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Fate and Mobility of Glyphosate Leachate in Palestinian Soil Using Soil Column

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Abstract

In recent years, pesticides were used heavily in Palestine, which led to the contamination of soil and water and causing many diseases. Many studies focused on the impact of pollutants such as pesticides and oil on soil, humans, animals, plants and the environment in general. Using column study the amount of glyphosate in soil decreases with increasing depth of soil, where it is for 0-30cm(11ppm) > 30-60cm(6ppm) > 60-100cm(2ppm) due to organic content and metal oxides founded in soil that can form stable complexes with glyphosate. When we increased the concentration of glyphosate, the amount of glyphosate (contaminant) in leachate where found to be 25x (15.96ppm) >15x (3.91) > 5x (3ppm) column.
The behavior of glyphosate leachate fits the first order reaction and the isotherm is in according with the Freundlich adsorption equation with R^2 value 0.98, k value 6.4 and n value 1.07 which indicates good adsorption to soil.

Keywords: glyphosate, adsorption, leachate, columns, kinetics, organic matter.

1. Introduction

Agriculture plays an important role in the Palestinian economy contributing to food requirements and providing jobs to more than 50% of the population. The total agricultural land in Palestine is approximately, 18,340 donums 83% in the West Bank and 17% in Gaza [1].

Agriculture needs good soil, clean water and sun light. Here in Palestine many factors affect soil, surface and ground water. The extensive use of pesticides, fertilizers in agriculture, as well as disposal of wastewater from Israeli settlements in the West Bank, is also cited as contaminating the soil and further reducing the water resources available for Palestinians.

Glyphosate [*N*-(phosphonomethyl)glycine] is a good example of such a compound. It was introduced by Monsanto (St. Louis, MO) in 1974 and is the most frequently used herbicide worldwide in both agricultural and nonagricultural applications. It is a nonselective herbicide that is taken up by plants after application on leaves and shoots and thereafter transported throughout the whole plant. Glyphosate is today often found in surface waters and occasionally also in groundwater, despite strong sorption to soil materials [2]. Studies investigating the mobility of glyphosate in soil also indicate that the potential for leaching appears to be limited [3], although there are studies showing that leaching may occur [4].

A leaching mechanism for strongly sorbed chemicals that has received increasing attention during recent years is what is referred to as colloid-facilitated transport [5]. Th rough this mode of transport, in combination with preferential flow, strongly sorbed compounds can potentially migrate long distances in soil. This can be one explanation why glyphosate is frequently found in surface waters and sometimes even in groundwater, although there is still no strong evidence for this hypothesis.

Inactivation is thought to be the result of strong sorption of the molecule to soil components [6] and rapid degradation by soil microorganisms.

Because of its strong sorption and rapid degradation, glyphosate is not supposed to cause environmental problems or affect the quality of the water resource [7-8]. However, not many studies have been undertaken under outdoor conditions [9] and they are not easy to compare because of different experimental conditions, and climate and/or soils whose consequences are difficult to assess. In addition, the results of these studies vary and are sometimes conflicting. Even the results of studies conducted in the laboratory [10] do not agree, although they tend to show weak leaching of glyphosate. However, this herbicide and its metabolite aminomethylphosphonic acid (AMPA) are frequently found in surface water and even in groundwater [11] at concentrations above the EC limit of 0.1 µg/L.

Hazardous chemicals and their intermediate metabolites may reach ground water and contaminate it. Once contaminating groundwater it is difficult and costly to treat it [12].

The aim of this study is to assess the risk of glyphosate leaching into deep layers of soils and to verify if observed leaching concentrations may have an impact on non-target organism.

The study of glyphosate will be investigated on two levels; the batch sorption and column experiment.

2. Experimental

2.1. Chemicals

Glyphosate(purity 98.5%) was purchased from Monsanto Company in USA. Other chemicals like carbon disulfide, copper nitrate and chloroform were available at the department of chemistry at An-Najah National University. All chemicals and solvents used in the experiment were of high performance liquid chromatography and high purity.

