UNIVERSITI PUTRA MALAYSIA

# *FATE OF GLYPHOSATE HERBICIDE IN MUNCHONG AND BENTA SOIL SERIES AMENDED WITH COW DUNG AND RICE HUSK ASH*

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By

**GARBA JAMILU**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

**November 2017**

**DEDICATION**

Dedicated to my family for their patience, support and encouragements toward achieving this goal.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

# FATE OF GLYPHOSATE HERBICIDE IN MUNCHONG AND BENTA SOIL SERIES AMENDED WITH COW DUNG AND RICE HUSK ASH

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**GARBA JAMILU**

**November 2017**

**Chairman : Samsuri Abd. Wahid, PhD**
**Faculty : Agriculture**

There is increasing environmental concern on herbicide application in soils due to its toxic effect on microorganism and contamination of food chain. Glyphosate (GLY) is one of the most widely used herbicide and its commercial formulations cause toxic effect to soil microorganism, aquatic habitat and human. Investigation on fates of GLY is necessary for predicting its bioavailability and possible risk of environmental pollution. Application of organic amendments increased soil sorption ability for organic and inorganic pollutants. There is no reported study on the influences of organic amendments on fates of GLY in Malaysian soils. The present study investigates adsorption-desorption, degradation and leaching of GLY in Munchong and Benta soil series amended with cow dung (CD) or rice husk ash (RHA). The physico-chemical properties of the soils, CD and RHA were analysed at the beginning of the study. The adsorption-desorption study was conducted on the selected agricultural waste, control soils, organic matter removed (OM-removed) soils and soils incorporated with CD or RHA (10: 1 w/w) using GLY concentrations ranged between 0 and 300 mg $L^{-1}$. This immediately followed by desorption study which employed addition of 0.01M $CaCl_2$ for every decanted adsorbent from adsorption study. The degradation study was carried out using control and soils amended with 10 ton $ha^{-1}$ equivalent rate of CD or RHA. All the soils were spiked with GLY, maintained at field capacity and GLY degradation was monitored for 65 days. At day's interval, $CO_2$ evolution was determined and on the other hand, extractable GLY residues were analyzed. Meanwhile, the enzymes dehydrogenase were assayed at the end of the incubation study. Three set of the earlier mentioned treatments each under condition of submerged, field capacity and permanent wilting point were monitored for 65 days to study soil GLY degradation at three moisture level. The column leaching study was performed by applying stimulated rainfall to GLY-spiked columns of controls and soils amended with 10 ton $ha^{-1}$ equivalent rate of CD or RHA at time intervals. The leachate were collected from each interval after 24 hours of water

application and analysed for GLY. At the end of the experiment, each column was divided into three layers, dried and analysed for GLY residues. All GLY residue analyses were conducted using high performance liquid chromatography. Results of the soils analysis show that, Munchong series had high clay contents and it is acidic in nature which was due to high Al saturation and contents of oxide minerals. Benta series on the other hand, was sandy in nature and had pH of near neutral. It was low in organic matter, C, N and P contents but had high CEC compared to Munchong which was due to its presence of mica and smectite. Chemical analysis of CD and RHA revealed both to be alkaline and had very low/no heavy metal contents but they have high content of Fe and Al. In addition to this, CD contains functional groups of amines, phenols, alcohols alkanes and alkenes while only siloxane, alkanes and ethers were present in RHA. The BET surface area of CD was lower than that of RHA but the former had higher internal surface area and both have relatively similar pore volume and radius. The adsorption study showed high percent (> 85%) removal of GLY by the adsorbent. The experimental isotherm data generally fitted more to Freundlich than Langmuir equation. Hence, the adsorption capacities of the adsorbents were in order of CD ($K_f$ =1.168 mg $g^{-1}$) > RHA ($K_f$ =1.166 mg $g^{-1}$). Desorption of GLY was minimal, indicating it strong adsorption to CD and RHA. Removing natural organic matter and application of CD or RHA affect the adsorption capacity of Munchong series. The sorption capacities ($K_f$) of the different adsorbent for GLY were in the following order: Munchong (544.879 mg $g^{-1}$) > Munchong + CD (123.908 mg $g^{-1}$) > Munchong + RHA (95.060 mg $g^{-1}$) > OM-removed Munchong (21.538 mg $g^{-1}$) > OM-removed Benta (11.572 mg $g^{-1}$) > Benta + RH (1.574 mg $g^{-1}$) > Benta + CD (1.405 mg $g^{-1}$) > Benta (1.186 mg $g^{-1}$). Adsorption of GLY by all adsorbents was favourable as indicated by Langmuir separation factor, thus, $0.011 < R \geq 0.910$. The percent desorption of GLY from Munchong series ranged between 0.013% and 2.564% with no desorption from the soils amended with CD or RHA. Meanwhile, GLY desorption from different samples of Benta series ranged between 8.10 and 14.57%. The GLY degradation occurred under natural attenuation but addition of CD and RHA stimulate microbial degradation of GLY in Munchong series while their addition showed low GLY degradation in Benta. The degradation in both soils occurred in two phase; initial rapid phase for the compound in solution and the final slow phase for the adsorbed compound. The GLY degradation data was fitted to first order exponential decay model. Munchong degradation data fitted more ($0.007 < r^2 \geq 0.993$) to this model than Benta ($0.371 < r^2 \geq 0.757$). There was higher rate of decay constant (k) for solution phase ($0.0371 < k_1 \geq 0.0688$) compared to sorbed phase ($0.0064 < k_2 \geq 0.0475$) from both soils. The half-life of GLY in Munchong from control and amended soil was less than 22 days for both solution and sorbed phase except for sorbed phase of Munchong amended with RHA which had 108.308 days. Similarly, the half-life of GLY in Benta from control and amended soil ranged from 11.476 – 41.506 days for both solution and sorbed phases. Application of GLY was shown to increase microbial respiration in Munchong while the reverse was observed in Benta hence suggesting its toxicity in the latter. The TPF concentration from control of both soils was higher compared to the treated samples indicating toxicity of GLY to soil enzyme dehydrogenase. Glyphosate was shown to rapidly degrade at field capacity in Munchong from both control and amended soils. But condition of permanent wilting points hasten GLY degradation in Benta soil applied with CD or RHA. Application of CD or RHA did not increased ($p > 0.05$) GLY leaching in both soils. However, more GLY residual concentration was obtained in both leachate from the soils amended with these agricultural waste, indicating their influence on increasing GLY mobility. The result of post-leaching GLY residue analysis showed its high contents at the top layer of both soils hence suggesting its low mobility in these soils even with the addition of CD or RHA. The present study therefore recommend the application of CD at the rate of 10 t $ha^{-1}$ for soil GLY remediation considering its physico-chemical composition and more influence on adsorption and degradation compared to RHA. In addition to this, field capacity was recommended as appropriate soil moisture condition for enhanced GLY degradation. Field trial is also recommended to validate the present laboratory result.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**NASIB RACUN RUMPAI GLIFOSAT DALAM TANAH SIRI MUNCHONG DAN BENTA YANG DITAMBAHBAIK DENGAN TINJA LEMBU DAN ABU SEKAM PADI**

Oleh

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Terdapat kebimbangan terhadap alam sekitar terhadap penggunaan racun herba di tanah akibat kesan toksiknya terhadap mikroorganisma dan pencemaran rantaian makanan. Glyphosate (GLY) adalah salah satu racun rumpai yang paling banyak digunakan dan formulasi komersilnya boleh menyebabkan kesan toksik kepada mikroorganisma tanah, habitat akuatik dan manusia. Kajian tentang nasib GLY adalah perlu untuk meramalkan kesediaan bio dan risiko terhadap pencemaran alam sekitar. Penggunaan bahan penambahbaik organik meningkatkan keupayaan penjerapan tanah terhadap bahan organik dan bukan organik. Tiada lagi kajian yang dilaporkan mengenai pengaruh penambahbaik organik terhadap nasib GLY dalam tanah di Malaysia. Kajian ini dijalankan untuk mengkaji penjerapan-pelepasan, penguraian dan larutlesap GLY pada tanah siri Munchong dan Benta yang ditambahbaik dengan tinja lembu (CD) atau abu sekam padi (RHA). Sifat kimia-fizik tanah, CD dan RHA dianalisis pada permulaan kajian. Kajian penjerapan-pelepasan dilakukan pada tanah siri Munchong dan Benta yang asal, tanah yang telah dihapuskan bahan organik dan tanah yang ditambahbaik dengan CD atau RHA (10: 1 w / w) menggunakan konsentrasi GLY antara 0 dan 300 mg $L^{-1}$. Ini diikuti dengan kajian pelepasan yang menggunakan 0.01M $CaCl_2$ yang ditambah untuk setiap penyerap yang telah diasingkan cairannya pada kajian penjerapan. Kajian penguraian dilakukan menggunakan tanah kawalan dan tanah yang ditambahbaik dengan 10 ton $ha^{-1}$ CD atau RHA. Kesemua tanah itu ditambah dengan GLY, dikekalkan pada kapasiti lapangan dan kandungan GLY dipantau selama 65 hari. Pada selang hari yang tertentu, evolusi $CO_2$ ditentukan dan residu GLY diekstrak dan dianalisis. Sementara itu, enzim dehidrogenase dianalisa pada akhir kajian inkubasi. Tiga set rawatan yang seperti dinyatakan terdahulu, dipantau selama 65 hari untuk mengkaji penguraian GLY pada tiga tahap kelembapan tanah iaitu keadaan tenggelam air, kapasiti lapangan dan titik layu kekal. Tanah kawalan dan tanah yang ditambahbaik dengan CD dan RHA dengan

