An-Najah National University
Faculty of Graduate Studies

The Kinetic Study of Glyphosate Leachate in Palestinian Soil at Different Concentrations

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Dedication

To My Mother, Father, Sisters, and Brothers
with Love & Respect

Acknowledgments

Prays be to Allah, the most graceful for granting me the power to finish this work.

I would like to express my deepest gratitude to my supervisors Dr. Shehdeh Jodeh and Prof .Dr. Marwan Haddad for their guidance, encouragements and supervision during this study and dissertation preparation. Thanks to all technicians in the chemistry labs, Chemical, Biological and Drugs Analysis Center (CBDA), Water and Environmental Studies Institute (WESI) and Department of Civil Engineering, soil laboratory for providing me with all research facilities.

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Finally, I thank my mother who supported my decision to undertake a three year long M.Sc.
My great thanks, gratitude and love to my family and friends for their support and sincere encouragement.

إقرار

أنا الموقع ادناه مقدم الرسالة التي تحمل العنوان :

The Kinetic Study of Glyphosate Leachate in Palestinian Soil at Different Concentrations

أقر بأن ما اشتملت عليه هذه الرسالة أنما هو نتاج جهدي الخاص، بإستثناء ما تمت الاشارة اليه حيثما ورد، و أن هذه الرسالة ككل، أو أي جزء منها لم يقدم لنيل اي درجة علمية أو بحث علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

Declaration

The work provide in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's name: اسم الطالب:
Signature: التوقيع
Date: التاريخ:

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The Kinetic Study of Glyphosate Leachate in Palestinian Soil at Different Concentrations

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Supervisors

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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. As a result of increasing environmental issues many centers were established like Water and Environmental Studies Institute (WESI) at An-Najah National University and Birzeit University and Chemical, Biological, Drugs Analysis Center (CBDA) at An-Najah National University.

Many studies focused on the impact of pollutants such as pesticides and oil on soil, humans, animals, plants and the environment in general.

The aim of this study was to study glyphosate kinetically in soil columns.

Laboratory analyses:

- Leachate: the samples were analyzed for glyphosate leachate (herbicides moved through the soil), pH and glyphosate were measured.
- Soil: the soil properties have been tested and classified under two different categories; physical and chemical properties.
    - Physical analyses are: pH, sieve analysis, hydrometer test.

- Chemical analyses are: Kjeldahl nitrogen, calcium carbonate, phosphorus, copper and iron.

The results of this study demonstrated that:

- 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.
- Glyphosate is highly adsorbed to soil due to metal oxides founded in soil where it is for 0-30cm (2000ppm) > 30-60cm (1900ppm) > 60-100cm (1800ppm).
- Doubling the concentration of glyphosate increases the amount glyphosate (contaminant) in leachate where it is for 25x (15.96ppm) >15x (3.91) > 5x (3ppm) column.
- The amount of glyphosate detected in leachate decreases with increasing time. It takes time for 25x (17days) > 15x (13days) > 5x (8days) until the inability to detect glyphosate in leachate for concentrations less than 1 ppm.
- Glyphosate fit the first order reaction.
- Isotherm is in accord with the Freundlich adsorption equation with R value 0.947, *k* value 0.9949 and n value 1.458 which is higher than one indicates good adsorption to soil (Helby, 1952).

- The adsorption isotherms for the soil is of S-type (Giles, 1960), this indicating the easiness of the adsorption, mainly at higher concentrations.

- Glyphosate has relatively rapid degradation; where DT_{50} values of glyphosate was 2, 3 & 3.75 days for 5x, 15x & 25x column respectively.

This study and others help to monitor soil erosion; number and amount of pollutants affect soil. Assessing the extent of soil degradation and identifying hot spots, where many steps and mitigation measures could be taken to reduce soil erosion and maintain soil fertility.

Chapter One
Introduction

1.1 Introduction

Agriculture in Palestine is the chief earner of the overseas exchange and provides the essential needs of the most of the local population (mapsofworld.com, 2010). It is divided into rain-fed and irrigated cultivation.

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.

Hazardous chemicals and their intermediate metabolites may reach ground water and contaminate it. Once contaminating groundwater it is difficult and costly to treat it (Viessman & Hammer, 2005). Glyphosate is a Broad-spectrum herbicide (Cummins & Ho, 2005). It can kill most or all unwanted weeds.

This work focuses on glyphosate residues in soils and ground water of Nablus using soil columns which indicate the first impression of ground water pollution with glyphosate.

There are many factors affect leaching of pesticides to ground water such as:

- Properties of the pesticide; chemical content, persistence, adsorption, solubility, volatility.
- Properties of the soil; permeability, soil texture, soil structure, organic matter, soil moisture, pH, microbial biomass and temperature.
- Site conditions including rainfall, depth to ground water, sinkholes, bedrock, light intensity, temperature, wind and humidity.
- Management practices, including method rate of application and irrigation practices.

All of these factors were taken into account in the study and provide the appropriate conditions similar to nature.

The method used consists of sample preparation, derivatization and UV-Spectrometer detection.

1.2 Palestine

Palestine is located on the western boundaries of the Asian continent directly on the southeastern coast of the Mediterranean Sea, as well as on the eastern boundaries of Africa. This geographical location provides the link between the Asian part and the African part of the Arab world (Palestinian Wildlife Society, 2005).

Agriculture plays an important role in the Palestinian economy contributing to food requirements and providing jobs to more than 50% of the population (ICARDA, 2003). The total agricultural land in Palestine is approximately, 18,340 donums 83% in the West Bank and 17% in Gaza (ICARDA, 2003). The total agricultural land in the West Bank and Gaza in 2000 was 1,860.7 Mio donums of which 1,557.4 Mio and 0.077 Mio donums are rain fed in the West Bank and Gaza Strip, respectively (IPEP, 2006). Palestine is famous of olive trees which are more than just a source of nourishment or profit. In the West Bank, approximately 750,000 donums of land are planted with olive trees, comprising about 50 percent of all cultivated agricultural land in Palestine (and about 80 percent of the orchard lands). Further, there are an estimated 10 million olive trees, producing on average 18,000 tons of olives per year, comprising 12 percent of the total value of agricultural output (Development Studies Programme, 2004). Approximately 19,000 donums of Palestinian agricultural land has been cut off by the separation wall (ACRI, 2009), 6 percent of the land dedicated to olive production in Palestine has been damaged, confiscated, restricted, or destroyed. As a result of the above violations the lost olive yield is estimated at approximately 2,100 tons of olives which mean approximately 8.4 million dollars (Development Studies Programme, 2004).

It is well known that the political situation in the West Bank and Gaza strip affect the agriculture sector. Most of the agricultural production is for domestic use, especially as the products exposed to competition from Israeli products that have freedom of access to Palestinian markets.

Soil and water are polluted in Palestine due to inappropriate agricultural practices (especially an inorganic fertilizers, pesticides), industrial activities (organic pollutants, heavy metals) and solid waste. As these problems increased in Nablus, Jericho, Gaza, Khan Younis and Hebron that suffering bad condition due to lack of waste management , outbreak of Intifada , partial and the total closures which related to public safety. In March 1999, 250 barrels of unknown chemical waste had been buried about near village of Umm al-Tut in Jenin (Sabri, 2005).

Pesticides' leaching through soil to groundwater is complex process controlled by environment conditions. In general leaching to ground water depends on four factors; properties of the soil, properties of the pesticides, hydraulic (total amount of water applied to the soil) loading on the soil and crop management pesticides.

1.3 Extent of Pesticide Usage in the West Bank and Gaza Strip

Pesticides are being heavily used in Palestine for various purposes in household and agriculture. More than 100 metric tons of formulated pesticides (about 75 pesticides) are used annually in Gaza Strip (Safi, et al., 1993). The amount of pesticides used in the Gaza Strip was almost 400 tons in the year 2000 (IPEP, 2006 & IPEN, 2006). 1,300 metric tons of pesticides were used in West Bank at a cost of over 15 million dollars yearly. Application rate of 7kg/donum and 11kg/donum in open agriculture and greenhouses, respectively per year (IPEN, 2006 & CEOHS, 1999). The average seasonal consumption of chemical pesticides was found to be 4kg/donum in open irrigated fields and 6.5kg/donum in irrigated fields covered with plastic houses or tunnels. Of the total pesticides used in the Palestinian territories (P.T), insecticides contribute at 49.4 %, fungicides 33.7 %, herbicides 12.8 % and others 4.1% (Batta, 2003).

In 1995 the total quantity of chemical pesticides used in the P.T was estimated at 730 tons per year in the West Bank, and 741 tons per year in Gaza Strip (Saleh, et al., 1995; Koch-Weser, 1994 & Batta, 2003). About 88.5% of the total irrigated land, and about 18.4% of the total land rain-fed in West Bank, dealing with pesticide where Jericho, Tulkarm and Jenin, consumes about 61% of the total pesticides marketed in West Bank (Rock, 1996 & Krzm, 1999).

Jericho has the worst soil in the region; it is suffering from high salinity and calcium because of the use of water containing high percentage of salt. Also it is suffering from excessive and reckless use of pesticides (Rock, 1996). It consumes about 29% of the total pesticides in the West Bank (Rock, 1996 & Saleh, 1995). Intensive use of pesticides will cause sterile soil and unfit for cultivation.

Table .1.1: Quantities of pesticides used by districts according to cropping pattern*

District Crop Pattern	Nablus	Tulkarem	Jenin	Jericho	Ramalla	Hebron	TOTAL
Irrig. Trees	0.780	9.050	1.514	2.735	0.000	0.000	14.079
Irrig. Field Crops	0.000	0.004	0.000	1.281	0.000	0.000	1.285
Vegetables in Plastic Houses	0.084	18.843	0.840	0.720	0.130	0.000	20.617
Vegetables in Open Fields	2.114	12.834	25.200	77.961	0.960	0.288	119.335
Subtotal	2.978	40.731	27.554	82.697	1.090	0.266	155.316
Rainfed Trees	5.958	12.262	1.986	0.000	17.867	45.407	83.480
Rainfed Field Crops	3.420	3.670	4.000	0.000	1.445	2.740	15.275
Rainfed Vegetable	4.390	1.560	2.500	0.000	6.410	20.888	35.748
Subtotal	13.768	17.492	8.468	0.000	25.722	69.035	134.503
TOTAL	16.476	58.223	36.040	82.697	26.812	69.301	289.819

* (Saleh, 1995)

In 1995a total of 123 pesticides were used in the West Bank, 23 of them are herbicides. Fourteen pesticides are banned (Saleh, 1995; WHO 1993; Safi 1991& Hassoun, 1991).

About 288 tons of glyphosate Isopropyl Amine Salt were used in 1998 (CBS, 1998).

1.4 Impact of Pesticides on the Health of Palestinians in Gaza Strip and West Bank

The extensive use of pesticides especially in agriculture the backbone of economy in Palestine causes harmful effect to environment, illnesses to humans and animals. Excessive amounts of chemical pesticide residues found in fresh commodities of fruits and vegetables which are usually much more than the tolerance limits (Batta, 2003). Many studies were carried out to evaluate the adverse health impact of all types of pesticides on Palestinian people. It was found that 87.5% of farm workers reported one or more symptoms potentially associated with exposures to pesticides burning sensation in the eyes/face, itching and skin irritation, chest symptoms, including cold symptoms, dyspnea, and chest pain, skin rash, and dizziness were the most prevalent symptoms (Abu Mourad ,2005).

Amount of pesticides used in West Bank and Gaza was significantly increasing since early nineties. At the same time there has been a clear increase in the number of infected cancerous diseases (in particular), beside sexually transmitted diseases, genetic, neurological, congenital malformations and abortions (Krzm, 1999). There are hundreds of cases of immediate poisoning of pesticides that reach Gaza hospitals. In the early nineties (of the twentieth century), in Gaza Strip, 19 compounds of pesticides had been monitored; which are internationally prohibited due to cancerous effect, however, pesticides were used there without restrictions or controls or censorship (Krzm, 1999). According to Alshifa'a Hospital in Gaza, since the eighties, cases of cancer was increased, especially cancers of blood (Leukemia), lymphoma, and breast cancer which is known medically that many of pesticides cause it. 3200 cases have been registered as cases of cancer in Alshifa'a hospital in the period between 1990 and 1997 (Krzm, 1999). In Gaza, at the same period, 1500 cases of cancer in men most of them were of lungs, lymphoma and leukemia cancer. It was also found that 40% of children in Gaza were exposed to carcinogens (Krzm, 1999).

Epidemiological association between chronic exposure to pesticides and recorded cases of human malignancy in Gaza Governorates during the years 1990–1999 was studied. Total cases recorded in males were 2277, with average annual incidence and age-adjusted rate/100 000 was 53.2 and 96.8 respectively, whereas the total for females was 2458 cases, average annual incidence and age-adjusted rate/100 000 was 59.7 and 105.3, respectively, over the same 10 years. Lung cancer, lymphomas, leukemia, cancers of the urinary bladder, prostate, brain, colon, stomach and liver were the most abundant among males, while breast cancer, leukemia, lymphomas, cancers of the brain, uterus, lung, thyroid gland and liver were the most abundant in females. There was a highly significant positive correlation between the type of pesticide and cancer incidence for male, female and both (Safi, 2002). In 1992, Birzeit University has examined fresh agricultural products existed in the markets of the West Bank. They found that 52% of the products contain organophosphorus residues. 34% of the same products contain pesticides residues higher than allowed by Israelis (Krzm, 1999& EXTOXNET).

Aims

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

The behavior of glyphosate was investigated on two levels:

- Batch sorption experiments.
- Column experiments.

This thesis consists of four chapters. In chapter Ш of this work the basic physiochemical properties of the soil were determined using standard methods. Sorption capacity of soil for glyphosate determined with batch sorption experiments.

The column experiments aims to investigate whether leaching of glyphosate via soil layers occurs at different concentrations.

Taking into account factors that affect leaching of glyphosate to ground such as:

- Properties of glyphosate; chemical content, persistence, adsorption, solubility, volatility.
- Properties of the soil; soil texture, organic matter, and soil depth.