2.2 Acid digestion of soil

To find the metals in soil a 0.5-1.0 gram of soil transfered into a clean 100 mL Teflon beaker and wet with 5 ml of distilled water. Two ml of $HClO_4$ (70%) and 12 mL of HF (40%) were added then heated to incipient (near dryness). Again 8 ml of HF were added and heated to dryness. Two ml of $HClO_4$ and about 5 mL of distilled water were added and heated to incipient. The remaining residue was dissolved in 8 mL of HCl and 20 mL of water. Volume was made up to the 100 mL volume and stored in polyethylene bottle. Fe and Cu in the supernatant were determined by AAS [13]. The physico-chemical soil properties (Table. 1) were determined using standard methods.

Table. 1: Physico-chemical characteristics of the soil column.

Soil texture	
• Sand [%]	35%
• Silt [%]	57.5%
• Clay [%]	7.5%
Moisture **%**	3.3%
Moisture correction factor (mcf)	1.033
pH	7.62
Organic Carbon %	2.11%
Organic Matter %	3.63%
Conductivity(µs)	530
N%	0.1934%
Ca CO_3 (mg)	0.795
Cu (mg/kg)	44
Fe (mg/kg)	1982.27
Available Phosphorous (P) (mg/kg)	62.41

2.3 . Sampling site and Collection

The soil was sampled in three layers; 0-30cm, 30-60cm and 60-100cm from agricultural locations in Nablus, Mount Gerizim before herbicide treatment of the fields. The soil samples were mixed well separately. The soil used for chemical analysis was air dried, sieved to 2mm stored in the dark at room temperature and protected from humidity. Basic physico-chemical properties of soil were conducted on soil before any treatment with glyphosate**.**

2.4 Leachate extraction columns

Leachate extraction columns consist of four columns of 1m long polyvinyl chloride (PVC) pipe and internal diameter of 15cm. A metal mesh screen was placed at the bottom end of each column and a plastic bottle was placed under each column to collect water. Soil column
was washed with distilled water to remove air bubbles from soil and to ensure that the pH of leachate water from each column is neutral.

2.5 Glyphosate application to soil-column experiment

Glyphosate (Monsanto Co, St. Louis, MO, USA) contains the monoisopropylamine salt of glyphosate (N-(phosphonomethyl)-glycine) (360g/L) was applied to each column with concentrations; 5X, 15X and 25X, where X equals amount of glyphosate applied to soil yearly (nearly 2L / dunom), numbers (5,15,25) are the years of applying glyphosate to soil. Blank soil samples were used as controls without glyphosate addition.
The concentrations of glyphosate added to soil columns are listed in Table. 2.

Table. 2: Main characteristics of soil after application of glyphosate at different depths.

Column	Depth (cm)	PH	C %	O.M %	N %	Available P mg/kg	$CaCO_3$ mg/kg	Fe mg/kg	Cu mg/kg
Blank	0-30	7.45	1.56	2.69	0.145	7.91	0.211	1941	43
	3-60	7.78	1.53	2.64	0.082	5.3	0.245	1997	38
	60-100	7.7	1.36	2.33	0.024	5.27	0.292	2008	52
5x	0-30	7.55	2.08	3.58	0.321	66.62	0.147	1853	30
	30-60	7.86	2.05	3.53	0.270	48.49	0.161	1953	35
	60-100	7.72	2.03	3.49	0.250	45.71	0.199	2000	64
15x	0-30	7.68	2.08	3.58	0.373	72.57	0.194	1909	35
	30-60	7.75	2.02	3.48	0.356	66.1	0.197	2053	44
	60-100	7.88	1.99	3.42	0.305	53.26	0.208	2103	52
25x	0-30	7.49	2.21	3.80	0.425	95.04	0.178	1909	24
	30-60	7.56	2.05	3.53	0.375	88.31	0.206	1985	29
	60-100	7.66	2.01	3.46	0.319	74.13	0.200	2032	34

The glyphosate was leached out from the column with water until glyphosate could no longer be detected in the column effluent.

