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Effects of Paraquat and Atrazine on Soil Microbial Activities and Soil Mineral Content

Research Article

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Abstract

Application of herbicides to remove weeds is now the most common method in mechanized agriculture. This study tested the consequences of using herbicides to kill weeds. Viable counts of bacteria and fungi were determined. Microbial activities such as microbial respiration, microbial biomass carbon, dehydrogenase activity, acid phosphatase activity and organic matter were analyzed. Physicochemical components of the soil were also analyzed. As the concentration of paraquat herbicide applied to the soil increased from 4 ml to 12 ml, the *Pseudomonas* spp became more dominant. *Aspergillus* spp were more dominant among the fungal species showing their ability to multiply and utilize paraquat as nutrient source. As the concentrations of paraquat and atrazine increased microbial activity values reduced. Treatment of soils with atrazine and paraquat resulted in significant ($P \leq 0.05$) reductions in the pH acidity (H^+), Na, K, Ca and Mg values of the soil samples. This study has shown that continual application of herbicides to soils caused significant changes in soil microbial activity.

Keywords: Paraquat, Atrazine, Viable counts, Microbial activities

1. INTRODUCTION

Paraquat and atrazine are contact and selective herbicides respectively. They can be used to control or destroy weeds when the chemicals are absorbed into the leaves, stems, or roots. These chemical pesticides inhibit growth, disrupt cell membrane, and control the proliferation of weeds with various modes of action. De Albuquerque *et al.*, [1] reported that herbicides have the potential to impact photosynthesis, pigment, lipid, and pigment biosynthesis as well as seedling growth. In order to meet the demand for agricultural products, herbicide use is growing annually. Herbicide treatments can result in a serious case of environmental pollution which immediately affects the water quality and eventually affects people. Herbicide contamination has negative impacts on the microflora and fauna in the environment [2].

Herbicides can be used alone when eliminating weeds from crop field. Paraquat and atrazine are acceptable and safe for use in the field. Herbicides are formulated so that mixing and stability are enabled. In Nigeria, the agricultural systems employ herbicides to control weeds. Continual accumulation of herbicides can result in limited accessibility of nutrients to crop plants when they accumulate in the soil to toxic amounts, thereby reducing the nutrients that eventually affect the plants. This herbicide percolation also poses a threat to humans and animals.

When herbicides are used to control weeds without taking proper precautions, they might end up destroying microbial communities and result in unnecessary impact negative impacts on soil functions. Nitrogen cycle and the degradation of organic matter are examples of these important soil processes. Herbicide residues in soil are a serious concern since they may directly affect soil microorganisms. When herbicides are used at the typical recommended field rates they result in no noticeable negative environmental impact. However, there are microorganisms which can break down the herbicide while others were adversely affected [3].

There is however paucity of information about the physiological effort, mechanism of action, and environmental impact on soil microbial communities [4]. Iriel *et al.* [5] and [6] reported that atrazine is a synthetic triazine chemical used for controlling green and broadleaf weeds in crops such as wheat, sorghum, sugarcane, nuts, conifers and corn. It was first displayed within the 20th century and is ordinarily utilized alone. With annual utilization range from 70,000 to 90,000 in tons [7], it is the second-most broadly utilized herbicide within the world.

Atrazine is widely used in many nations because of its practical and affordable benefits even though it is prohibited and has been reported as one of the 45 priority pollutants in terms of research in water policy and with the maximum permitted absorption. Atrazine accumulates significantly in the environment due to its slow biodegradation in soils and extended half-life, which are typically found in water and soil. Atrazine has been reported to have harmful impacts on humans, including the ability to cause cancer and reproductive problems [8]. For this reason, it's important to find dependable and efficient ways to remove atrazine from water and soil.

The high toxic efficacy and low cost of atrazine have made it one of the most widely used triazine herbicides worldwide [9]. Atrazine can cause widespread and persistent pollution of soil and deposits due to its high dosage and prolonged use on a global scale. However, Nigeria has placed a strict ban on the import and usage of atrazine and paraquat due to severe public health and environmental risks. The ban on paraquat took effect on January 1, 2024. The ban on atrazine took effect on January 1, 2025. NAFDAC has been actively enforcing this ban through raids and confiscation of banned agrochemicals. Atrazine and paraquat have also been prohibited in the European Union and many other countries for years. This prohibition in the European union was primarily due to paraquats high toxicity to humans and atrazine's link to reproductive system issues and environmental contamination. The ability of soil to absorb and break down waste products by its microflora, producing nutrients as a result, makes it an important growth medium. However, soil microbial activity loses a lot of its efficiency if the intake of pollutants exceeds the soil purifying limit. As a result, the physicochemical characteristics of the soil will deteriorate, which will have an impact on the growth and development of crop plants [10]. Microorganisms oversee several biogeochemical cycles and help maintain healthy soil processes. Microorganisms also aid plant growth and development by, among other things, mineralizing organic compounds, raising the production of phytohormones and antibiotics, and boosting resistance to stress factors [11]. Feyzi *et al.* [12] reported that living organisms are valuable for removing soil contamination. The foremost solid markers of soil contamination are soil microorganisms since they are in coordinate touch with the soil environment and are in this manner vulnerable to any environment in confusion. The removal of toxic compounds, conservation of the soil, control of bugs and development in plants are all important forms in which soil organisms play a key part.

As an important component of agricultural biological systems, soil microflora not only contributes to fundamental soil forms but also effectively contributes to moving forward soil fertility and crop efficiency. According to Prashar and Shah,[13] microbial movement in soil encompasses a critical effect on its physical characteristics, and it is regarded too basic to seek after ecologically friendly activities like bioremediation and biocontrol of phytopathogens in agricultural soils. In addition to microorganisms, enzymes play a significant role in the biochemical process and nutrient cycle, making them crucial evaluation markers for soil quality. To support plant growth and control the microbiological ecology in the soil, soil enzymes may accelerate the conversion of organic materials into inorganic nutrients or help in the breakdown of external toxic compounds.

