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Herbicide Residue Dissipation Dynamics And Residual Effects On Soil Physicochemical Parameters Of A Pilot Maize Farm

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Abstract: ***Herbicide application to control the growth of weeds in farming has its attendant effect on the ecosystem. The rate of reduction of applied herbicides concentration (pre-plant: glyphosate, pre-emergence: atrazine, and post-emergence: 2,4 D amine) were studied on a pilot maize farm and the impacts on the soil physicochemical parameters using standard methods. Glyphosate and atrazine followed a linear regression equation while 2,4 D followed quadratic regression equations. The regression equations were fit for the predictions of the residues by having high R^2 values (0.82-0.98) and their ANOVA P-value was less than 0.05. Regression Model prediction of half life for glyphosate, atrazine and 2,4 D were 80 days, 63 days and 10 days respectively whereas first order equation prediction of half life for glyphosate, atrazine and 2,4 D were 16 days, 37 days and 10 days respectively. There is convergence of prediction on 2,4 D half life. This is as a result of high decomposition rate of 2,4 D in the environment. These are within the range in literature. Soil pH was slightly increased by glyphosate and atrazine application whereas 2,4 D application reduced the soil pH. Soil fertility index and cation exchange capacity of the farmland were slightly improved whereas organic carbon content and percentage base saturation showed no significant difference with herbicide application. Herbicide applications have slight impact on the ecosystem but could be significant if application persist over a long period of time.***

I. INTRODUCTION

Herbicide soil persistence or residual life is the length of time an herbicide remains active in a soil. The soil persistence of an herbicide is often stated as "half-life" which is the amount of time it takes to decompose 50 percent of the applied chemical to an herbicidal inactive form (Aaron and Dawn, 2007). The stated half-life of an herbicide is determined under standard conditions in the laboratory. The half-life of an herbicide in the field will vary depending on environmental and soil conditions. For example, an herbicide with a half-life of 4 weeks would be 50 percent decomposed, with 50 percent remaining in the soil 4 weeks after application. After 8 weeks, 75 percent of the herbicide would be degraded, with 25 percent remaining, and after 12 weeks, only 12.5 percent would remain (Bradberry *et al*, 2004). The time it takes to degrade half of the applied herbicide (half-life) is independent of the herbicide rate that is applied. The herbicide concentration in the soil and the susceptibility of the following crops determines whether rotational crop injury will occur. Most crops on which an herbicide is labeled will tolerate two to four times the highest labeled herbicide application rate. In

the example, the herbicide rate applied is not high enough to injure the tolerant crop, but would kill both the less susceptible and very susceptible weed species present and the susceptible rotational crop. By 4 weeks following application, the herbicide concentration would be low enough that the less susceptible weed species would not be con-trolled, but high enough to injure the susceptible rotational crop. By 6 to 8 weeks after application, the herbicide concentration should be low enough to avoid injury to the susceptible rotational crop (Guyton *et al*, 2015).

The half-life of herbicide in soil is the time it takes for 50% of the chemical to degrade or break down. Metribuzin has an average half life of 60 days. So, after 60 days, only half of what was applied will remain. After 120 days, this 50% of the original amount will have decreased by half again, only 25% will remain. And so on. Soil half-lives are only an indicative guide. Half-life varies with soil type. There are not data for all soil types and the half-life may be expressed as a range or an average (Rachel, 2014). Within soil types, half-lives are affected by pH, temperature, moisture content, sunlight and concentration of active ingredient. Higher temperatures, greater soil moisture, high bacterial activity and high levels of organic matter tend to accelerate degradation; dry and cold conditions tend to lengthen degradation. In Australia, dry or drought conditions are the main factor in causing herbicide residues to persist longer than normal (William, 2001). Some herbicides with persistent soil residues, like hexazinone, do not have agricultural uses but are restricted to industrial and forestry uses instead. These recommendations are made for herbicides which are used to control weeds in crops and pastures. When adopting a crop or pasture rotation, selection of an herbicide needs to take into account following crops as well as the crop and weed to which the herbicide is applied (Andrea *et al*, 2003). Obviously, the selection of the herbicide is made upon grounds such as efficacy, resistance management and integrated weed management. However, as many herbicides are residual, the label needs to be checked for this as well. It is no good selecting an herbicide that gives good weed control only to in its residues in the soil mean you can't plant the following crop you intended. Even if an herbicide is persistent, it may not affect following crops if it is not available to be taken up by the plant, e.g. glyphosate. Some herbicides have a long residual. The residual is not the same as the half-life (Vicente and Yolanda, 2004). Although the amount of chemical in the soil may break down to half the original amount rapidly, what remains can be persistent for long periods, e.g. sulfonylureas.

These warnings let the applicator know the product can damage existing nearby valuable vegetation or can harm crops or pastures that may be planted in the ground if it is cleared (William, 2001). The fact that many herbicides are soil residual is just one reason why it is helpful to keep accurate application records.

II. MATERIALS AND METHODS

THE STUDY SITE

This study was conducted at the pilot farmland situated behind Food Science and Technology Complex, Osun State Polytechnic, Iree (7°55′N, 4°43′E), Osun State, Nigeria. The location is characterised by a bimodial pattern of rainfall with an annual mean of about 300mm. the soil at the experimental site was sandy clay loam.

LAND PREPARATION AND PLANTING

The experimental site was manually prepared using cutlass and hoe, but no fertilizer application was employed. The planting was carried out on plots measuring 5×2 m at a spacing of 60×30 cm with 1 m alley-way between plots. Three seeds of Downy Mildew Resistant (DMR) variety of maize were sown per stand but subsequently thinned to one seeding per stand at two weeks after planting (WAP).

