Biochar use for reducing agrochemical leaching in tropical agricultural soils

By

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Abstract

Biochar amendments to soils have sparked remarkable research interests in agricultural and environmental sustainability. However, limited studies have focused on the use of biochar for reducing agrochemical leaching in tropical soils. Also, limited studies have focused on understanding agricultural stakeholders’ perspectives on biochar use, which are essential for the development of its implementation. This thesis aims to: (i) devise a stakeholder analysis for implementing biochar in agricultural systems of Belize; (ii) use laboratory approaches to identify biochars that reduce agrochemical leaching in tropical soils; and (iii) apply a groundwater pesticide-fate model to simulate biochar-amended soils and predict its effects on pesticide concentrations in groundwater.

A mixed-method design consisting of thematic and descriptive analyses were used to understand the perspectives of Belizean agricultural stakeholders. Batch and column leaching studies were performed to analyse leachate agrochemicals using analytical methods such as High-Performance Liquid Chromatography and Liquid Chromatography-Mass Spectrometry. Standard scenarios of the PEARL pesticide-fate model, used to predict concentrations of pesticides in groundwater, were modified to simulate the leaching of pesticides in biochar-amended soils.

Results from the stakeholder analysis showed that biochar could be implemented in Belize if major challenges in its agricultural sector are resolved. These challenges include agricultural research and education advances, funding availability and collaboration amongst agricultural stakeholders. Also, laboratory experiments and pesticide fate model showed that tropical soils amended with rice husk biochar were able to decrease the leaching of agrochemicals in groundwater. These results are noteworthy mainly since atrazine, although being banned in the European Union due to its tendency and persistency to contaminate groundwater is still widely used in tropical agricultural soils that are vulnerable to agrochemical leaching. Biochar use offers an excellent opportunity for agricultural stakeholders to reduce agrochemical leaching in tropical agricultural soils.

Declaration

This thesis has been composed by Gerardo Ofelio Aldana unless otherwise stated, and has not been submitted as part of any previous application for a degree. All sources of information have been acknowledged explicitly by reference.

Gerardo Ofelio Aldana
September 2019

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Chapter 1. Introduction

1.1. Introduction to biochar

Increasing agricultural production while simultaneously adapting to climate change has never been more demanding. More food is needed for an increasing population. Strategies to combat climate change must be reinforced. These demands have sparked research interests in biochar technology (Glaser et al., 2001). Biochar is the production of carbonaceous material derived from the thermochemical conversion of biomass in an oxygen-limited environment (Lehmann, 2015). There are many agricultural and environmental benefits associated with the use of biochar (Jeffery et al., 2011; Xu et al., 2012a). These include helping to reduce soil and water contamination by agrochemicals, mitigate climate change, produce energy and manage agricultural waste (Jeffery et al., 2011; Xu et al., 2012a). Different biochar types can have either general or specific benefits based on their physicochemical properties. Therefore, an accumulation of biochar research could create a matrix of recommendations associated with biochar type and its corresponding benefit.

Firstly, the biochar's porous structure and rich surface functional groups allow the biochar to absorb pesticides, antibiotics and other pollutants that leach down a soil profile (Liu et al., 2018). Secondly, biochar improves the soil to optimum conditions by adjusting the pH, cation exchange capacity, bulk density and nutrient availability of the soil, among other soil improvements, to suitable soil conditions (Scholz et al., 2014). Thirdly, some biochars are characterised as highly recalcitrant aromatic carbon materials resistant to decomposition (Lehmann, 2017). These biochars are capable of sequestering carbon, lessening greenhouse gas emissions, and storing carbon in the soil for several hundreds of years (Hussain et al., 2016). Furthermore, a variety of biomass feedstock can be used to produce biochar. Woody biomass, leaves, crop residues, grass, manure and sludge can all be converted into biochar. Agricultural waste can be managed by producing biochar. Using agricultural waste for biochar production can help to move away from more expensive waste management techniques (Jaria et al., 2017). Also, converting agricultural waste into biochar is an agro-environmentally friendly option (Scholz et al., 2014). Lastly, biochar production via pyrolysis produces several high energy valued liquids and gases. The heat energy can be harnessed and used for cooking and heating in homes (Lehmann and Joseph, 2015). Heat energy produced from making biochar can be beneficial for cooking, especially in developing countries where other energy sources are scarce, and much agricultural waste is available. The life cycle of biochar proves itself very efficient.