Higher animals and humans may get malignancies, immune system suppression, organ failure, and impairments in reproduction if they consume food crops that contain pesticides. Evaluation of the genotoxicity of organisms in such environments and groundwater monitoring, particularly close to agricultural areas and sources of primary drinking water, are crucial given that pesticides, such as herbicides, have contaminated the environment as a result of the widespread use of chemicals to control weeds [14]. The genotoxic effects of some herbicides have been evaluated by several researchers through several test systems. Due to the stress that pesticide application causes, the population of organisms that received sublethal dosages may exhibit a high number of DNA changes, which can result in pesticide resistance [15; 16]. This study assessed the effects of the widely used herbicides atrazine and paraquat on the soil's microbial flora.

2. MATERIAL AND METHODS

2.1. Study Area

Ijebu-Ode is a prominent town and Local Government Area (LGA) located in Ogun State, southwestern Nigeria. It serves as the administrative capital of Ijebu North Local Government Area and is one of the major towns in the Ijebu ethnic region. Geographically, Ijebu-Ode lies within the tropical zone, characterized by a mix of dry and wet seasons, with rich vegetation and fertile soil that supports agriculture, especially crop farming and palm oil production. The coordinates of Ijebu-Ode are approximately 6.7906° N latitude and 3.9319° E longitude. The town experiences a tropical climate, with average annual temperatures ranging between 27°C and 32°C. The wet season typically lasts from March to October with heavy rainfall from June to September while the dry season runs from November to February, marked by the harmattan winds. Ijebu-Ode covers an area of about 1,121 square kilometers, making it one of the larger LGAs in Ogun State. The area is well known for its cultural heritage, particularly the famous Ijebu kingdom, which has a long history of trade and royal significance. Today, Ijebu-Ode continues to grow as a key economic hub with its proximity to major highways and cities like Lagos, fostering both local and regional commerce.

2.2. Soil Sampling and Soil Treatment

Topsoil samples (up to 5 cm deep) that had no history of pesticide applications were collected in triplicates with the aid of hand trowel from a field plot (the research field of Biological Sciences Department, Tai Solarin Federal University of Education, Ijebu Ode, Ogun State, Nigeria) at 5 cm – 15 cm depth. The samples were sieved with wire mesh (size < 2 mm), sorted to remove stones, plant debris and any visible soil fauna. Then, they were thoroughly mixed with the hand trowel. The soil was allowed to stabilize for seven days by incubating at 27°C to permit the disturbances caused by sampling and sieving to subside [22]. 180 g of atrazine powder was mixed with 15 l of water in a 15 l Knapsack sprayer (recommended application rate ranges between 2.5-5.0 L/ha depending on the type of weed present). 180 ml of paraquat was mixed with 15 l of water in 15 l Knapsack sprayer (recommended application rate ranges between 2-6 L/ha). Soil treatments were replicated three times and carried out using the complete randomized block design. Soil treatments of 4ml, 6ml, 8ml, 10ml and 12ml of paraquat and atrazine were applied to 5kg soil samples in plastic pots. Untreated soil samples were used as control. Soil samples were incubated in the dark at 40°C ± 0.5 for a period of twelve days. Soil moisture content was maintained at 50% water holding capacity by weighing and correcting for any weight loss, using distilled water. One hundred grams of soil samples were taken from the pots before and after incubation and analyzed for soil dehydrogenase and urease activities, total viable counts of bacteria and fungi.

2.3. Herbicides

The test chemicals used in this study were obtained from a local agricultural dealership outlet located in Ogun state, Nigeria. The test chemicals were: Paraquat (by Syngenta Crop Protection AG, Switzerland) and Atrazine (by Hepu Pesticide Co. Ltd., Guangxi, China, 536100).

2.4. Microbial Isolation, Enumeration and Identification

Nutrient agar (NA) was used to assess the total heterotrophic bacteria by the pour plate method and incubated at 30°C for 24h-48 h. We also used Potato Dextrose Agar (PDA) to enumerate and isolate fungi and incubated at 25°C for 7 days. Characterization of bacterial isolates was done with respect to biochemical and staining reactions, and cultural characteristics. Bergey's Manual of Systemic Bacteriology (1984) was used as guide for identification while morphological and cultural characteristics were especially used for fungi identification. After bacteria and fungi emerged from plates, they were sub-cultured continuously until pure cultures were achieved. We used Quebec colony counter to conduct microorganism counting from plates containing 15-150 colonies per plate and then calculated the number of colony forming units per gram (cfu/g) in each soil sample.

2.5. Acid Phosphatase Activity

Two grams of soil sample were extracted with 20ml sodium carbonate buffer at pH 6.0. The suspension obtained was centrifuged at 5000 rpm in a high-speed Gerber centrifuge (Gallenkamp model) at 5°C for 30 min. The supernatant obtained at the end of 30 min centrifugation was decanted into 30 ml centrifuge stoppered bottle and stored in a deep freezer at -20°C prior to analysis. One ml of enzyme extract of sample was pipetted into a 50 ml test tube. 5 ml of disodium-p-nitrophenol phosphate was added, mixed thoroughly by shaking to obtain a homogenous solution and left to stay for 5 minutes in order to yield the yellowish coloration. A standard solution of phosphatase enzyme was prepared from stock phosphatase solution and treated similarly like the sample above. The absorbance of the yellowish color solution and standard solution was measured as change in 60s (1 min) at wavelength of 475nm. One unit of phosphatase activity was estimated as the quantity of enzyme which catalyzed 0.01 absorbance change in 1 min at wavelength of 475 nm.

$$\text{Phenol } (\mu\text{g g}^{-1} \text{ dwt h}^{-1}) = C \times \frac{100}{\text{dwt}} \times t \times 10$$

Where C = the measured phenol concentration ($\mu\text{g phenol ml}^{-1}$) filtrate

dwt = the dry weight of 1g moist soil,

t = the incubation time hours,

100 is the total volume of the soil suspension in milliliters,

10 is the weight of the soil used in the test.

2.6. Determination of Microbial Biomass Carbon

The analysis was performed using the ISO [36] method. 250 g of soil moistened to 50% retention capacity were pre-incubated for 3 days and then 25 g of soil was weighed. Three samples were fumigated in a desiccator using boiling chloroform and left in the dark for 24 h. To the remaining samples, 200 mL of 0.5 M K_2SO_4 were added, and the samples were shaken for 30 min. The same process was carried out for the fumigated samples after 24 h. MBC was determined by dichromate oxidation. All samples were filtered and 8 mL were taken. Subsequently, 2 mL 0.07 M $\text{K}_2\text{Cr}_2\text{O}_7$ and 15 mL acid mixture (H_2SO_4 , H_3PO_4) were added. After refluxing for 30 min, titration was carried out using 0.04 M Mohr's salt $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{SO}_4$.

