UNIVERSITI PUTRA MALAYSIA

FATE OF GLYPHOSATE IN THE SOIL AND WATER SYSTEM OF AN OIL PALM PLANTATION.

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By

NURFARADILLA BT OTHMAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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DEDICATION

This thesis is dedicated to my beloved parents, siblings and friends

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in the fulfillment of the requirement for the degree of Master of Science

FATE OF GLYPHOSATE IN THE SOIL AND WATER SYSTEM OF AN OIL PALM PLANTATION

By

NURFARADILLA OTHMAN

July 2013

Chairman : Rosenani Abu Bakar, PhD

Faculty : Agriculture

The herbicide glyphosate is widely used in oil palm plantations for the control of a wide range of broadleaf weeds, woody plants and grasses, to ease the collection of palm fruits and to ensure the safety of workers against wild animals hiding among the tall weeds. Currently, lifecycle assessment of environmental impacts is a requirement particularly for exported products such as palm oil and there is insufficient documented data on the residue of glyphosate in the oil palm ecosystem to support the lifecycle assessment. Adsorption and degradation are the most important factors that affect the fate of pesticides in the soil and consequently determine their distributions in the soil/water environment. Thus, this project was carried out to determine the behaviour and possible residues of glyphosate in soil and water of oil palm ecosystem through three specific objectives: 1) to investigate the adsorption and desorption of glyphosate in different soils under oil palm cultivation, 2) to determine the half-life of glyphosate in soils under oil palm cultivation and 3)

to determine the residues of glyphosate in the soil and water of oil palm plantation.

The first objective was achieved when adsorption and desorption study was conducted on four mineral soils, Inceptisol (Selangor soil), Inceptisol (Briah Soil) and Ultisol (Serdang and Rengam soils) and Histosol (a peat soil) collected under oil palm plantation from 0 - 15 cm and 15 - 30 cm depths using batch equilibrium technique. The concentrations of glyphosate used were 0, 20, 40, 60, 80, 100, and 120 µg/mL. The adsorption and desorption isotherms were fitted to the linear and Freundlich equations. Adsorption of glyphosate was in the following decreasing order: Selangor > Briah > Rengam > Serdang > peat with the highest adsorption being 85.5 L kg^{-1}. The results indicated that adsorption of glyhosate was positively correlated with soil oxides and clay content. The high adsorption of the Selangor soil was expected and can be explained by the high soil oxides and clay content in the soil series compared to the other soil series. In contrast, desorption of glyphosate was in the following order: Rengam > Serdang > Peat > Selangor > Briah. This result revealed that adsorption capacity of glyphosate was strongly correlated with soil oxides and clay content.

The second objective was achieved through a degradation study in the laboratory using incubation technique. The effect of microbial activity on glyphosate was studied in a Selangor soil collected at 0 - 15 cm depth. The sterilized and non-sterilized soils and both were treated with either a 100% recommended field dosage (41 g.a.i/ha) of glyphosate and 200%

recommended dosage. Each soil treatment was done in triplicates. Samples were analyzed at 0, 3, 7, 21, 42, 60, 100, 120 and 140 days after treatment. Degradation rates of glyphosate in Selangor soil (sterilized and non-sterilized) follow the first order kinetics. For non-sterilized soil, the residue of glyphosate can be detected until 35 days after the incubation period for single recommended field dosage and for double recommended dosage the residue can be detected until 60 days after incubation. Whereas, for sterilized soil, the degradation of glyphosate in the recommended field dosage is detected until 80 days and for double recommended dosage is detected until 120 days after the incubation period. The half-life ($t_{1/2}$) of glyphosate in sterilized soil for double recommended field dosage was 4 and 8.3 days for recommended field dosage. The half-life ($t_{1/2}$) of glyphosate in non- sterilized soil for double recommended field dosage is 17.7 and for recommended field dosage is 12.2 days. From the results obtained, we can see that sterilized soil gave the longer $t_{1/2}$ compared to non-sterilized soil in Selangor soil 5% level of significance.

A field experiment was carried out at Ladang Telok Datok, Banting. The type of soil at this site was clay soil and the series was Selangor (Typic Tropaquept). The study plots were conducted in Completely Randomized Design (CRD). The study was conducted at two different seasons, the wet and dry season. In this study, glyphosate was applied at a recommended and double recommended field dosage. During the wet season, glyphosate was not detected at all in the soil and water which indicates that glyphosate was washed away or the soil and water did not contain glyphosate in detectable quantities. On the other hand, for the dry season, residue of glyphosate on the topsoil (0 – 15 cm) was detected until day 7 and 35 for recommended and double recommended dosage, respectively. Whereas, residue of glyphosate on the subsoil (15 – 30 cm) was detected until day 1 and 3, for recommended and double recommended dosage, respectively. However, the level is below the threshold level of 6 µg/L which is considered harmful for soil flora and fauna. The higher concentration of glyphosate applied will cause its residue to stay longer in the soil. Glyphosate residue was not detected in soil below 30 – 45 cm in each single and double recommended field dosage. The residues in water collected from PVC tube installed in the field and sub stream were not detected for both dosages.