In chapter IV glyphosate leaching through packed laboratory columns is presented, which aimed to investigate whether leaching of glyphosate via soil occurs. Batch sorption data also presented.

In this study conditions were similar to nature.

Chapter Two

Literature Review

2.1 Glyphosate

Glyphosate (N-(phosphonomethyl) glycine) is a white and odorless crystalline solid, broad-spectrum, nonselective, post emergence herbicide in both agricultural, forestry and aquatic weed control (WHO, 2004). It's used to kill unwanted plant. It was first introduced for agricultural use in 1974 by the Monsanto Company (Baylis, 2000 & Bingzi, et al., 2009).

Glyphosate is very soluble in dilute bases and in strong acids, forming soluble salts. Glyphosate is amphoteric (can be read as a base or an acid) and may exist as different ionic forms, dependent on the pH of the soil or water as shown in (Fig.2.2) (Mensink and Janssen, 1994).

The toxicity of the compound depends on the pH where it is more toxic at a higher pH values (Folmar, et al., 1979 & Vereecken, 2005).

In recent years, glyphosate becomes the biggest selling and fastest growing agrochemical in the world (Baylis, 2000). It has the ability to control perennial weeds which make it essential tool in modern agriculture (Baylis, 2000).

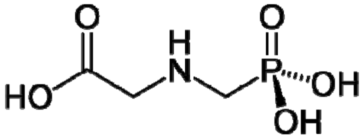
The major formulation of glyphosate is ROUNDUP@ which is made up of glyphosate, a surfactant and water (Monsanto, 1995). Manufacturers add these components to create products that are convenient to handle, mix well with other agricultural products, or facilitate movement of the active ingredient into plants (Hartzle, et al., 2006). ROUNDUPQS, contains

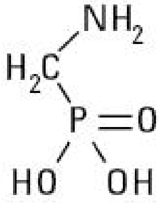
480g/L of glyphosate as an isopropylamine sodium salt, which is equivalent to 360g/L of glyphosate as a free acid (WHO, 1994).

Glyphosate is the major export variety of Chinese technical. From 2006 to April 2008, the glyphosate price was rising gradually (CRI[a], 2009). Due to the successive increases of the global crude oil price in the previous time, the advantages of the biological energy were showed fully. Besides, the global planting areas of the glyphosate resistance genetically modified crops were increased (CRI[a], 2009). It is predicted that the demands will be about 700 thousand tons in 2010. Because of the yield capacity surplus, the price will not increase unseasonably in the next several years (CRI[b], 2009). In china the glyphosate yield capacity will reach 900 thousand tons in 2010, accounting for 70% of the worlds yield capacity (CRI[a], 2009).

Scientists are interested in studying current and future impact of glyphosate on the environment. More attention to the practical aspects of the glyphosate formulations with new adjuvants, or mixtures with other herbicides used to enhance performance.

Table .2.1: Overview of glyphosate's general data*

IUPAC name	N-(phosphonomethyl)glycine
CAS name	N-(phosphonomethyl)glycine
CAS registry number	1071-83-6
Common name	Glyphosate
Molecular formula	$C_3H_8NO_5P$
Relative molecular mass	169.1
Structural formula	
Melting point (decomposes)	below 234˚C
Density	1.7 g/cm³
Solubility	12 g/L at 25 ºC in water, and is practically insoluble in most organic solvents.
Vapour pressure, Pa at 20˚C	Negligible (<1 × 10-5 Pa)
Primary use	Herbicide
Chemical group	Organophosphonate
Physical characteristics	Colorless, odorless, crystalline solid
Stability	Glyphosate formulations are stable for extended periods below 60˚C
Freundlich sorption coefficient(K_F)	0.6-303 LKg^{-1}
Half–life in soil fields	DT_{50} 3-174 day
Half–life in water	DT_{50} 5-91 day

Main degradation product	Aminomethylphosphonic acid (AMPA) 	
Manufacturers	Monsanto,Cenex/Land O'Lakes, DowAgroSciences, Du Pont,Helena, and Platte, Riverside/Terra, Dow AgroSciences, and Zeneca	
Flammability	Not highly flammable	
Solubility in organic solvents	Acetone	0.078 g/l
	dichloromethane	0.233 g/l
	ethyl acetate	0.012 g/l
	Hexane	0.026 g/l
	Methanol	0.231 g/l
	n-octanol	0.020 g/l
	propan-2-ol	0.020 g/l
	Toluene	0.036 g/l

* (Mensink and Janssen, 1994; WHO, 2004; chemyq.com & IPCS, 1994)

2.1.1 Application Scenarios

Application should not take place if the vegetation or soil is very wet or if rain is expected within 6 hours of application (and preferably not within 24 hours of application) (Chris, et al., 2003 & Monsanto UK Ltd, 2007). This is because rain after an application can wash glyphosate off before it has a chance to enter the leaf. Rain also reduces the activity by dilution, so plant may not receive a lethal dose of the herbicide. Glyphosate products are formulated to be mixed with water to facilitate application (Jaffer Company, 2010 & Hartzle, et al., 2006). Water quality (soft or hard) affects on glyphosate's effectiveness. Hard water contains large amounts of dissolved salts as calcium and magnesium salts these salts have a positive charge and may associate with the negatively charged glyphosate molecule, displacing the isopropylamine or other salt used in the formulated product. Plants absorb less glyphosate bound with calcium or magnesium salts than the formulated salt of glyphosate, thus reducing glyphosate activity (Hartzle, et al., 2006).

Glyphosate's performance is affected by many factors, and applicators have little or no control over many of them. The primary cause of weed control failures is a delay in application that allows weeds to reach sizes that are difficult to kill consistently. Timely application and using the proper rate for the specific situation minimizes the effects of factors outside of the applicator's control and reduces the likelihood of performance failures (Hartzler, et al., 2006).

2.1.2 Mode of Action

Glyphosate is systemic, post-emergence herbicide that is phloem-mobile and is readily translocated throughout the plant (Franz, et al., 1997). Glyphosate's primary action is the inhibition of the enzyme 5 enolpyruvylshikimate-3-phosphate synthase (EPSPS) (Della-Cioppa, et al., 1986). EPSPS is the sixth key enzyme on shikimic acid pathway that catalyzes production of 5-enolpyruvylshikimate-3-phosphate from sikimate -3-phosphate (Grossbard and Atkinson, 1985). It occurs only in plant and microbes generate the aromatic amino acids phenyl-alanin, tyrosine, and tryptophane (Uldis and Ronald, 1991).

2.1.3 Persistence

Glyphosate is mainly degraded biologically by soil micro-organisms and has a minimal effect on soil microflora (USDA-FS, 1984 & Massachustts, 2005). Doses of glyphosate <10 ppm were stimulatory to soil microflora including actinomycetes, bacteria, and fungi, while concentrations > 10 ppm had detrimental impacts on microflora populations in one study (Chakravarty & Sidhu 1987). Microbial biodegradation of glyphosate occurs in soil (Sprankle, et al., 1975), aquatic sediment and water, the major metabolite being aminomethylphosphonic acid (AMPA) (CH_6NO_3P). Chemical degradation is negligible and photodegradation occurs in small extent (Franz, et al., 1997). No data on biodegradation under anaerobic conditions are available.

Glyphosate is retained strongly by various soil components (Franz, et al., 1997; Ravanel, et al., 1999 & Patsias, et al., 2001), due to the phosphate functional group strong adsorption of glyphosate to clay minerals such as Fe and Al oxides and organic matter (Glass, 1987; Piccolo, et al., 1996; Morillo, et al., 2000 & Candela, et al., 2007).

Glyphosate is chemically stable in water and is not subjected to photochemical degradation. The low mobility of glyphosate in soil indicates minimal potential for contamination of ground water. Glyphosate can, however, enter surface and subsurface waters after direct use near aquatic environments or by runoff or leaching from terrestrial applications (WHO, 2004).

Glyphosate is considered to be a moderately persistent herbicide with a half-life, $t_{1/2}$, ranging between 10 to 100 days (average 47 days) (Hornsby, et al., 1996). The main route of biodegradation of glyphosate appears to be by splitting the C-N bond to produce AMPA. A second route with splitting of the C-P bond can also occur. AMPA is biologically degradable where the end product is carbon dioxide. Degradation occurs more rapidly in aerobic than in anaerobic conditions. Half-lives for biodegradation in soil between a few days and several months; in water, half-lives between 12 hours and 7 weeks (CCME, 1989).

Leaching of glyphosate was only observed at the sandy and loamy site and, low concentrations (0.1μg/L) of both glyphosate and its metabolite

AMPA have been found in shallow aquifers (Heinz, 1995& Kjaer, et al., 2003).

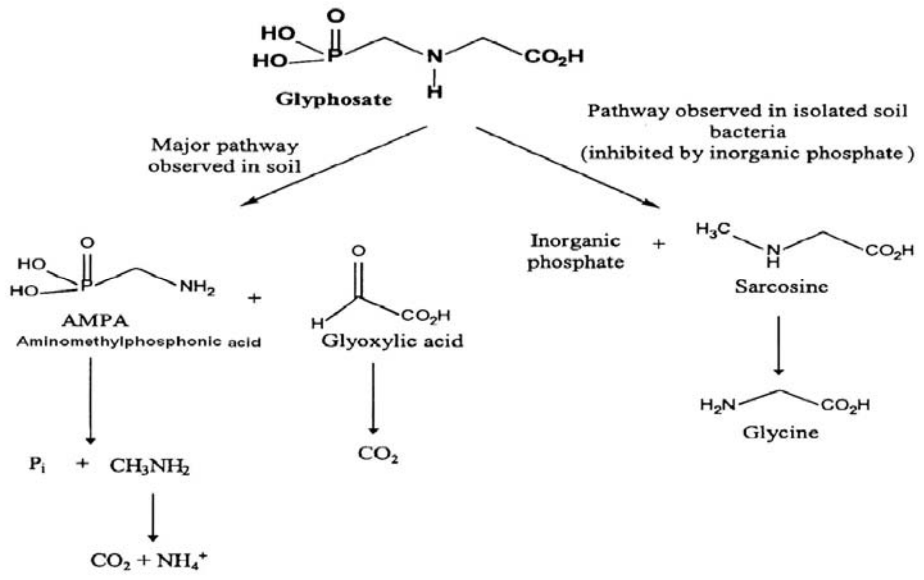


Fig. 2.1: Glyphosate degradation pathway (Schuette, 1998).

2.1.4 Adsorption on Soil

Mobility or leachability of any compound in soil depends on its sorption characteristics; where strong sorption to soil solid decreases mobility of compound, while weakly sorbed compound can readily leached. Glyphosate strongly sorbed after application to soil (Piccolo and Celano, 1994; Tiberg, et al., 1998; De Jonge and De Jong, 1999; Gimsing and Borggaard, 2001; Autio, et al., 2004 & Mamy and Barriuso, 2005). It is a small molecule with three polar functional groups (carboxyl, amino and phosphonate groups). It is strongly sorbed by soil minerals (Gimising, et al., 2004; Gimsing and Borggaard, 2002 & Gimsing, et al., 2007). Glyphosate primary adsorption to soil occurs through the phosphonic acid (organic compounds containing $C\text{-}PO(OH)_2$ or $C\text{-}PO(OR)_2$) moiety in its phosphonate anion form as phosphate (PO_4^{3-}) does in soil (Sprankle, et al., 1975; Piccolo, 1994; Gerritse, et al., 1996; Gimsing and Borggaard, 2001 & Wang, et al., 2005), even though the carboxylic group can also participate in this process. Ion exchange and hydrogen bonding can explain glyphosate soil adsorption (Miles & Moye, 1988).

In literature, there are several papers describing that the adsorption of glyphosate by soils or clays depends on cation exchange capacity (CEC) (the capacity of a soil for ion exchange of cations between the soil and the soil solution. CEC is used as a measure of fertility, nutrient retention capacity, and the capacity to protect groundwater from cation contamination.), clay content (Glass, 1987), organic matter iron and aluminum amorphous oxides (Morillo, et al., 2000). Glyphosate forms mono- and divalent anions with high affinity for, in particular, trivalent cations such as Al^{3+} and Fe^{+3} within the pH rang 4-8 which found in most soils (Sheals, et al., 2002 & Barja and Dos Santos Afonso, 2005).

Phosphate reacts similarly as glyphosate so it may influence the adsorption of glyphosate to soil surface sites it could compete with glyphosate for the surface sites, which may affect glyphosate sorption, and mobility, in phosphate-rich soils (Gimsing , et al.,2004; Gimsing, et al., 2007; De Jonge, et al., 2001& Hill, 2001).

Many studies agreed that by the increase of pH the adsorption of glyphosate decrease (Nomura, et al., 1977; McConnell, 1985; Morillo, et al., 2000 & Sheals, 2002). However, increasing pH by liming seems to have the opposite effect however, increasing of the formation of (more) glyphosate-sorbing aluminium and iron oxides at higher pH (De Jonge, et al., 2001). However, Glass (1987) showed that pH had no effect on the adsorption of glyphosate.

A metal-chelating herbicide (Subramaniam, 1988) is strongly binds to cations, most especially transition metals form metal - glyphosate complexes due to three functional groups carboxyl, amino and phosphonate (Tsui, et al., 2005). The formation of these complexes leads to reduction in the herbicidal activity of glyphosate as well as affecting its bioavailability to microorganisms (Hall, et al., 2000; Tsui, et al., 2005).

Besides the mineral phase, the pH strongly influences the sorption of glyphosate as it governs its electrical charge (McConnel and Hossner 1985; De Jonge and De Jong, 1999& Gimsing and Borggaard, 2004).

Glyphosate can only be sorbed onto variable-charge surfaces, not onto permanent-charge (negative) sites on layer silicates, as it is an anion in the relevant pH range of soils.