2.6 Leachate

Leachate was collected from each column in plastic bottle at the end of every period. Leachate volumes were determined gravimetrically, stored at 2°C in dark prior to analysis and analyzed within a week.
Leachate water was centrifuged to remove solid particles and then the supernatant was filtered through a 0.45μm membrane filter paper before analysis. Glyphosate extracted by the method described below (2.7) and derivatized using the method shown below (2.8) then measured by Spectrometer at 435 nm.

2.7 Procedure for Solid-Phase Extraction (SPE) of glyphosate from water samples

A cation exchange resin was used for the pre concentration and cleanup of glyphosate. A slurry of the Amberlite IR-120, Na-ion exchange resin (cationic) (ACROS ORGANICS, New Jersey, USA) was made in 10 mL distilled water and packed into a narrow glass column (4.8mm wide, 30cm long), plugged with glass wool at the bottom. The resin was rinsed with distilled water and then with 1M HCl at a flow rate of 2 mL/min several times before sample application. The pH of water sample spiked with glyphosate was adjusted to 2 and amine group of glyphosate was
converted into its protonated form. The protonated sample (25 mL) was passed through the column at a flow rate of 0.5mL/min in order to have maximum exchange of protonated sample. After the loading step, the sorbent was washed with 25mL of 2M NaCl solution (used as eluent) at the same flow rate. The eluted solution was evaporated to about 10mL at 70ºC then evaluated by the proposed method [14].

2.8 Derivatization procedure of glyphosate

Glyphosate was derivatized using carbon disulfide to convert the amine group into dithiocarbamic acid. The dithiocarbamate group was used as chelating group for reaction with transition metal ion Cu (II). The resultant yellow colored complex was measured at 435 nm using UV- Spectrophotometer.

Carbon disulfide (1% CS_2) solution was prepared by mixing 0.5mL CS_2 in chloroform and diluted to 50 mL with chloroform. An aliquot of 10 mL of glyphosate were added to a series of 100 mL separating funnels followed by the addition of 5mL of 1% CS_2 solution. Then the mixture was shaken for 3 minutes for the formation of dithiocarbamic acid. A 0.4 mL ammonical solution of Cu(II) (1000 mg/L) was added to the mixture, shaken again vigorously to form complex with dithiocarbamic acid and then kept for separation of two phases. The yellow colored chloroform layer containing the complex was separated in a 10 mL flask and diluted with ethanol. The absorbance of the complex was measured at 435 nm. (The product is slightly soluble in lower alcohols) [15]. Ammonical solution of Cu(II) prepared by dissolving an appropriate amount of Cu $(NO_3)_2$ in (20 mL) distilled water and diluted to 100 mL with ammonia solution.

2.9 Soil columns after glyphosate application

At the end of the experiment, soil columns were cut into three parts. Three samples were taken from each part, air dried and stored in an air tight polythene bottle to analyze their parameters in soil lab at An Najah National University. Glyphosate were extracted from the three parts of soil columns, derivatized and measured spectrophotometrically.

2.10 Instruments

Absorbance readings of glyphosate were detected using Spectrophotometer (Spectro 23 RS from LaboMed, inc.USA) at 435 nm using a glass cell with an optical path length of 1cm. pH was measured using pH and conductivity meter(3540 JENWAY).

2.11 Batch sorption experiment

Sorption kinetics was analyzed by altering the contact time at a constant concentration of 20 and 30 ppm per vessel for determination of an appropriate equilibrium time at room temperature for the sorption isotherm experiments. They were shaken for 1, 2, 4, 6, 8, 24, 48 and 72 hours, respectively. Samples were equilibrated and processed.