kadar 10 ton $ha^{-1}$ ditimbang kedalam tiub larutlesap dan dicampur dengan GLY kemudian dilarutlesapkan dengan air hujan simulasi dan hasil larutlesap dikumpulkan pada setiap selang 24 jam dan dianalisis untuk GLY. Pada akhir eksperimen, setiap tiub larutlesap dibahagikan kepada tiga lapisan, dikeringkan dan dianalisis untuk residu GLY. Semua analisis residu GLY dijalankan menggunakan kromatografi cecair prestasi tinggi (HPLC). Keputusan analisis tanah menunjukkan bahawa, siri Munchong mempunyai kandungan lempung yang tinggi dan sifatnya berasid yang disebabkan oleh ketepuan dan kandungan mineral oksida yang tinggi. Sebaliknya, Siri Benta adalah berpasir dan mempunyai pH hampir neutral. Ia rendah dalam kandungan organik, kandungan C, N dan P tetapi mempunyai CEC tinggi berbanding Munchong disebabkan oleh kehadiran mika dan smektit. Analisis kimia CD dan RHA mendedahkan keduanya adalah alkali dan mempunyai kandungan logam berat yang sangat rendah/tiada, tetapi tinggi kandungan Fe dan Al. Di samping itu, CD mengandungi kumpulan amina, fenol, alkana alkohol dan alkenea sementara hanya siloksan, alkana dan eter yang terdapat dalam RHA. Luas permukaan BET CD lebih rendah daripada RHA tetapi mempunyai permukaan dalaman yang lebih tinggi dan kedua-duanya mempunyai isipadu dan radius liang yang sama. Kajian penjerapan menunjukkan peratus penyingkiran GLY yang tinggi (> 85%) oleh adsorben. Data isotherma penjerapan secara umumnya lebih bersesuain dengan isotherma Freundlich berbanding Langmuir. Kapasiti penjerapan oleh penjerap adalah CD ($K_f$ = 1.168 mg $g^{-1}$) > RHA ($K_f$ = 1.166 mg $g^{-1}$). Pelepasan GLY adalah minimum, menunjukkan penjerapan yang kuat oleh CD dan RHA. Mengeluarkan bahan organik semula jadi dan aplikasi CD atau RHA memberi kesan terhadap keupayaan penjerapan siri Munchong. Kapasiti penyerapan ($K_f$) penjerap yang berlainan untuk GLY adalah seperti berikut: Munchong (544.879 mg $g^{-1}$)> Munchong + CD (123.908 mg $g^{-1}$)> Munchong + RHA (95.060 mg $g^{-1}$) > Munchong yang dinyah OM (21.538 mg $g^{-1}$) > Benta dinyah OM (11.572 mg $g^{-1}$) > Benta + RH (1.574 mg $g^{-1}$)> Benta + CD (1.405 mg $g^{-1}$) > Benta (1.186 mg $g^{-1}$). Penjerapan GLY oleh semua penjerap adalah baik seperti ditunjukkan oleh faktor pemisahan Langmuir, iaitu $0.011 < R \geq 0.910$. Peratusan pernjerapan GLY oleh siri Munchong berjulat antara 0.013% dan 2.564%, dan tiada pelepasan GLY dari tanah yang dipinda dengan CD atau RHA. Sementara itu, penjerapan GLY dari sampel berbeza dalam siri Benta berjulat antara 8.10 dan 14.57%. Penguraian GLY berlaku secara semulajadi tetapi penambahan CD dan RHA merangsang penguraian GLY oleh mikrob dalam siri Munchong sementara penambahan mereka memperlihatkan penguraian GLY yang rendah di Benta. Penguraian GLY dalam kedua-dua tanah berlaku dalam dua fasa; fasa awal awal bagi sebatian dalam larutan dan fasa akhir yang perlahan untuk sebatian yang terjerap. Data degradasi GLY padan dengan model pengurain eksponen pertama. Data penguraian untuk siri Munchong lebih padan ($0.007 < r^2 \geq 0.993$) kepada model ini berbanding Benta ($0.371 < r^2 \geq 0.757$). Kadar pemalar penguraian (k) lebih tinggi untuk fasa larutan ($0.0371 < k_1 \geq 0.0688$) berbanding fasa terjerap ($0.0064 < k_2 \geq 0.0475$) untuk kedua-dua tanah. Separuh hayat GLY dalam tanah siri Munchong dan tanahsiti Munchong yang telah ditambahbaik adalah kurang daripada 22 hari untuk kedua-dua fasa larutan dan fasa terjerap kecuali fasa terjerap untuk tanah Munchong yang ditambahbaik dengan RHA di mana separuh hayatnya ialah 108.308 hari. Begitu juga separuh hayat GLY dalam tanah siri Benta dan tanah Benta yang ditambahbaik adalah dari 11.476 - 41.506 hari untuk kedua-dua fasa larutan dan fasa terjerap. Aplikasi GLY meningkatkan pernafasan mikrob di tanah Munchong manakala sebaliknya diperhatikan di tanah Benta, dan ini menunjukkan keracunan GLY di dalamnya. Kepekatan TPF dari kedua-dua tanah kawalan adalah lebih tinggi berbanding dengan sampel yang dirawat yang menunjukkan ketoksikan GLY kepada enzim dehidrogenase tanah. Glifosat mengurai dengan cepat pada kapasiti lapangan di tanah Munchong dan tanah Munchong yang ditambahbaik. Tetapi penguraian GLY adalah cepat pada titik layu tetap di tanah Benta yang ditambahbaik dengan CD atau RHA. Aplikasi CD atau RHA tidak meningkatkan ($p > 0.05$) larutlesap GLY di kedua-dua tanah. Walau bagaimanapun, lebih banyak kepekatan residu GLY diperolehi di kedua-dua larutresapan dari tanah yang ditambahbaik dengan sisa pertanian. Ini menunjukkan pengaruh mereka terhadap peningkatan pergerakan GLY. Hasil analisis residu GLY selepas proses larutlesap menunjukkan kandungannya yang tinggi di lapisan atas kedua-dua tanah dengan itu menunjukkan pergerakannya yang rendah di tanah ini walaupun dengan penambahan CD atau RHA. Oleh itu, kajian ini mengesyorkan penggunaan CD pada kadar 10 t $ha^{-1}$ untuk merawat GLY dalam tanah memandangkan komposisi kimiafiziknya dan ia lebih banyak berpengaruh terhadap penjerapan dan penguraian berbanding dengan RHA. Di samping itu, kapasiti lapangan disyorkan sebagai keadaan kelembapan tanah yang sesuai untuk meningkatkan penguraian GLY. Kajian lapangan juga disyorkan untuk mengesahkan keputusan makmal ini.

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I certify that a Thesis Examination Committee has met on 21 November 2017 to conduct the final examination of Garba Jamilu on his thesis entitled "Fate of Glyphosate Herbicide in Munchong and Benta Soil Series Amended with Cow Dung and Rice Husk Ash" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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| | |
|---|---|
| IPA | Isopropylamine |
| AMPA | Aminomethylphosphonic acid |
| GLY | Glyphosate |
| CD | Cow dung |
| RHA | Rice husk ash |
| CEC | Cation exchange capacity |
| SEM | Scanning electron microscopy |
| BET | Brunauer-emmett-teller |
| UV | Ultraviolet |
| FLD | Flourescent detector |
| FMOC-CL | 9-fluoremethyloxycarbonyl chloride |
| FMOC | 9-fluoremethyloxycarbonyl |
| GC | Gas chromatogramy |
| LC | Liquid chromatogramy |
| HPLC | High pressure liquid chromatogramy |
| LOD | Limit of detection |
| LOQ | Limit of quantification |
| FTIR | Fourier transform infrared spectroscopy |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of the study

Modern agriculture of today is associated with mechanization, the use of genetically modified crops and animals, chemical fertilizers and pesticides for increased productivity. Pesticides are chemicals used in controlling insect, plant disease organisms and weeds (Ortiz-hernández et al., 2011) that endangered our food supply. They generally alter the biological processes of the pest organism (Damalas, 2009). Pesticides are commonly classified based on their chemical composition and the types of pathogens they control (Avav and Ayuba, 2006; Ortiz-hernández et al., 2011). Herbicides are chemicals used in controlling unwanted plants (weeds) and is achieved through their suppression or killing of the weed (Akobundu, 1987). Glyphosate N-(phosphonomethyl) glycine is a broad-spectrum herbicide and its basic ingredients are isopropylamine (IPA) salt, polyethoxylated tallowamine (surfactant) and water. (Giesy et al., 2000; Mackay et al., 2006; NPIC, 2014). Its mode of action in plant is disruption of shikimic pathway which is essential in the synthesis of aromatic amino acids; phenylalamine, tyrosine and tryptophan (Krüger et al., 2013). Plant exposed to glyphosate display stunted growth, loss of green coloration, leaves wrinkling and tissue death, hence death of plant takes 4-20 days to occur (NPIC, 2014).

Glyphosate is a foliage applied herbicide but significant amount can reach the soil through spray drift, direct surface application, plant roots exudate and decomposition of sprayed foliage. The fates and behaviour of glyphosate in soils is controlled by properties of soils and environmental factors (Borggaard and Gimsing, 2008; Rampazzo et al., 2013) which determines its pollution effect on soil microorganism and ground water contamination. Glyphosate undergoes processes of adsorption, degradation and leaching in soil. Glyphosate is strongly adsorbed by soil oxide minerals and organic matter through its phosphonic acid moiety ( Sprankle et al., 1975; Piccolo et al., 1994). This restrict its bioavailability and mobility in soils. However, increase in soil pH results in glyphosate deprotonation leading to possession of more negative charges and subsequent desorption from soil. Once in soil solution, glyphosate will completely be degraded to either aminomethylphosphonic acid (AMPA) or sarcosine then lastly to $CO_2$ and $NH_4^+$. This is achieved by several species of bacteria, fungi and actinomycetes (Kononova and Nesmeyanova, 2002; Romero et al., 2004; Abdel-megeed et al., 2013; Arfarita et al., 2013) which is predominantly a co-metabolic process as it is not used as C and energy source by soil microorganism (Forlani et al., 1999; Singh and Walker, 2006). However there are several species of bacteria and fungi identified as degraders of glyphosate in soil which most of them use glyphosate as source of C, N and P (Kononova and Nesmeyanova, 2002; Lipok et al., 2003; Singh and Walker, 2006). Leaching of glyphosate is negligible due to its strong adsorption by soil and complete degradation by microorganisms. Nonetheless, a soil with low or no oxides minerals and high hydraulic conductivity is vulnerable to glyphosate leaching (Borggaard and Gimsing, 2008).