All results showed that glyphosate adsorption in soil were significantly influenced by clay content, type of clay and soil oxides. Glyphosate detected in the soil up to 35 days. However, the glyphosate residue was not detectable in groundwater even though with stimulated double recommended dosage. Glyphosate residue has a short half-life (8 days) in the soil and could be considered as essentially non-leachable to the groundwater and safe for the environment.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KESAN SISA BAKI RACUN GLIFOSAT DI DALAM JENIS TANAH BERLAINAN DAN AIR DI SEKITAR KAWASAN LADANG KELAPA SAWIT

Oleh

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Racun herba glifosat digunakan secara meluas di ladang-ladang kelapa sawit terutamanya bagi bagi mengawal pelbagai rumput, pokok renek dan rumpai. Ini bagi memudahkan kerja-kerja pengumpulan buah sawit dan bagi memastikan keselamatan pekerja dari ancaman haiwan luar. Dewasa ini, penilaian kitar hidup bagi kesan terhadap alam sekitar adalah kemestian terutama bagi produk yang dieksport seperti minyak sawit dan kurangya data yang didokumentasikan berkaitan sisabaki glifosat terutama bagi kelapa sawit menyebabkan kajian ini perlu dilakukan. Kadar jerapan dan nyahjerapan dan penguraian adalah penting dalam mengetahui kemungkinan kehadiran sisa baki glifosat dalam tanah dan air. Dengan itu, kajian ini telah dilaksanakan untuk menentukan kewujudan kesan sisa baki racun glifosat di dalam sistem tanah dan air di sekitar kawasan ladang kelapa sawit. dengan objektif yang berikut: 1) menentukan kadar jerapan dan nyahjerapan glifosat dalam bebrapa jenis tanah berlainan di sekitar kawasan tanaman kelapa sawit, 2) mengenalpasti tempoh penguraian

glifosat dalam tanah jenis Selangor di kawasan kelapa sawit dan 3) mengenalpasti kesan sisa baki glifosat dalam tanah dan air di ladang kelapa sawit.

Untuk mencapai objektif pertama, kajian jerapan dan nyahjerapan telah dijalankan ke atas empat jenis tanah mineral iaitu, Inseptisol (siri Selangor), Inseptisoll (siri Briah), Utisol (siri Rengam dan Serdang) dan Histosol (tanah gambut) yang di ambil dari kawasan tanaman kelapa sawit pada kedalaman 0-15 cm dan 15- 30 cm menggunakan teknik keseimbangan berperingkat.

Kepekatan glifosat yang digunakan adalah 0, 20, 40, 60, 80, 100, and 120 µg/ml. Isoterma bagi jerapan dan nyahjerapan glifosat disesuaikan menggunakan persamaan garis lurus dan Freundlich. Jerapan glifosat adalah mengikut turutan menaik berikut iaitu Selangor > Briah > Rengam > Serdang > gambut. Keputusan ini menunjukkan bahawa jerapan glifosat adalah berkadaran positif dengan kandungan oksida tanah dan kandungan liat. Jerapan yang tinggi pada tanah siri Selangor adalah kerana tanah ini mengandungi kadar oksida tanah dan liat yang paling tinggi. Walaubagaimanapun, bagi nyahjerapan glifosat ,turutan adalah berlawanan iaitu Rengam > Serdang > gambut > Selangor > Briah. Keputusan ini kerana nyahjerapan bergantung kepada tahap penjerapan glifosat pada tanah.

Objektif kedua dicapai melalui kajian penguraian di dalam makmal dan dalam keadaan terkawal menggunakan teknik inkubasi. Kesan aktiviti mikrob pada penguraian glifosat telah dikaji pada tanah siri Selangor yang mempunyai kadar penjerapan paling tinggi pada kadar kedalaman 0 – 15 cm. Sampel bagi tanah steril dan tidak steril dirawat dengan glifosat pada kadar 41 L/ha dan dua kali ganda kadar disyorkan ladang. Setiap tanah yang dirawat disediakan dalam tiga replikasi. Sampel dianalisis pada 0, 3, 7, 21, 42, 60, 100, 120 dan 140 hari selepas rawatan. Penguraian glifosat bagi tanah steril bagi kadar yang disyorkan ladang dapat diperhatikan sehingga hari ke 80 dan 120 hari bagi kadar dua kali ganda disyorkan ladang. Penguraian glifosat bagi tanah tidak steril bagi kadar yang disyorkan ladang dapat diperhatikan sehingga hari ke 35 dan 60 hari bagi kadar dua kali ganda disyorkan ladang.