TREATMENT APPLICATION AND EXPERIMENTAL DESIGN

The experiment consisted of four treatments:

- ✓ Glyphosate applied preplant at the rate of 1.41 kg *a.e* ha^{-1}
- ✓ Atrazine applied preemergence at the rate of 3.0 kg *a.i.*ha^{-1}
- ✓ 2,4 D applied postemergence at the rate of 1.0 kg *a.i* ha^{-1} and
- ✓ Handweeding at 3 and 7 weeks after planting. All the treatments were assigned to plots arranged in a randomized complete block design involving three replications per treatment.

SOIL SAMPLING AND PRE-TREATMENT

Soil samples were obtained in dynamics (at 0, 3, 6, 9 and 12 WAT) from each of the treatment plots by sampling randomly about 5 points at 0-15 cm depth. Samples from individual plot was later bulked to form a composite sample and then homogenised and reduced to laboratory size by applying Quartering Techniques. Each soil sample was transported to the laboratories in polythene bags and sieved (<2 mm) to remove plant materials from the soil. The soil samples were stored at temperature <4 ^{0}C prior to analysis.

Maize grains and Stems samples were also obtained by randomly sampling 5 points also, they were bulked, homogenised and reduced to laboratory size by Quartering Techniques. The samples were sieved (<2 mm) and stored in polythene bags and kept in cool and dry place prior to analysis.

HERBICIDE RESIDUES DETERMINATION

Extraction of the herbicide residue: The herbicide residues extraction and analysis were carried out by the following the modified standard test methods of:

- ✓ Modified Luke and Doose (1984) method for multiple residue determinations.

- ✓ Manual of Analytical Methods for the Analysis of pesticide Residues in Human and Environmental Samples, EPA – 600/8-80-30

The samples were kept in less than 4 degree centigrade until analysis. 50.0 g of the sample was weighed into the borosilicate container and 20.0 g of the dried Aluminium Oxide was added along with 25 ml of deionised water and 280 ml of the Acetonitrile. The mixture was stirred for about 2 minutes with magnetic stirrer. The mixture was filtered through the suction to recover the filtrate. 250 ml of the filtrate after the addition of the surrogate standard solution to the sample and later transfer to the extraction bottle that was cocked with TFE-Flourocarbon which was extracted by addition of 100 ml of the Petroleum Ether, 10 ml of the Sodium Chloride saturated solution along with 500 ml of the deionised water. The procedure was repeated twice after the recovery of the organic layer in the separating bottle and the extras of the first and second extraction combined. The extract was washed twice with 100 ml of the deionised water.

The combine extract was dried by pouring through a drying column containing a 10 cm column of anhydrous Sodium Sulphate (previously rinsed with Ethylene Chloride), and the filtrate was concentrated in the concentrator flask with a stream of Nitrogen. The wall of the concentrator flask was rinsed with Methyl Tertiary Butyl Ether (MTBE) so as to bring the final volume of the extract to 5.0 ml.

CLEANING UP THE EXTRACT: The clean-up of the concentrated extract was followed by packing the column with any of the florisil. The extract was eluted with the MTBE and later concentrated to 2 ml.

CHROMATOGRAPHY QUANTIFICATION OF THE HERBICIDE RESIDUE: The gas chromatography with Pulsed Flame Photometric Detector (PFPD) was employed. 2 ml of the extract was injected through the sample port, the equipment was made to run at standard conditions and the chromatograms obtained. The standards were run first and integrated into the equipment for subsequent quantification of the samples.

SOIL CHEMICAL PARAMETERS DETERMINATION

PH DETERMINATION: Equal volume of air-dry soil was passed through 2 mm sieve and distilled water was measured into a beaker, it was allowed to stand for 30 minutes and stirred with a glass rod. The electrode of the pH meter was inserted into the suspension and the pH is recorded.

DETERMINATION OF EXCHANGEABLE BASES (CA, MG, K, NA): 2.5 g of sieved air – dried soil was taken and 25 ml of N ammonium acetate was added to make it to pH 7.0 and was shaken for 30 minutes and filtered through whatman filter paper. N, K and Na were determined on the Flame Photometer whereas Mg, Mn, and Ca were determined on the Atomic Absorption Spectrophotometer.

% ORGANIC CARBON AND ORGANIC MATTER USING WALKEY BLACK METHOD

3.0 g of well ground soil sample was weighed which passed through 0.2 mm non – ferrous sieve depends on how dark the colour of the soil is. 10 ml of 1 N K_2 Cr_2 O_7 was added from an automatic burette, then approximately 20 ml Conc. H_2SO_4 was carefully added using the acid dispenser gently shaken and left to cooled. Distilled water was added to make up to approximately 150 ml mark on the conical flask. 8 – 10 drops of diphenylamine indicator was added the colour was made to be dark violet. 0.4 N ferrous ammonium sulphate was titrated until violet colour changed to green. If a titre required value of less than 5 ml of the ferrous ammonium sulphate, then the sample was repeated with less soil weighed.

Duplicate blank determinations were carried out on 10ml of normal K_2 Cr_2 O_7. All reagents each time a set of determination was done were used.

Calculation: Let y be the volume of millilitres of 0.4 N ferrous ammonium sulphate used to react with the remaining 1 N potassium dichrometer is 0.4y eq. since 10 ml of K_2 Cr_2 O_7 were used in the first place, then the amount used to oxidized and carbon in the soil will be (10.0 – 0.47). 1 ml of $K_2Cr_2O_7$ = 0.003 g Carbon.