2.12 Adsorption isotherm experiment

Soil samples were air-dried, sieved to 2 mm, stored in the dark at room temperature (23 ◦C), and protected from humidity. Sorption experiments were carried out using the standard batch equilibration method. A series of five selected glyphosate concentrations were carried out to determine the adsorption isotherms of glyphosate on soil. The adsorption measuring steps were as follows:

- 200 ml of a PTFE vessels containing 25g air dried weight soil.
- 100 ml aqueous solutions containing 0-50mg/L glyphosate were equilibrated for 24 hr at room temperature on a reciprocating shaker at low speed 120 excursions per minute.
- The supernatant equilibrium concentration is obtained after centrifuging at 3000 rpm (round per minute) for 20 minutes.
- Blank without glyphosate was also equilibrated. The equilibrium concentrations of each soil were measured spectrophtometrically after derivatization.

Consequently, the differences between the initial and equilibrium concentrations were assumed to be due to sorption onto soil. Sorption isotherms were obtained by plotting the amount of glyphosate sorbed per weight of soil at equilibrium (Q_e, μg/g) versus the amount of glyphosate per volume of solution at equilibrium (C_e, μg/mL). The sorption data were described using the Freundlich equation:

$$Q_e = K_f \, .C_e^{nf} \qquad \text{eq. 1}$$

where Qe is the concentration of glyphosate sorbed onto the solid phase (μg/g), Ce is the concentration of glyphosate in solution at equilibrium (μg m/L), and Kf (in $\mu g^{1-nf}\, mL^{nf}\, g^{-1}$)
and nf are empirical constants which are related to the adsorption phenomenon and calculated by regression analysis. K_f can be considered as a characterisation of the intensity of sorption, modulated by the deviation from the unity of the nf exponent [16].

2.13 Glyphosate extraction from soil samples

Homogenized soil sample (10g) was extracted for 60 min with 25mL of 2 M NH_4OH solution. The extraction was repeated three times. The pH of eluted sample was re-adjusted to pH 5.4 and was evaluated by the proposed method[14]. Each recovery was performed in triplicates.

3. Results and Discussion

3.1 Batch sorption experiments

The sorption kinetics of the soil were studied to determine an appropriate shaking time for the sorption isotherm experiments. Readings were recorded until 72 hours, no changes in concentrations were observed after 24 hours

for all samples, and therefore 24 hours were chosen as equilibrium time for the sorption isotherm experiment due to the quick degradation of glyphosate [17].
The equilibrium adsorption data over the range of concentrations studied here were used to fit Freundlich adsorption equation (eq. 1).
The values of n within the range of 2-10 represent good adsorption [18]. Higher values of *k* indicate high adsorption capacity. The isotherm equilibrium results for the examined soil are shown in Fig.1. Freundlich isotherm constants (*k* & n) for glyphosate, the correlation coefficient "R" were obtained from Fig. 1. and listed in Table. 2. Glyphosate sorption at 25°C in the studied soils was evidenced to be a kinetics process, with a reasonable equilibration time of 24 hours.

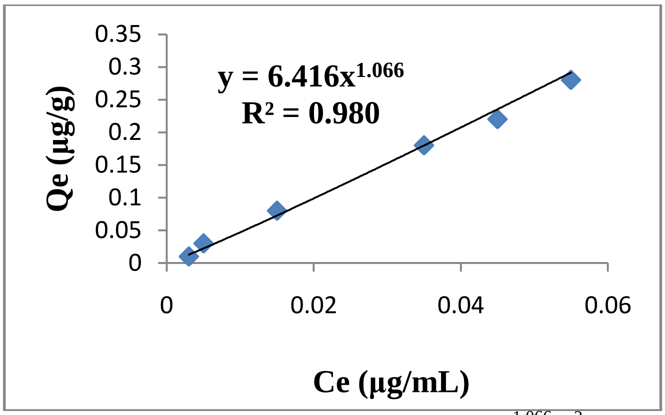

Figure 1: Adsorption isotherm of glyphosate for Palestenian soil($Q_e = 6.416C_e^{1.066}$, $r^2 = 0.9803$).