Application of organic materials for enhanced removal of soil pollutants (biostimulation) has proven to be an effective technique of remediation due to its lower cost, affordability, fewer disturbance of soil and improvements of soil general condition through addition of nutrients, increase in sorption capacity of soil, growth and function of microorganisms (Briceño et al., 2007; Pal et al., 2010; Kanissery and Sims, 2011). These organic amendments also serve as source of micro-organism in soil (Sánchez et al., 2004) a primary agent of pesticide degradation. Cow dung (CD) is the faeces of bull, cow, heifer and calves which is usually applied to agricultural lands as manure. Application of CD to farm lands is an economical and environmentally sustainable mechanism for increasing nutrients and soil organic matter which will result in increase in crop productivity and soil health. Cow dung mainly consists of cellulose, hemicellulose and lignin, and contains several nutrients like N, P, K, basic cations and trace elements essentially for plant and microbial growth (Gupta et al., 2016). Cow dung contains different strains of bacteria and fungi which makes it useful for degradation of pollutants in soil. There are several report on natural ability of CD in decontamination of soil with petroleum hydrocarbons (Agamuthu et al., 2013; Obasi et al., 2013; Oladotun and Adekunle, 2014), heavy metals removal/stabilisation (Marques et al., 2008; Uwumarongie-Ilori et al., 2012; Ngorwe et al., 2014) and remediation of pharmaceutical waste (Randhawa and Kullar, 2011). Rice husk ash (RHA) is a by-product of burnt rice husk used as a source of renewable fuel in the operation of rice driers installed at the mills (Theeba et al., 2012). It has granular structure with high mechanical strength, it is insoluble in water and chemically stable (Raju and Naidu, 2013). This makes it suitable materials in remediation processes especially adsorption of pollutants from wastewater. Rice husk ash has been found to be a good adsorbent of textile dye (Lakshmi et al., 2009), phenol (Mahvi et al., 2004), heavy metals (Srivastava et al., 2006, 2007), and glyphosate (Herath et al., 2016). It also served as a bulking agent in accelerating composting and reduction of N loss (Theeba et al., 2012).

## 1.2 Problem statement

There is rise of environmental concern on increasing glyphosate application due to its environmental contamination and toxicity effect. Waste disposal is also an important issue of environmental concern. Biochar production from these waste is now receiving much attention as a remedy of their deposition. However the energy required in pyrolysis can serve as a constraint to its production. The direct incorporation of these organic residues as manure has been in practice time immemorial. This helps in soil improvement and increased fertility but, their alternative used in soil pollution control still remained unexplored. Glyphosate is increasingly applied in Malaysia for weed control and this necessitates an investigation on its fates in soils with different properties for predicting its potential pollution effect. Considerable studies have been reported by the local researchers on the utilization of RHA for adsorptive removal of heavy metal however, there is little or no attention paid to CD on that aspect. Currently, there is no specific study on the utilization of CD or RHA as amendments for glyphosate adsorption, degradation and leaching on Malaysian soils. Hence utilization of CD and RHA as amendments for investigating fates of glyphosate in Malayasian soils will add knowledge to organic waste utilization and unveils the potential of these agricultural residues as biostimulants. The present study therefore, was undertaken to evaluate the potential of CD and RHA for enhanced adsorption of glyphosate and its metabolite by soil as well as degradation and leaching of glyphosate in selected soils of Peninsular Malaysia.

## 1.3 Significance of the study

In Malaysia, glyphosate is increasingly applied to weedy young oil palm plantation (Abdullah, 2002) and to a large number of problematic weeds found in rice paddies, other cultivated and non-cultivated area (Mohamad et al., 2011). Glyphosate is a foliar applied herbicide, therefore, usually applied using a knap sack sprayer. As a result, siginificant amount of glyphosate go into the soils and undergo adsorption-desorption, leaching and degradation processes depending on properties and composition of the soil. Adsorption-desorption determines bioavailability and mobility of glyphosate in soil. On the other hand, microbial degradation of glyphosate helps in controlling it toxicity effect while it leaching result in underground water pollution. Soil clay, oxide minerals and organic matter significantly increase adsorption of glyphosate in soil (Franz et al., 1997; Piccolo et al., 1994; Piccolo et al., 1995; Sprankle et al., 1975; Sprankle et al, 1975b). Therefore, glyphosate desorb in soil containing less percent clay, oxide minerals and organic matter. This result in increasing bioavailabilty and mobility of glyphosate leading to soil and ground water contamination. Even though, glyphosate is completely mineralized by soil microorganisms (Giesy et al., 2000) but still pose toxicity effect to them. This is due their possession of a shikimic pathway similar to plants and the main action of glyphosate even in plant is disruption of this pathway which is essential for the synthesis of essential amino acids required for growth (Krüger et al., 2013). Investigating adsorption-desorption, degradation and leaching of glyphosate in Malaysian soils therefore, help in predicting its potential pollution to soil and underground water.

## 1.4 Objectives of the study

The present study aimed at investigating the fates of glyphosate and aminomethylphosphonic acid in Oxisols and Alfisols of Malaysia amended with CD or RHA. The specific objectives were;

- To study adsorption-desorption of glyphosate and its major metabolite-aminomethylphosphonic acid- by CD or RHA and in Munchong and Benta soil series in their natural form, added with CD or RHA and after removal of organic matter.
- To evaluate the stimulatory effect of CD or RHA on microbial degradation of glyphosate in Munchong and Benta soil series.
- To examine the influence of three moisture regimes (permanent wilting point, field capacity and submerged) on glyphosate degradation in Munchong and Benta soil series amended with CD or RHA.
- To assess the effect of CD or RHA incorporation on leaching of glyphosate in Munchong and Benta soil series.

# REFERENCES


Abdel-megeed, A., Suliman, A. A., Eman, A., and Sholkamy, E. (2013). In Vitro Detection of Herbicide-Tolerant Fungi Isolated from Pesticides Polluted-Soil. *Journal of Agricultural Science and Technology*, *3*, 960–972.

Abdelhafid, R., Houot, S., and Barriuso, E. (2000). Dependence of atrazine degradation on C and N availability in adapted and non-adapted soils. *Soil Biology and Biochemistry*, *32*(3), 389–401.

Abdullah, A. R. (2002). Pesticide use in Malaysia. *Pesticide Residues in Coastal Tropical Ecosystems: Distribution, Fate and Effects*, 159.

Abdulrazzaq, H., Jol, H., Husni, A., and Abu-bakr, R. (2014). Characterization and Stabilisation of Biochars Obtained from Empty Fruit Bunch, Wood, and Rice Husk. *Bioresources*, *9*(2), 2888–2898.

Accinelli, C., Koskinen, W. C., Seebinger, J. D., Vicari, A., and Sadowsky, M. J. (2005). Effects of incorporated corn residues on glyphosate mineralization and sorption in soil. *Journal of Agricultural and Food Chemistry*, *53*(10), 4110–7.

Agamuthu, P., Tan, Y. S., and Fauziah, S. H. (2013). Bioremediation of Hydrocarbon Contaminated Soil Using Selected Organic Wastes. *Procedia Environmental Sciences*, *18*, 694–702.

Agbenin, J. O., Ibitoye, S. O., and Agbaji, A. S. (2008). Nutrient Mineralization from Deoiled Neem Seed in a Savanna Soil from Nigeria. *Communications in Soil Science and Plant Analysis*, *39*(3–4), 524–537.

Akma, N. M. H., and , Samsuri, A.W.1 , Ainie, H.K. and Rosenani, A. B. (2009). Sorption-Desorption Study of a Herbicide 2 , 4- Dichlorophenoxyacetic Acid on Acidic Tropical Soils. *Malaysian Journal of Soil Science*, *13*, 119–131.

Akobundu, I. O. (1987). *Weed science in the tropics. Principles and practices.* John Wiley.

Al-Rajab. (2014). Behavior of the Non-Selective Herbicide Glyphosate in Agricultural Soil. *American Journal of Environmental Sciences*, *10*(2), 94–101.

Al-Rajab, A. J., Amellal, S., and Schiavon, M. (2008). Sorption and leaching of 14C-glyphosate in agricultural soils. *Agronomy for Sustainable Development*, *28*(3), 419–428.

Al-Rajab, A. J., and Schiavon, M. (2010). Degradation of 14C-glyphosate and aminomethylphosphonic acid (AMPA) in three agricultural soils. *Journal of Environmental Sciences*, *22*(9), 1374–1380.

Albers, C. N., Banta, G. T., Hansen, P. E., and Jacobsen, O. S. (2009). The influence of organic matter on sorption and fate of glyphosate in soil - Comparing different soils and humic substances. *Environmental Pollution*, *157*(10), 2865–2870.

Alef, K. (1995). Estimating of soil respiration. *Methods in Soil Microbiology and Biochemistry, Alef, K., and P. Nannipieri (Eds.). Academic Press, New York*, *464*, 470.

Araújo, A. S. F., Monteiro, R. T. R., and Abarkeli, R. B. (2003). Effect of glyphosate on the microbial activity of two Brazilian soils. *Chemosphere*, *52*(5), 799–804.

Arfarita, N., Imai, T., Kanno, A., Yarimizu, T., Xiaofeng, S., Jie, W., Higuchi, T and Akada, R. (2013). The potential use of trichoderma viride strain FRP3 in biodegradation of the herbicide glyphosate. *Biotechnology and Biotechnological Equipment*, *27*(1), 3518–3521.

Aronsson, H., Stenberg, M., and Ulén, B. (2011). Leaching of N, P and glyphosate from two soils after herbicide treatment and incorporation of a ryegrass catch crop. *Soil Use and Management*, *27*(March), 54–68.

Aslam, S., Garnier, P., Rumpel, C., Parent, S. E., and Benoit, P. (2013). Adsorption and desorption behavior of selected pesticides as influenced by decomposition of maize mulch. *Chemosphere*, *91*(11), 1447–1455.

Aslam, S., Iqbal, A., Deschamps, M., Recous, S., Garnier, P., and Benoit, P. (2015). Effect of rainfall regimes and mulch decomposition on the dissipation and leaching of S-metolachlor and glyphosate: A soil column experiment. *Pest Management Science*, *71*(2), 278–291.

Autio, S., Siimes, K., Laitinen, P., Rämö, S., Oinonen, S., and Eronen, L. (2004). Adsorption of sugar beet herbicides to Finnish soils. *Chemosphere*, *55*(2), 215–226.

Avav, T. and Ayuba, S. . (2006). *Fertilizers and pesticides calculations and application techniques*. Jolytta publication, No 154A Gyado villa, KM 3 Gboko road Makurdi, Benue state-Nigeria.

Ayawei, N., Ebelegi, A. N., and Wankasi, D. (2017). Modelling and Interpretation of Adsorption Isotherms: A Review. *J. Chemistry*. doi.org/10.1155/2017/3039817

Báez, M. E., Espinoza, J., Silva, R., and Fuentes, E. (2015). Sorption-desorption behavior of pesticides and their degradation products in volcanic and nonvolcanic soils: interpretation of interactions through two-way principal component analysis. *Environmental Science and Pollution Research*, *22*(11), 8576–8585.

Bailey, G. W., and White, J. L. (1970). Factors influencing the adsorption, desorption, and movement of pesticides in soil. In *Single Pesticide Volume: The Triazine Herbicides* (pp. 29–92). Springer.

Barot, N. S., and Bagla, H. K. (2012). Biosorption of radiotoxic 90Sr by green adsorbent: Dry cow dung powder. *Journal of Radioanalytical and Nuclear Chemistry*, *294*(1), 81–86.