However the reaction is only approximately 75% completed. Therefore, 1ml of $K_2Cr_2O_7$ = 0.003 x 100/75 = 0.004gL.

$$\text{The \% C in soil } = \frac{(10-0.41)\times 0.004\times 100}{\text{Vol. of soil taken}}$$

Calculation the % organic matter from the relation

% organic matter = 2% organic carbon x 1.724

TOTAL NITROGEN DETERMINATION IN SOIL (EXTRACTION): 0.7 g of soil samples in digestion tube was weighed and 4 ml of sulphuric acid was added with one kjeldahl tablet. The rack of tubes in the UD 40 Blocks digestor was placed and digested at 350^{0}C for 4 hours. The block from the digestor was removed and cooled about 50ml distilled water was added and the content was mixed vigorously. Wash into a 100ml flask and made up to mark. The flask was shaken properly, allowed to cooled and settled down, %N by distillation method using 40% N and 4% boric acids with methyl red indicator was determined. Green condensate was titrated against 0.01 N HCl

Calculation

$$\%N = \frac{NHCl\times VHCl\times Vt\times 14}{Vs\times 1000\times Ws}\times\frac{100}{1}$$

N HCl = Normally of HCl used in titration

VHCl = Titre value

Vt = total volume made up after digestion (extract volume)

Vs = volume of sample taken (aliquot) 100

Ws = weight of sample 0.2

Determination of Available Phosphorus in Soil Bray 1 Method

Phosphorus A Reagent.

30 ml of 2 N NH_4F + 25 ml of 2 N HCl and made up to 2 L with distilled water. The resulting solution is known as Bray 1.

2 N NH_4 F: 37g of Ammounium Fluoride was weighed in 450 ml of distilled water then make up to 500 ml. 2 N HCl: 768 ml of HCl made up to 1L

Phosphorus B Reagent: Ammonium Molybdate solution

20 g of $(NH_4)_6$ $Mo_7.4H_2O$ (Ammonium molybdate) was dissolved in 170 ml of distilled water heated to 60^{0}C filtered

and cooled. 340ml of conc. HCl was mixed with 32ml of distilled water and cooled.

A to B was added slowly and cooled. 20 g of boric acid (H_3BO_3) was weighed into 500 ml flask and made up to marked with C

Phosphorus C reagent – f – s reducing agent

2.5 g of 1- amino – 2 - naphtha – 4 – sulphuric acid: 5.0 g of sodium metabisulphate and 146.25 g of sodium metabisulphate ($Na_2S_2O_5$) was mixed together. 8.0 g of the mixture in 50 ml of warm distilled water was dissolved and allowed to stand overnight before use in long standing crystallization may occur but this does not interfere with action of the reagent. Fresh phosphorus 'C' reagent was made up from 8.0g of the mixture every 7 days.

Standard Phosphorus solutions

Standard stock (1000 g/ml): 4.390 g of analar potassium dihydrogen phosphate (KH_2PO_4) was distilled in about 900 ml of distilled water in a 1000 ml volumetric flask, made up to marked with distilled water. 1,2,3,4, and 5 ppm standards was prepared from the 1000 ppm

5 g of air dried soil was weighed and 25 ml of 'A' reagent was measured in extraction cup shaken or mechanical shaker for 5 minutes, alternatively stirred for 1 minute. 8 ml of sample or standard solution or blank was pipette into a set of cups. 5 drops of phosphorus 'B' reagent was added and mixed thoroughly. Then 5 drops of phosphorus 'C' reagent was added and mix thoroughly. The solution was allowed to stand for 30 minutes. Then red on the calorimeter at 660 nm wavelength, reading was recorded. P value from standard curve was determined.

Working standard solution (2.5 ppm): 25 ml of the 100 ppm stock solution was pipetted and diluted to 100 ml with distilled water. This of and air solution contains 25 mgs per ml.

Extracting solution – KH_2 PO_4 solution containing 500 ppm P, 4.39g of KH_2PO_4 was weighed into 2 litres of water = 500ppm

5 g of soil was weighed and 25 ml of the extracting solution was added and shaken for 30 minutes. 10 ml of the sample aliquot was pipette into 25 ml volumetric flask. Distilled water was added to make the volume to approximately 20 ml.

1 ml of the gelatin – $BaCl_2$ reagent was added, made up to volume with distilled water the content was mixed thoroughly and it was allowed to stand for 30 minutes. The %T and optical density at 420 sp. was determined within 30 to 60 minutes on spectronic 20 colorimeter. The content was shaken in the flask before pouring into the photo test tube. A set of standard S solution containing EOPPA, 1ppm 2ppm, 3ppm, 3ppm, 5ppm, or 25, 50, 75, 100, 125, veg 304 – 5 per 25 ml was prepared from the working standard solution. The standard solution should of course contain 1 ml of gelatin $BaCl_2$ reagent and 10 ml of the blank digest or extracting solution.

TRACE ELEMENT IN SOILS (AVAILABLE COPPER, IRON, MANGANESE AND ZINC)

Extracting solution: 1.9 g EDTA in 1litre of 1N ammonium acetate pH 7

5 g of air-dried 2 mm sieved soil was weighed into the extraction bottle 25 ml of 1 N ammonium acetate containing 0.01 N EDTA pH 7 was added. The bottle was covered and shaken for 30 minutes on the mechanical shake. Filtered through Whitman filter paper No1, the elements were determined on the Atomic Absorption Spectrophotometer (AAS).

III. RESULTS AND DISCUSSION

Herbicide decompositions and dissipations in the soil is shown in Figure 1 and it shows the residual amounts of glyphosate, atrazine and 2,4 D in the soil measured as the amount of the concentration of the herbicides detectable in the soil, measured at 3-weekly intervals over a period of twelve weeks after treatment. Significant difference ($P<0.05$) in soil residual amounts of the foregoing herbicides occurred with increasing time after application. The residues of the herbicides in the soil significantly decreased with increasing time after application. The decomposition is gradual and progresses as the week after treatment increases. The lowest amount of the residues were recorded at 12th week after treatment. The decomposition of the herbicides in the soil were found to be linearly and negatively correlated for glyphosate and atrazine but quadratic for 2,4 D.