2.7. Microbial Respiration

The method used in ISO [35] was used to determine microbial respiration. 150 g of soil moistened to 50% retention capacity was pre-incubated for 3 days and then 25 g of soil was weighed into breathable bags (in three replications). The breathable bags were hung in a 750 mL sealed glass bottle with 20 mL of 0.05 M NaOH at the bottom for 3 days. Before titration, 2 mL of 0.5 M BaCl₂ and phenolphthalein were added. Subsequently, titration was then carried out using 0.1 M HCl.

2.8. Analysis of Organic Matter in Soils

The method of Tyurin [34] was used to determine soil organic matter. 0.1 g of soil (<0.25 mm) was weighed in triplicate for each location. Subsequently, 0.3 M K₂Cr₂O₇ and concentrated H₂SO₄ were mixed to form a chromo-sulfur mixture. The titration cups with the weighed soil were added to 12.5 mL of the chromo-sulfur mixture and then the samples were burned in an oven at 135° for 30 min. Then, titration was carried out with 0.2 M Mohr's salt ((NH₄)₂Fe(SO₄)₂·6H₂O + H₂SO₄). The following formula was then used to determine the amount of organic matter:

$$\% \text{ Organic matter} = \frac{(\mu\text{s K}_2\text{S}_4 - \mu\text{s FeSO}_4) \times 0.003 \times 100 \times G \times 1.729}{\text{Weight of air-dried soil}}$$

Where, correlation factor "G" = 1.33, us = normality of solution × milliliter of solution used and 1.729 = conversion.

2.9. Determination of the Dehydrogenase Activity

The research was carried out in triplicates. Six grams of the soil were weighed into flasks and 0.06 g of CaCO₃, and 1 cm³ 3 % aqueous solution of 1,3,5-phenyl-tetrazolium chloride with 2.5 cm³ distilled water were added to it successively. The samples were incubated for 24 h in 37 °C. After the incubation, twenty-five cm³ methyl alcohol was introduced into every sample. The resultant solution was thoroughly mixed and filtered using a 50 cm³ volumetric flask and a funnel with a quantitative hard filter at diameter of 9 cm. It was repeated twice. The flasks were then made up to the mark with methyl alcohol, their contents were thoroughly mixed and absorbances were measured on a spectrophotometer Aquarius CE7500 Cecil Instruments, at a wavelength of λ=485 nm.

2.10. Determination of Soil Minerals and Cation Exchange Capacity

The method described by Blakemore *et al.* [33] was used to determine the mineral contents of the soil samples. Concentrations of Na, K, Ca and Mg in the soil samples were determined using the atomic absorption spectrophotometer. Soil solutions from were injected into the atomic absorption spectrophotometer. The concentrations of the minerals were then calculated. The heavy metals were analyzed using soil samples obtained from the farmlands after the soils have been air dried and homogenized. Cationic exchange capacity (CEC) was determined using the method described by Ibitoye [31]

2.11. Statistical Analysis

The version 20 statistical package for social sciences (SPSS) software was used to analyze data from the microbial count, soil nutrient content, soil microbial respiration and soil biomass carbon. Duncan's tests and the One-Way ANOVA were used to test statistical differences between the various treatment groups. Continuous data are presented as Mean ± standard deviation and were considered statistically significant when the p-values were less than 0.05.

3. RESULTS

In Table 1, microorganisms capable of adapting, growing and utilizing paraquat as nutrient and carbon sources are presented. The most predominant group of bacteria are the *Bacillus* and *Pseudomonas* spp. As the concentration of paraquat herbicide applied to the soil increased from 4 ml to 12 ml, the *Pseudomonas* spp became more dominant. In the control samples, the soil samples showed no initial presence of herbicides. As Paraquat was applied in increasing concentrations to the soil samples, the bacterial species adapted to the conditions paraquat presented. Their growth rate increased showing their adaptability and abilities to utilize paraquat as nutrient source. The fungi followed the same pattern. *Aspergillus* spp were more dominant among the fungal species showing their ability to multiply and utilize paraquat as nutrient source.