Literature usually reports Frendlich adsorption constants for glyphosate adsorption by soils [19] which are consistent with that founded in our study. It is indicated from Table. 3 and Fig. 1. that "n" of glyphosate adsorption is higher than 1. The adsorption isotherms for the soil is of S-type [20], which indicates the easiness of the adsorption, mainly at higher concentrations.

Table. 3: Freundlich isotherm constants for glyphosate.

Coefficient	K	1/n	n	R^2
Glyphosate	6.41	0.93	1.07	0.98

3.2 Glyphosate in leachate

It is indicated that the amount of glyphosate detected in leachate decreases with increasing time. It takes time for 25x > 15x > 5x until the inability to detect glyphosate in leachate for concentrations less than 1ppm. Doubling the concentration of glyphosate increases the amount
glyphosate (contaminant) in leachate. The above resulting curves shows that the best fit of the glyphosate degradation data was obtained using a first-order reaction as shown in Fig. 2. DT50 values of glyphosate was 2, 3 and 3.75 days for 5x, 15x & 25x column respectively. This indicate relatively rapid degradation.

3.3 Glyphosate in column soil

The results indicated that the glyphosate mobility in the soil columns increased with application rate. With more glyphosate applied, more glyphosate in the soil columns was capable of moving out of the columns. Amount of glyphosate detected in soil columns was increased in the order :

25x > 15x > 5x.

The amount of glyphosate was decreased with depth increasing due to decreasing organic content. It means that the adsorption tendency decreases as the depth increases. No glyphosate detected in 60- 100cm depth as shown in Fig. 3. This due to low concentration of glyphosate less than 1ppm that couldn't be measured by the method used here. Lowest concentration was used also most of glyphosate adsorbed on the upper layer of soil (0-30cm). This study indicates that glyphosate can be extensively mobile in soil environment if it is applied on soils unable to retain the molecule long enough for its microbial degradation. This may also lead to herbicide leaching to lower soil layers where a limited biological activity occurs.