The control represent determination of the herbicide content of the soil before any herbicide is applied; the result in part per billion is a safe condition as described by Aaron and Dawn (2007). The rate of decomposition for 2,4 D was higher compared with the rates of decomposition for glyphosate and atrazine. This is noticeable in the sharp significant decrease in concentration from the 1st week to the 3rd week. This trend continued until the end of the experiment. The rate of atrazine decomposition was also higher than that of glyphosate and seen in the extent of decomposions with the time interval. Glyphosate on the other hand decomposes gradually with the least reduction in residue concentration as determined in the soil. The reduction in concentration is linear, just like for atrazine, and negatively correlated. The decomposition continued beyond the period of the experiment, therefore a regression model was established in Table 1. The regression model was formulated based on the rate of decomposition of the herbicides in the soil as measured by the amount of residues of the herbicides (Y) detectable in the soil at 3-weekly interval after treatment (X) for 12 weeks. The accuracy of the model was measured by determining the P^2 value for each model which is an indication of the accuracy of the model and the ANOVA P-value which measured the fitness of the model. The model is only significant and applicable when the ANOVA P-value is less than 0.05. The model was used to estimate the half life of the herbicide residues in the soil of the pilot maize farmland and compared with half life estimations through first order kinetic equation. From Table 1 below, the regression equations for glyphosate and atrazine were linear and negatively correlated while that of 2,4 D was quadratic in nature with negative correlation. The ANOVA P-values for all the equations were less than 0.05 which indicated that all the model equations are fit for prediction. Glyphosate model is 90% fit, atrazine model is

82% fit while 2,4 D model is 98% fit. The regression model gave half life of glyphosate herbicide to be 80 days, atrazine to be 63 days and 2,4 D to be 10 days.

These predictions are in consonance with the range in literature by Andrea *et al.,* (2013), Vicente and Yolanda (2004), US EPA (2003), Tomlinson (2000) among others. Tomlinson edition of pesticide manual of the British Crop Protection Council (2000) gives the half life of glyphosate to range from 3 – 130days, atrazine to range from 60 – 100days and 2,4 D to be 7 days. National Pesticide Information Centre Technical Fact sheet of US Environmental Protection Agency (EPA, 2003) gives the half life of glyphosate to be between 2 – 197days, atrazine to be between 13 to 261 days and 2, 4 D to be between 6 – 10days. First order kinectic equation, ($Y= \ln 2/\lambda$, where λ is the decay constant and equal to the slope of the plotted graph of residue concentration vs time after treatment), predicted half life of glyphosate in the soil of the farmland to be 16 days, atrazine to be 37 days and 2,4 D to be 10 days. There is a point of convergence on the half life of 2,4 D. This could be because 2,4 D decomposition rate is high compare to others, natural factors that could interfere with decomposition process is minimal. This is not the case with glyphosate and atrazine decomposition in the soil, environmental factors could have been responsible for the disparities observed. Soil factors, such as, soil composition, chemistry and microbial activities determine what the half life of the herbicide will be in a particular soil. The climatic variables of various environments are also a determinant coupled with the properties of the chemicals in which the herbicide is made of (William, 2001). Half life of respective herbicides differ with different environments, climatic conditions and soil properties. The persistence of glyphosate and atrazine over a longer period of time in the soil is an indication that they could exhibit residual effects both on the soil and the plant growing on it. Atrazine is known to have residual herbicide effects on soil application (US EPA, 2007). 2,4 D is known not to be persistent under most environmental conditions (National Pesticide Information Center, 2003). The persistence of herbicide in the soil is responsible for contamination of surface and underground waters by glyphosate and atrazine. The long residual effects of herbicide sometimes are not the same as half life; half life refers to the breaking down of the original components of the herbicide applied to half its concentration.

Effect of Exposure to glyphosate is said to be dose related, acute fatal toxicity has been reported in deliberate overdose (Bradberry *et al.*, 2004; Sribanditmongtol *et al.*, 2012). EPA 1993 review considers glyphosate to be non-carcinogenic and relatively low in dermal and oral acute toxity (EPA, 1993). Daniel Cressey reported an on-going review as at March, 2015 of the toxicity of glyphosate. A 2013 systematic review by German Institute for Risk Assessment conducted epidemiological studies, animal studies and in vitro studies that it found valid and found that no classification and labeling for carcinogenicity is warranted for glyphosate. In March 2015, the International Agency for Research on cancer published a summary of their forthcoming in humans (category 2A) based on epidemiological studies, animal studies and in vitro studies; it noted that there was limited evidence of carcinogenicity in humans for non-Hodgkin lymphoma (Daniel, 2015; Guyton *et al.*, 2015; WHO, 2015; Michael, 2015). So, glyphosate is relatively safe except for recent concern.

Exposure to atrazine on the other hand does not enjoy the same recommendation; it was banned in European Union in 2004 when found in ground water in levels exceeding the limits set by regulators. Studies suggest it is an endocrine disrupter, an agent that can alter the natural hormonal system (EC 2004; Danny, 2015). EPA's 2009 review concluded that the agency's scientific bases for its regulation of atrazine are robust and ensure prevention of exposure levels that could lead to reproductive effects in humans. According to Extension Toxicology Network in the US, the oral median lethal Dose (LD_{50}) for atrazine is 3090 mg/kg in rats, 1750 mg/kg in mice, 750 mg/kg im rabbits and 1000 mg/kg in hamsters. The Dermal LD_{50} in rabbits is 7500 mg/kg and greater than 300 mg/kg in rats. The 1hour inhalation LC_{50} is greater than 0.7 mg/kg in rats and 4hour inhalation LC_{50} is 5.2 mg/h in rats. The maximum contaminant level is 0.003 mg/h and the reference dose is 0.035 mg/kg/day (Pesticide Information Profile, 1996).