Glyphosate is a weak acid have the ability to dissociate in aqueous solution to have four acidity constants: two for the phosphonic group (pK_{a1}, pK_{a3}), one for the amino group (pK_{a4}), and one for the carboxylic group (pK_{a2}) where pK_{a2}, pK_{a3} and pK_{a4} values that have been determined by different analytical methods such as potentiometric titration (Madsen, et al., 1978 & Barja and Dos Santos Afonso,1998), NMR (Appleton, et al.,1998 & Motekaitis and Martell, 1985) or Attenuated Total Reflection (ATR) infrared spectroscopy ATR-FTIR Spectra. However, only three of them can be measured due to the formation of a zwitterion between the amino and the phosphono groups in aqueous solution.

Glyphosate is a zwitterionic molecule that has the ability to form chelating and bridging structures with metal ions and surfaces. The structures of metal complexes commonly consist of two chelating rings where PMG (phosphonomethyl glycine) coordinates through the phosphonate, amine and carboxylate groups (Sheals, et al., 2001, Ramstedt, et al, 2004, Appleton, et al., 1986 & Heineke, et al, 1994).

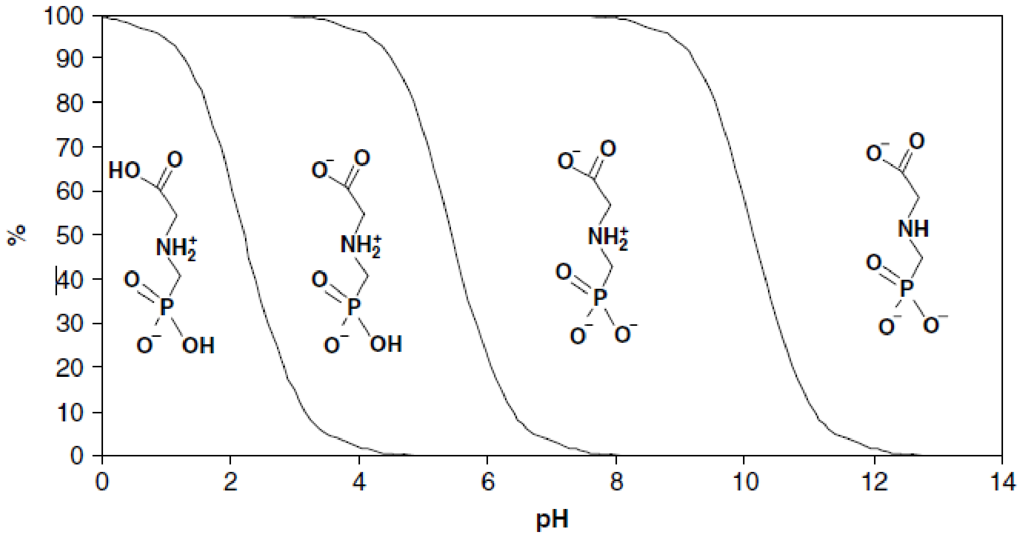


Fig. 2.2: Distribution of glyphosate species as a function of pH (Bjerrum diagram). Acid dissociation constants: $pK_{a1} = 2.22$, $pK_{a2} = 5.44$ and $pK_{a3} = 10.13$. The zwitterionic structure of carboxyl and amino groups is shown in the entire pH range (Borggaard and Gimsing, 2008).

In the presence of Fe and Al mineral surfaces, PMG forms bonds to the surface primarily through the phosphonate group, leaving the amine and carboxylate groups free to interact with metal ions in the solution (Sheals, et al., 2002 & Sheals, 2002) as shown in Fig.2.3

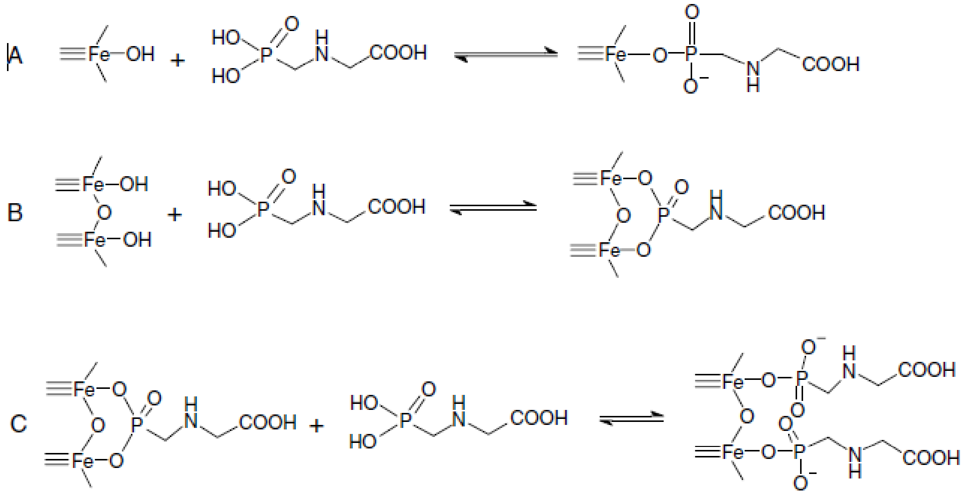


Fig. 2.3: Tentative reaction schemes for glyphosate sorption by an iron oxide:

A: formation of mononuclear, monodentate surface complex.

B: formation of binuclear, bidentate surface complex.

C: formation of dense packed mononuclear, monodentate surface complexes from binuclear, bidentate surface complex at increased glyphosate concentration. Zwitterionic structure of carboxyl and amino groups omitted (Borggaard and Gimsing, 2008).

In contrast to almost all other pesticides, which are mainly sorbed by soil organic matter (SOM) because of their domination by a polar groups, i.e. aliphatic or aromatic carbon, glyphosate is due to its three polar functional groups (carboxyl, amino and phosphonate groups) mainly sorbed by soil minerals.

Soil organic matter only seems to have an indirect effect by blocking sorption sites. However, C_{org} content and clay content have previously been correlated with the ability of soils to adsorb glyphosate (Glass, 1987& Piccolo, et al., 1996).

Glyphosate adsorption to soil is usually described by the Freundlich sorption isotherm. However large variations in sorption capacity of soils are reported in literature with Freundlich sorption coefficients (K_F) ranging from 0.6 to 500000 mg $^{1-n}$ L^n kg^{-1} (Vereecken, 2005).

2.2 Environmental Fate of Glyphosate

2.2.1 Water

Glyphosate is highly soluble in water 11,600 ppm at 25˚C (Kollman and Segawa, 1995), stable in water at pH 3, 5, 6, and 9 at 35˚C (Brightwell and Malik, 1978). Glyphosate enters surface water by direct application to aquatic system, binding to soil that washes of treated terrestrial sites, or drift from treated areas that are near water (monsato, 2003). It is moderately persistent in water and not removed by normal drinking water processing. Glyphosate is more likely to occur in surface waters than ground waters (poptel.org.uk; PAN, 1999 & water-matters.org) due to direct application to aquatic system; stable to hydrolysis in water but undergoes rapid microbial degradation in natural surface waters. Some photolysis can also occur (Brønstad and Friestad, 1985). No appreciable degradation of glyphosate was observed in water via chemical, microbiological or photolytic processes for 78 days (Anton, et al., 1993). Glyphosate's half-life in surface waters after forestry spraying in Manitoba was less than 24 hours.

The maximum contaminant level (MCL) for glyphosate in water stated by EPA is 0.7 ppm (Kollman and Segawa, 1995). According to Canadian Drinking Water Quality the interim maximum acceptable concentration (IMAC) for glyphosate in drinking water is 0.28 mg/L (280 µg/L) (hc-sc.gc.ca).

2.2.2 Soil

In general, glyphosate is moderately persistent in soil. The soil field dissipation half-life averaged 44-60 days (Kollman and Segawa, 1995). The primary metabolite of glyphosate is aminomethylphosphonic acid (AMPA). Degradation of AMPA is generally slower than that of glyphosate possibly because AMPA may adsorb onto soil particles more strongly than glyphosate and/or because it may be less likely to permeate the cell walls or membranes of soil microorganisms (U.S.D.A., Forest Service, 1984).

Glyphosate has a potential toxic effect when applied to soil which is inhibition of symbiotic N_2 fixation (King, et al., 2001) observed in greenhouse and growth chamber experiments using potting media that early applications of glyphosate at a rate of 1.68kg.ha^{-1} delayed N_2 fixation and decreased biomass and N accumulation in glyphosate-tolerant soybean, especially when soil water content was low (Motavalli, et al., 2004).

In the U.S it has been suggested that herbicides, including glyphosate reduce winter hardiness in trees and their resistance to fungal disease (ENDS, 1991). It has been suggested that damage to maple trees increases during the second year following treatment with glyphosate, and that clover planted 120 days following treatment showed reduced nitrogen fixation and growth. This implies that glyphosate which is bound to soil particles can remain active and may be released from soil and taken up by plants (Esty, 1991). The US-EPA has also stated that many endangered plants may be at risk from glyphosate use (US-EPA R.E.D, 1993).

2.2.3 Health Impacts

The producer of herbicide containing glyphosate is Monsanto Company. Its popular trademark is Roundup. It has been reported that exposure to glyphosate causes problems with kidneys or reproductive difficulties, eye and skin irritations. The direct toxicity of pure glyphosate to mammals and birds is low (Pan-uk, 1996). Monsanto claims that extensive testing of glyphosate has shown that it has a low order of toxicity and exhibits no unusual toxicological effects in animals (Monsanto, 1985).

Glyphosate has United States Environmental Protection Agency Toxicity Class of III in 1993 (U.S. EPA, 1993). It has been rated as class I (Severe) for eye irritation. Glyphosate is being evaluated for effects to unborn fetuses and their development. It is currently on the USEPA Endocrine Disrupter Screening list, published in 2007(U.S. EPA, 2007).

It causes many problems as excess fluid in the lungs, pneumonia, lung dysfunction, clouding of consciousness, destruction of red blood cells, abnormal electrocardiograms, low blood pressure, kidney damage and damage to the larynx. Glyphosate is one of ninth chemicals (which are alachlor, beryllium,chromium, 1,1-dichloroethylene, diquat, glyphosate, lindane, oxamyl and picloram) that is cancer assessments postdating the Maximum Contaminant Level Goal (MCLG) (Office of Water, 2003).

Japanese researchers analyzing suicides have found that drinking 3/4 of a cup (200 milliliters) of commercial glyphosate products is fatal (Leu, 2007). However, glyphosate's broad spectrum of herbicidal activity has led to the destruction of habitats and food sources for some birds and amphibians leading to population reductions.

There is, indeed, direct evidence that glyphosate inhibits RNA transcription in animals at a concentration well below the level that is recommended for commercial spray application .Transcription was inhibited and embryonic development delayed in sea urchins following exposure to low levels of the herbicide and/or the surfactant polyoxyethyleneamine. The pesticide should be considered a health concern by inhalation during spraying (Marc, et al., 2005).

It's shown that a brief exposure to commercial glyphosate caused liver damage in rats, as indicated by the leakage of intracellular liver enzymes (Benedetti, et al., 2004). A study of effect of the herbicide glyphosate on liver lipoperoxidation in pregnant rats and their fetuses shows that the effects that 1% glyphosate oral exposure has on lipoperoxidation and antioxidant enzyme systems in the maternal serum and liver of pregnant rats and their term fetuses at 21 days of gestation. The excessive lipid peroxidation induced with glyphosate ingestion leads to an overload of maternal and fetal antioxidant defense systems (Beuret, et al., 2005). Glyphosate has reported oral LD_{50} of 4,320 and 5,600 mg/kg in male and female rats (RTECS, 1982; Massachusetts, 2005& USDA, 1984). In a number of human volunteers, patch tests produced no visible skin changes or sensitization (Weed Science Society of America, 1994). In 2004 WHO said in their report that there was no toxic effects were observed on mice and rates (WHO/FAC, 2004).

Applying of glyphosate to soil increases carbon and nitrogen contents in the soil. An increase in the concentrations of CO_2 in the soil lead to an increase of nitrifying bacteria, which in turn leads to an increase in the concentration of nitrites, making the food grown there also have greater concentrations of nitrites that combined with amines produce nitrosoamines that defined as cancerous substances. In addition, nitrites in high concentrations can produce metahemoglobinemia in animals and human beings. So glyphosate could indirectly lead to carcinogenesis and other pathologies (Ministry of Health and National Institute of Health, 1992).

An Egyptian study of the effects of glyphosate on soil fungi and the decay of organic matter found that treatment with Roundup influenced the soil fungal community structure, reducing some species while enhancing others, and affected soil respiration and rate of decay of organic matter (Abdel-Mallek, et al., 1994).

2.3 Methods of Glyphosate Analysis

Glyphosate is one of the most difficult herbicide to analyze. The difficulty of analysis of glyphosate residues due to its chemical properties , highly solubility of water and polar nature, so it needs to be derivatized because of the lack of chromophore or flurophore (Sahasrabuddhey, et al., 1999; Kun, et al., 2009).

A great variety of analytical methods have been applied for determination of glyphosate residues in soil and water but limited published for food samples. Many analytical methods to determine phosphonic and amino acid group-containing pesticides, which included glyphosate, glufosinate..etc have been published.

Analytical methods for analysis of glyphosate include thin layer chromatography (TLC) (Franz, et al., 1997), gas chromatography (GC) (Alferness& Iwata ,1994), liquid chromatography (LC) (Piriyapittaya, et al., 2008) capillary electrophoresis (Hsu & Whang, 2009 & Goodwin, et al., 2003), electrochemiluminescence (Hsu & Whang, 2009), conductivity detection (Zhu, et al.,1999), inductively coupled plasma–mass spectrometry (ICP–MS) (Guo, et al., 2005), integrated pulsed amperometric detection

(IPAD) at gold electrodes (Sato, et al., 2001), detection by immunosensors (Gonzalez-Martinez, et al., 2005), and the enzymelinked immunosorbent assay (ELISA) method (Rubio, et al., 2003). LC is preferred over GC because of the ionic character of glyphosate. Overview of chromatographic methods, e.g. gas chromatography (GC), liquid chromatography (LC) and ion chromatography (IC) has been presented below.