Benbrook, C. M. (2016). Trends in glyphosate herbicide use in the United States and globally. *Environmental Sciences Europe*, *28*(1), 3. http://doi.org/10.1186/s12302-016-0070-0

Bennicelli, R. P., Szafranek-Nakonieczna, A., Wolinska, A., Stepniewska, Z., and Bogudzinska, M. (2009). Influence of pesticide (glyphosate) on dehydrogenase activity, pH, Eh and gases production in soil (laboratory conditions). *International Agrophysics*, *23*(2), 117–122.

Boehm, H. P. (2002). Surface oxides on carbon and their analysis : a critical assessment. *Carbon*, *40*, 145–149.

Boivin, A., Cherrier, R., and Schiavon, M. (2005). A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. *Chemosphere*, *61*(5), 668–676.

Borggaard, O. K. and Gimsing, A. L. (2008). Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: areview. *Pest Management Science*, *64*, 441–456.

Brady, N. C., and Weil, R. R. (1999). *The nature and properties of soil 12th ed*. Prentice-Hall Inc. Upper Saddle River, New Jersey.

Briceño, G., Palma, G., and Durán, N. (2007). *Influence of Organic Amendment on the Biodegradation and Movement of Pesticides*. *Critical Reviews in Environmental Science and Technology* (Vol. 37). http://doi.org/10.1080/10643380600987406

Bronstad, J. O., and Friestad, H. O. (1985). Behaviour of glyphosate in the aquatic environment. *Herbicide Glyphosate/edited by E. Grossbard, D. Atkinson*.

Cáceres-Jensen, L., Gan, J., Báez, M., Fuentes, R., and Escudey, M. (2009). Adsorption of Glyphosate on Variable-Charge, Volcanic Ash-Derived Soils. *Journal of Environmental Quality*, *38*(4), 1449–57.

Carter, M. R., and Gregorich, E. G. (eds). (2006). *Soil sampling and methods of analysis*. CRC Press.

Cassigneul, A., Benoit, P., Bergheaud, V., Dumeny, V., Etiévant, V., Goubard, Y., Maylin, A., Justes, E and Alletto, L (2016). Fate of glyphosate and degradates in cover crop residues and underlying soil: A laboratory study. *Science of the Total Environment*, *545–546*, 582–590.

Castillo, J. M., Romero, E., Fernández-Bayo, J., Vivas, A., and Nogales, R. (2011). Effect of Natural Vegetation Strips and Herbicides on Enzyme Activities and Bacterial Diversity in Olive-Orchard Systems. In *Soil Enzymology in the Recycling of Organic Wastes and Environmental Restoration* (pp. 255–270). Springer.

Cederlund, H., Börjesson, E., Lundberg, D., and Stenström, J. (2016). Adsorption of pesticides with different chemical properties to a wood biochar pre-treated with heat and iron. *Water, Air, and Soil Pollution*, *227*, 203–215.

Chai, L. K., Wong, M. H., and Bruun Hansen, H. C. (2013). Degradation of chlorpyrifos in humid tropical soils. *Journal of Environmental Management*, *125*, 28–32.

Cheah, U.-B., Kirkwood, R. C., and Lum, K.-Y. (1998). Degradation of Four Commonly Used Pesticides in Malaysian Agricultural Soils. *Journal of Agricultural and Food Chemistry*, *46*(3), 1217–1223.

Cheah, U., Kirkwood, C., and Lum, K. (1997). Adsorption , Desorption and Mobilit y of Four Commonl y Used Pesticides in Mala y sian Agricultural Soils . *Pesticide Science*, *50*, 53–63.

Chowdhury, A., Pradhan, S., Saha, M., and Sanyal, N. (2008). Impact of pesticides on soil microbiological parameters and possible bioremediation strategies. *Indian Journal of Microbiology*, *48*(1), 114–127.

Claoston, N., Samsuri, A., Ahmad Husni, M., and Mohd Amran, M. (2014). Effects of pyrolysis temperature on the physicochemical properties of empty fruit bunch and rice husk biochars. *Waste Management and Research : The Journal of the International Solid Wastes and Public Cleansing Association, ISWA*, *32*(4), 331–9.

Cserháti, T., Forgács, E., Deyl, Z., Miksik, I., and Eckhardt, A. (2004). Chromatographic determination of herbicide residues in various matrices. *Biomedical Chromatography*, *18*, 350–359.

Dąbrowska, D., Kot-Wasik, A., and Namieśnik, J. (2004). The Importance of Degradation in the Fate of Selected Organic Compounds in the Environment. Part II. Photodegradation and Biodegradation. *Polish Journal of Environmental Studies*, *13*(6), 617–626.

Damalas, C. (2009). Understanding benefits and risks of pesticide use. *Scientific Research and Essay*, *4*(10), 945–949.

De Andréa, M. M., Peres, T. B., Luchini, L. C., Bazarin, S., Papini, S., Matallo, M. B., and Tedeschi Savoy, V. L. (2003). Influence of repeated applications of glyphosate on its persistence and soil bioactivity. *Pesquisa Agropecuaria Brasileira*, *38*(11), 1329–1335.

De Jonge, H., and De Jonge, L. W. (1999). Influence of pH and solution composition on the sorption of glyphosate and prochloraz to a sandy loam soil. *Chemosphere*, *39*(5), 753–763.

De Jonge, H., De Jonge, L. W., and Jacobsen, O. H. (2000). [14C]glyphosate transport in undisturbed topsoil columns. *Pest Management Science*, *56*(10), 909–915.

de Santana, H., Toni, L. R. M., Benetoli, L. O. de B., Zaia, C. T. B. V, Rosa, M., and Zaia, D. A. M. (2006). Effect in glyphosate adsorption on clays and soils heated and characterization by FT-IR spectroscopy. *Geoderma*, *136*(3–4), 738–750.

Dion, H. M., Harsh, J. B., and Hill, H. H. (2001). Competitive sorption between glyphosate and inorganic phosphate on clay minerals and low organic matter soils. *Journal of Radioanalytical and Nuclear Chemistry*, *249*(2), 385–390.

Duke, S. O., Lydon, J., Koskinen, W. C., Moorman, T. B., Chaney, R. L., and Hammerschmidt, R. (2012). Glyphosate effects on plant mineral nutrition, crop rhizosphere microbiota, and plant disease in glyphosate-resistant crops. *Journal of Agricultural and Food Chemistry*, *60*(42), 10375–10397.

Durovic, R., Gajic-Umiljendic, J., and Dordevic, T. (2009). Effects of organic matter and clay content in soil on pesticide adsorption processes. *Pesticides and Phytomedicine, 24*(1), 51–57.

Eberbach, P. (1998). Appl y ing Non-stead y -state Compartmental Anal y sis to Investigate the Simultaneous Degradation of Soluble and Sorbed Gl y phosate ( N - ( Phosphonomethyl ) glycine ) in Four Soils. *Pesticides Science*, 52, 229-240.

Eberbach, P. L. (1999). Influence of Incubation Temperature on the Behavior of Triethylamine-Extractable Glyphosate ( N -Phosphonomethylglycine ) in Four Soils. *Journal of Agricultural and Food Chemistry*, *47*(1979), 2459–2467.

Ekhwan, M., Toriman, H., and Mokhtar, M. B. (2009). Analysis of the Physical Characteristics of Bris Soil in Coastal Kuala Kemaman , Terengganu. *Research Journal of Earth Sciences*, *1*(1), 1–6.

Eman, A., Abdel-megeed, A., Suliman, A. A., and Sadik, M. W. (2013). Biodegradation of Glyphosate by fungal strains isolated from herbicides polluted-soils in Riyadh area. *International Journal of Current Microbiology and Applied Sciences, 2*(8), 359–381.

Enio, M. S. K., Shamshuddin, J., Fauziah, C. I., and Husni, M. H. A. (2011). Pyritization of the Coastal Sediments in the Kelantan Plains in the Malay Peninsula during the Holocene. *American Journal of Agricultural and Biological Sciences*, *6*(3), 393–402.

Fidel, R. B., Laird, D. a., and Thompson, M. L. (2013). Evaluation of Modified Boehm Titration Methods for Use with Biochars. *Journal of Environment Quality*, *42*(6), 1771–1778.

Flury, M. (1996). Experimental evidence of transport of pesticides through field soils—a review. *Journal of Environmental Quality*, *25*(1), 25–45.

Forlani, G., Mangiagalli, A., Nielsen, E., and Suardi, C. M. (1999). Degradation of the phosphonate herbicide glyphosate in soil: Evidence for a possible involvement of unculturable microorganisms. *Soil Biology and Biochemistry*, *31*, 991–997.

Franz, J. E., Mao, M. K., and Sikorski, J. A. (1997). *Glyphosate: a unique global herbicide.* American Chemical Society.

Gaillardon, P., and Dur, J. C. (1995). Influence of Soil Moisture on Short-Term Sorption of Diuron and Isoproturon by Soil. *Pesticide Science*, *45*, 297–303.

Gasnier, C., Dumont, C., Benachour, N., Clair, E., Chagnon, M. C., and Séralini, G. E. (2009). Glyphosate-based herbicides are toxic and endocrine disruptors in human cell lines. *Toxicology*, *262*(3), 184–191.

Geisseler, D., Horwath, W. R., and Scow, K. M. (2011). Soil moisture and plant residue addition interact in their effect on extracellular enzyme activity. *Pedobiologia*, *54*(2), 71–78.

Gerritsea, R. G., Beltranb, J., and Hernandeg, F. (1996). Adsorption of atrazine, simazine, and glyphosate in soils of the Gnangara Mound, Western Australia. *Australian Journal of Soil Research*, *34*, 599–607.

Getenga, Z. M. (2003). Enhance mineralization of Atrazine in Compost-Amended soil in Laboratory studied. *Bulletin of Environmental Contamination and Toxicology*, *71*, 933–941.

Getenga, Z. M., and Kengara, F. O. (2004). Mineralization of glyphosate in compost-amended soil under controlled conditions. *Bulletin of Environmental Contamination and Toxicology*. http://doi.org/10.1007/s00128-003-9004-9

Gianfreda, L., and Rao, M. A. (2004). Potential of extra cellular enzymes in remediation of polluted soils: a review. *Enzyme and Microbial Technology*, *35*(4), 339–354.

Giesy, J. P., Dobson, S., and Solomon, K. R. (2000). Ecotoxicological Risk Assesment for Roundup Herbicide. *Rev Environ Contam Toxicol*, *167*, 35–120.

Gimsing, A. L., Borggaard, O. K., Jacobsen, O. S., Aamand, J., and Sørensen, J. (2004). Chemical and microbiological soil characteristics controlling glyphosate mineralisation in Danish surface soils. *Applied Soil Ecology*, *27*, 233–242.