Figure 2 represent the effects of the selected herbicide application on the soil pH of the farmland. The pH of the soil obtained in the experiment is similar to the one obtained by Cartes *et al.*, (2009); Krzywy – Gawronska (2012); Nannipier *et al.*, (2003); Borkar (2014); Doi and Ranamukhaarachchi (2009); among others. The applications of the herbicide increase the soil pH till about the 6th week, after which it start to stabilize back towards the neutral pH. Application of glyphosate increase the pH of the farm from initial 6.93 ± 0.07 to 7.59 ± 0.14 after the 3rd week and 7.89 ± 0.66 after the 6th week, before it start to stabilize back to 7.32 ± 0.1 after the 9th week and 7.27 ± 0.09 after the 12th week. Application of Atrazine also has similar effect on the soil pH. It increases the pH from initial value of 7.16 ± 0.08 to 7.39 ± 0.11 after the 3rd week, to 7.89 ± 0.10 after the 6th week, before it start to stabilize from the 9th week 7.40 ± 0.13 and 12th week 7.18 ± 0.03. 2, 4 D on the other hand shows different variation compared to glyphosate and atrazine, the soil pH decreases from initial value of 7.13 ± 0.14 to 6.84 ± 0.13, after the 3rd week, and to 6.44± 0.13 after the 6th week, and 6.23 ± 0.14 after the 9th week and 6.05 ± 0.04 after the 12th week. Glyphosate and atrazine had an increasing effect on the pH of the soill whereas 2, 4 D had a decreasing effect on the pH of the soil. The control experiment showed slight significant difference in the pH of the soil over the time of the experiment. The increase observed in the pH of soil of the farmland with glyphosate is justified by the decomposition pathway of glyphosate in which ammonia was released into the soil (Giesy *et al.*, 2000). In the same way, atrazine decomposition also utilises hydrogen ion to release ammonium ion into the soil which leads to observed increase. 2,4 D is acidic in nature, its addition to the soil lead to the observed decrease in soil pH.

Table 2 represents the correlation between soil pH (Y) and the sampling period (X) affected by herbicides treatments, the correlation coefficient for glyphosate, atrazine and the control follows a quadratic equation rather than linear equation. For glyphosate application, the coefficient for quadratic equation is 0.867 and 0.180 for linear, atrazine

application has 0.822 for quadratic and linear and quadratic equations for 2,4 D is very close, 0.952 and 0.958 respectively, which indicated that the two equation is applicable to determine the pH of the soil at any sampling time (X).

Figure 3 represents the effects of selected herbicide on soil fertility index of the farmland. The soil fertility index obtained in this study compare favourably with values obtained by Doi and Rammulchaarachchi (2009). The fertility index is a summation of pH, organic matter, phosphorus content, exchangeable potassium, calcium and magnesium with the values of exchangeable Aluminum deducted from the summation. In order word; soil fertility index = pH + organic matter + available P + exch. K + exch.Ca + exch. Mg – exch. Al (Lu *et al*., 2002). It is an indication of how fertile the soil is. The application of the herbicide to the farmland increases the fertility index of the farmland. This could have resulted from the fact that when the pesticide is applied, the vegetation on the farmland get affected and decomposed on the land; their decomposition on the farmland could have a direct effect on soil fertility index of the farmland. Leaving the vegetation to decompose on the farmland leads to increase in the fertility index of the soil. 0.086 for linear, whereas control has 0.902

for quadratic and 0.287 for linear. The higher the soil fertility index the higher the element and organic matter constituent of the soil available to the plants growing on the farmland (Lu *et al*., 2002).

Table 3 presents the correlation between soil fertility index(Y) and the sampling period(X) affected by the herbicide application. Soil Index of farmland in which glyphosate, 2, 4 D and the control (hand weeding) were applied follow a quadratic equation more than a linear equation because their correlation coefficient(r) for quadratic equation is higher than that of linear. For glyphosate application, the coefficient for quadratic is 0.883, and for linear is 0.348, for 2,4 D application, the coefficient for quadratic is 0.845 and for linear is 0.669 whereas for control, the coefficient for quadratic is 0.918 and for linear is 0.386. So, quadratic application of regression equation is more applicable to predict the soil fertility index at any sampling period (X). The coefficient for linear and quadratic of atrazine is very close, 0.956 and 0.961 respectively. Therefore, the two could be employed to predict the soil fertility index of the farmland at any sampling period (X).

Figure 4 represents the effects of selected herbicides on Cation Exchange Capacity of the soil. The Cation exchange capacity compare favourably with the work of Doi and Ranamukhaarachchi (2009). The cation exchange capacity of the soil is a contribution of soil exchangeable cations (Ca, K, Na and Mg) and the exchangeable acidity. The cation exchange capacity of the farmland follows the same trend with soil fertility index. Cation exchange capacity of the farmland increased with herbicides application (glyphosate, atrazine and 2,4 D). Reduction was observed in the cation exchange capacity of the farmland toward the end of the experiment except for atrazine applied farmland. The initial increase could be due to vegetative decomposition of weeds on the farmland and other organic substances while the usage of cations by plants could be responsible for the reduction.