2.3.1 Gas Chromatography

Gas chromatography is one of the most sensitive methods for residue analysis. Glyphosate, being very polar and non-volatile compound, has to be derivatized for GC analyses. In the literature trifluoroacetic acid (TFAA)–trifluoroacetic anhydride–trimethyl orthoacetate reagent (Watanabe, 2004) , N-methyl-N-(tert-butyldi methylsilyl) trifluoroacetamide **(**MTBSTFA**)** 1% tertbutyldimethyl chlorosilane (TBDMCS) **(**Hori, et al., 2003**)** have been used for derivatisation of glyphosate for GC analyses.

In most cases, derivatization is performed to convert polar N-H, O-H and S-H groups into thermally stable, nonpolar groups. GC derivatization methods can be classified into four groups according to the reagents used and the reaction achieved; silylation, acylation, alkylation and esterification (Sigma-Aldrich, 2002).

2.3.2 Liquid Chromatography

Liquid chromatography (LC) is a method where the compounds are separated according to their partition between stationary and mobile phases. The mobile phase acts as a carrier for the sample solution. The stationary phase is solid support contained within the column over which the mobile phase continuously flows. In general three primary characteristics of chemical compounds can be used to create HPLC separations; polarity, electrical charge and molecular size. In LC exploit polar differences. If the stationary phase is more polar than the mobile phase the chromatography is called a normal phase chromatography. If the mobile phase is more polar the chromatography is called a reversed phase chromatography (RPC). Sample components that partition strongly into the stationary phase spend greater time in the column and are separated from components that stay predominantly in the mobile phase and pass through the column faster.

HPLC analysis of herbicides is most often performed on reversed-phase columns (Tadeo, et al., 2000) with fluorescence detection using precolumn dirivatization with FMOC-Cl (9- fluorenylmethylchloroformate) to give the fluorescenscent derivative (Sancho, et al .,1996& Hogendoorn, et al., 1999). 4-Fluoro-7-nitrobenzofurazan (NBD-F) (Lei, et al., 2006), Phthaldialdehyde (OPA) (California Dept, 1997), Trifluorethanol (TFE) and Trifluoracethic anhidride (TFAA) (Alexa, et al., 2008) are used for glyphosate derivatization.

2.4 Derivatization

Derivatization is a technique which transforms a chemical compound into a product of similar chemical structure. It is change chemical and physical properties. Chemical derivatives may be used to facilitate analysis (wikipedia.org). Derivatization reactions are also difficult to implement quantatively at very low concentrations of analyte (sub-nanogram per milliliter) (Venn, 2001). Derivatization reactions should produce stable derivatives that achieved by pre-column (before analytical separation), post-column the reaction is performed automatically by adding a derivatization reagent after separation, and before detection, by means of a second HPLC pump. A specific detection method as fluorescence or absorption in visible light, at a long wavelength will be used.

Chemical derivatization modifies or converts substances with a low UV absorption into highly sensitive products. Post column derivatization procedures represent a powerful analytical tool. The methodology is suitable for trace and ultra trace analysis and offers enhancement of both detectability and specificity compared to conventional HPLC methods (Stewart, 1982).

The disadvantages are the post column is not always amenable to automation, also the danger of there being insufficient reagent due to sample matrix reaction. Thiofluor (N,N-dimethyl-2mercaptoethyl aminehydrochloride), ortho-phthalaldehyde (Patsias, et al., 2001) and ortho-phthalaldehyde with 2-mercaptoethanol (Tadeo, et al., 2000) have been used for glyphosate determination with fluorescence detection.

The advantages of using pre-column derivatization for increasing the sensitivity of an assay are that the chromatography, particularly of basic compounds, can be improved; less complex equipment is required than for the post-column derivatization and the wavelength of absorbance can be shifted into the visible band where very few impurities or interfering peaks absorb (Venn, 2001).

Pre-column derivatization studied p-toluenesulphonyl with HPLC method and UV detector (Khlorenko and Wieczorek, 2005), mostly FMOC-Cl with HPLC method with MS/MS (shimadzu application News). In some papers e.g. 4-chloro-3, 5-dinitrobenxotrifluoride reaction with glyphosate has been studied to optimize reagent's concentration, reaction time, temperature, and pH. The derivative was more stable than that with FMOC-Cl and more mildly and it has applied to the quantaive determination of glyphosate in environmental water (Kun, et al., 2009). The secondary amino group in glyphosate treated with nitrous acid, and converted to an N-nitro group (March, 1992). This one can be easily reduced, making possible its determination by voltammetric strategies (Smyth, et al., 1975). Bronstad and Friestad (Bronstad and Friestad, 1976 & Friestad and Bronstad, 1985) showed the possibility of applying differential pulse polarography (DPP) as an inexpensive and fast technique for glyphosate determination.

In this study a method used for derivatization of glyphosate was based on reaction of glyphosate with carbon disulphide 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 using spectrophotometer at 435 nm using a glass cell and pH measured using pH meter (pH & Conductivity Meter, 3540 JENWAY) (Rasul, et al., 2009).

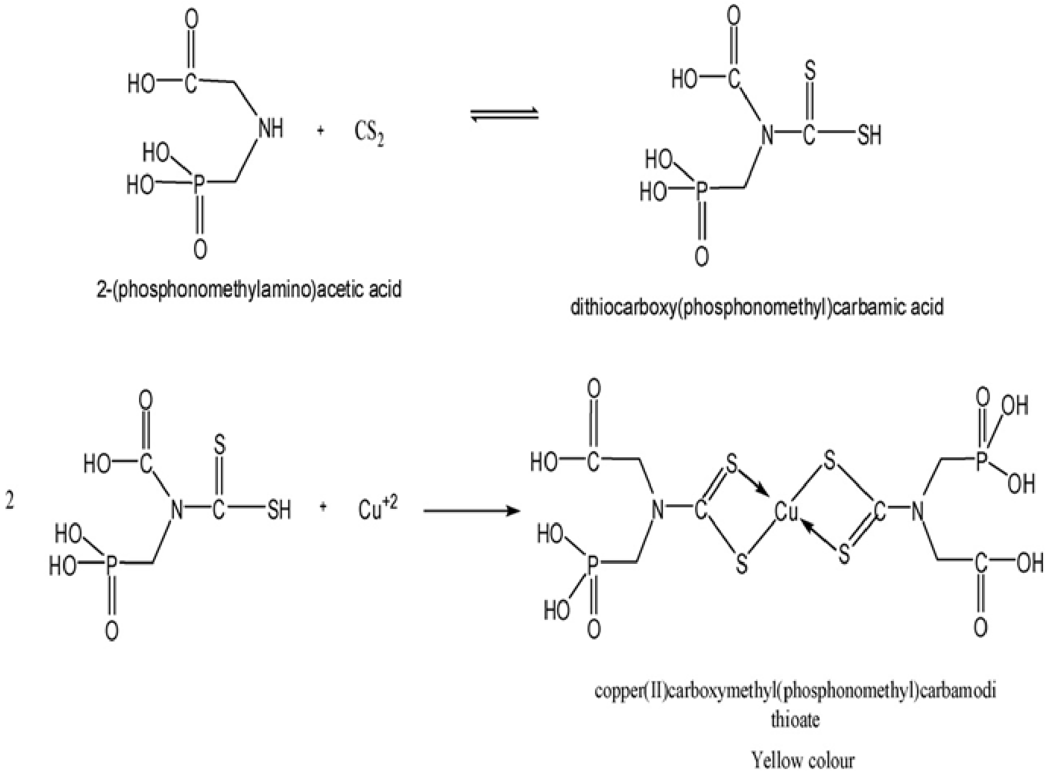


Fig .2.4: Proposed reaction mechanism (Rasuel, et al., 2009).

The aim of sample preparation is a sample aliquot that is relatively free of interferences that may be caused by contaminants in solvents , reagents, glassware and other sample processing that elevated baselines in the UV-Spectrophotometer.

Glassware, Collection of a sample, storage of a sample, preservation of a sample , high purity reagents and solvents preliminary sample processing, weighing or volumetric dilution, alternative sample processing, removal of particulates, sample extraction and derivatization have critical effects on the accuracy and precision on the final method. The solid particles centrifuged and the supernatant filtered through a 0.45µm membrane filter before analysis for greater precision and accuracy.

To analyze low concentrations of glyphosate, methods of purification of analytes are required. Purification methods are well established techniques as: liquid-liquid extraction, solid phase extraction (SPE), ion exchange chromatography, and supported extraction technique (SLM) that could considered as alternative for pretreatment of liquid samples containing herbicides. SLM is a porous polymeric hydrophobic membrane with organic solvent immobilized in its ports. The membrane separates the aqueous (donor) phase and the receiving aqueous (acceptor) phase. It depends on the charge of the extracted analytes where in case of acidic and basic compounds the enrichment is achieved by adjusting the pH to appropriate values (Wieczorek, et al., 1997). SLM samples more cleanly than other extraction techniques (Maxim, et al., 2005).

2.5 Chemical Kinetics

2.5.1 Rate of Reaction

The rate is defined as change in concentration (Δc) with time **(**Δt**)**. The rate can be positive or negative: a positive rate means that the concentration is increasing with time e.g. a product; a negative rate means that the concentration is falling with time e.g. a reactant. A rate law is a mathematical equation that describes the progress of the reaction. In general, rate laws must be determined experimentally.

There are two forms of a rate law for chemical kinetics:

- Differential rate law.
- Integrated rate law.

The differential rate law describes how the rate of reaction varies with the concentrations of various species, usually reactants, in the system. Each rate law contains a constant, k, called the rate constant. The units for the rate constant depend upon the rate law, because the rate always has units of mole L^{-1} sec^{-1} and the concentration always has units of mole L^{-1}.

The rate is the derivative of concentration with respect to time.

$$r = -\frac{d[\mathrm{A}]}{\mathrm{dt}} \quad \text{.....................................(2.1)}$$

Integrated rate law relates the concentration to time.

$$r = k\,[A]^n \quad \text{..................................... (2.2)}$$

2.5.2 Order of Reaction

The power to which its concentration term in the rate equation is raised. For example, given a chemical reaction 2A + B → C with a rate equation.

$r = k\,[A]^{2}[B]^{1}$ …………………..……..………. (2.3)

The reaction order with respect to A would be 2 and with respect to B would be 1; the total reaction order would be 2 + 1 = 3.

Reaction orders can be determined only by experiment. It is not necessary that the order of a reaction be a whole number.

2.5.2.1 Zero-Order Reaction

The rate of reaction is a constant when the limiting reactant is completely consumed.

Differential Rate Law:

$r = k$…………………………………….... (2.4)

the rate constant, k, has units of mole L^{-1} sec^{-1}.

2.5.2.2 First-Order Reaction

For a first-order reaction, the rate of reaction is directly proportional to the concentration of one of the reactants.

Differential Rate Law:

$r = k\,[A]$ ……………………………….....…….. (2.5)

$$-\frac{d[\mathrm{A}]}{\mathrm{dt}} = k[\mathrm{A}] \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.6)}$$

$[\mathrm{A}] = [\mathrm{A}]_0\ \mathrm{e}^{-kt}$…………………………..…….. (2.7)

$[\mathrm{A}]/\ [\mathrm{A}]_0 = 1/2 = e^{-kt_{1/2}}$ ……………………..... (2.8)

Taking the ln of both sides

$\ln(\ 1/2\ ) = -\ \ln 2 = -\ \mathrm{k}\ \mathrm{t}_{1/2}$…..………………….. (2.9)

or $\mathrm{t}_{1/2} = (\ \ln 2\ )\ /\ \mathrm{k}$……………….………… (2.10)

For any order other than first order, the half-life of the reaction is dependent on the concentration. The rate constant, k, has units of $\sec^{-1}$.

2.5.2.3 Second-Order Reaction

For a second-order reaction, the rate of reaction is directly proportional to the square of the concentration of one of the reactants. Differential Rate Law:

$\mathrm{r} = \mathrm{k}\ [\mathrm{A}]^2$ ....… (2.11)

$$-\frac{d[\mathrm{A}]}{\mathrm{dt}} = \mathrm{k}[\mathrm{A}]^2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.12)}$$

$$\frac{[\mathrm{A}]}{1+\mathrm{kt}[\mathrm{A}]_0} = [\mathrm{A}] \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.13)}$$

$\mathrm{t}_{1/2} = 1\ /\ \mathrm{k}[\mathrm{A}]_0$ ………………..……………… (2.14)

The rate constant, k, has units of L $\mathrm{mole}^{-1}\ \sec^{-}$.

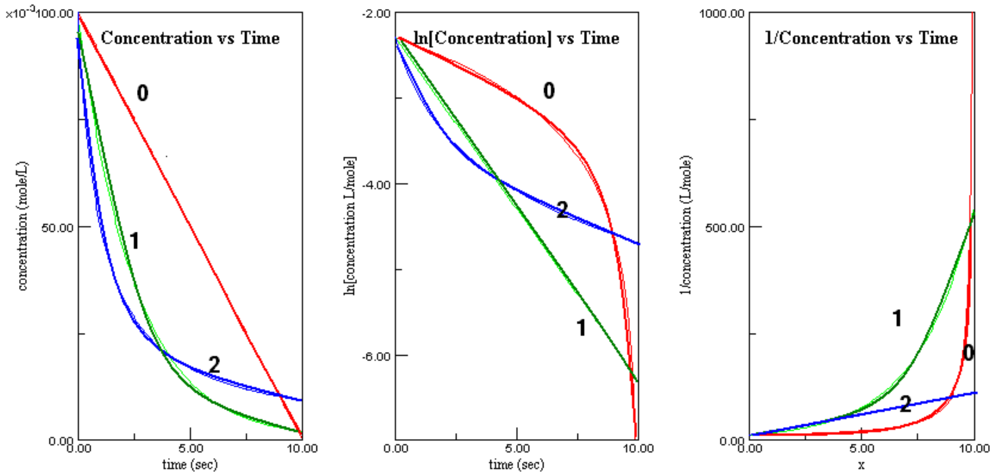


Fig. 2.5: The use of the characteristic kinetic plots (chem. davidason.edu, 2010).