Di dalam tanah steril, bagi kadar yang disyorkan ladang yang digunakan, jangka hayat separa yang didapati ialah 4 dan kadar dua kali ganda disyorkan adalah 8.3 hari. Di dalam tanah tidak steril, bagi kadar yang disyorkan ladang yang digunakan, jangka hayat separa yang didapati ialah 12.2 dan kadar dua kali ganda disyorkan adalah 17.7 hari.

Eksperimen ladang telah dijalankan bagi mencapai objektif ketiga. Jenis tanah di ladang eksperimen adalah tanah liat. Plot kajian disusun secara rawak lengkap (CRD). Kajian telah dijalankan pada dua musim berbeza iaitu musim hujan dan musim kering. Dalam kajian ini, aplikasi glifosat dijalankan pada kadar disyorkan dan dua kali ganda kadar yang disyorkan ladang. Tiada kesan sisa baki dikesan pada tanah dan air pada musim hujan. Ini kerana hujan lebat yang turun mencairkan glifosat sehingga tidak dapat dikesan dalam kuantiti yang boleh dikenalpasti. Sisa baki glifosat dapat dikesan sehingga hari ke tujuh bagi tanah bahagian atas (0 -15 cm) bagi kadar yang disyorkan dan hari ke tiga puluh lima bagi kadar dua kali disyorkan. Manakala, sisa baki glifosat dapat dikesan sehingga hari pertama bagi tanah bahagian kedua atas (15 – 30 cm) bagi kadar yang disyorkan dan hari ketiga bagi kadar dua kali disyorkan. Kesan sisa baki tidak didapati pada tanah bahagian ketiga (30 -45 cm) bagi kesemua eksperimen. Tiada kesan sisa baki glifosat didapati pada sampel air. Ini kerana kadar taburan hujan yang agak tinggi pada sepanjang eksperimen dilakukan. Dari semua keputusan yang diperolehi, dapat diputuskan bahawa glifosat adalah selamat untuk digunakan kerana ia mempunyai jangka hayat separa yang pendek dan potensi yang rendah untuk racun herba ini dipindahkan atau meluntur ke dalam air bawah tanah sekiranya digunakan seperti yang disyorkan.

Keputusan kajian menunjukkan penjerapan glifosat dalam tanah bergantung kepada tanah yang mempunyai tanah kandungan liat yang tinggi, kandungan oksida tanah yang tinggi dan jenis liat. Sisa glifosat dikesan dalam tanah sehingga hari 35 hari. Walaubagaimanapun, kesan sisa baki glifosat dalam air tanah tidak dapat dikesan walaupun pada dos dua kali ganda digunakan.

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This thesis was submitted to Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the supervisory committee were as follows:

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Date: 15 July 2013

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledge. I also declare that it has not been previously or concurrently, submitted for any other degree at Universiti Putra Malaysia or other institutions.

NURFARADILLA OTHMAN

Date : 15 July 2013

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LIST OF ABBREVIATIONS

CRD	Completely Randomized Design
HPLC	High Performance Liquid Chromatography
MPOB	Malaysian Palm Oil Board
$t_{1/2}$	Half-life
US EPA	United State Environmental Protection Agency
GAP	Good Agricultural Practice
DAT	Day at treatment

CHAPTER 1

INTRODUCTION

Palm oil industry is the main sources of Malaysian economy. Currently, Malaysia is the second largest producers and exporters of oil palm oil in the world, which is supplied for 41% of the world palm oil production and 47 % of world exports. MPOB, (2012) stated that total exports of oil palm products increased from 23.06 million tonnes in 2010 to 24.27 million tonnes in 2011. The area of oil palm plantation in 2011 reached 5.00 million hectares and this number increasing to of 3.0% against 4.85 million hectares. This related to increase in oil palm plantation area in Sarawak which recorded to increase from to 1049, 987 hectares. Sabah is the largest oil palm planted state with 1.43 million hectares or 28.6% of total oil palm planted area and this is followed by Sarawak with 1.05 million hectares (MPOB, 2012).