Table 4 presents the correlation between Cation Exchange Capacity (Y) of the farmland and the Sampling Period (X) and their regression equation. The correlation coefficients for glyphosate and control are higher for quadratic equation than linear equations. Correlation coefficient for glyphosate application is 0.570 for quadratic and 0.329 for linear, for control is 0.957 for quadratic and 0.149 for linear. So, quadratic equations are applicable for glyphosate and control treatments. 2, 4 D treatment showed a close correlation values for quadratic and linear equations (0.872 and 0.750 respectively), the quadratic is favoured above the linear for the predictions. Atrazine treatment correlation coefficient is very close (0.888 for linear and 0.898 for quadratic) which indicated that the two equations are applicable.

Figure 5 represents the effect of the selected herbicide on Percentage Base Saturation of the soil. Percentage Base Saturation refers to the percentage of the number of basic cations that are held on the soil exchange (Cation Exchange Capacity site) in comparison to the total number of site. It is the amount of basic cations that occupy the cation exchange sites divided by the total cation exchange capacity (CEC) multiply by 100 so as to express it in percentage. The result obtained compare favourably with the work of Doi and Ranamukharachchi (2009). There is similarity in values of base saturation obtained with the different sampling period. Glyphosate, 2, 4 D and the control treatments showed an increment in values till the 6^{th} week and followed by decrease in values from that point whereas for 2,4 D, it showed highest values at the first week with constant reduction the end of the experiment. This shows that herbicides has transient effect on the Percentage Base Saturation of the farmland soil.

Table 5 presents the correlation between percentage base saturation(Y) and sampling period (X) and their regression equations as affected by herbicide application. Glyphosate and control treatments follow a quadratic regression equation more than linear because the correlation coefficient (r) of quadratic is higher than that of linear (for glyphosate, quadratic has 0.914 and linear has 0.713, for control, quadratic has 0.969 and linear has 0.722). In the case of Atrazine and 2, 4 D treatments, the correlation coefficient for linear and quadratic are not too different (for atrazine, quadratic has 0.464 and linear has 0.422; for 2,4 D, quadratic has 0.851 and linear has 0.837). So, the two is applicable with quadratic preferred.

Figure 6 represents the effect of selected herbicide on Organic Carbon Content of the soil. The result obtained here also compare favourably with the work of Doi and Ranamukhaarachchi (2009). For Glyphosate and Atrazine treatment, there is no significant difference in the Organic Carbon Content of the soil over the sampling period whereas slight decrease were observed in 2, 4 D and control experiment. This indicated that application of herbicide for cultivation of plant has minimal effects on its Organic Carbon Content.

Table 6 represents the correlation between Organic Carbon (Y) and the Sampling Period (X) and their regression equations as affected by herbicide application. The trend is similar to Percentage Base Saturation correlation. Glyphosate and Control treatments follow a quadratic regression equation more than linear equation. Correlation coefficient of glyphosate application for quadratic is 0.988 and for linear is

0.453. Correlation coefficient of control treatment for quadratic is 0.959 and for linear is 0.549. Atrazine and 2, 4 D treatments correlation coefficient for linear and quadratic are close (for atrazine 0.826 for quadratic and 0.725 for linear, for 2,4 D for quadratic 0.825 and 0.797 for linear).

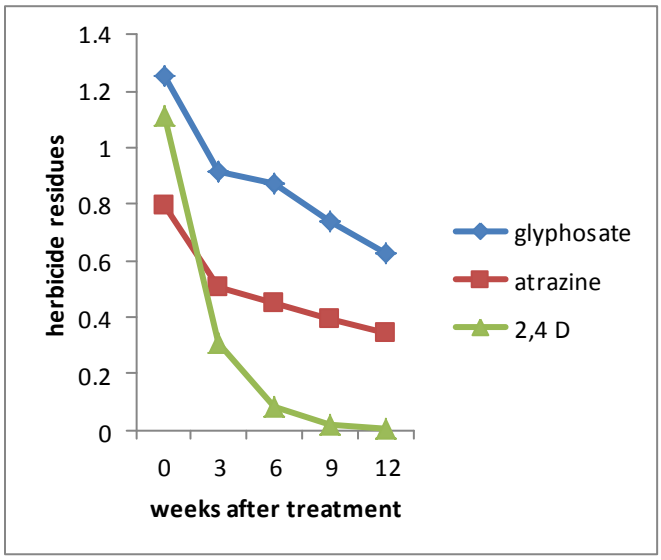

Figure 1: Herbicide residues decomposition in the soil of the pilot maize farm

Herbicide	Correlation Coefficient (r)	Regression equation (Y = a + bx)
Glyphosate	- 0.95	Y = 1.168 – 0.0048x
Atrazine	- 0.91	Y = 0.704 – 0.0341x
2, 4 – D	-0.93	Y= 0.990 – 0.0527x

Table 1: Correlation between Herbicide Residues (Y) and Sampling Period (X) and their Regression Equations