0: zero-order

1: first-order

2: second-order

2.6 Adsorption onto Surface

Adsorption Theory

Adsorption is adhesion of the molecules of liquids, gases, and dissolved substances to the surfaces of solids, on the contrary absorption, in which the molecules enter the absorbing medium (answers.com). The adsorption process is classified as physical and chemical adsorption. Physisorption (or physical adsorption) is result of intermolecular forces between the adsorbate and the adsorbent (Roberts, 2006). Physical adsorption is a readily reversible process (Frank, et al., 2004); the forces involved are (van der Waals forces) (weak bonds) (old.iupac.org , 2001) , repulsion through dipole-dipole interactions and dispersing interactions, and hydrogen bonding (Roberts, 2006). While Chemisorption (or chemical adsorption), is produced by the transfer of electrons and the formation of chemical bonds between the adsorbate and the adsorbent (strong bonds). It may be an irreversible reaction bonding (Roberts, 2006), have high activation energies takes place only in a monolayer and high enthalpy change (an exothermic chemical reaction) (en.wikipedia.org) ranging from 80 to 400 Btu/lb. mole (2.326 Btu/lb mole equals 1 kJ/kg mole) (Roberts, 2006).

Strong sorption to soil particles reduces the risk of leaching (Walker, et al., 2005). Adsorption is described by isotherm where the adsorption and desorption rates balance each other at equilibrium. The quantity of adsorbate that can be bound up on a particular adsorbent is a function of the concentration of the adsorbate and the temperature (Walker, et al., 1995). The amount of material which is adsorbed on the surface at a particular temperature depends upon the amount of that substance in the gas or liquid phase which is in contact with the surface, and this is called the adsorption isotherm. The isotherm is useful in determining the interactions between the adsorbate and the adsorbent.

The isotherm can be determined in batch experiments by varying the solute mass or the phase ratio this could be performed in a vessel with a known liquid volume and known amounts of solute at different time till equilibrium. The two most common equations used to describe the equilibrium between a surface (adsorbent) and a chemical in solution (adsorbate) are the Langmuir and Freundlich adsorption equations. Freundlich was published by Freundlich and Küster (1894) for gaseous adsorbate (en.wikipedia[a]). Langmuir published in 1916 (en.wikipedia[a]). The Langmuir equation treats the interaction between the adsorbent and the adsorbate as a linear, reversible, monolayer chemical reaction (Roberts, 2006).

It is based on four hypotheses (en.wikipedia[a]):

- The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
- Adsorbed molecules do not interact.
- All adsorption occurs through the same mechanism.
- At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

$$M = \frac{A_{\max} Kc}{1 + \mathrm{Kc}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; (2.15)$$

Where:

M is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent at equilibrium, the unit of M is $mol.g^{-1}$, $mol.kg^{-1}$ respectively. A_{max} is the maximal substance amount of adsorbate per gram (or kg) of the adsorbent. The unit of A_{max} is $mol.g^{-1}$, $mol.kg^{-1}$ respectively. K is the adsorption equilibrium constant $mol^{-1}.L$; c $mol.L^{-1}$ is the concentration of adsorbate in liquid.

Chapter Three

Methodology

3.1 Study Area: Nablus

Nablus district is in the northern part of the West Bank. It is the capital of the Nablus Governorate and a Palestinian commercial and cultural center. Its population is 320,830 people, according to statistics in 2007 (Palestinian Central Bureau of Statistics, 2007) and it has a total area of 613582 dunoms (613.5 Km^2) (ICCPR, 2006).

The relatively temperate Mediterranean climate brings hot, dry summers and cool, rainy winters to Nablus. Spring arrives around March-April and the hottest months in Nablus are July and August with the average high being 28.9˚C (84˚F). The coldest month is January with temperatures usually at 3.9˚C (39˚F). Rain generally falls between October and March, with annual precipitation rates being approximately 23.2 inches (589mm) (en.wikipedia). Cumulative amounts of rain that fell on the governorates of the country since the beginning of the current rainy season 2010/2009 mid-morning on Monday 03/05/2010 is 581.2mm and average of 660.1mm (Meteorological Palestinian, 2010). The hottest months in Nablus are July and August with the mean monthly temperature 25.2˚C and 25.4˚C respectively for the year 2008 (Meteorological Palestinian, 2008).

3.2. Sampling Site and Sample 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.

3.3 Soil Analysis

The soil used for chemical analysis was sieved in 2mm sieve, and dried at 105˚C. Basic physico-chemical properties of soil were conducted on soil before any treatment with glyphosate**.**

3.3.1-Soil Texture (Hydrometer Test)

The particle size distribution of a soil expresses the proportions of the various size classes (clay < 0.002mm, silt 0.002-0.02mm and sand 0.02-2.0mm particle size), commonly represented by weight percentages of the total soil. The proportions of these fractions are determined by Hydrometer method (Bouyoucos, 1962) based on the Stokes`s Law which states that the rate of fall of particles in a suspension is directly proportional to their size (Bouyoucos, 1962 & Dhyan,et al., 1999). The soil was sieved using 2mm sieve, and dried at 105˚C for 24 hours using Elle oven. The soil texture was determined by ASTM 152-H hydrometer.

3.3.2- Moisture

The results of soil analysis were calculated on the basis of an oven dried sample weight. Therefore, the moisture analysis was executed before any other analysis. The results on the basis of the air-dry weight were multiplied by a moisture correction factor (mcf).

A porcelain crucible was placed in Ari J. Levy oven at a temperature of 105°C and left for 2 hours, then cooled down to room temperature in a desiccator. The weight of the empty crucible was recorded. Ten grams of soil sample were weighed in the crucible. The crucible was placed for 12 hours in the oven at 105°C. Then cooled down to room temperature in a desiccator and reweighed again. The moisture content and moisture correction factor were calculated using the following equations (Buurman, 1996 & Dhyan, et al., 1999):

$$M\,(moisture\ content) = \frac{(B-C)\times 100\%}{(\mathrm{B - A})}$$

Where:

A: Empty crucible weight

B: Sample + Crucible weight before drying

C: Sample + Crucible weight after drying

$$mcf\,(moisture\ \ corrction\ \ factor) = \frac{100 + M\%}{100}$$

3.3.3- pH

pH of the soil is measured potentiometrically in a 1:5 soil – water suspensions. Twenty grams of an oven dried - sieved soil were weighed, transferred into 200 ml beaker; 100 ml of distilled water were added while stirring for one hour using Electric magnetic stirrer. The pH conductivity meter (JENWAY) was calibrated using pH buffer 4.0, 7.0 & 9.0, and then the pH of suspension was measured (Dhyan, et al., 1999 & USSL, 1954).

3.3.4 Electrical Conductivity

The measurement of EC will give the concentration of soluble salts in the soil at any particular temperature. EC measured in 1:5 soil-water suspension using conductivity meter.

3.3.5 Organic Carbon (Walkely and Black 1934)

The organic carbon in the sample is oxidized with potassium dichromate and sulphuric acid. The excess potassium dichromate is titrated against ferrous ammonium sulphate.

One gram soil was weighed and transferred into 500mL conical flask. 10 mL of 1N $K_2Cr_2O_7$ and 20 mL of conc. H_2SO_4 were added. Swirled carefully then let to stand for 30 minutes. Slowly 200 mL distilled water and 10 mL H_3PO_4 were added. Then 1 mL of diphenylamine indicator was added and the resulted suspension was titrated against 0.5 N ferrous ammonium sulphate solution until green color started appearing indicating the end point. Blank must run simultaneously (Walkely and Black, 1934 & Jackson, 1962).

The carbon content was calculated using the following equation:

$$Organic\ Carbon = \frac{10(B - S) \times 0.39 \times mcf}{(\mathrm{B} \times \mathrm{W})}$$

Where:

B = mL of ferrous ammonium sulphate solution used for blank.

S = mL of ferrous ammonium sulphate solution used for sample.

mcf = moisture correction factor.

W = sample weight (g).

0.39 = conversion factor (including a correction factor for a supposed 70% oxidation of organic carbon.

% of organic matter = 1.72 x % of organic carbon

3.3.6 Total Nitrogen (Kjeldhal Method)

Nitrogen in soil/sediments is mostly present in the organic form with small quantities of ammonium and nitrate. This method measures only organic and ammoniacal form, therefore nitrate is excluded.

One gram of the soil sample was placed in digestion tube. Two and a half grams of a catalyst mixture (containing K_2SO_4, $CuSO_4.5H_2O$) were added. A 10 mL of conc. H_2SO_4 was added. Mixture was heated to about 400˚C until the mixture became transparent, then allowed to cool. 50 mL sample of 2% boric acid were added into 250 mL conical flask, and the flask was placed under the condenser of the distillation apparatus. The end of the condenser was dipped into the solution. 20 mL of 40% NaOH were added in digest till the colour changed to blackish. About 200 mL of the condensate were distilled. The condenser was rinsed and few drops of indicator (0.1g of bromocresol green, 0.02g of methyl red in 100 mL ethanol) were added to the distillate. Then sample titrated with 0.01N HCl till the pink colour started to appear. The percent nitrogen was calculated using the following equations (AOAC, 2002):

$$Total\ Nitrogen\ (mg/kg) = \frac{(S-B)\times N\times 14\times 100\%}{\text{weight of soil}}$$

Where:

S: Volume of acid used against sample.

B: Volume of acid used against blank.

N: Normality of acid.

3.3.7 Calcium carbonate

Five grams of soil were added into a 250mL conical flask. 100 mL of 1M HCl were added using pipette and swilled gently and let to stand overnight, then shaked for two hours. The suspension let settled, then 5 mL of the supernatant was pipetted into a 100mL conical flask and 10 mL of water were added. 2-3 drops of phenolphthalein indicator were added and titrated with 0.25M NaOH till colour change to purple (Piper, 1966; Buurman, et al., 1996; Dhyan,et al., 1999 & Page, et al., 1982).

The percent calcium carbonate was calculated using the following equations:

$$CaCO_3 = \frac{(B - S) \times N \times 100}{\text{weight of soil (g)}} \times mcf$$

Where:

B = mL NaOH used for blank.

S = mL NaOH used for sample.

N = Normality of NaOH.

mcf = moisture correction factor.

100 = conversion factor.

3.3.8 Available Phosphorous (P- Olsen)

Five grams of soil transferred into a 250mL shaking bottle. 100mL of sodium bicarbonate extractante (0.5M $NaHCO_3$ adjusted to pH 8.5 with 1M NaOH) was added. Then shaken for 30 minutes and filtered through whatman # 42 filter paper. 5mL of the standard series sample or blank were pipetted into a test tube and 5mL of mixed reagent (50mL 4M sulphuric acid, 15mL 4% ammonium molybdate, 30mL 1.75% ascorbic acid, 5 mL 0.275% potassium antimony tartrate and 200mL water were added successively to a 500mL bottle) was added. Mixture was shaked and stood for one hour for the blue colour development. The concentration of the solution was measured at 882 nm or 720 nm using spectrophotometer (Olsen, et al., 1954; Buurman, et al., 1996 & Dhyan, et al., 1999).

$$Available\ P\ (mg/kg) = \frac{(S-B)\times D\times[100+\{W-\frac{W}{mcf}\}\ ]}{\text{weight of soil (g)}} \times mcf$$

Where:

S = P concentration in sample (mg/L) read by spectrophotometer.

B = P concentration in blank (mg/L) read by spectrophotometer.

D = Dilution factor (standard 1 for undiluted samples).

W = sample weight (g).

mcf = Moisture correction factor.

100 = Volume of extractant.

3.3.9 Metal contents (Fe&Cu)

3.3.9.1 $HClO_4$-HF Digestion

0.5-1.0gram of soil transfered into a clean 100 mL teflon beaker and wet with 5mL 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 8mL of HCl and 20mL 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 (Dahlquist and Knoll, 1978; Blancher, et al., 1965; EPA, 1992; Jackson, 1958 & Hossner, 1996).

The physico-chemical soil properties (Tab.3.1) were determined using standard methods.

Table.3.1: 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%
$CaCO_3$ %	0.795%

Cu (mg/kg)	44
Fe (mg/kg)	1982.27
Available Phosphorous (P) (mg/kg)	62.41

The physico-chemical soil properties after glyphosate application were listed in table (4.7)

3.4 Leachate Extraction Columns

Leachate extraction columns consist of four columns of 1m long polyvinyl chloride (PVC) pipe and internal diameter of 15cm (6inch). 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.

3.5 Glyphosate Application to Soil-Column Experiment

Glyphosate (Monsanto Co, St. Louis, MO, USA) contains the monoisopropylamine salt of glyphosate (N-(phosphonomethyl)-glycine) (360g L^{-1}) 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

.3.2

Table 3.2: Glyphosate amounts applied to soil columns.

Column	***Blank***	***5x***	***15x***	***25x***
Glyphosate (g)	0	63.585	190.755	317.925
Kg /dunom	0	3.6	10.8	18

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

3.6 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 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 before analysis. Glyphosate extracted by the method described below (3.12.1) and derivatized using the method shown below (3.12) then measured by Spectrometer at 435nm.

3.7 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.

3.8 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 & conductivity meter(3540 JENWAY).

3.9 Calibration Curve

Stock solution of glyphosate 1000 ppm (purity = 99% purchased from SUPLECO analytical) was diluted in water to a concentration of 100 ppm as a working standard. A series of glyphosate standards of 1, 5, 10, 20, 30 and 50 ppm. 0.5, 2.5, 5, 10, 15 and 25mL transferred into 50ml volumetric flasks. Distilled water was added to volume. 50mL distilled water without glyphosate used as blank. Standards and blank were derivatized with CS_2 by the method described in section (3.12). The absorbance measured spectrophotometrically at 435 nm.