Gimsing, A. L., Szilas, C., and Borggaard, O. K. (2007). Sorption of glyphosate and phosphate by variable-charge tropical soils from Tanzania. *Geoderma*, *138*(1–2), 127–132.

Glass, R. L. (1987). Adsorption of Glyphosate by Soils and Clay Minerals. *Journal of Agricultural and Food Chemistry*, *35*, 497–500.

Goetz, A. J., Wehtje, G., Walker, R. H., and Hajek, B. (1986). Soil solution and mobility characterization of imazaquin. *Weed Science*, 788–793.

Gupta, K. K., Aneja, K. R., and Rana, D. (2016). Current status of cow dung as a bioresource for sustainable development. *Bioresources and Bioprocessing*, *3*(1), 28. http://doi.org/10.1186/s40643-016-0105-9

Güven, D. E., and Akinci, G. (2011). Comparison of acid digestion techniques to determine heavy metals in sediment and soil samples. *Gazi University Journal of Science*, *24*(1), 29–34.

Häggblom, M. M. (1992). Microbial breakdown of halogenated aromatic pesticides and related compounds. *FEMS Microbiology Reviews*, *9*(1), 29-71.

Hamdaoui, O., and Naffrechoux, E. (2007). Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I . Two-parameter models and equations allowing determination of thermodynamic parameters. *J. Hazardous Material*, *147*, 381–394.

Hameed, B. H., Tan, I. A. W., and Ahmad, A. L. (2008). Adsorption isotherm , kinetic modeling and mechanism of 2 , 4 , 6-trichlorophenol on coconut husk-based activated carbon. *Chemical Engineering Journal*, *144*, 235–244.

Haney, R. L., S. A . Senseman, L. J. Kruzt, F. M. H. (2002). Soil carbon and nitrogen mineralization as affected by atrazine and glyphosate. *Biology and Fertility of Soils*, *35*(1), 35–40.

Haney, R., Senseman, S., Hons, F., and Zuberer, D. (2000). Effect of glyphosate on soil microbial activity and biomass. *Weed Science*, *48*(1), 89–93.

Harper, S. S. (1994). Sorption-desorption and herbicide behavior in soil. *Reviews of Weed Science (USA)*.

Hart, M. R., Quin, B. F., and Nguyen, M. (2004). Phosphorus runoff from agricultural land and direct fertilizer effects. *Journal of Environmental Quality*, *33*(6), 1954–1972.

Henry, C. J., Higgins, K. F., and Buhl, K. J. (1994). Acute toxicity and hazard assessment of Rodeo??, X-77 Spreader??, and Chem-Trol?? to aquatic invertebrates. *Archives of Environmental Contamination and Toxicology*, *27*(3), 392–399.

Herath, I., Kumarathilaka, P., Al-Wabel, M. I., Abduljabbar, A., Ahmad, M., Usman, A. R. A., and Vithanage, M. (2016). Mechanistic modeling of glyphosate interaction with rice husk derived engineered biochar. *Microporous and Mesoporous Materials*, *225*, 280–288.

Herath, I., Mayakaduwa, S. S., and Vithanage, M. (2015). Potential of Different Biochars for Glyphosate Removal in Water ; Implications for Water Safety. In *6th International Conference on Structural Engineering and Construction Management 2015, Kandy, Sri Lanka, 11th-13th December 2015* (pp. 163–168).

Hiera Da Cruz, L., De Santana, H., Zaia, C. T. B. V, and Zaia, D. A. M. (2007). Adsorption of glyphosate on clays and soils from Paraná State: Effect of pH and competitive adsorption of phosphate. *Brazilian Archives of Biology and Technology*, *50*(3), 385–394.

Houot, S., Topp, E., Yassir, A., and Soulas, G. (2000). Dependence of accelerated degradation of atrazine on soil pH in French and Canadian soils. *Soil Biology and Biochemistry*, *32*(5), 615–625.

Hu, Y. S., Zhao, Y. Q., and Sorohan, B. (2011). Removal of glyphosate from aqueous environment by adsorption using water industrial residual. *Desalination*, *271*(1–3), 150–156.

Ismail, B. S., Kadir, Z. A., Jusoh, K., and Mat, N. (2002). Adsorption-Desorption , Mobility and Degradation of 14 C-Glyphosate in Two Soil Series. *Jurnal Sains Nuklear Malaysia, 20*(1), 17–29.

Jalaludin, A., Yu, Q., and Powles, S. B. (2015). Multiple resistance across glufosinate, glyphosate, paraquat and ACCase-inhibiting herbicides in an Eleusine indica population. *Weed Research*, *55*(1), 82–89.

Johnson, T. A., and Sims, G. K. (2011). Introduction of 2, 4-dichlorophenoxyacetic acid into soil with solvents and resulting implications for bioavailability to microorganisms. *World Journal of Microbiology and Biotechnology*, *27*(5), 1137–1143.

Kadian, N., Gupta, A., Satya, S., Mehta, R. K., and Malik, A. (2008). Biodegradation of herbicide (atrazine) in contaminated soil using various bioprocessed materials. *Bioresource Technology*, *99*(11), 4642–4647.

Kah, M., and Brown, C. D. (2006). Adsorption of ionisable pesticides in soils. *Reviews of Environmental Contamination and Toxicology*, *188*, 149–217.

Kanissery, R. G., and Sims, G. K. (2011). Biostimulation for the Enhanced Degradation of Herbicides in Soil. *Applied and Environmental Soil Science*, *2011*, 1–10.

Kanissery, R., Welsh, A., and Sims, G. (2015). Effect of Soil Aeration and Phosphate Addition on the Microbial Bioavailability of Carbon-14-Glyphosate. *Journal of Environmental quality, 44*(1), 137–144.

Keeney, D. R., Nelson, D. W., and Page, A. L. (1982). Methods of soil analysis. Part. 2. Chemical and microbiological properties. *Eds. CA Black et Al*, 711–733.

Khan, S. U. (1980). *Pesticides in the soil environment*. Elsevier scientific publishing company, Amsterdam.

Khanif, Y. M., Fauziah, I. C., and Shamshuddin, J. (1999). Toxic Metals and Agrochemicals in Soils in Malaysia: Current Problems and Mitigation Plans. *Soils and Groundwater Pollution and Remediation: Asia, Africa, and Oceania*, 330.

Kishore, G. M., and Jacob, G. S. (1987). Degradation of glyphosate by Pseudomonas sp. PG2982 via a sarcosine intermediate. *Journal of Biological Chemistry*, *262*(25), 12164–12168.

Kjær, J., Ernsten, V., Jacobsen, O. H., Hansen, N., de Jonge, L. W., and Olsen, P. (2011). Transport modes and pathways of the strongly sorbing pesticides glyphosate and pendimethalin through structured drained soils. *Chemosphere*, *84*(4), 471–479.

Kjær, J., Olsen, P., Ullum, M., and Grant, R. (2005). Vadose zone processes and chemical transport leaching of glyphosate and amino-methylphosphonic cid from Danish agricultural field sites. *Journal of Environmental Quality*, *34*, 608–620.

Kononova, S. V, and Nesmeyanova, M. A. (2002). Phosphonates and Their Degradation by Microorganisms. *Biochemistry (Moscow)*, *67*(2), 184–195.

Krüger, M., Schrödl, W., Neuhaus, J., and Shehata, A. A. (2013). Field Investigations of Glyphosate in Urine of Danish Dairy Cows. *Journal of Environmental and Analytical Toxicology*, *3*(5), 186. http://doi.org/http://dx.doi.org/10.4172/2161-0525.1000186

Krzyśko-Łupicka, T., and Orlik, A. (1997). Use of glyphosate as the sole source of phosphorus or carbon for the selection of soil-borne fungal strains capable to degrade this herbicide. *Chemosphere*, *34*(12), 2601–2605.

Kwabiah, A. B., Stoskopf, N. C., Palm, C. A., and Voroney, R. P. (2003). Soil P availability as affected by the chemical composition of plant materials: Implications for P-limiting agriculture in tropical Africa. *Agriculture, Ecosystems and Environment*, *100*(1–3), 53–61.

Lakshmi, U. R., Srivastava, V. C., Mall, I. D., and Lataye, D. H. (2009). Rice husk ash as an effective adsorbent: Evaluation of adsorptive characteristics for Indigo Carmine dye. *Journal of Environmental Management*, *90*(2), 710–720.

Lancaster, S. H., Hollister, E. B., Senseman, S. A., and Gentry, T. J. (2010). Effects of repeated glyphosate applications on soil microbial community composition and the mineralization of glyphosate. *Pest Management Science*, *66*(1), 59–64.

Landry, D., Dousset, S., Fournier, J.-C., and Andreux, F. (2005). Leaching of glyphosate and AMPA under two soil management practices in Burgundy vineyards (Vosne-Romanée, 21-France). *Environmental Pollution*, *138*(2), 191–200.

Lane, M., Lorenz, N., Saxena, J., Ramsier, C., and Dick, R. P. (2012). The effect of glyphosate on soil microbial activity, microbial community structure, and soil potassium. *Pedobiologia*, *55*(6), 335–342.

Lipok, J., Dombrovska, L., Wieczorek, P., and Kafarski, P. (2003). The ability of fungi isolated from stored carrot seeds to degrade organophosphonate herbicides. In *Pesticide in Air, Plant, Soil and Water System, Proceedings of the XII Symposium Pesticide Chemistry*.

Liu, C.-M., McLean, P. A., Sookdeo, C. C., and Cannon, F. C. (1991). Degradation of the herbicide glyphosate by members of the family Rhizobiaceae. *Applied and Environmental Microbiology*, *57*(6), 1799–1804.

Locke, M. A., and Zablotowicz, R. M. (2004). Pesticides in soil–benefits and limitations to soil health. In *Managing soil quality: challenges in modern agriculture* (pp. 239–260). CABI Publishing Wallingford.

Lu, J. H., Li, J. F., Li, Y. M., Chen, B. Z., and Bao, Z. F. (2012). Use of Rice Straw Biochar Simultaneously as the Sustained Release Carrier of Herbicides and Soil Amendment for Their Reduced Leaching. *Journal of Agricultural and Food Chemistry*, *60*(26), 6463–6470.

Mackay, D., Shiu, W.-Y., Ma, K.-C., and Lee, S. C. (2006). *Handbook of physical-chemical properties and environmental fate for organic chemicals*. CRC press.

Mahvi, A.H., Maleki, A., Eslami, A. (2004). Potential of Rice Husk and Rice Husk Ash for Phenol Removal in Aqueous Systems. *American Journal of Applied Sciences*, *1*(4), 321–326.