Table 1 Microorganisms Isolated From Paraquat and Atrazine Treated Soils

	Micro-organisms Isolated
Control	<i>B. subtilis</i> , <i>Micro. varians</i> , <i>Serri mercezens</i> , <i>S. aureus</i> , <i>A. niger</i> , <i>A. tamari</i> , <i>P. oxalicum</i> , <i>B. macerans</i> , <i>B. subtilis</i> , <i>Micro. luteus</i> , <i>Serri marscences</i> , <i>S. aureus</i> , <i>A. niger</i> , <i>A. tamari</i> , <i>P. oxalicum</i> , <i>Fusarium oxysporum</i> , <i>B. cereus</i> .
4ml	<i>Bacillus subtilis</i> , <i>Bacillus licheniformis</i> , <i>S. aureus</i> , <i>Pseudomonas aureginosa</i> , <i>Pseudomonas Putida</i> , <i>Aspergillus tamari</i> , <i>Aspergillus niger</i> , <i>Pseudomonas oxalicum</i> , <i>Micro. varians</i> , <i>Serri marscences</i> , <i>Bacillus coagulans</i> , <i>Trichoderma viridie</i> , <i>Aspergillus terrus</i> , <i>Bacillus macerans</i> , <i>Staphylococcus aureus</i> , <i>Bacillus subtilis</i> .
6ml	<i>Bacillus subtilis</i> , <i>Bacillus cereus</i> , <i>Staphylococcus aureus</i> , <i>Pseudomonas aureginosa</i> , <i>Pseudomonas putida</i> , <i>Micrococcus luteus</i> , <i>Aspergillus tamari</i> , <i>Pseudomonas oxalicum</i> , <i>Pseudomonas aureginosa</i> , <i>B. subtilis</i> , <i>Micrococcus varians</i> , <i>Trichodama Viridie</i> , <i>Aspergillus niger</i> , <i>Aspergillus terreus</i> , <i>Bacillus macerans</i> , <i>Staphylococcus aureus</i> .
8ml	<i>Ps. putida</i> , <i>Micro. acidiphilus</i> , <i>B. subtilis</i> , <i>Proteus vulgaricus</i> , <i>A. niger</i> , <i>A. terrus</i> , <i>Fusarium oxysporum</i> , <i>B. coagulans</i> , <i>Micro. acidiphilus</i> , <i>Pro. Morganii</i> , <i>Trich. Viridie</i> , <i>A. tamari</i> , <i>B. subtilis</i> , <i>Micro. varians</i> , <i>Klebsiella aerogenes</i> , <i>P. oxalicum</i> .
10ml	<i>Ps. putida</i> , <i>Micro acidiphilus</i> , <i>B. subtilis</i> , <i>Pr. Vulgaricus</i> , <i>A. niger</i> , <i>A. tamari</i> , <i>P. oxalicum</i> , <i>B. subtilis</i> , <i>B. cogulans</i> , <i>Micro. varians</i> , <i>Trich. Viridie</i> , <i>A. terreus</i> , <i>A. niger</i> , <i>B. cereus</i> , <i>B. macerans</i> , <i>B. subtilis</i> , <i>P. oxalicum</i> , <i>A. niger</i> , <i>A. flavus</i> .
12ml	<i>B. subtilis</i> , <i>Micro. varians</i> , <i>B. licheniformis</i> , <i>Ps. aureginosa</i> , <i>A. niger</i> , <i>A. tamari</i> , <i>P. oxalicum</i> , <i>Ps. aureginosa</i> , <i>Ps. putida</i> , <i>B. subtilis</i> , <i>A. niger</i> , <i>T. viride</i> , <i>B. subtilis</i> , <i>Micro.varians</i> , <i>P. oxalicum</i> .

Table 2 shows that in this study there were significant ($P \leq 0.05$) reductions in the viable counts of bacteria and fungi obtained from soils treated with atrazine and paraquat. The highest viable counts of bacteria and fungi obtained from soils treated with atrazine were $16.00 \pm 6.00 \times 10^5$ CFUg⁻¹, and $5.33 \pm 1.20 \times 10^5$ CFUg⁻¹. However, in paraquat treated soils, the highest viable counts of bacteria and fungi were $20.667 \pm 0.333 \times 10^5$ CFUg⁻¹ and $6.333 \pm 0.333 \times 10^5$ CFUg⁻¹, respectively. The values were obtained after the first herbicide treatments (4ml). Meanwhile as the treatments increased from 4ml to 12ml, the viable counts reduced. The lowest viable counts of $5.333 \pm 0.882 \times 10^5$ CFUg⁻¹ and $2.000 \pm 0.000 \times 10^5$ CFUg⁻¹ were obtained from soils treated with paraquat while the soils treated with atrazine recorded the lowest values of $5.66 \pm 0.33 \times 10^5$ CFUg⁻¹ (bacteria) and $2.33 \pm 0.33 \times 10^5$ CFUg⁻¹ (fungi) at 4g/100ml treatment.

Table 2. Viable counts of bacteria ($\times 10^5$ Cfug⁻¹) and fungi ($\times 10^5$ Cfug⁻¹)

	CONC	TBC	TFC
PARAQUAT	Control	33.333 $\pm$ 1.667 ^d	11.000 $\pm$ 0.577 ^d
	4ml	20.667 $\pm$ 0.333 ^c	6.333 $\pm$ 0.333 ^c
	6ml	15.667 $\pm$ 0.667 ^b	5.667 $\pm$ 0.333 ^b
	8ml	12.667 $\pm$ 1.202 ^b	4.333 $\pm$ 0.667 ^b
	10ml	8.333 $\pm$ 0.882 ^a	3.000 $\pm$ 0.000 ^a
	12ml	5.333 $\pm$ 0.882 ^a	2.000 $\pm$ 0.000 ^a
	SAMPLE VOLUME	TBC	TFC
ATRAZINE	Control	36.00 $\pm$ 2.08 ^c	9.67 $\pm$ 0.88 ^d
	4ml	16.00 $\pm$ 6.00 ^b	5.33 $\pm$ 1.20 ^c
	6ml	15.66 $\pm$ 0.33 ^b	5.00 $\pm$ 0.58 ^{bc}
	8ml	13.00 $\pm$ 0.58 ^{ab}	42.33 $\pm$ 0.33 ^{ab}
	10ml	10.00 $\pm$ 1.15 ^{ab}	3.00 $\pm$ 0.00 ^{ab}
	12ml	5.66 $\pm$ 0.33 ^a	2.33 $\pm$ 0.33 ^a

Values followed by the same superscript along the same vertical column are not significantly different ($P \geq 0.05$), while values followed by different superscript along the same vertical column are significantly different ($P \leq 0.05$). TBC =Total Bacterial Count, TFC = Total Fungi Count, CFUg⁻¹ = Colony forming unit / gram.

There were significant reductions ($P \leq 0.05$) in the dehydrogenase and phosphatase activities as the concentration values of paraquat and atrazine increased (Table 3). Soils treated with atrazine recorded the lowest value of dehydrogenase activity value of $0.85 \pm 0.7 \mu\text{g g}^{-1}$ at the 12g/100ml concentration while soils treated with paraquat recorded the lowest dehydrogenase activity value of $0.419 \pm 0.061 \mu\text{g g}^{-1}$ at 12g/100ml concentration. Also, at the 12g/100ml concentration atrazine treated soils recorded the lowest phosphatase activity value of $5.83 \pm 5.81 \mu\text{g g}^{-1} \text{ dwt h}^{-1}$ and paraquat treated soils also recorded the lowest phosphatase activity value of $0.0182 \pm 0.003 \mu\text{g g}^{-1} \text{ dwt h}^{-1}$. As herbicides accumulated in the soil samples, microbial activities reduce significantly.