1.2. Reducing agrochemical leaching by using biochar

Agricultural production in tropical regions continues to use agrochemicals such as antibiotics and herbicides. Antibiotics are used to prevent diseases and promote growth in livestock and aquaculture, while herbicides are used as crop protection products that control, eradicate or change the cycle of individual plants. However, if misused and managed improperly, contamination to soil and water may cause detrimental effects to human health and the environment (Gibson et al., 1998; Chaukura et al., 2016; Wu et al., 2000). Also, tropical soils may be particularly prone to agrochemical leaching due to unsustainable agricultural practices that deteriorate soil health. A distinctive in situ technique for retaining herbicides and antibiotics through the soil profile is to integrate carbon-based materials such as biochar into the soil. Contaminants can be directly absorbed to the biochar, thus reducing its leaching through the soil.

Several studies have investigated the effects of biochar on the absorption of pesticides and veterinary antibiotics. Cederlund et al. (2017) studied the effects of wood-based biochar produced at 380-430°C on the leaching reduction of chlorpyrifos, diuron, glyphosate and MCPA in a sand column test. Cederlund et al. (2017) recommended biochar to be used as an absorptive layer directly on the surface of soils where pesticides are handled or may be spilt. Essandoh et al. (2017) used switchgrass biochar produced at 425°C to absorb phenoxy herbicides such as 2, 4-D, and MCPA from aqueous solutions. The surface area of the switchgrass biochar absorbed 2, 4-D, and MCPA effectively. The bioavailability of the insecticide thiacloprid was reduced after applying biochar made from magnolia tree wood chips at 500°C applied to the soil (Li et al., 2017). Cassava waste biochar produced at 750°C was used to reduce the transport of atrazine within agricultural soils, showing a positive correlation between the mobility of the pesticide and the addition of biochar (Deng et al., 2017).

Mandal and Singh (2017) used several agricultural wastes to produce biochar. The biochars were made from eucalyptus bark, corncob, bamboo chips, rice husk, and rice straw biochars along with acid-treated rice husk biochar produced at 600°C. These biochars were used for the sorption of atrazine and imidacloprid. The results indicated that the physiochemical properties such as aromaticity, polarity, pore-volume, pore diameter, pH and surface acidity of various feedstock determined the biochar absorption. Cabrera et al. (2011) also observed that the sorption of fluometuron and 4-chloro-2-methylphenoxyacetic acid (MCPA) was variable due to the biochar feedstock type, physiochemical structure, and organic matter in the soil. Qiu et al. (2009) found that pH and dissolved organic matter significantly affects the adsorption of 2, 4-Dichlorophenoxyacetic acid using black carbon. Furthermore, equilibrium sorption experiments were conducted to determine the sorption of glyphosate using birch wood biochar produced at 500°C, indicating that the soil-biochar interactions significantly affect the absorption of glyphosate (Kumari et al., 2016).

Other studies such as Cabrera et al. (2014) found that wood pellet biochars completely sorbed herbicides aminocyclopyrachlor and bentazone, and Cederlund et al. (2016) modified the chemical properties of wood biochar by applying a heat and iron treatment, which caused a significant increase in sorption of diuron, chlorpyrifos, (4-chloro-2-methylphenoxy) acetic acid and glyphosate. Herath et al. (2016) observed that glyphosate was removed by rice husk biochar pyrolysed at 700°C (pH 4) while Kumari et al. (2016) found that sorption of glyphosate increased after 7-18 months of soil birch wood biochar interaction. According to Tang et al. (2013), biochar has the ability to increase sorption and reduce the dissipation of pesticides, thus creating a very cost-effective and eco-friendly method for remediating a polluted environment. These studies suggest that applying biochar to agricultural soils is an effective mitigation strategy to reduce agrochemical leaching.