Malik, J., Barry, G., and Kishore, G. (1989). The herbicide glyphosate. *BioFactors (Oxford, England)*, *2*(1), 17–25.

Mallory-Smith Carol, and Retzinger, J. (2003). Revised Classification of Herbicides by Site of Action for Weed Resistance. *Weed Technology*, *17*(2), 605–619.

Mamy, L., and Barriuso, E. (2007). Desorption and time-dependent sorption of herbicides in soils. *European Journal of Soil Science*, *58*(1), 174–187.

Marc, J., Mulner-Lorillon, O., Boulben, S., Hureau, D., Durand, G., and Bellé, R. (2002). Pesticide Roundup provokes cell division dysfunction at the level of CDK1/cyclin B activation. *Chemical Research in Toxicology*, *15*(3), 326–331.

Marques, A. P. G. C., Oliveira, R. S., Rangel, A. O. S. S., and Castro, P. M. L. (2008). Application of manure and compost to contaminated soils and its effect on zinc accumulation by Solanum nigrum inoculated with arbuscular mycorrhizal fungi. *Environmental Pollution*, *151*(3), 608–620.

Marrs, R. H., Frost, A. J., Plant, R. A., and Lunnis, P. (1993). Determination of buffer zones to protect seedlings of non-target plants from the effects of glyphosate spray drift. *Agriculture, Ecosystems and Environment*, *45*(3–4), 283–293.

Martin-Neto, L., Vieira, E. M., and Sposito, G. (1994). Mechanism of atrazine sorption by humic acid: a spectroscopic study. *Environmental Science and Technology*, *28*(11), 1867–1873.

Maurya, N. S., and Mittal, A. K. (2010). Biosorptive Color Removal: Applicability of Equilibrium Isotherm Models. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, *14*(1), 25–36.

Mayakaduwa, S. S., Kumarathilaka, P., Herath, I., Ahmad, M., Al-Wabel, M., Ok, Y. S., Usman, A., Abduljabar, A., and Vithanage, M. (2016). Equilibrium and kinetic mechanisms of woody biochar on aqueous glyphosate removal. *Chemosphere*, *144*, 2516–2521.

Mazzei, P., and Piccolo, A. (2012). Quantitative evaluation of noncovalent interactions between glyphosate and dissolved humic substances by NMR spectroscopy. *Environmental Science and Technology*, *46*(11), 5939–5946.

Mcconnell, J. S., and Hossner, L. R. (1985). pH-Dependent Adsorption Isotherms of Glyphosate. *Journal of Agricultural and Food Chemistry*, *33*(6), 1075–1078.

McGuinness, M., and Dowling, D. (2009). Plant-Associated Bacterial Degradation of Toxic Organic Compounds in Soil. *International Journal of Environmental Research and Public Health*, *6*(8), 2226–2247.

Mesnage, R., Bernay, B., and Séralini, G. E. (2013). Ethoxylated adjuvants of glyphosate-based herbicides are active principles of human cell toxicity. *Toxicology*, *314*(2–3), 122–128.

Moeskops, B., Sukristiyonubowo, Buchan, D., Sleutel, S., Herawaty, L., Husen, E., Saraswati, R., Setyorini, D., and De Neve, S. (2010). Soil microbial communities and activities under intensive organic and conventional vegetable farming in West Java, Indonesia. *Applied Soil Ecology*, *45*(2), 112–120.

Mohamad, R. B., Awang, Y., Jusoff, M. S., and Puteh, A. (2011). Effect of glufosinate-ammonium, glyphosate and imazapyr herbicides at two spraying volumes on Imperata cylindrica (L.) Raeuschel. *Journal of Food, Agriculture and Environment*, *9*(3–4), 854–857.

Mohamad, R. B., Wibawa, W., Mohayidin, M. G., Puteh, A. B., Juraimi, A. S., Awang, Y., and Lassim, M. B. M. (2010). Management of mixed weeds in young oil-palm plantation with selected broad-spectrum herbicides. *Pertanika Journal of Tropical Agricultural Science*, *33*(2), 193–203.

Mohan, D., Rajput, S., Singh, V. K., Steele, P. H., and Pittman, C. U. (2011). Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. *Journal of Hazardous Materials*, *188*(1–3), 319–333.

Mohapatra, D., Mishra, D., and Chaudhury, G. R. (2008). Removal of Arsenic from Arsenic Rich Sludge by Volatilization Using Anaerobic Microorganisms Treated with Cow Dung. *Soil and Sediment Contamination*, *17*, 301–311.

Mohsen Nourouzi, M., Chuah, T. G., and Choong, T. S. Y. (2012). Adsorption of glyphosate onto activated carbon derived from waste newspaper. *Desalination and Water Treatment*, *24*(1–3), 321–326.

Morillo, E., Undabeytia, T., Maqueda, C., and Ramos, A. (2000). Glyphosate adsorption on soils of different characteristics.: Influence of copper addition. *Chemosphere*, *40*(1), 103–107.

Myers, J. P., Antoniou, M. N., Blumberg, B., Carroll, L., Colborn, T., Everett, L. G., Hansen, M., Landrigan, P.J., Lanphear, B. P., Mesnage, R., Vandenberg, N.V., vom Saal, F. S., Welshons, W. V., and Benbrook, C. M. (2016). Concerns over use of glyphosate-based herbicides and risks associated with exposures: A consensus statement. *Environmental Health: A Global Access Science Source*, *15*(1), 1–13. http://doi.org/10.1186/s12940-016-0117-0

Nafziger, E. D., Widholm, J. M., Steinrücken, H. C., and Killmer, J. L. (1984). Selection and characterization of a carrot cell line tolerant to glyphosate. *Plant Physiology*, *76*(3), 571–4.

Nannipieri, P., Kandeler, E., and Ruggiero, P. (2002). Enzyme Activities and Microbiological and Biochemcial Processes in Soil. In *Enzymes in the environment: Activity, ecology, and applications*. CRC Press.

Neumann, G., Kohls, S., Landsberg, E., Stock-Oliveira Souza, K., Yamada, T., and Römheld, V. (2006). Relevance of glyphosate transfer to non-target plants via the rhizosphere. *Journal of Plant Diseases and Proctection, Supplement*, *969*(20), 963–969.

Ngorwe, E. N., Nyambaka, H. N., and Murungi, J. I. (2014). Use of Low Cost Soil Amendments Reduces Uptake of Cadmium and Lead by Tobacco ( Nicotiana tabacum ) Grown in Medially Polluted Soils. *Journal of Environment and Human*, *1*(2), 104–113.

Nguyen, D. B., Rose, M. T., Rose, T. J., Morris, S. G., and van Zwieten, L. (2016). Impact of glyphosate on soil microbial biomass and respiration: A meta-analysis. *Soil Biology and Biochemistry*, *92*, 50–57.

Novak, J. M., Busscher, W. J., Watts, D. W., Laird, D. A., Ahmedna, M. A., and Niandou, M. A. S. (2010). Short-term CO2 mineralization after additions of biochar and switchgrass to a Typic Kandiudult. *Geoderma*, *154*(3–4), 281–288.

NPIC. (2014). *Glyphosate fact sheet.* National Pesticide Information Centre Oregun state university, 333 Weniger Hall, Corvallis. Weniger.

Obasi, N. A., Eze, E., Anyanwu, D. I., and Okorie, U. C. (2013). Effects of organic manures on the physicochemical properties of crude oil polluted soils. *African Journal of Biochemistry Research*, *7*(6), 67–75.

Okada, E., Costa, J. L., and Bedmar, F. (2016). Adsorption and mobility of glyphosate in different soils under no-till and conventional tillage. *Geoderma*, *263*, 78–85.

Okalebo, J. R., Gathua, K. W., and Woomer, P. L. (2002). Laboratory methods of plant and soil analysis: a working manual. *TSBF-UNESCO, Nairobi, Kenya*.

Oladotun, A., and Adekunle, I. (2014). Remediation of crude oil polluted soil using cow dung manure in relations to the growth of maize ( Zea mays L . ). *Canadian Open Agricultural and Soil Science Journal*, *1*(1), 1–16.

Ololade, I. A., Oladoja, N. A., Oloye, F. F., Alomaja, F., Akerele, D. D., Iwaye, J., and Aikpokpodion, P. (2014). Sorption of Glyphosate on Soil Components: The Roles of Metal Oxides and Organic Materials. *Soil and Sediment Contamination: An International Journal*, *23*(5), 571–585.

Ortiz-hernández, M. L., Sánchez-salinas, E., Olvera-velona, A., and Folch-mallol, J. L. (2011). Pesticides in the Environment : Impacts and Their Biodegradation as a Strategy for Residues Treatment. *Pesticides - Formulations, Effects, Fate*, 552–574.

Pal, R., Chakrabarti, K., Chakraborty, A., and Chowdhury, A. (2005). Pencycuron dissipation in soil: effect of application rate and soil conditions. *Pest Management Science*, *61*(12), 1220–1223.

Pal, R., Chakrabarti, K., Chakraborty, A., and Chowdhury, A. (2006). Degradation and effects of pesticides on soil microbiological parameters - a review. *International Journal of Agricultural Research*. http://doi.org/10.3923/ijar.2006.240.258

Pal, S., Patra, A. K., Reza, S. K., Wildi, W., and Poté, J. (2010). Use of bio-resources for remediation of soil pollution. *Natural Resources*, *1*(2), 110.

Panettieri, M., Lazaro, L., López-Garrido, R., Murillo, J. M., and Madejón, E. (2013). Glyphosate effect on soil biochemical properties under conservation tillage. *Soil and Tillage Research*, *133*, 16–24.

Paramananthan. (2000). Malaysian Soil Taxonomy- A Unified Malaysian Soil Classification System. *Soils of Malaysia, Volume 1*.

Pasaribu, A., Mohamad, R. B., Awang, Y., Othman, R., and Puteh, A. (2011). Growth and development of symbiotic Arbuscular mycorrhizal fungi , Glomus mossea ( Nicol . and Gerd .), in alachlor and glyphosate treated soils. *African Journal of Biotechnology*, *10*(55), 11520–11526.

Payne, N. J. (1992). Off- target glyphosate from aerial silvicultural applications, and buffer zones required around sensitive areas. *Pest Management Science*, *34*(1), 1–8.

Pérez, G. L., Vera, M. S., and Miranda, L. A. (2011). Effects of Herbicide Glyphosate and Glyphosate-Based Formulations on Aquatic Ecosystems. *Herbicides and the Environment*, 343–368.