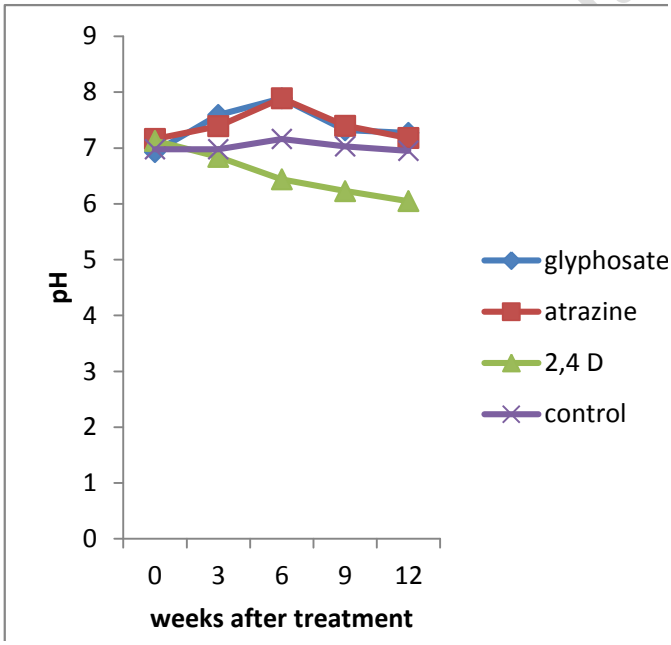

Figure 2: Herbicide application effects on Soil pH

Herbicide	Correlation coefficient(r)	Regression equation (Y = a + bX) (Y = aX^2 + bX + c)
Glyphosate	L = 0.180 Q = 0.867	Y = 7.318 + 0.014X Y = 6.991 + 0.232X – 0.018X^2
Atrazine	L = 0.086 Q = 0.822	Y = 7.454 – 0.005X Y = 7.213 + 0.156X – 0.013X^2
2, 4 D	L = 0.952 Q = 0.958	Y = 7.472 – 0.129X Y = 7.545 – 0.17X + 0.004X^2
Control (Handweeding)	L = 0.287 Q = 0.902	Y = 6.962 + 0.006X Y = 6.866 + 0.070X – 0.005X^2

Table 2: Correlation between Soil pH (Y) and the Sampling Period (X) and their Regression Equations as affected by Herbicide Treatment

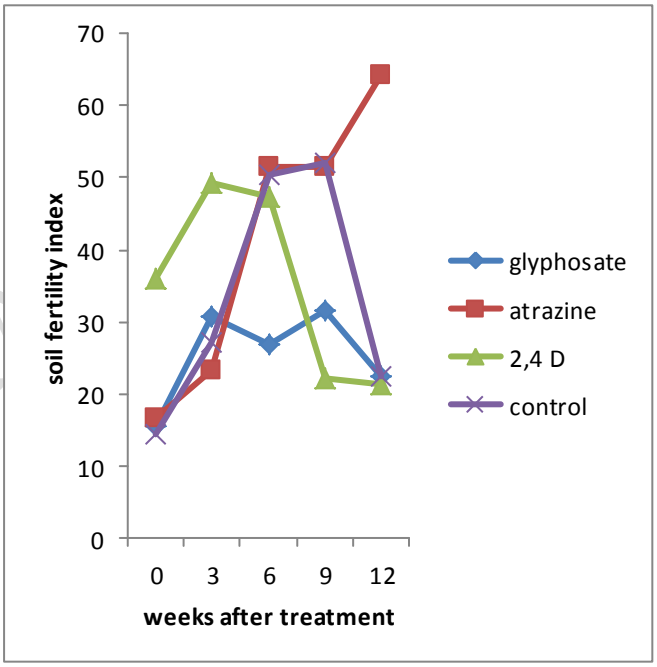

Figure 3: Herbicide application effects on soil fertility index

Herbicide	Correlation coefficient(r)	Regression Equation (Y = a + bX), (Y = aX^2 + bX + c)
Glyhosate	L = 0.348 Q = 0.883	Y = 22.538 + 0.485X Y = 16.812 + 4.302X – 0.318X^2
Atrazine	L = 0.956 Q = 0.961	Y = 16.696 + 4.118X Y = 14.386 + 5.658X – 0.128X^2
2, 4 – D	L = 0.669 Q = 0.845	Y = 46.588 – 1.894X Y = 39.194 + 3.036X – 0.411X^2
Control (Handweeding)	L = 0.386 Q = 0.918	Y = 24.920 + 1.381X Y = 9.786 + 11.471X – 0.841X^2

Table 3: Correlation between Soil Fertility Index (Y) and the Sampling Period (X) and their Regression Equations as affected by Herbicide Application

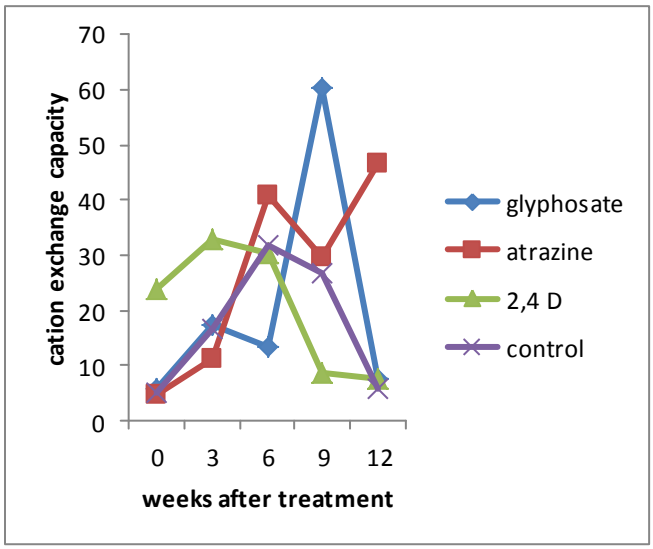

Figure 4: Herbicide application effects on cation exchange capacity of the soil

Herbicide	Correlation Coefficient (r)	Regression Equations Y= a + bX, Y= aX^2+bX+c
Glyphosate	L = 0.329	Y = 1.244 + 1.572X
	Q = 0.570	Y = 9.069X – $0.625X^2$
Atrazine	L = 0.888	Y = 5.998 + 3.418X
	Q = 0.898	Y = 3.282 + 5.229X – $0.151X^2$
2, 4 – D	L = 0.750	Y = 31.782 – 1.865X
	Q = 0.872	Y = 26.169 + 1.877X – $0.312X^2$
Control (Handweeding)	L = 0.149	Y = 14.918 + 0.380X
	Q = 0.957	Y = 2.714 + 8.517X – $0.678X^2$