The calibration curve for glyphosate was used linear in the range (1-50) ppm as shown in Fig. 3.1

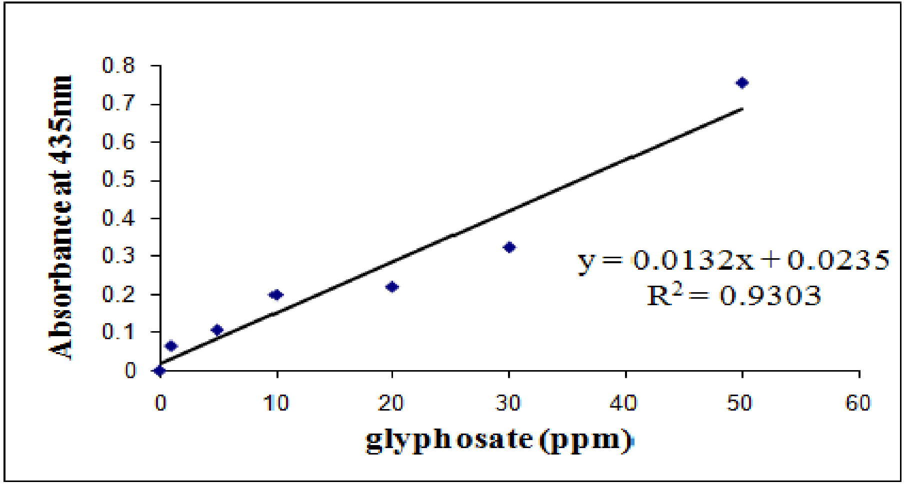


Fig .3.1: Calibration curve for estimation of glyphosate at 435 nm.

3.10 Batch Sorption Experiments

Sorption kinetics was analyzed by altering the contact time at a constant concentration of 20 & 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.

3.11 Adsorption Isotherm Experiment

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 equilibriated.

The equilibrium concentrations of each soil were measured spectrophtometrically after derivatization.

The equilibrium concentrations were determined with respect to a standard curve Fig (3.1).

Sorption parameters were estimated from the Freundlich equation:

$C_s = K_F . C_e^{\,n}$ …………………… (3.1)

Where C_s is the concentration in the soil (mg kg^{-1}), K_F is the Freundlich sorption coefficient (mg^{1-n} L^n kg^{-1}), C_e is the concentration in the solution after 24 hours (mg L^{-1}) and n is a linearity factor (Freundlich exponent).

3.12 Derivatization Procedure of Glyphosate

Glyphosate was derivatized using carbon disulphide 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.

Carbon disulphide (1% CS_2) solution was prepared by mixing 0.5mL CS_2 in chloroform and diluted to 50mL with chloroform. An aliquot 10mL 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. 0.4 mL ammonical solution of Cu(II) (1000ppm) 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 10mL flask and diluted with ethanol. The absorbance of the complex was measured at 435 nm. (The product is slightly soluble in lower alcohols) (Catherine, et al., 1949). Ammonical solution of Cu(II) prepared by dissolving an appropriate amount of Cu $(NO_3)_2$ in (20mL) distilled water and diluted to 100mL with ammonia solution.

3.12.1 Procedure for Solid-Phase Extraction (SPE) of Glyphosate from Water Samples

A cation exchange resin was used for the preconcentration and clean-up of glyphosate. A slurry of the Amberlite IR-120, Na-ion exchange resin (cationic) (ACROS ORGANICS, New Jersey, USA) was made in 10mL 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 $mL.min^{-1}$ several times, before sample application. The pH of water sample spiked with glyphosate was adjusted to pH 2 and amine group of glyphosate was converted into its protonated form. The protonated sample (25mL) was passed through the column at a flow rate of $0.5mL.min^{-1}$, 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 $70^{\circ}C$ then evaluated by the proposed method (Rasul, et al., 2009).

3.12.2 Glyphosate Extraction from Soil Samples

Homogenized soil sample (10g) was extracted for 60 min with 25mL of 2M NH_4OH solution (Hu, et al., 2006). 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 (3.12.1 & 3.12). Each recovery was performed in triplicates (Rasul, et al.,2009).

Chapter Four
Results & Discussion

4.1Batch Sorption Experiments

The sorption kinetic of the soil was 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. Glyphosate degrades quickly (Nomura and Hilton 1977; Rueppel et al. 1977; Strange-Hansen et al. 2004).

The equilibrium adsorption data over the range of concentrations studied here were used to fit Freundlich adsorption equation.

$x/m = k\,C_e^{1/n}$ ………………………..(4.1)

Where:

k and n are Freundlish constant

x/m = moles adsorbed per unit wt of adsorbent

x: mol compound adsorbed

m: weight of soil (g)

C_e = equilibrium concentration (mol/L)

Log $S = \log (k_F) + 1/n (\log C)$………… (4.2)

Where:

S is the sorbed amount (mg kg^{-1}), C is the concentration in equilibrium solution (mg L^{-1}), k_F is the Freundlich adsorption coefficient (L kg^{-1}), and 1/n (-) is a correction term needed to describe the nonlinearity of the sorption isotherm.

The Freundlich equation constants "k" & "n" could be obtained form the empirical Freundlich adsorption equation (4.1)

k related to the adsorption capacity.

1/n is the intensity of adsorption.

n: is the linearity factor.

The values of n within the range of 2-10 represent good adsorption (Teng and Hsieh, 1998; Ozer and Pirincci, 2006& Dhir, et al., 2009). Higher values of k indicate high adsorption capacity.

The isotherm equilibrium results for the examined soil are shown in Fig. 4.2 for glyphosate as the amount of glyphosate adsorbed against the equilibrium concentration.

Fig.4.1 showed that adsorption equilibrium was obtained after 24 hours of contact time between soil and solution.

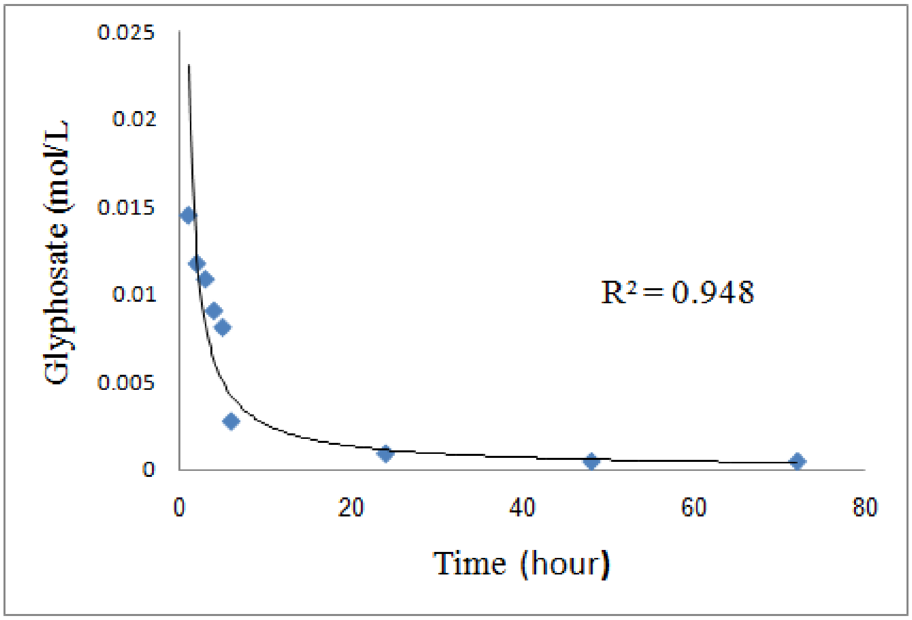


Fig .4.1: Plot of time vs. concentration of glyphosate.

The isotherm equilibrium results are shown in Fig.4.2 as the amount adsorbed against the equilibrium concentrations after 24 hours of adsorption. All concentrations were converted into mol/L.

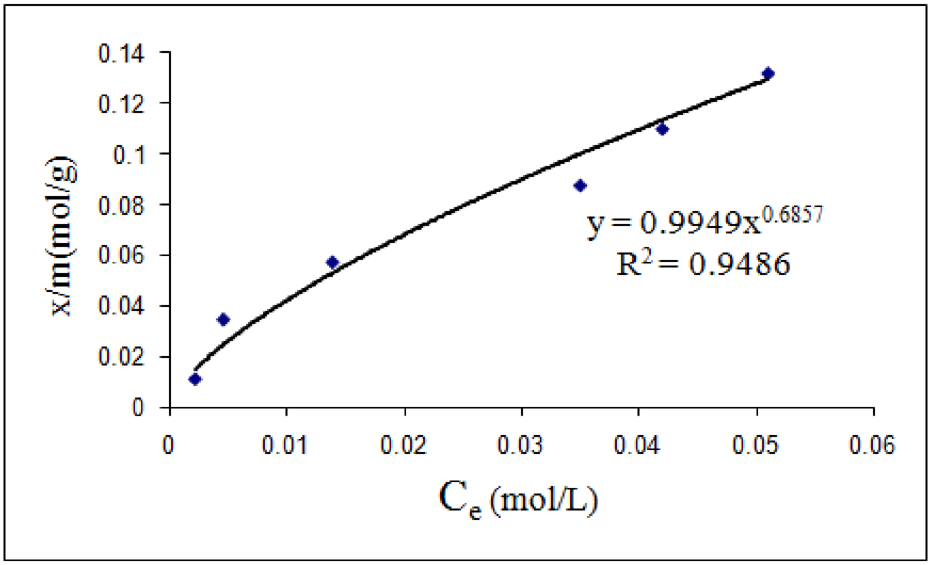


Fig .4.2: Plot of C_e vs. x/m for Glyphosate.

Freundlich isotherm constants (*k* & n) for glyphosate, the correlation coefficient "R" were obtained from Fig. 4.2 and listed in tab. 4.1.

Table.4.1: Freundlich isotherm constants (*k* & n) & the correlation coefficient R for glyphosate.

Substance	***k***	***1/n***	***n***	R^2	***R***
Glyphosate	0.9949	0.6857	1.458	0.9484	0.974

Glyphosate sorption at 25°C in the studied soils was evidenced to be a kinetics process, with a reasonable equilibration time of 24 hours. Literature usually reports Frendlich adsorption constants for glyphosate adsorption by soils (Hance, 1976; Glass, 1987) which are consistent with that founded in our study.

It is indicated from the previous table 4.1 and Fig 4.2 that "n" of glyphosate adsorption is higher than 1. According to Helby (1952) represents good adsorption. The adsorption isotherms for the soil is of S-type (Giles, 1960), this indicating the easiness of the adsorption, mainly at higher concentrations.

4.2 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 1 ppm. Doubling the concentration of glyphosate increases the amount glyphosate (contaminant) in leachate.

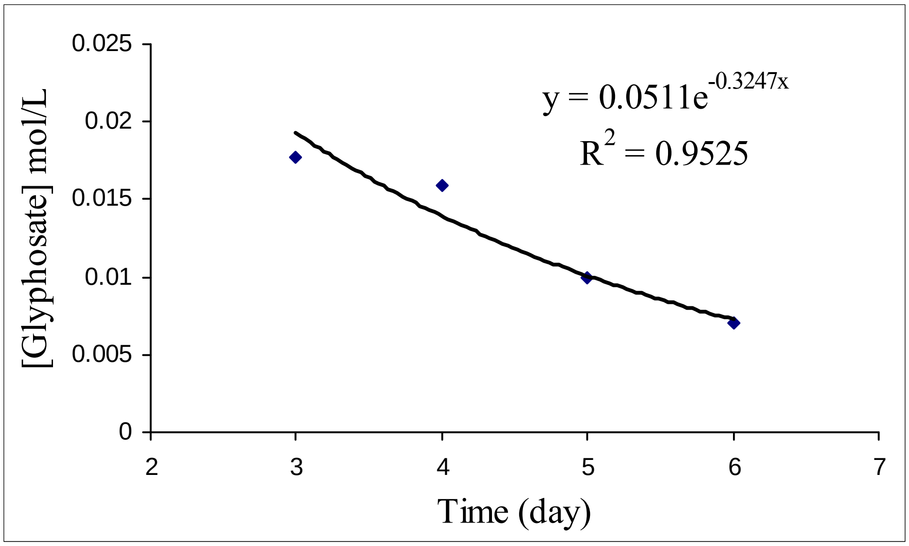


Fig 4.3: Plot of time vs. concentration for 5 times glyphosate in leachate.

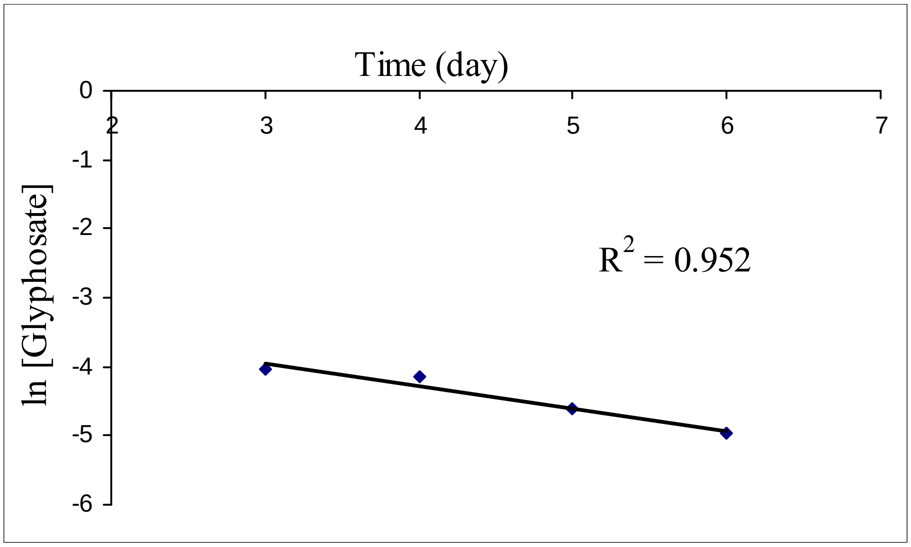


Fig.4.4: Plot of time vs. ln concentration for 5 times glyphosate in leachate.