1.3. Biochar for reducing agrochemical leaching in tropical Belize

In 2008, approximately 50% of pesticides produced globally were used by developing countries (Chaukura et al., 2016). Furthermore, there are instances where the distribution, production, application and disposal of pesticides are poorly governed, therefore posing a threat to protected and sensitive ecosystems (Wu et al., 2000). Several studies have shown the effects of pesticide contamination onto Belize's ecosystems. Wu et al. (2000) found the presence of organochlorine contaminants in the eggs of the Morelet's crocodile species in Belize. Kaiser (2011) also found that pesticides drifted from areas of anthropogenic activities and into protected areas of Belize. Since the economy of most developing countries relies mainly on the agriculture sector, there is a high demand for the use of agrochemicals (Chaukura et al., 2016).

As instructed by the EU Directive 98/83/EC, the maximum threshold limit for herbicides in drinking water is 0.1 µg/L (Boesten et al., 2000). Due to soil and water persistence, herbicides such as diuron and atrazine are banned in most of the EU (PPDB, 2018), while atrazine is banned in the UK. However, these two herbicides are still being used in countries such as Australia, Belize, Brazil and other countries in the Americas (Arias-Estévez et al., 2008; Arraes & Maur, 2008). Atrazine at 47 metric tons of active ingredient and diuron at 40 metric tons of active ingredient were two of the top ten most imported pesticides in Belize in 2015, as reported by the Belize Pesticide Control Board. However, there may be illegal importation of these herbicides. Therefore, their total amount may be underestimated. In addition to using persistent herbicides, slash-and-burn farming is still practised in Belize. Slash-and-burn farming eventually causes soils to become of poor quality and health. Tropical soils of poor quality and health are especially prone to the leaching of persistent herbicides such as atrazine and diuron. It is crucial to protect the natural environment from agrochemical leaching while at the same time increasing agricultural production.

In addition, Belize has available agricultural waste that can be used as feedstock for the production of biochar. However, although biochar is being implemented in many agricultural systems of the world, there are limited studies pertaining to the use of biochar in Belize. A stakeholder analysis of the acceptance of biochar is non-existent in Belize. In addition, studies dedicated to the application of biochar for the attenuation of agrochemicals in tropical soils of Belize and mathematical modelling of the fate of a pesticide in a biochar-amended soil are also minimal. Therefore, laboratory, field and modelling studies of biochar must be intertwined with the social aspects of implementing biochar in a developing country to propose reliable recommendations for agricultural stakeholders.

1.4. Aims of the Study

This thesis seeks to understand the absorption effects of biochar on agrochemicals that have been applied to tropical soils. This thesis also seeks to understand the perspectives of Belizean stakeholders about the feasibility of implementing biochar in agricultural systems for agrochemical attenuation. This thesis, therefore, addresses the following aims: (1) to devise a stakeholder analysis to determine the feasibility of implementing biochar in agricultural systems of Belize; (2) to use laboratory approaches to identify biochar materials that will retain agrochemicals from leaching in tropical soils; and (3) to use mathematical pesticide fate models to simulate a biochar-amended soil and determine its effects on pesticide leaching.

1.5. Outline

This thesis is divided into six sections (See Figure 1-1):

Chapter 1 introduces the research, the aims of the study and outline of chapters.

Chapter 2 gives an overall literature review and is divided into sections that relate to the upcoming chapters 3, 4 and 5.

Chapter 3 is entitled 'Implementation of Biochar in Agricultural Systems of Belize: Stakeholder Analysis'. The aims of this chapter are to determine the familiarity of biochar and necessity for its use in agricultural systems of Belize. It also examines the perceptions of different agricultural stakeholders regarding biochar implementation. It also gathers information about the future opportunities and constraints of Biochar in Belize.