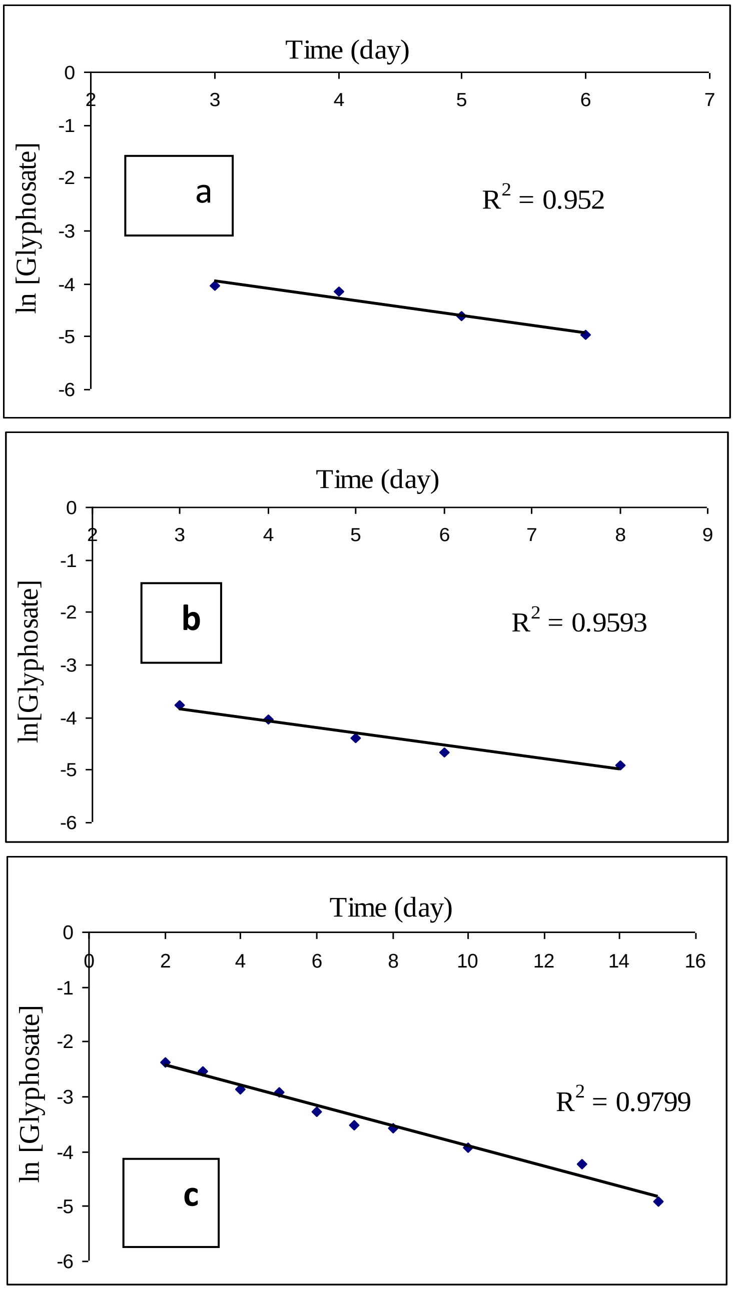

Figure. 2: Plot of time vs. Ln concentration for 5X(a), for 10X and (c) for 25X times glyphosate

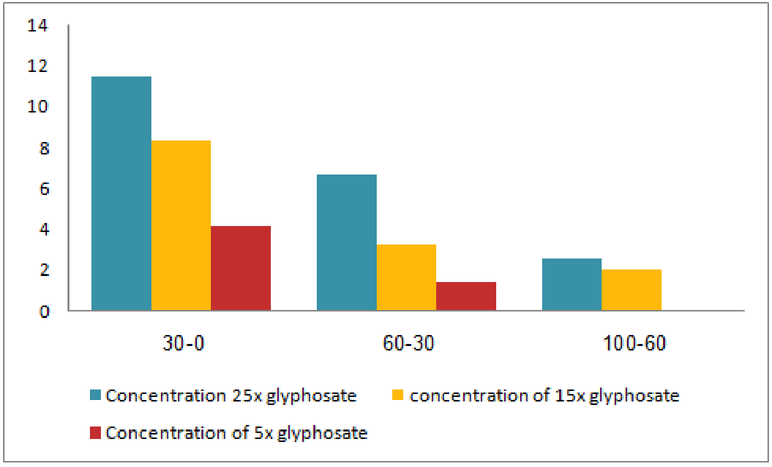

Figure 3: Concentration(mg/L) of glyphosate in soil column at different depths.

3.4 The effect of organic matter

Soil organic matter consists of a variety of components. These include, in varying proportions and many intermediate stages:

- Raw plant residues and microorganisms (1 to 10 %).
- "Active" organic traction (10 to 40 %).
- Resistant or stable organic matter (40 to 60 %) also referred to as humus [21].

Table 4.2 shows that organic matter content of the soil at different depths ranges between 2-3.8% which is considered as a moderate organic matter soil. Organic matter content of the soil at different depths for each column nearly the same as shown in Fig. 4. It is indicated that organic matter only may not affect the adsorption of glyphosate at different depths and it could affect sorption in two ways:

- Reducing glyphosate sorption by blocking sorption sites.
- Increasing glyphosate sorption because poorly ordered aluminium and iron oxides with high sorption capacity are favored at higher soil organic matter content.