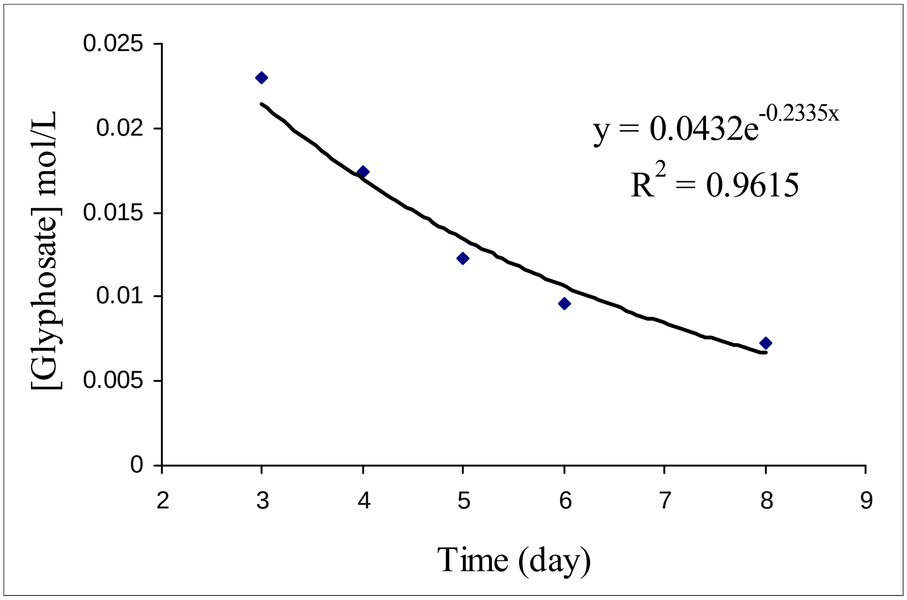


Fig.4.5: Plot of time vs. concentration for 15 times glyphosate in leachate.

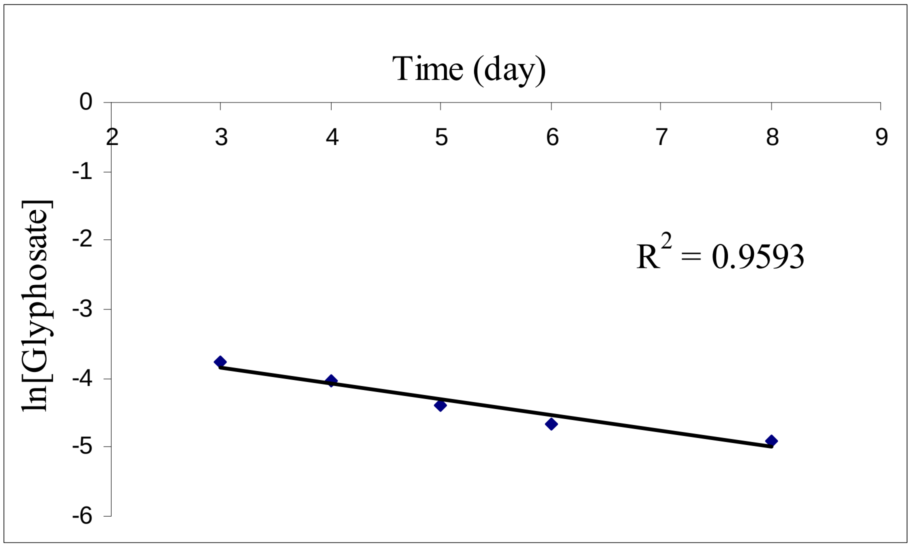


Fig.4.6: Plot of time vs. ln concentration for 15 times glyphosate.

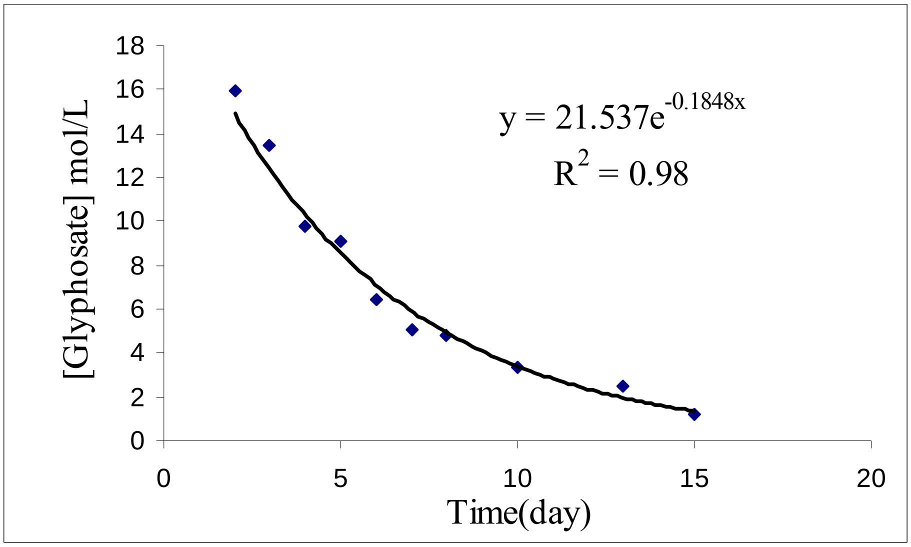


Fig .4.7: Plot of time vs. concentration for 25 times glyphosate.

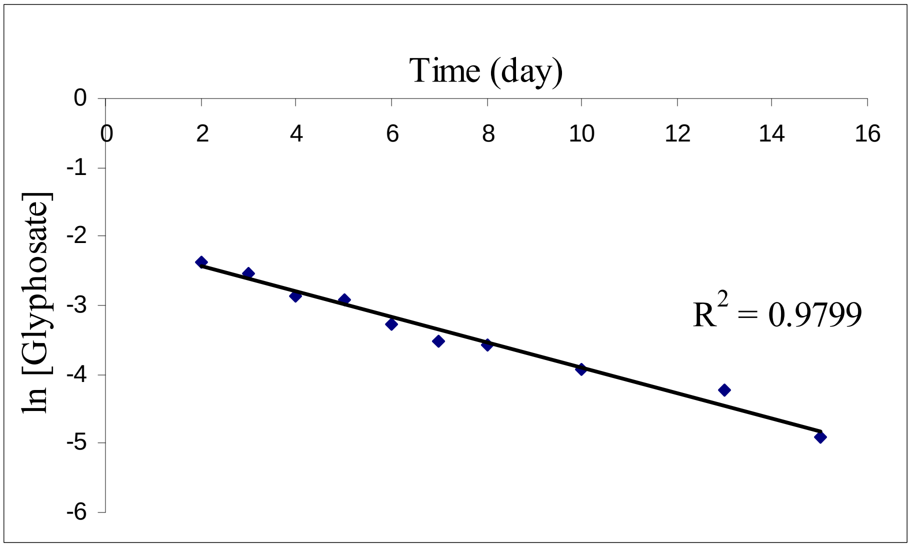


Fig .4.8: Plot of time vs. ln concentration for 25 times glyphosate

The above resulting curves shows that the best fit of the glyphosate degradation data was obtained using a first-order reaction. DT_{50} values of glyphosate was 2, 3 & 3.75 days for 5x, 15x & 25x column respectively this indicate relatively rapid degradation.

4.3 Glyphosate in 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.4.9. 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).

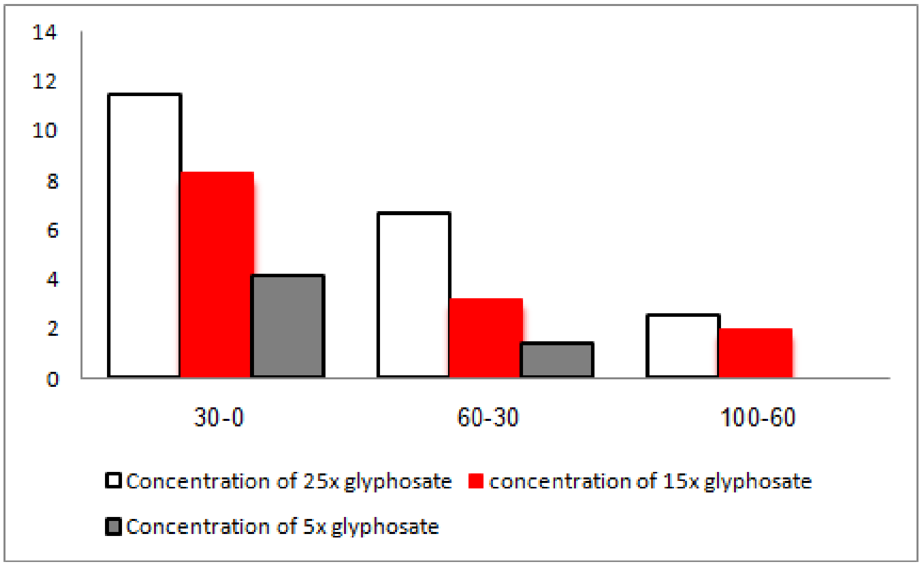


Fig .4.9: Concentration of glyphosate in soil column at different depths.

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.

Table 4.2: 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

4.4 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 (Lickacz and Penny, 2010).

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. 4.10, 4.11&4.12

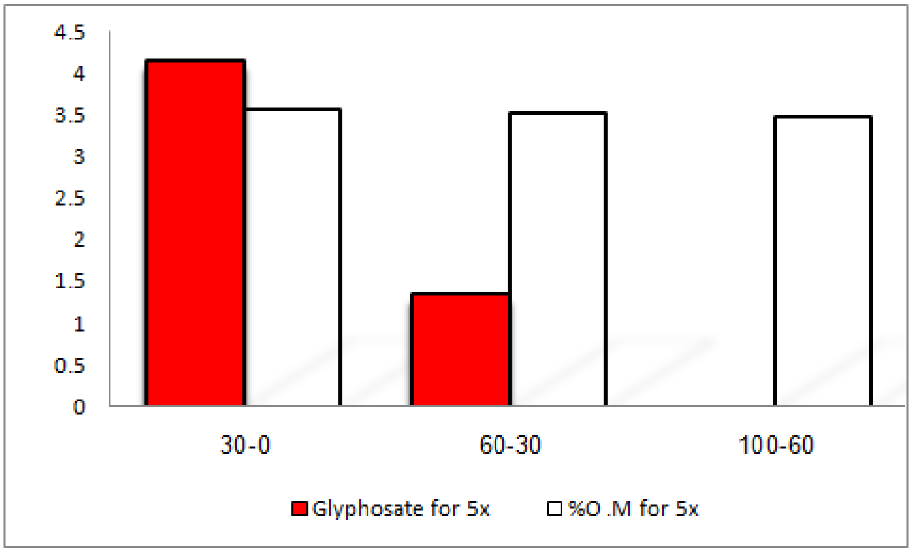


Fig .4.10: Organic matter content in 5x column and concentrations of glyphosate at certain depths.

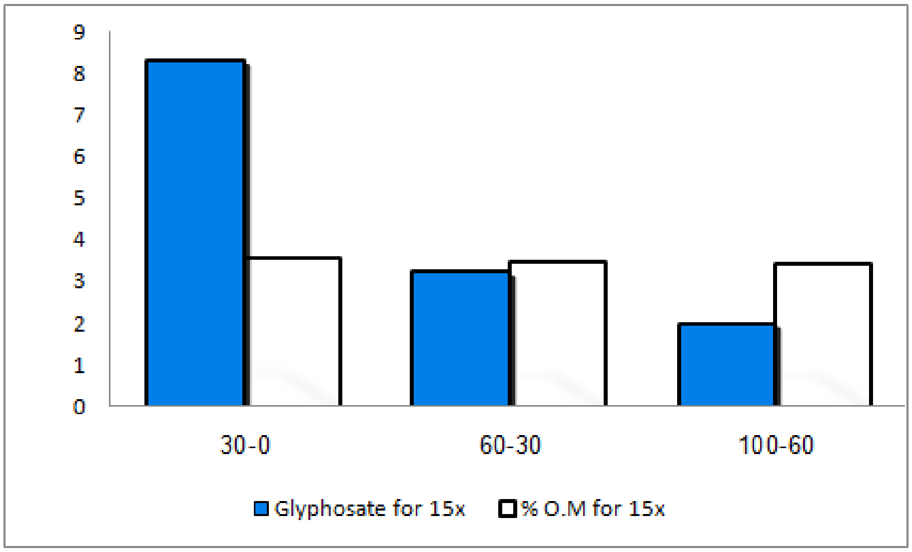


Fig. 4.11: Organic matter content in 15x column and concentrations of glyphosate at certain depths.

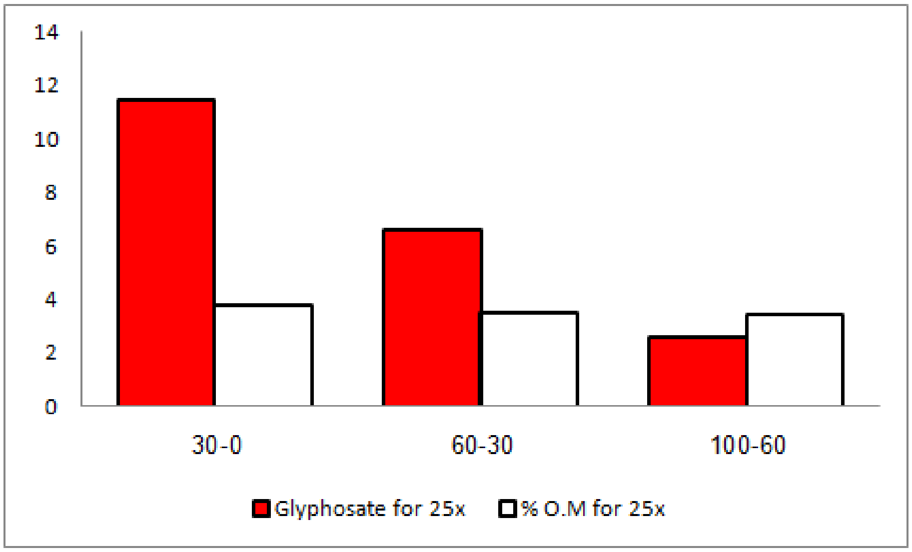


Fig. 4.12: Organic matter content in 25x column and concentrations of glyphosate at certain depths.

It's indicated that organic matter only may not affect the adsorption of glyphosate at different depths.

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.

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 4.13 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.4.13& 4.14 and table 4.2.