Table 3. Effect of atrazine and paraquat on dehydrogenase ($\mu\text{g g}^{-1}$) and phosphatase ($\mu\text{g g}^{-1} \text{ DWT H}^{-1}$) activities

	Control	4ml	6ml	8ml	10ml	12ml
ATRAZINE						
DHY($\mu\text{g g}^{-1}$)	2.77 $\pm$ 0.00 ^a	1.69 $\pm$ 0.69 ^a	1.68 $\pm$ 0.69 ^a	1.66 $\pm$ 0.69 ^a	1.62 $\pm$ 0.67 ^a	0.85 $\pm$ 0.71 ^a
PHOS ($\mu\text{g g}^{-1}$)	0.05 $\pm$ 0.00 ^a	0.03 $\pm$ 0.00 ^a	0.03 $\pm$ 0.00 ^a	0.03 $\pm$ 0.00 ^a	0.02 $\pm$.00 ^a	5.83 $\pm$ 5.81 ^a
PARAQUAT						
		4ml/100ml	6ml/100ml	8ml/100ml	10ml/100ml	12ml/100ml
DHY ($\mu\text{g g}^{-1}$)	2.939 $\pm$ 0.114 ^c	2.149 $\pm$ 0.392 ^b	2.179 $\pm$ 0.067 ^b	1.732 $\pm$ 1.137 ^b	0.574 $\pm$ 0.080 ^a	0.419 $\pm$ 0.061 ^a
PHOS ($\mu\text{g g}^{-1}$)	0.044 $\pm$ 0.002 ^c	0.037 $\pm$ 0.002 ^d	0.033 $\pm$ 0.001 ^{cd}	0.030 $\pm$ 0.001 ^{cb}	0.026 $\pm$ 0.001 ^b	0.0182 $\pm$ 0.003 ^a

Note: DA= Dehydrogenase Activity, PHOS = Phosphatase Activity

In Table 4, soil microbial respiration and microbial biomass carbon content of the soil samples were significantly suppressed ($P \leq 0.05$). The lowest microbial respiration values of $10.70 \pm 1.80 \mu\text{g g}^{-1}$ (in atrazine treated soils) and $17.583 \pm 0.536 \mu\text{g g}^{-1}$ (in paraquat treated soils). The microbial biomass activity also followed similar trends. The lowest and the highest microbial biomass activity values of $165.24 \pm 81.48 \text{ KgC m}^{-2}$ and $280.62 \pm 0.61 \text{ KgCm}^2$ were obtained in atrazine treated soils.

Table 4. Effect of Atrazine and Paraquat on Soil Microbial Respiration (μgg^{-1}) and Microbial Biomass Carbon (KgC m^{-2})

	Control	4ml	6ml	8ml	10ml	12ml
ATRAZINE						
MR	29.07 $\pm 0.11^c$	24.22 $\pm 1.11^b$	22.29 $\pm 2.00^b$	20.85 $\pm 1.75^{bc}$	19.27 $\pm 1.81^{bc}$	10.70 $\pm 1.80^a$
BC	280.62 $\pm 0.61^c$	263.13 $\pm 1.37^{ac}$	259.28 $\pm 0.94^{ac}$	255.13 $\pm 1.66^{ac}$	249.97 $\pm 0.92^{ac}$	165.24 $\pm 81.48^a$
PARAQUAT						
MR	28.348 $\pm$ 0.272 ^f	25.633 $\pm 0.262^e$	23.950 $\pm 0.229^d$	22.268 $\pm 0.260^c$	20.683 $\pm 0.203^b$	17.583 $\pm 0.536^a$
BC	274.317 $\pm$ 1.894 ^e	259.917 $\pm 1.830^d$	255.717 $\pm 0.934^c$	251.067 $\pm$ 0.667 ^b	247.367 $\pm 0.242^a$	245.050 $\pm$ 0.715 ^a

Note: BC=Microbial Biomass Carbon, MR= Microbial respiration

In Table 5, treatment of soils with paraquat resulted in significant ($P \leq 0.05$) reductions in the pH, acidity (H^+), Na, K, Ca and Mg values of the soil samples after treatment with paraquat (Table 6). The highest mineral contents of the soil samples after analysis occurred in the soils that had no record of herbicide treatments. The highest pH, Na, K, Ca and Mg values of 6.767 ± 0.033 , 0.043 ± 0.006 , 0.501 ± 0.012 , 0.233 ± 0.004 and 0.687 ± 0.009 were recorded in the control samples. However, the H^+ values of the soil samples increased showing the accumulation of acid in the samples as a result of the metabolic activities of the microorganisms.

Table 5: Effect of Paraquat on Soil Minerals

	Control	4ml	6ml	8ml	10ml	12ml	P-Value
pH	6.767 $\pm$ 0.033 ^d	6.317 $\pm 0.142^c$	6.233 $\pm 0.120^c$	6.117 $\pm 0.167^{bc}$	5.933 $\pm$ 0.067 ^{ab}	5.817 $\pm 0.101^a$	0.000
H^+	0.072 $\pm$ 0.002 ^a	0.094 $\pm 0.007^{ab}$	0.098 $\pm 0.006^{bc}$	0.104 $\pm 0.001^{bcd}$	0.123 $\pm$ 0.013 ^{cd}	0.129 $\pm 0.079^d$	0.004
Na(mg/kg)	0.343 $\pm$ 0.006 ^c	0.270 $\pm 0.016^b$	0.248 $\pm 0.019^b$	0.230 $\pm 0.010^{ab}$	0.207 $\pm$ 0.010 ^a	0.190 $\pm 0.0173^a$	0.000
K(mg/kg)	0.501 $\pm$ 0.012 ^d	0.318 $\pm 0.013^a$	0.350 $\pm 0.008^{ab}$	0.380 $\pm 0.013^{bc}$	0.388 $\pm$ 0.034 ^{bc}	0.427 $\pm 0.019^c$	0.000
Ca(mg/kg)	0.233 $\pm$ 0.004 ^d	0.212 $\pm 0.007^c$	0.192 $\pm 0.011^c$	0.193 $\pm 0.003^c$	0.170 $\pm$ 0.006 ^b	0.148 $\pm 0.006^a$	0.000
Mg(mg/kg)	0.687 $\pm$ 0.009 ^d	0.632 $\pm 0.019^c$	0.592 $\pm 0.024^{bc}$	0.590 $\pm 0.008^{bc}$	0.552 $\pm$ 0.011 ^{ab}	0.528 $\pm 0.017^{ab}$	0.000

Treatment of soils with atrazine resulted in reduction in the pH, acidity (H^+), Na, K, Ca and Mg values of the soil samples (Table 6). Table 6 followed similar trends with were obtained in Table 5. The highest mineral contents of the soil samples after analysis were obtained in the soils that had no record of herbicide treatments. The highest pH, Na, K, Ca and Mg values of 6.73 ± 0.0 , 0.35 ± 0.0 mg/kg, 0.50 ± 0.00 mg/kg, 0.24 ± 0.00 mg/kg and 0.70 ± 0.00 mg/kg were recorded in the control samples. However, the H^+ values of the soil samples increased showing the accumulation of acid as a result of the metabolic activities of the microorganisms. In Table 7, the P values for K, Ca, mg and P are 0.755, 0.612 and 0.624 respectively.