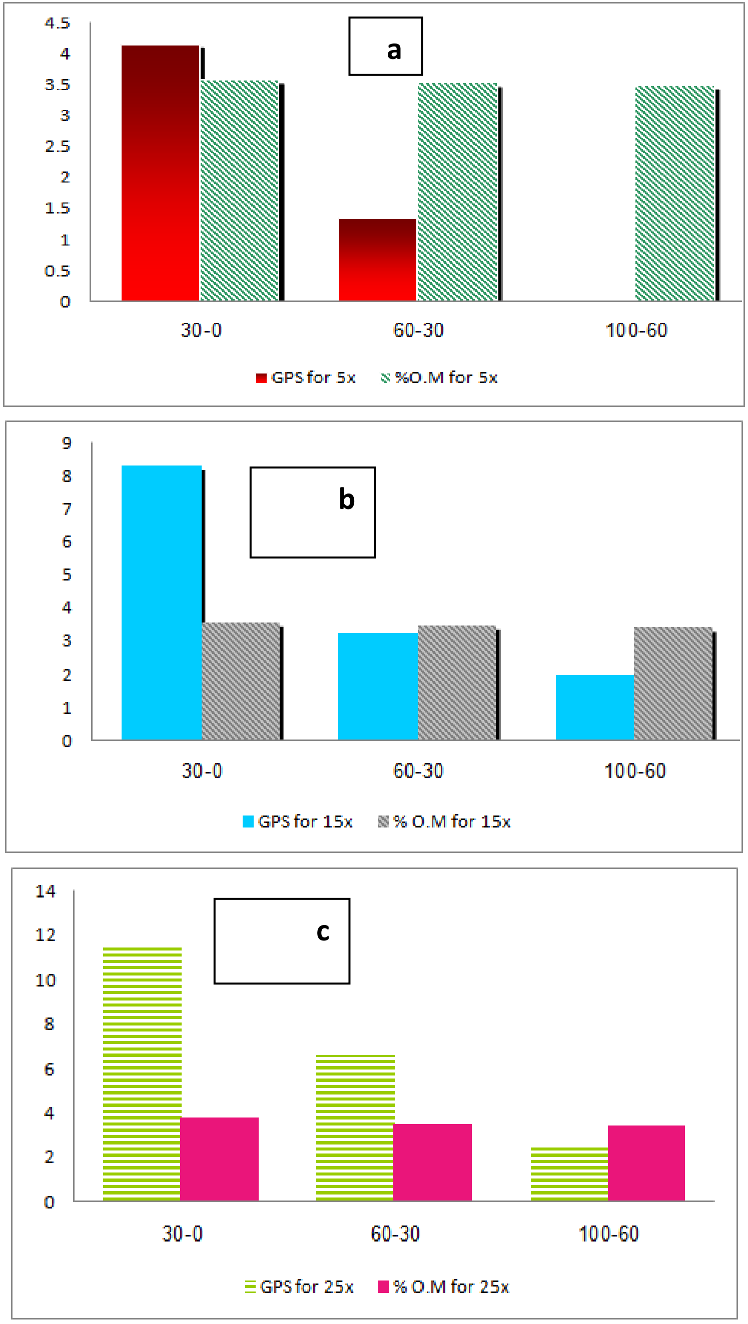

Figure 4: Organic matter content in 5X (a), 15X(b) and 25X(c) column and concentrations of glyphosate at certain depths.

4.5 The effect of soil metals

The high sorption values for glyphosate can be in part due to the pH values of soils and to the presence of iron oxides, copper and other metalls that can form stable complexes with glyphosate. Glyphosate coordinates strongly to Cu, and Cu–glyphosate complexes formed seem to have higher ability to be adsorbed on the soil than free glyphosate. Copper acts as a bridge between the soil and glyphosate.

At these pH values glyphosate is a dianion and both the carboxylate and the phosphonate functional groups in its molecule are deprotonated, being able to compete for the surface adsorption sites on the metal oxides.

4.6 Available phosphorous after glyphosate application

Fig. 5. shows that the amount of phosphorous in soil columns after application of glyphosate increased this indicates degradation of glyphosate to its components where phosphorous is one of the degradation products. Glyphosate could be source of phosphorous, nitrogen and carbon in soil as it’s shown in Fig. 6 and Table 1. The nitrogen content of soil has been increased after glyphosate application to soil columns due to biodegradation of glyphosate.