Pessagno, R. C., Torres Sánchez, R. M., and dos Santos Afonso, M. (2008). Glyphosate behavior at soil and mineral–water interfaces. *Environmental Pollution*, *153*(1), 53–59. http://doi.org/10.1016/j.envpol.2007.12.025

Piccolo, A., G. Celano, G., and Conte, P. (1996). Adsorption of Glyphosate by Humic Substances. *Journal of Agricultural and Food Chemistry*, *44*(2), 2442–2446.

Piccolo, A., Celano, G., Arienzo, M., & Mirabella, A. (1994). Adsorption and desorption of glyphosate in some european soils. *Journal of Environmental Science and Health B*, *Pesticides, Food Contaminants, and Agricultural Wastes*, *29*(6), 1105–1115.

Piccolo, A., and Celano, G. (1994). Hydrogen- bonding interactions between the herbicide glyphosate and water- soluble humic substances. *Environmental Toxicology and Chemistry*, *13*(11), 1737–1741.

Piccolo, A., Celano, G., and Pietramellara, G. (1992). Adsorption of the herbicide glyphosate on a metal-humic acid complex. *Science of the Total Environment, The*, *123–124*(C), 77–82.

Piccolo, A., Gatta, L., and Campanella, L. (1995). Interactions of glyphosate with a humic acid and its iron complex. *Annali Di Chimica*, *85*(1–2), 31–40.

Raju, K. S., and Naidu, S. V. (2013). A Review on Removal of Heavy Metal Ions from Wastewater by Rice Husk as an Adsorbent. *Journal of Chemical , Biological and Physical Sciences*, *3*(2), 602–606.

Rampazzo, N., Rampazzo Todorovic, G., Mentler, a., and Blum, W. E. H. (2013). Adsorption of glyphosate and aminomethylphosphonic acid in soils. *International Agrophysics*, *27*(2), 203–209.

Rampoldi, A., Hang, S., and Barriuso, E. (2008). Glyphosate Mineralization: Effect of Temperature and Soybean and Corn Crop Residues. *Chilean Journal of Agricultural Research*, *68*(1), 13–20.

Randhawa, G. K., and Kullar, J. S. (2011). Bioremediation of Pharmaceuticals, Pesticides, and Petrochemicals with Gomeya/Cow Dung. *ISRN Pharmacology*, *2011*, 1–7. http://doi.org/10.5402/2011/362459

Raymond, J. W., Rogers, T. N., Shonnard, D. R., and Kline, A. A. (2001). A review of structure-based biodegradation estimation methods. *Journal of Hazardous Materials*, *84*(2–3), 189–215.

Reddy, T. R. K. (2013). Hardness , chemical resistance and void content of reinforced cow dung- glass fiber polyester hybrid composites. *National Journal on Chembiosis, 4*(2), 14–20.

Regitano, J. B., Alleoni, L. R. F., Vidal-Torrado, P., Casagrande, J. C., and Tornisielo, V. L. (2000). Imazaquin sorption in highly weathered tropical soils. *Journal of Environmental Quality*, *29*(3), 894–900.

Reimer, M., Farenhorst, A., and Gaultier, J. (2005). Effect of Manure on Glyphosate and Trifluralin Mineralization in Soil. *Journal of Environmental Science and Health, Part B*, *40*(4), 605–617.

Richard, S., Moslemi, S., Sipahutar, H., Benachour, N., and Seralini, G.-E. (2005). Differential effects of glyphosate and roundup on human placental cells and aromatase. *Environmental Health Perspectives*, 716–720.

Rochette, E. A., and Koskinen, W. C. (1996). Supercritical carbon dioxide for determining atrazine sorption by field-moist soils. *Soil Science Society of America Journal*, *60*(2), 453–460.

Rojano-Delgado, A. M., and Luque de Castro, M. D. (2014). Capillary electrophoresis and herbicide analysis: Present and future perspectives. *Electrophoresis*, 2509–2519. http://doi.org/10.1002/elps.201300556

Roy, C., Gaillardon, P., and Montfort, F. (2000). The effect of soil moisture content on the sorption of five sterol biosynthesis inhibiting fungicides as a function of their physicochemical properties. *Pest Management Science*, *56*(9), 795–803.

Rueppel, M. L., Brightwell, B. B., Schaefer, J., Marvel, J. T., and Agri-, M. (1977). Metabolism and Degradation of Glyphosate in soil and water. *Journal of Agricultural and Food Chemistry*, *25*(3), 517–528.

Sadegh Zadeh, F. (2010). *Sorption-Desorption, Degradation and Leaching of Napropamide in Selected Malaysian Soils*. Universiti Putra Malaysia.

Sailaja, K. K., and Satyaprasad, K. (2006). Degradation of glyphosate in soil and its effect on fungal population. *Journal of Environmental Science and Engineering*, *48*(3), 189–190.

Salazar, S., Sánchez, L. E., Alvarez, J., Valverde, A., Galindo, P., Igual, J. M., Peix, A., Santa-Regina, I. (2011). Correlation among soil enzyme activities under different forest system management practices. *Ecological Engineering*, *37*(8), 1123–1131.

Samsuri, A. W., Sadegh-Zadeh, F., and Seh-Bardan, B. J. (2013). Characterization of biochars produced from oil palm and rice husks and their adsorption capacities for heavy metals. *International Journal of Environmental Science and Technology*, *11*(4), 967–976.

Sánchez, M. E., Estrada, I. B., Martínez, O., Martín-Villacorta, J., Aller, a., and Morán, A. (2004). Influence of the application of sewage sludge on the degradation of pesticides in the soil. *Chemosphere*, *57*(7), 673–679.

Sánchez Martín, M. J., Villa, M. V., and Sánchez-Camazano, M. (1999). Glyphosate-hydrotalcite interaction as influenced by pH. *Clays and Clay Minerals*, *47*(6), 777–783.

Sarmah, A. K., and Close, M. E. (2009). Modelling the dissipation kinetics of six commonly used pesticides in two contrasting soils of New Zealand. *Journal of Environmental Science and Health. Part. B, Pesticides, Food Contaminants, and Agricultural Wastes*, *44*(6), 507–517.

Savitz, D. A., Arbuckle, T., Kaczor, D., and Curtis, K. M. (1997). Male pesticide exposure and pregnancy outcome. *American Journal of Epidemiology*, *146*(12), 1025–1036.

Schnurer, Y., Persson, P., Nilsson, M., Nordgren, A., and Giesler, R. (2006). Effects of surface sorption on microbial degradation of glyphosate. *Environmental Science and Technology*, *40*(13), 4145–50.

Schrijver, A. De, and Mot, R. De. (1999). Degradation of pesticides by actinomycetes. *Critical Reviews in Microbiology*, *25*(2), 85–119.

Schroll, R., Becher, H. H., Dörfler, U., Gayler, S., Grundmann, S., Hartmann, H. P., and Ruoss, J. (2006). Quantifying the effect of soil moisture on the aerobic microbial mineralization of selected pesticides in different soils. *Environmental Science and Technology*, *40*(10), 3305–3312

Schrübbers, L. C., Masís-Mora, M., Carazo Rojas, E., Valverde, B. E., Christensen, J. H., and Cedergreen, N. (2016). Analysis of glyphosate and aminomethylphosphonic acid in leaves from Coffea arabica using high performance liquid chromatography with quadrupole mass spectrometry detection. *Talanta*, *146*, 609–620.

Scott, N. A., Cole, C. V., Elliott, E. T., and Huffman, S. A. (1996). Soil textural control on decomposition and soil organic matter dynamics. *Soil Science Society of America Journal*, *60*(4), 1102–1109.

Shahgholi, H., and Ahangar, A. G. (2014). Factors controlling degradation of pesticides in the soil environment : A Review. *Agriculture Science Developments*, *3*(8), 273–278.

Shamshuddin, J., and Anda, M. (2008). Charge properties of soils in Malaysia dominated by kaolinite, gibbsite, goethite and hematite. *Bulletin of the Geological Society of Malaysia*, *54*(54), 27–31.

Shamshuddin, J., and Daud, N. W. (2011). Classification and Management of Highly Weathered Soils in Malaysia for Production of Plantation Crops. *Principles, Application and Assessment in Soil Science*, 13. http://doi.org/ISBN 978-953-307-740-6

Shamshuddin, J., Fauziah, C. I., Anda, M., Kapok, J., and Shazana, M. R. S. (2011). Using ground basalt and/or organic fertilizer to enhance productivity of acid soils in Malaysia for crop production. *Malaysian Journal of Soil Science*, *15*(1), 127–146.

Shamshuddin, J., Salleh, R., Husni, M. H. A., and Awang, K. (1996). Charge Characteristics in Relation to Mineralogy of Selected Soils from South-east Asia. *Pertanika Journal of Tropical Agricultural Science, 19*(1), 55–60.

Shareef, K. M. and Hamadamin, S. I. (2009). Adsorption of Metalaxyl and Glyphosate on Six Erbilian Agricultural Soils. *Asian Journal of Chemistry*, *21*(4), 2673–2683.

Sheals, J., Persson, P., and Hedman, B. (2001). IR and EXAFS spectroscopic studies of glyphosate protonation and copper(II) complexes of glyphosate in aqueous solution. *Inorganic Chemistry*, *40*(17), 4302–4309.

Sheals, J., Sjöberg, S., and Persson, P. (2002). Adsorption of glyphosate on goethite: molecular characterization of surface complexes. *Environmental Science and Technology*, *36*(14), 3090–3095.

Si, Y.-B., Xiang, Y., Tian, C., Si, X.-Y., Zhou, J., and Zhou, D.-M. (2013). Complex Interaction and Adsorption of Glyphosate and Lead in Soil. *Soil and Sediment Contamination: An International Journal*, *22*(1), 72–84.

Sidoli, P., Baran, N., and Angulo-Jaramillo, R. (2016). Glyphosate and AMPA adsorption in soils: laboratory experiments and pedotransfer rules. *Environmental Science and Pollution Research*, *23*(6), 5733–5742.

Simonsen, L., Fomsgaard, I. S., Svensmark, B., and Spliid, N. H. (2008). Fate and availability of glyphosate and AMPA in agricultural soil. *Journal of Environmental Science and Health. Part. B, Pesticides, Food Contaminants, and Agricultural Wastes*, *43*(5), 365–375.

Singh, B. K., and Walker, A. (2006). Microbial degradation of organophosphorus compounds. *FEMS Microbiology Reviews*, *30*(3), 428–471.

Solomon, K. R., Anadón, A., Cedeira, A. L., Marshall, J., and Sanin, L.-H. (2007). Environmental and Human Health Assessment of Aerially Applied Glyphosate in Colombia. *Rev Environ Contam Toxicol*, *190*, 43–125.