Table 6 Effect of Atrazine on Soil Minerals

	Control	4ml	6ml	8ml	10ml	12ml	P - Value
Soil pH	6.73 ± 0.02 ^c	6.33 ± 0.03 ^b	6.25 ± 0.03 ^a	6.23 ± 0.03 ^a	6.20 ± 0.00 ^a	6.22 ± 0.02 ^a	0.000
H ⁺	0.07 ± 0.00 ^a	0.09 ± 0.00 ^a	0.24 ± 0.14 ^a	0.10 ± 0.02 ^a	0.10 ± 0.00 ^a	0.10 ± 0.10 ^a	0.412
Na (mg/kg)	0.35 ± 0.05 ^d	0.26 ± 0.02 ^c	0.24 ± 0.02 ^{bc}	0.22 ± 0.02 ^{bc}	0.19 ± 0.02 ^{ab}	0.17 ± 0.01 ^a	0.000
K(mg/kg)	0.50 ± 0.00 ^a	0.44 ± 0.03 ^a	0.40 ± 0.03 ^a	0.37 ± 0.04 ^a	0.41 ± 0.11 ^a	0.38 ± 0.11 ^a	0.755
Ca(mg/kg)	0.24 ± 0.00 ^a	0.22 ± 0.02 ^a	0.19 ± 0.02 ^a	0.17 ± 0.02 ^a	1.99 ± 1.85 ^a	1.96 ± 1.84 ^a	0.612
Mg(mg/kg)	0.70 ± 0.00 ^a	0.65 ± 0.04 ^a	0.62 ± 0.04 ^a	0.57 ± 0.05 ^a	3.60 ± 3.11 ^a	3.54 ± 3.09 ^a	0.624

There were significant changes ($P \leq 0.05$) in cation exchange capacity, total organic carbon and total nitrate values (Table 7). The cation exchange capacity, total organic carbon and total nitrate values reduced as the atrazine levels applied to soil samples increased. Therefore, the highest cation exchange capacity, total organic carbon and total nitrate values were obtained in the control soil samples (24.44 ± 0.01 (meq/g, 5.91 ± 0.00 % and 0.05 ± 0.00 %).

Table 7 Effect of Atrazine concentrations on Cation Exchange Capacity, Total Organic Carbon and Total Nitrogen

	Control	4ml	6ml	8ml	10ml	12ml	P - Value
Cation Exchange Capacity (meq/g)	24.44 ± 0.01 ^c	23.29 ± 0.38 ^b	23.15 ± 0.34 ^b	22.56 ± 0.37 ^{ab}	22.13 ± 0.25 ^a	21.76 ± 0.32 ^a	0.001
Total Organic Carbon(%)	5.91 ± 0.00 ^a	5.70 ± 0.06 ^a	5.66 ± 0.07 ^a	5.60 ± 0.07 ^a	3.67 ± 1.82 ^a	3.60 ± 1.79 ^a	0.422
Total Nitrate(%)	0.05 ± 0.00 ^a	0.04 ± 0.00 ^a	0.04 ± 0.00 ^a	0.03 ± 0.00 ^a	0.19 ± 0.16 ^a	0.19 ± 0.16 ^a	0.622

Similar to what was obtained in Table 8, there were significant changes ($P \leq 0.05$) in cation exchange capacity, total organic carbon and total nitrate values (Table 9). The cation exchange capacity, total organic carbon and total nitrogen content values reduced as the paraquat levels applied to soil samples increased. The highest CEC, organic carbon and total nitrogen values of 1.837 ± 0.021 meq/g, 5.785 ± 0.023 % and 0.725 ± 0.070 % respectively were all obtained in the control soil samples.

Table 8: Effect of Paraquat Concentrations on Cation Exchange Capacity, Total Organic Carbon and Total Nitrogen Content

	Control	4ml	6ml	8ml	10ml	12ml	P-Value
CEC(meq/g)	24.44 ± 0.01 ^c	16.34 ± 0.049 ^c	15.23 ± 0.080 ^{bc}	14.99 ± 0.013 ^{bc}	14.00 ± 0.031 ^{ab}	13.17 ± 0.023 ^a	0.000
TOC(%)	5.91 ± 0.00 ^a	5.722 ± 0.044 ^{bc}	5.652 ± 0.050 ^{ab}	5.647 ± 0.029 ^{ab}	5.603 ± 0.029 ^a	5.550 ± 0.028 ^a	0.007
TN (%)	0.05 ± 0.00 ^a	0.042 ± 0.004 ^a	0.035 ± 0.029 ^a	0.032 ± 0.007 ^a	0.033 ± 0.033 ^a	0.030 ± 0.000 ^a	0.270