Table 4: Correlation between Cation Exchange Capacity (Y) of the Soil and the Sampling Period (X) and their Regression Equations as affected by Herbicide Application

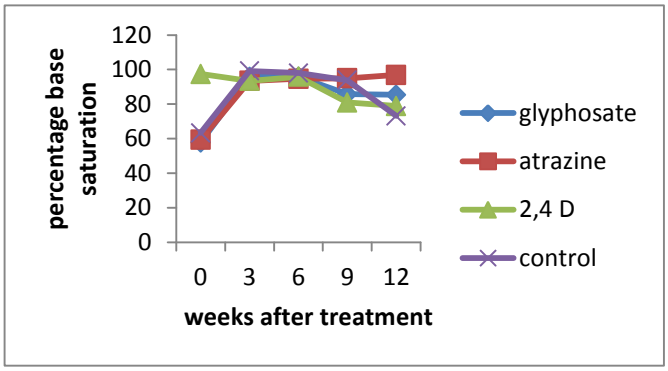

Figure 5: Herbicide application effects on percentage base saturation of the soil

Herbicide	Correlation Coefficient (r)	Regression Equation Y= a + bX, Y= aX^2+bX+c
Glyphosate	L = 0.713	Y = 1.2.178 – 0.963X
	Q = 0.914	Y = 97.821 + 1.942X – $0.242X^2$
Atrazine	L = 0.422	Y = 99.452 – 0.099X
	Q = 464	Y = 99.223 + 0.054X – $0.013X^2$
2, 4 D	L = 0.837	Y = 101.492 – 0.917X
	Q = 0.851	Y = 100.635 – 0.346X – $0.048X^2$
Control (Handweeding)	L = 0.722	Y = 1.2.214 – 1.065X
	Q = 0.969	Y = 97.383 + 2.156xX– $0.268X^2$

Table 5: Correlation between Percentage Base Saturation (Y) and Sampling Period (X) and their Regression Equations as affected by Herbicide Application

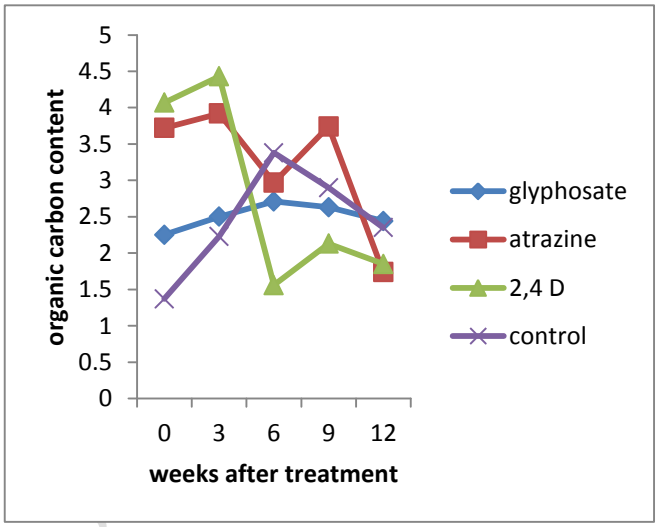

Figure 6: Herbicide application effect on organic carbon content of the soil

Herbicide	Correlation Coefficient (r)	Regression Equation Y= a + bX, Y= aX^2+bX+c
Glyphosate	L = 0.453	Y = 2.404 + 0.017X
	Q = 0.988	Y = 2.237 + 0.128X – $0.009X^2$
Atrazine	L = 0.725	Y = 4.046 – 0.138X
	Q = 0.826	Y = 3.663+ 0.117X – $0.021X^2$
2, 4 D	L = 0.797	Y = 4.156 – 0.225X
	Q = 0.825	Y = 4.465 – 0.430X + $0.017X^2$
Control (Handweeding)	L = 0.549	Y = 1.920 + 0.088X
	Q = 0.959	Y = 1.284 + 0.511X – $0.035X^2$

Table 6: Correlation between Organic Carbon content (Y) and the Sampling Period (X) and their Regression Equations as affected by Herbicide Application

IV. CONCLUSION

Herbicide decompositions in the pilot maize farm were gradual. It was linearly and negatively correlated for glyphosate and atrazine. The rate of decomposition of 2,4 D was higher and negatively correlated but quadratic in nature. Regression model was developed based on the reduction in the concentration of the residues in the soil of the pilot maize farm with increasing time after treatment. Glyphosate and atrazine followed a linear regression equation while 2,4 D followed a

quadratic regression equations. The regression equations were fit for the predictions of the residues by having high R^2 values (0.82-0.98) and their ANOVA P-value was less than 0.05. Regression Model prediction for glyphosate, atrazine and 2,4 D were 80 days, 63 days and 10 days respectively whereas first order equation prediction for glyphosate, atrazine and 2,4 D were 16 days, 37 days and 10 days respectively.

There is convergence of prediction on 2,4 D half life. This is as a result of high decomposition rate of 2,4 D in the environment. The divergence observed on glyphosate and atrazine prediction could be dependent on natural environmental factors surrounding the field experiment different from laboratory environment Glyphosate and atrazine application to the farm slightly increase its soil pH whereas 2,4 D application slightly decreases its soil pH. Soil fertility index and cation exchange capacity of the farmland is slightly improved by vegetation decomposing on it but depleted as crops grow on it. Organic carbon content shows no significant effects with herbicide applications. Percentage base saturation indicated a transient increase till the 6^{th} week and subsequent reduction till the 12^{th} week.

V. RECOMMENDATION

The use of herbicide on a farmland should be controlled to limit an adverse effect long period application could bring. Manual weeding sometimes maybe employed or the land left for some time to avoid pesticide accumulation on the farmland.

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