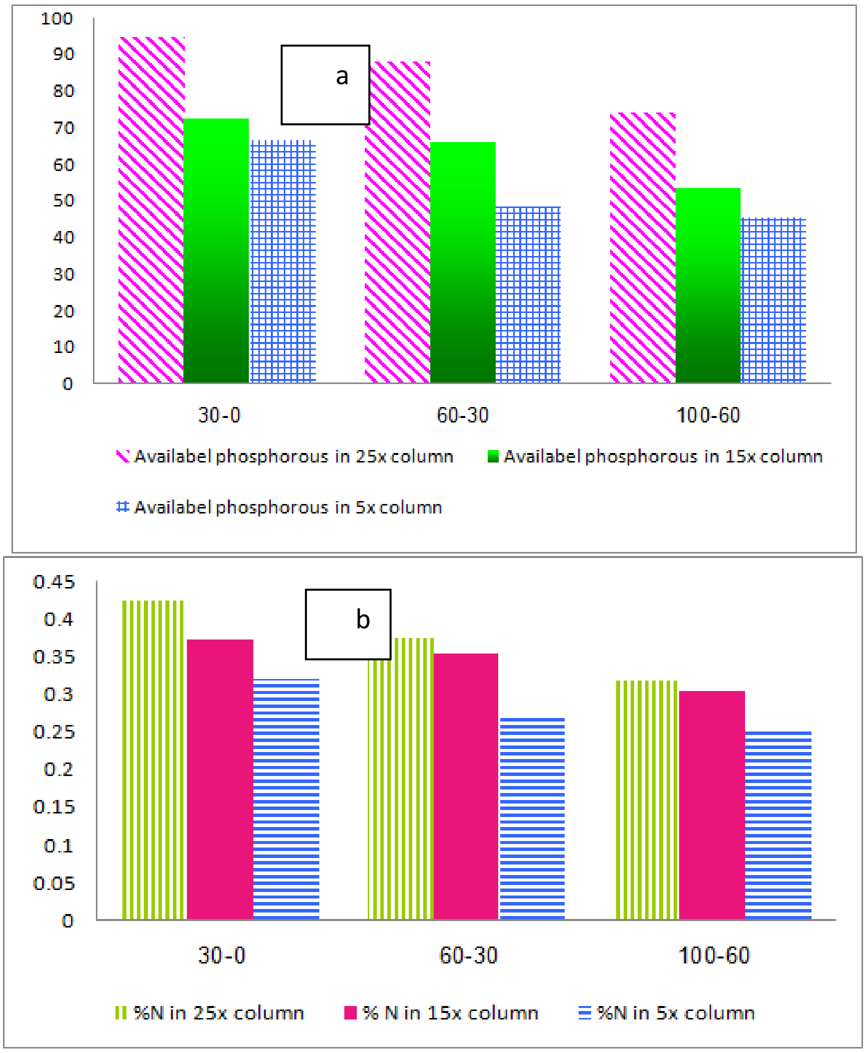

Figure 5: Phosphorous content (a) and nitrogen content(b) in soil columns after application of glyphosate.

Conclusion

Adsorption is an important process in determining the fate of glyphosate in soil. The texture for soil used has been found to be silty clay and the total organic matter (T.O.M) close to 4 %.

Batch equilibrium technique was used to evaluate the extent of glyphosate adsorption on soil as adsorbent. Isotherm is in accord with the Freundlich adsorption equation with R^2 value 0.98; the parameters of this isotherm have been calculated. The adsorption isotherm was fit the S-type isotherm according to Giles. The values of "n" in Freundlich equitation was more than one indicating good adsorption for glyphosate with the soil used. Freundlich constant "*k*" indicates the tendency of glyphosate in this study to be adsorbed on soil particles. *k* increases with increasing the soil minerals and decreases with increasing the depth of soil where the main

binding mechanism for glyphosate is the covalent bond between the herbicide and the metals from soil oxides, and so the adsorption decreasing due to decreasing the organic matter content as depth increases.

Many factors affect the adsorption of glyphosate as phosphorous content, pH, and temperature. The high sorption values for glyphosate can be in part due to the presence of metal oxides that can form stable complexes with glyphosate

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