4. DISCUSSION

Atrazine (6 – chloro - N2 – ethyl - N4 – isopropyl - 1, 3, 5 – triazine - 2, 4 - diamine) belongs to the group of triazines. Triazines interfere with photosynthesis in plants. Atrazine is a selective systemic herbicide used for pre - and post - emergence control of annual grasses and broad leaf weeds in a variety of cultivated crops. However, The dipyridylum herbicides, paraquat and diquat, were introduced as effective

nonselective herbicides. Application of paraquat and atrazine at increased concentrations beyond the company recommended rates resulted in decreased population of bacteria and fungi which played important roles in soil nutrient availability and in the biodegradation of complex and toxic chemicals. Paraquat is a total contact herbicide used to control broad-leaved and grassy weeds. It should be sprayed when the weeds are young and less than 30 cm high. It kills all green tissues but does not harm the mature bark. Paraquat is used for plantation crops (banana, cocoa palm, oil-palm, rubber, etc.) and for citrus fruits, apples, plums, vines and tea. On certain crops (potato, pineapple, sugarcane, sunflower), it is used as a desiccant. It is also used as a cotton defoliant. It is applied around the trees in orchards and between the rows of crops. Teke *et al.* [23] similarly reported that bacterial and fungal population decreased in paraquat treated soils, compared to the control. This study suggests that the exposure of soil microorganisms to pesticides negatively impacts their proliferation and survival. Abdullahi *et al.* [24] further reported that in their study, the various heterotrophic bacterial colony counts obtained from the various treatments ranging from the control (Day 1, no herbicide applied), to days 3, 6, 9 and 15 after the applications of the various herbicides, respectively show two general trends are readily observed: the first is that upon the application of the herbicide, the microbial growth steadily diminishes, up to the 6th day. However, from there it continues to increase till the end of the experiments (day 15).

According to Mili *et al.* [27], bacteria are the most widely reported microorganism for atrazine elimination from polluted sites. Due to its potential for bioremediation, a large variety of strains of Gram-positive and Gram-negative bacteria that degrade atrazine have been isolated and identified. Atrazine degrading bacteria produce various catalytic enzymes that break down atrazine (i.e., atrazine chlorohydrolase, allophanate amidohydrolase, HA hydrolase, N-isopropylammelide amidohydrolase, triazine hydrolase, 1-carboxybiuret amidohydrolase, and cyanuric acid amidohydrolase) and enhance the metabolic mechanisms. They reduce the degradation of half-life of atrazine a variety of metabolic processes which include dichlorination, dealkylation, hydroxylation, and ring cleavage. The atrazine-degrading strains, for example, *Pseudomonas* strain ADP break down atrazine into cyanuric acid through three enzymatic steps, and cyanuric acid acts as a source of nitrogen for many other bacteria [24]. Moreover, some other bacteria belonging to the genera *Rhodococcus*, *Acinetobacter*, *Streptomyces*, *Pseudomonas*, *Clavibacter*, *Arthrobacter*, *Bacillus*, *Alcaligenes*, *Klebsiella*, and *Agrobacterium*, transform atrazine into cyanuric acid.

The dominant microorganisms obtained here are *Pseudomonas* spp and *Aspergillus* spp. This, however, indicates the ability of the bacteria and fungi isolated to utilize atrazine and paraquat as nutrient and carbon sources. Oladele and Ayoade [30] reported that beneficial bacteria such as *Pseudomonas* spp, *Bacillus* spp, *Enterobacter* spp etc. were the dominant colonies across the herbicide treated fields in their study. Under the atrazine treated plots, *Pseudomonas fluorescens* was the highest bacteria genera population (20×10^{-8} cfu/g) while the lowest population was *Chromobacterium lividium* and *Xanthomonas* spp (12×10^{-8} cfu/g) respectively. In the glyphosate treated plot, isolated bacteria genera; *Bacillus subtilis* and *Thiobacillus thiooxidans* were the dominant colonies at (20×10^{-8} cfu/g) respectively, while *Citrobacter freundii* was observed to have the lowest colony (8×10^{-8} cfu/g). Paraquat treated plots generally recorded low bacteria colonies, beneficial bacteria such as *Rhizobium*, *Bacillus subtilis*, were isolated under this plot; however, *Bacillus subtilis* recorded the highest colony count (5×10^{-8} cfu/g)

Labouyrie *et al.* [19] reported that bacteria were more predominant than the fungi isolated in their work. It was observed that the microbial population observed in this study declined significantly as the concentration of atrazine and paraquat used in killing weeds increased significantly. Similar to what was obtained in this study Teke *et al.* [23] also reported that Isolates capable of growing at different Paraquat concentrations were isolated in their study. This includes five (5) bacterial isolates which were recovered from the Bushnell-Haas medium, and were identified as: *Arthrobacter* sp., *Bacillus* sp., *Micrococcus* sp., *Pseudomonas* sp. and *Staphylococcus* sp. The pesticide-utilizing fungi detected include *Penicillium* sp., *Aspergillus* sp., *Trichoderma* sp., and *Fusarium* sp. Oladele and Ayoade [30] reported that fungal colonies

which are isolated from herbicide treated plots were generally low with respect to population count irrespective of the different herbicide types. However, *Aspergillus* spp, *Fusarium* spp and *Geotrichum* spp were the dominant colonies identified in all herbicide treated plots. *Aspergillus* Flavus was the dominant colony in the atrazine treated plots (15×10^{-8} cfu/g).

In this study, there were significant ($P \leq 0.05$) reductions in the viable counts of bacteria and fungi obtained from soils treated with atrazine and paraquat. The highest viable counts of bacteria and fungi obtained from soils treated with atrazine were $16.00 \pm 6.00 \times 10^5$ CFUg⁻¹ and $5.33 \pm 1.20 \times 10^5$ CFUg⁻¹. However, in paraquat treated soils the highest viable counts of bacteria and fungi were $20.667 \pm 0.333 \times 10^5$ CFUg⁻¹ and $6.333 \pm 0.333 \times 10^5$ CFUg⁻¹ respectively. The values were obtained after the first herbicide treatments (4ml). Meanwhile as the treatments increased from 4ml to 12ml, the viable counts reduced. However, Teke *et al.* [23] reported that in the second treatment (with paraquat) bacterial population decreased from 2.49×10^3 CFU/g on day 1 to 2.25×10^3 CFU/g on day 7; in T3, it decreased from 2.5×10^3 CFU/g to 2.18×10^3 CFU/g; in T4, it decreased from 2.4×10^3 CFU/g to 1.96×10^3 CFU/g and in T5, it decreased from 2.43×10^3 CFU/g to 1.83×10^3 CFU/g. In the control (unpolluted soil), the population varied from 2.24×10^3 CFU/g to 2.33×10^3 CFU/g.