The high increased in yield is influenced by a subsequent rise in utilization of agrochemicals (MPOB, 2009). Pesticides are one of the main agrochemicals used in oil palm plantation besides fertilizers. The use of pesticides is a necessary in an oil palm plantation and minimal amount of herbicides, insecticides, fungicides and rodenticides is now applied. The use of pesticides in Malaysian agriculture accounts for 75.1% of total market, followed by insecticides,16.0% fungicides, 5.4% and rodenticides,3.5% (Source: Malaysian Agricultural Directory & Index, 2010).

Weed is a major component in oil palm production system. The composition of weeds is a mixture of grasses, sedges, broad-leaved and woody plants, and it will change due to the oil palm growth stages which can provide suitable climatic and environmental conditions for the growth of specific weeds. The shade provided by the palm canopy influences the nature of weed composition, and grass species tend to dominate as the oil palms get bigger (Wan Mohamed *et al*., 1987).

In oil palm industry, herbicides are the most used pesticide group. Herbicides are used to control weeds and to eradicate unwanted plants. Herbicides such as paraquat, glyphosate, glufosinate ammonium, 2, 4-D and lindane are actively used in oil palm plantations for the control of a wide range of broad-leaved weeds , woody plants and grasses. One of the herbicide commonly used in many plantations is glyphosate. It has been on the market since 1974 by Monsanto and constitutes the active substance of several commercially available products such as Roundup®, Rodeo®, Accord®, and Touchdown®. These glyphosate containing herbicides are used not only in agriculture but also in forests, along highways, and in private gardens. The herbicide is taken up by the leaves, and no plants are known to be naturally resistant to the action of glyphosate. It functions by inhibiting an enzyme in the biosynthesis of aromatic amino acids in plants (Carlisle *et al*, 1988).

Glyphosate is actively used in oil palm plantations for the control of a wide range of broad-leaved weeds, woody plants and both annual and perennial grasses. This is to ease the collection of palm oil fruits and to ensure the workers safety against wild animals. Glyphosate was introduced in Malaysia market in 1975 (Cheah *et al*., 1996).

The fate of glyphosate in soil in an important consideration since most of the applied pesticide can be expected eventually reach the soil (Lonsjo *et al*, 1980) and a number of very important processes in normal ecosystems functions occur in soil. Glyphosate meets a variety of fates after application. Glyphosate can be applied onto soil either by direct application, through spraying, and subsequently may evaporate, destroyed by sunlight, or washed away to surface water before reaching their targets. When reaching soil, glyphosate may be taken up by plants, adsorbed onto soil particles, broken down by soil microorganisms and sometimes can be moved off-target to water resources (Tu *et al*., 2001). The most important criteria to determine the behavior of pesticide in the environment is the rate of degradation in soil (Goring and Hamaker, 1975). The persistence of glyphosate in the environment depends partly on the microbial activity of the soil, since the degradation of the molecule is mainly determined by microbial processes. On the other hand, the inactivation of glyphosate in soils occurs mainly through adsorption onto mineral surfaces. However, as a consequence of frequent usage, glyphosate has been introduced to many different compartments of the environment, and there have been a number of incidents where glyphosate and its primary metabolite, aminomethylphosphonic acid (AMPA), have been found in surface and ground (Vreckeen *et al*, 2005). The mobility and leaching of glyphosate may increase, for example due to high rainfall events shortly after application (Vreckeen *et al*, 2005). Glyphosate adsorbs mainly through the phosphonate moiety of the molecule and as a consequence, phosphate can be expected to compete with glyphosate for binding sites on the minerals (Sheals *et al*, 1975).

Field studies are good sources of information on the degradation rates of pesticide. However, variability of climate, pesticide application and sampling exercise are beyond the control of the experimental set up (Laskowski *et al*, 1983). Baylis, (2000) reported that glyphosate is widely used because it's have high- weed killing efficiency, low toxicity to non-target organism and have a limited risk of leaching to groundwater. According to Cheah (1996), the studies of environmental fate of pesticides in Malaysia have been done but the studies on the adsorption, desorption, biodegradation and leaching of pesticides in Malaysia agroecosystems are relatively new and limited. So that, this study is crucial to this oil palm industry for the lifecycle assessment. This project is also much related to MPOB's research and development goals to promote the use, consumption and marketability of oil palm products and to ensure that the oil palm industry is environmentally-friendly.

The main objective of this project is to investigate the behaviour and residue of glyphosate in soil and water of oil palm through three specific objectives. The specific objectives were:

1) To investigate the sorption and desorption of glyphosate on soils with different texture (laboratory experiment)
2) To determine the half-life of glyphosate in Selangor soil (sterilized and non-sterilized soil) applied at 2 rates (laboratory experiment)
3) To determine the residues of glyphosate in soil and water of oil palm plantation (field experiment).

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