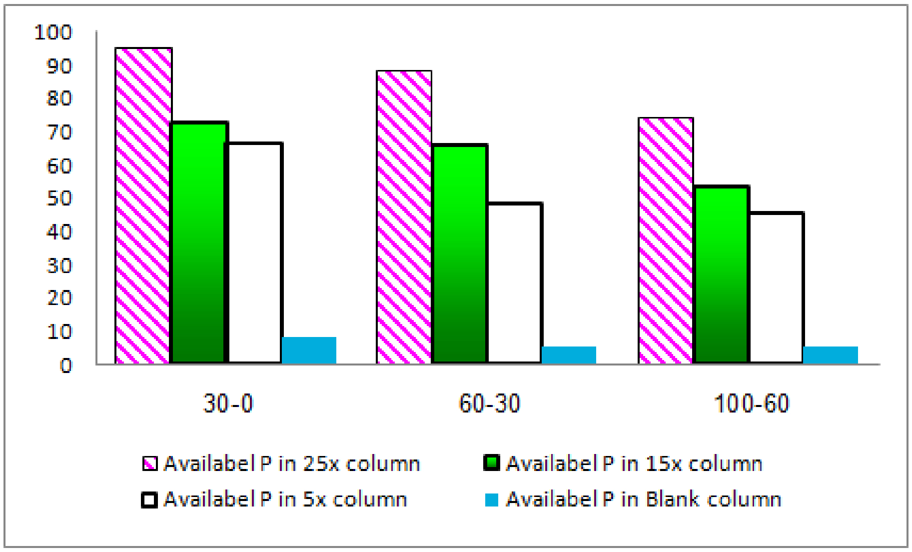


Fig. 4.13: phosphorous content in soil columns after application of glyphosate.

4.7 Available Nitrogen after Glyphosate Application

The nitrogen content of soil has been increased after glyphosate application to soil columns due to biodegradation of glyphosate.

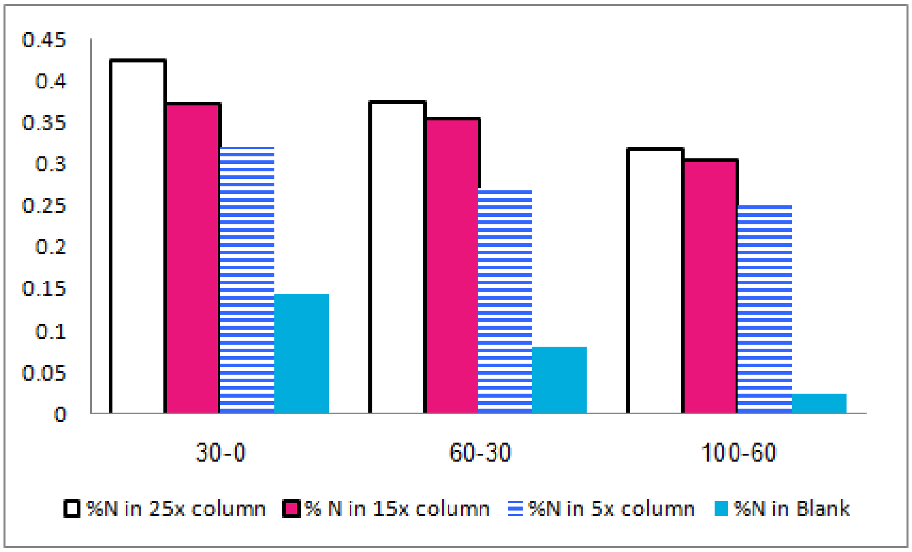


Fig.4.14: Nitrogen content in soil columns after application of glyphosate.

Chapter Five

Conclusion & Recommendations

5.1Conclusion:

Adsorption is an important process in determining the fate of glyphosate in soil. The texture for soil used has been founded 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 value 0.947; 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.

Simple and sensitive method has been used for derivatization of glyphosate after extraction from water and soil.

It is based on formation of dithiocarbamic acid from glyphosate and further reaction of dithiocarbamic acid with copper (II) to form a yellow coloured complex. The method is applicable to environmental samples.

Compared with chromatographic methods which are based on derivatization of glyphosate but the derivatization procedures are quite complicated and also produce unstable products.

The molar absorptivity (ε) equals 1.864×10^{3} ($Lmol^{-1}$ cm^{-1}) and stability constant (K_F) 1.06×10^{5}.

This study and others showed that the use of glyphosate can be problematic under certain circumstances.

According to our experimental conditions, leaching through the three soil columns, and therefore the potential risk of groundwater contamination, is greater for higher concentration of glyphosate. This study is just a step forward in the right way and it is thought that there is still a lot to be done.

A field study concerning glyphosate, pesticides contamination of the ground water should be carried out to study the behavior and fate in Palestinian soils.

5.2 Recommendations:

Alternative methods of weed control such as mechanical weeding and grazing by sheep should be encouraged to preserve the quality of surface water and groundwater in Palestine.

If the application of glyphosate is inevitable, the following points should be considered:

- As leaching of glyphosate through the soil can't be excluded, the soil as well as the ground water levels should be included in the assessment of the risk of ground water contamination by glyphosate or its biodegradation product.

- The application of glyphosate should be limited to once a year, due to measured background concentrations of glyphosate.
- At any rate, glyphosate should only be applied if no rain is likely as claimed in the principles of Good Professional Practice (BMELV, 2005).
- Integrated pest management should be used and followed.
- Farmers and agriculturists must take the necessary precautions when using herbicides.

New methods should be founded to remove glyphosate residues from water using safe and economic methods such as natural organic substances, olive stones, rice bran, rice husk, date stones, chickpea husk, and avocado stones.

Appendices

Appendix .1: Concentrations of Glyphosate at different times.

Time (hour)	**Glyphosate (mol/L)**
1	0.01456
2	0.01180
3	0.01090
4	0.00909
5	0.00814
6	0.00276
24	0.00091
48	0.00045
72	0.00046

Appendix .2: Equilibrium concentrations (C_e) & amount of Glyphosate adsorbed per gram of soil (x/m)

x/m (mol/g of soil)	**C_e (mol/L)**
0.0114	0.0022
0.0348	0.0046
0.0574	0.0139
0.0876	0.035
0.1098	0.042
0.1317	0.051

Appendix .3: Concentrations of 5 Times Glyphosate solution at different times.

Time (day)	**Glyphosate (ppm)**	**[Glyphosate] mol/L**	**ln [Glyphosate]**
3	3	0.0177	-4.034
4	2.69	0.0159	-4.14
5	1.72	0.01	-4.605
6	1.19	0.007	-4.961
8	Not detected	Not detected	Not detected

Appendix .4: Concentrations of 15 times Glyphosate in leachate.

Time (day)	**Glyphosate (ppm)**	**[Glyphosate] mol/L**	**ln [Glyphosate]**
3	3.91	0.023	-3.77
4	2.95	0.01745	-4.048
5	2.08	0.0123	-4.39
6	1.62	0.0096	-4.65
8	1.238	0.0073	-4.91
13	*Not detected*	*Not detected*	*Not detected*

Appendix .5: Concentrations of 25 Times Glyphosate solution at different times.

Time (day)	**[Glyphosate] (ppm)**	**[Glyphosate] mol/L**	**ln [Glyphosate]**
2	15.96	0.094	-2.36
3	13.46	0.0795	-2.53
4	9.77	0.058	-2.85
5	9.08	0.054	-2.92
6	6.46	0.038	-3.26
7	5.07	0.03	-3.51
8	4.77	0.028	-3.57
10	3.31	0.0196	-3.93
13	2.46	0.0145	-4.23
15	1.23	0.0073	-4.92
17	Not detected	Not detected	Not detected

Appendix .6: Glyphosate concentrations in soil columns at different depths.

Depth (cm)	**25x (ppm)**	**15x (ppm)**	**5x (ppm)**
0-30	11.460	8.310	4.150
30-60	6.620	3.230	1.345
60-100	2.540	2.000	Not detected

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جامعة النجاح الوطنية
كلية الدراسات العليا

دراسة حركة الجلايفوسات المرتشحة في التربة الفلسطينية بتراكيز مختلفة

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قدمت هذه الأطروحة استكمالاً لمتطلبات درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2011

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الملخص

يتزايد الاهتمام حديثا بالآثار السلبية الناتجة عن تراكم المبيدات بشكل عام في التربة وإمكانية انتقالها إلى مصادر المياه الجوفية خاصة في المناطق ذات المستوى المائي القريب من السطح نتيجة لتلوث المياه و التربة بكميات من المبيدات و التي غالبا ما تستعمل بطريقة غير صحيح و دون تطبيق التعليمات اللازمة من حيث الوقاية و الكمية المضافة و عدد المرات اللازمة خلال السنة.

تركز هذا البحث حول دراسة حركة الجليكوسايد في التربة في محاولة لفهم آلية حركة و نقل ذلك المبيد العشبي و التفاعلات الحادثة له مع التربة .كما و تهدف الدراسة الى تقييم الخواص الادمصاصية للجليكوسايد للتراب تحت الدراسة ، و تأثير تراكيز مختلفة منه مع ثبات معدل إضافة الماء إلى الأعمدة على حركة الجليكوسايد و توزيعه في عمود التربة .

تمت الدراسة الحالية في قسم الكيمياء في جامعة النجاح –نابلس و قسمت الدراسة إلى جزأين:

- في الجزء الأول تمت دراسة عملية ادمصاص الجليكوسايد على نوع من التربة جمعت من ارض مزروعة بأشجار الزيتون في جبل جرزيم في نابلس بغرض التعرف على سلوك الجليكوسايد في التربة . تم رج 25غم تربة مع 200 مل من محلول الجليكوسايد بتركيزات متدرجة من 0- 50ملغم/لتر و ذلك لفترات زمنية من 0-72 ساعة و بعد ذلك تم تقدير التركيز في الراشح لحساب الكمية المدمصة من الجليكوسايد و التعبير عنها رياضيا .

- في الجزء الثاني من الدراسة تم دراسة انتقال وتوزيع الجليكوسايد في أعمدة التربة بعد عملية غسل التربة و تخلص من الفراغات الموجودة في التربة . وقد تم تصنيع وحدة دراسة الانتقال في المختبر حيث تتكون من حامل للأعمدة و عمود من البلاستيك (PVC) و قرص ذو ثقوب على شكل شبكة يوضع أسفل العمود.

تم تعبئة أعمدة التربة بطول 100سم وقطر 15سم ، من ثم إضافة المحلول على سطح التربة بعد ذلك تمت عملية اضافة الماء الى الاعمدة و استقبل الراشح إن وجد أسفل العمود على فترات زمنية كل يوم تقريبا وبعد انتهاء و استخلاص الجليكوسايد منه .

في التجربة تم تقطيع عمود التربة إلى مقاطع بسمك 30سم، وأخذت هذه المقاطع وقدر فيها المحتوى الرطوبي و تركيز الجليكوسايد المدمص باستخدام الطرق المناسبة للاستخلاص. أخذت النتائج المتحصل عليها وتم جدولتها وإجراء التحليلات الإحصائية والرياضية المناسبة.

ويمكن تلخيص النتائج المتحصل عليها في الأتي:

- **تجارب الأدمصاص:**

أظهرت النتائج الاتجاهات التالية:

- زيادة في تركيز الجليكوسايد عند الاتزان مع زيادة تركيز المادة المضافة للتربة.
- حدوث الاتزان في عملية الادمصاص بعد 24 ساعة.
- زيادة الكمية المدمصة مع زيادة تركيز المضاف، ادمصاص الجليكوسايد كان أعلى في التركيز الأعلى من المادة المضافة.
- نجحت معادلة فرندليش الخطية و غير الخطية في التعبير عن ادمصاص الجليكوسايد وأظهرت هذه المعادلات توافقا كبيرا مع البيانات التجريبية (معامل التقدير في حدود ال 95% وأكثر).

أظهرت النتائج أن ادمصاص هذه العناصر يختلف تبعا لاختلاف المواد العضوية و المعادن المتواجدة في التربة.

- **تجارب الانتقال**

أوضحت النتائج النقاط التالية:

- تركز الجليكوساید في الطبقة السطحية للتربة مع وجود تدرج في تركيز ابتداء من السطح (التركيز الاعلى) الى العمق المحدد و بعد ذلك يقل التركيز مع ازدياد العمق ليختفي تماما في في العمود المحتوي على خمسة اضعاف الجليكوساید في العمق الاخير (60-100).
- يفسر التركيز العالي للجليكوساید في الطبقات العليا السطحية الى ارتباط الجليكوساید بالمعادن المتواجدة في التراب و تكوين رابطة مع المواد العضوية و التي تتواجد اكثر في سطح التربة عنه في المناطق الاكثر عمقا .
- أسفرت النتائج أن تركيز الجليكوساید في الراشح يبدا بالاختفاء مع زيادة الزمن.

الدراسة الحالية تقدم تصورا لحركة الجليكوساید في اعمدة التربة بالاضافة الى توزيع وانتقال الجليكوساید تحت تاثير صفات التربة و التراكيز المختلفة من المبيد.

نظرا لخطورة هذه المبيدات على الإنسان والنبات فان الفهم الجيد لآليات انتقال هذه المواد وتوزيعها يؤدى إلى معرفة الطرق الصحيحة لتفادى هذه المخاطر مستقبلا حيث أصبح التلوث بالمبيدات مشكلة بيئية خطيرة في العصر الحالي نظرًا لكثرة مصادر التلوث في البيئة وأهمها استخدام النفايات الصلبة والسائلة أو دفنها بطرق غير سليمة و الاستعمال الخاطيء و المتزايد لها دون سبب مما يؤدى إلى تراكم هذه المواد في التربة أو انتقالها على المدى الطويل إلى المياه الجوفية السطحية مؤدية إلى تلوثها.

لابد من وجود دراسات مستقبلية و الاخذ بالاعتبار عكس عملية الإدمصاص للجليكوساید .

لابد من استخدام النتائج و الإستفادة في اخذ الإحتياطات و الإجراءات اللازمة للحد من تلوث المياه و التربة .