The increased concentrations of the herbicides used in this study resulted in reductions in dehydrogenase activity, microbial respiration, phosphatase activity, microbial biomass, total nitrogen, mineral concentration and total organic carbon. The increase in organic carbon observed in the herbicide treated soils in this study could be attributed to the faster breakdown of herbicides by the dynamic microbial activity which further influences the movement and persistence of these herbicides due to increasing organic carbon levels which aids a faster biodegradation process.

Similar to what was obtained in this study, Oladele and Ayoade [30] reported that there was no significant ($P=0.05$) difference in soil pH values obtained in their atrazine treated soil samples. However, atrazine treated plots had the highest statistical soil pH (6.55) values while glyphosate + paraquat treated plots recorded the lowest values (4.96). The atrazine treated plot recorded a 14.3% increase in pH values when compared to the control, which makes the soil on this plot to be slightly acidic and in a range where most plant nutrients are available for uptake. The increase in soil pH could become disadvantageous as this could increase the persistence of some herbicide due to restricted hydrolysis associated with high pH levels and increase in exposure period by soil microbes thereby causing mortality and a decrease in microbial biomass carbon. According to Oladele and Ayoade [30] Atrazine + paraquat treated plots and singly treated atrazine plots showed increased soil organic matter when compared with other treatments and the control (untreated plots). Paraquat treated plots (1.05%) recorded the lowest SOM values while the control (untreated) plot had values of (3.98%). Soil available P was significantly ($P=0.05$) higher in Atrazine + Glyphosate treated plot (49.93mg/kg) while paraquat treated plots recorded the lowest value of available P (6.77mg/kg).

This, however, indicates that increased herbicide application will eventually result in reduction in soil nutrients hence resulting in reduced productivity of crops. The reduction in microbial activities which include dehydrogenase activity, phosphatase activity, microbial biomass, will eventually result in limiting the rate of removal of these herbicides from the environment via biodegradation of the herbicides. Similar results were also reported by Ataikiru *et al.* [20]. They discovered that the phosphatase activities dropped from day 7 to day 21 before increasing on day 28. They also reported that dehydrogenase activity in the treated soils increased from day 1 to day 28. They stated that phosphatase activity showed a decrease in paraquat treated soils from day 7 (13.00 µg nitrophenol/g soil) today 21 (10.855 µg nitrophenol/g soil) and then increased on day 28 (12.07 µg nitrophenol/g soil). There were variations in the values of carbofuran and the control during the investigation. The variation in phosphatase activity with respect to different pesticides and days was significant at $P=0.05$ value. However, in their study, Wolinska and Stepniewska [21] reported that dehydrogenase activities significantly decreased following the application of atrazine, primextra, paraquat, and glyphosate in field settings. Wolinska and Stepniewska [21] also discovered that atrazine and Nicolsulfuron significantly reduced the amount of microbial biomass carbon in soils. They

also explained that applying herbicides to the soil can have both positive and negative effects on several soil microorganisms, which may change how soil carbon cycles. This research demonstrated that microbial respiration reduced significantly. This correlated with the research report of Wolinska and Stepniewska [21], who found that herbicides did not significantly increase soil microbial respiration. Dennis *et al.* [25] also reported that when applied as Gramoxone or as a pure compound, paraquat suppresses culturable soil bacteria (Gramoxone), reduce dehydrogenase activity, (Gramoxone), increase urease activity (pure) and exert both positive (pure) and negative (Gramoxone) effects on soil fungi and invertase activity (pure). Paraquat is also mixed with diquat in commercial herbicides, which have been observed to increase soil fungi (Sprayseed), reduce soil nematodes and bacteria, and suppress nematode diversity (Preeglone Extra). Soil, treated with recommended rate of herbicides significantly ($P \leq 0.05$) increase the organic carbon content of the soil at the end of the sampling period. Olanrewaju *et al.* [26] reported that soils treated with twice the recommended rate of pre and post emergence herbicide significantly decreased the organic carbon content of the soil at 10-12 weeks after herbicides application compared to the control plot. Significant decrease in the carbon content of soils treated with 6 L/ha of S-metolachlor and 3 L/ha of Nicosulfuron could be adduced to lysis of microbial cell following the adsorption of the chemicals by the soil microorganisms due to the toxicity created by the herbicide at such high concentration.

In this study, treatment of soils with paraquat and atrazine resulted in significant ($P \leq 0.05$) reductions in the pH, acidity (H^+), Na, K, Ca and Mg values of the soil samples after treatment with paraquat. The highest mineral contents of the soil samples after analysis occurred in the soils that had no record of herbicide treatments. Olanrewaju *et al.* [26] similarly reported that herbicides applied at twice the recommended rate significantly ($P \leq 0.05$) decreased the exchangeable bases, such as Na^+ , Ca^{2+} , K^+ and Mg^{2+} , when compared to all the treatments. Lemma [28] also reported that Magnesium, Sodium, Calcium and Potassium have been established to decrease with decrease in soil organic carbon. In addition, the use of pre and post emergent herbicides significantly ($P \leq 0.05$) increased the magnesium content of the soil. This may be due to the herbicide's degradation processes in the soil, which produced breakdown products containing magnesium and helped in the release of magnesium from soil minerals, boosting the soil's magnesium concentration [29]. The cation exchange capacities of the atrazine and paraquat treated soils reduced drastically after treatment. The values obtained in the paraquat treated soils were significantly lower compared to the soils treated with atrazine. This might be as a result of the mode of actions of the two herbicides with atrazine being a selective systemic herbicide and paraquat a contact herbicide. Tudarado-Aherobo and Ataikiru [32] reported that the cation exchange capacity in the soil of carrot and maize farms (which had a history of chronic use of atrazine and glyphosate) were higher relative to the control at 15-30cm depth, while at 0-15 cm depth, the cation exchange capacity was higher in the carrot farm, but lower in the soil of maize farm (78.65 ± 0.08 meq/g) at 0-15 cm. The CEC values for control soil were 82.86 ± 0.16 meq/g and 68.79 ± 0.10 meq/g at 0-15 cm and 15-30 cm, respectively.

5. CONCLUSION

The results obtained in this study revealed that atrazine and paraquat caused significant reduction in soil microbial activities and soil nutrient status. This study has also shown that increased treatment with doses higher than company recommended rates caused significant depletion of the microbial population and soil microbial activities. The nutrient status in soils treated with paraquat showed lower values compared to the atrazine treated soils.

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