Song, W., and Guo, M. (2012). Quality variations of poultry litter biochar generated at different pyrolysis temperatures. *Journal of Analytical and Applied Pyrolysis*, *94*, 138–145.

Sophie Guimont, Corinne Perrin-Ganier, Beno ̂ ıt Real, M. S. (2005). Effects of soil moisture and treatment volume on bentazon mobility in soil. *Agronomy for Sustainable Development*, *25*, 321–329.

Sparks, D. L. (2003). *Environmental soil chemistry*. Academic press.

Sprankle, P., Meggitt, W. F., and Penner, D. (1975). Adsorption , Mobility , and Microbial Degradation of Glyphosate in the Soil. *Weed Science*, *23*(3), 229–234.

Sprankle, P., Meggitt, W. F., Penner, D., Science, S. W., and May, N. (1975). Rapid Inactivation of Glyphosate in the Soil Rapid Inactivation of Glyphosate in the Soil1. *Weed Science*, *23*(3), 224–228.

Srivastava, V. C., Mall, I. D., and Mishra, I. M. (2006). Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. *Journal of Hazardous Materials*, *134*(1–3), 257–267.

Srivastava, V. C., Mall, I. D., and Mishra, I. M. (2007). Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA). *Chemical Engineering Journal*, *132*(1–3), 267–278.

Stevenson, F. J. (1994). *Humus chemistry: genesis, composition, reactions*. John Wiley and Sons.

Strange- Hansen, R., Holm, P. E., Jacobsen, O. S., and Jacobsen, C. S. (2004). Sorption, mineralization and mobility of N- (phosphonomethyl) glycine (glyphosate) in five different types of gravel. *Pest Management Science*, *60*(6), 570–578.

Suhadolc, M., Schroll, R., Hagn, A., Dörfler, U., Schloter, M., and Lobnik, F. (2010). Single application of sewage sludge – Impact on the quality of an alluvial agricultural soil. *Chemosphere*, *81*(11), 1536–1543.

Sviridov, A. V, Shushkova, T. V, Ermakova, I. T., Ivanova, E. V, Epiktetov, D. O., and Leontievsky, A. A. (2015). Microbial Degradation of Glyphosate Herbicides (Review). *Applied Biochemistry and Microbiology*, *51*(2), 188–195.

Tan, K. H. (2010). *Principles of soil chemistry*. CRC press.

Tariq, F. S., Samsuri, A. W., Karam, D. S., and Aris, A. Z. (2016). Phytoremediation of Gold Mine Tailings Amended with Iron-Coated and Uncoated Rice Husk Ash by Vetiver Grass (Vetiveria zizanioides (Linn.) Nash). *Applied and Environmental Soil Science*, *2016*. http://doi.org/10.1155/2016/4151898

Tarley, C. R. T., and Arruda, M. A. Z. (2004). Biosorption of heavy metals using rice milling by-products. Characterisation and application for removal of metals from aqueous effluents. *Chemosphere*, *54*(7), 987–995.

Teh, C. B. S., and Talib, J. (2006). *Soil physics analyses: volume 1*. Universiti Putra Malaysia Press.

Tejada, M. (2009). Application of different organic wastes in a soil polluted by cadmium: Effects on soil biological properties. *Geoderma*, *153*(1–2), 254–268.

Tévez, H. R., and Afonso, M. dos S. (2015). pH dependence of Glyphosate adsorption on soil horizons. *Boletin de La Sociedad Geologica Mexicana*, *67*(3), 509–516.

Theeba, M., Bachmann, R. T., Illani, Z. I., Zulkefli, M., Husni, M. H. A, and Samsuri, A. W. (2012). Characterization of local mill rice husk charcoal and its effect on compost properties. *Malaysian Journal of Soil Science*, *16*(1), 89–102.

Thibaud, C., Erkey, C., and Akgerman, A. (1993). Investigation of the effect of moisture on the sorption and desorption of chlorobenzene and toluene from soil. *Environmental Science and Technology*, *27*(12), 2373–2380.

Thongprakaisang, S., Thiantanawat, A., Rangkadilok, N., Suriyo, T., and Satayavivad, J. (2013). Glyphosate induces human breast cancer cells growth via estrogen receptors. *Food and Chemical Toxicology*, *59*, 129–136.

Topp, E., Vallaeys, T., and Soulas, G. (1997). Pesticides: microbial degradation and effects on microorganisms. *Modern Soil Microbiology*, 547–575.

Tsui, M. T. K., and Chu, L. M. (2003). Aquatic toxicity of glyphosate-based formulations: Comparison between different organisms and the effects of environmental factors. *Chemosphere*, *52*(7), 1189–1197.

Ucun, H., Aksakal, O., and Yildiz, E. (2009). Copper(II) and zinc(II) biosorption on Pinus sylvestris L. *Journal of Hazardous Materials*, *161*(2–3), 1040–1045.

Ulén, B., Gunborg, A., Kreuger, J., Svanbäck, A., and Etana, A. (2012). Particulate-facilitated leaching of glyphosate and phosporus from a marine clay soil via tile drains. *Acta Agriculturae Scandinavica, Section B - Plant Soil Science*, *62*, 241–251.

Usharani, K., Muthukumar, M., and Kadirvelu, K. (2012). Effect of pH on the degradation of aqueous organophosphate (methylparathion) in wastewater by ozonation. *International Journal of Environmental Research*, *6*(2), 557–564.

Uwumarongie-Ilori, E.G., Aisueni N.O., Sulaiman-Ilobu, B.B., Ekhator, F. Eneje, R. C. and, and Efetie-Osie, A. (2012). Immobilization Effect of Cow Dung on Lead and Chromium in Soil Cultivated With Oil Palm. *Bulletin of Environment, Pharmacology and Life Sciences*, *1*(August), 74–80.

Van Eerd, L. L., Hoagland, R. E., Zablotowicz, R. M., and Hall, J. C. (2003). Pesticide metabolism in plants and microorganisms. *Weed Science*, *51*(4), 472–495.

Van Ranst, E., Verloo, M., Demeyer, A., and Pauwels, J. M. (1999). *Manual for the soil chemistry and fertility laboratory: analytical methods for soils and plants equipment, and management of consumables*. University of Ghent Belgium.

Vereecken, H. (2005). Mobility and leaching of glyphosate: A review. *Pest Management Science*, *61*(12), 1139–1151.

von Wirén-Lehr, S., Scheunert, I., and Dörfler, U. (2002). Mineralization of plant-incorporated residues of 14C-isoproturon in arable soils originating from different farming systems. *Geoderma*, *105*(3–4), 351–366.

Wang, Yu-jun; Zhou, Dong-mei; Sun, R. (2005). Effect of phosphate of the adsorption of glyphosate on three different types of Chinese soils. *Journal of Environmental Sciences*, *17*(5), 711–715.

Wang, H., Lin, K., Hou, Z., Richardson, B., and Gan, J. (2010). Sorption of the herbicide terbuthylazine in two New Zealand forest soils amended with biosolids and biochars. *Journal of Soils and Sediments*, *10*(2), 283–289.

Wang, H. Z., Zuo, H. G., Ding, Y. J., Miao, S. S., Jiang, C., and Yang, H. (2014). Biotic and abiotic degradation of pesticide Dufulin in soils. *Environmental Science and Pollution Research*, *21*(6), 4331–4342.

Wang, Y. J., Zhou, D. M., Sun, R. J., Cang, L., and Hao, X. Z. (2006). Cosorption of zinc and glyphosate on two soils with different characteristics. *Journal of Hazardous Materials*, *137*(1), 76–82.

Wibawa, W., Mohamad, R. B., Omar, D., Zain, N. M., Puteh, A. B., and Awang, Y. (2010). Comparative impact of a single application of selected broad spectrum herbicides on ecological components of oil palm plantation. *African Journal of Agricultural Research*, *5*(16), 2097–2102.

Wolińska, A., and Bennicelli, R. P. (2010). Dehydrogenase activity response to soil reoxidation process described as varied conditions of water potential, air porosity and oxygen availability. *Polish Journal of Environmental Studies*, *19*(3), 651–657.

Worrall, F., Fernandez-Perez, M., Johnson, a C., Flores-Cesperedes, F., and Gonzalez-Pradas, E. (2001). Limitations on the role of incorporated organic matter in reducing pesticide leaching. *Journal of Contaminant Hydrology*, *49*(3–4), 241–62.

Yu, Y., and Zhou, Q. X. (2005). Adsorption characteristics of pesticides methamidophos and glyphosate by two soils. *Chemosphere*, *58*(6), 811–816.

Zabaloy, M. C., Gómez, E., Garland, J. L., and Gómez, M. a. (2012). Assessment of microbial community function and structure in soil microcosms exposed to glyphosate. *Applied Soil Ecology*, *61*, 333–339.

Zabaloy, M. C., and Gomez, M. A. (2008). Microbial Respiration in Soils of the Argentine Pampas after Metsulfuron Methyl, 2, 4- D, and Glyphosate Treatments. *Communications in Soil Science and Plant Analysis*, *39*(3–4), 370–385.

Zabaloy, M. C., Zanini, G. P., Bianchinotti, V., Gomez, M. a, Garland, J. L., Sur, N., and Corp, D. (2006). Herbicides in the Soil Environment : Linkage Between Bioavailability and Microbial Ecology. In *Herbicides, Theory and Applications*.

Zablotowicz, R. M., Accinelli, C., Krutz, L. J., and Reddy, K. N. (2009). Soil depth and tillage effects on glyphosate degradation. *Journal of Agricultural and Food Chemistry*, *57*(11), 4867–4871.

Zain, N. M. M., Mohamad, R. B., Sijam, K., Morshed, M. M., and Awang, Y. (2013). Effect of selected herbicides in vitro and in soil on growth and development of soil fungi from oil palm plantation. *International Journal of Agriculture and Biology*, *15*(5), 820–826.

Zhang, J., Lü, F., Luo, C., Shao, L., and He, P. (2014). Humification characterization of biochar and its potential as a composting amendment. *Journal of Environmental Sciences (China)*, *26*, 390–397.

Zhao, B., Zhang, J., Gong, J., Zhang, H., and Zhang, C. (2009). Glyphosate mobility in soils by phosphate application: Laboratory column experiments. *Geoderma*, *149*(3–4), 290–297.

Zhou, D. M., Wang, Y. J., Cang, L., Hao, X. Z., and Luo, X. S. (2004). Adsorption and cosorption of cadmium and glyphosate on two soils with different characteristics. *Chemosphere*, *57*(10), 1237–1244.