Chapter 4 is entitled 'Sorption Effects of Biochar on Herbicides and Veterinary Antibiotics in Different Soil Types'. The aim of this chapter is to determine the most suitable sorbent from different biochar types for the sorption of atrazine, diuron, enrofloxacine, oxytetracycline and tetracycline in one temperate oceanic and three tropical soils through batch and column leaching studies.

Chapter 5 is entitled 'Modelling of Pesticide Fate in a Biochar Amended Soil'. The aim of this chapter is to simulate the fate of pesticides in a biochar-amended soil matrix. It also compares the behaviour of different pesticides based on modified soil parameters. In addition, it identifies feasible methods of applying biochar to the soil.

Chapter 6 presents a general discussion, implications and future biochar research.

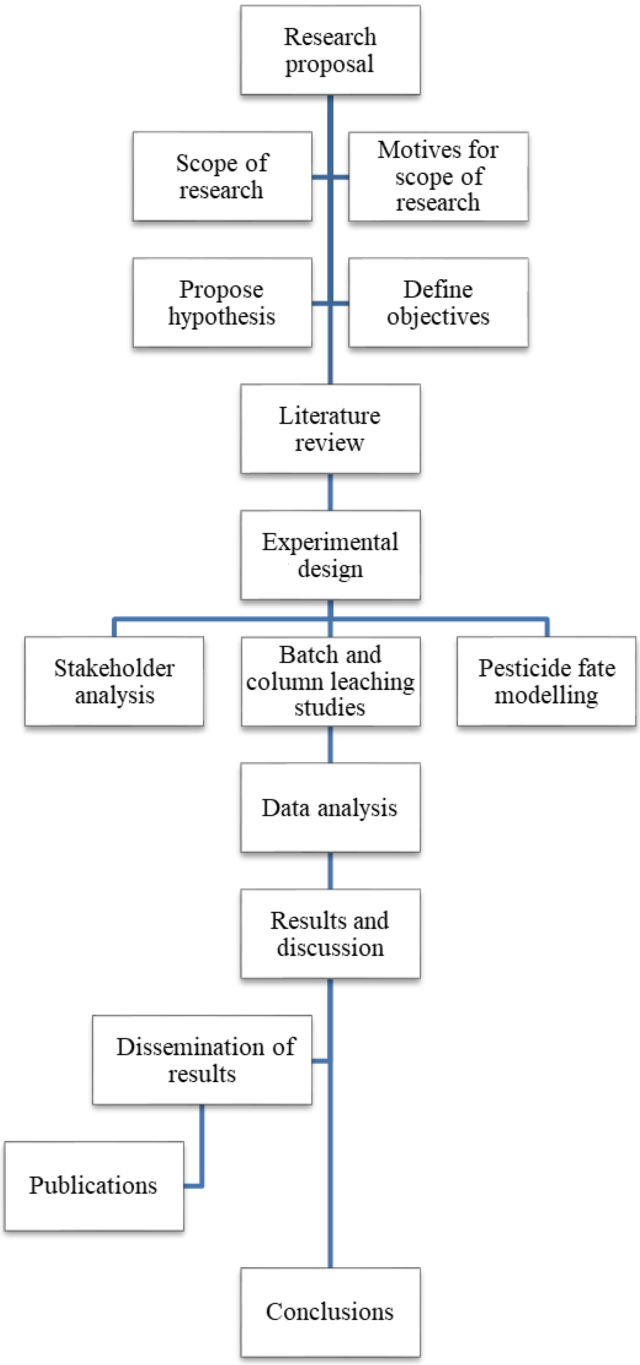

Figure 1-1. Research framework identifying the structure of this study

Chapter 2. Literature Review

2.1. Fundamentals of Biochar

Biochar is produced through the process of pyrolysis. Pyrolysis is defined as the production of carbonaceous material through the thermochemical conversion of organic material at high temperatures in an oxygen-limited environment (MJeong et al., 2016; Trigo et al., 2016; Llorach-Massana et al., 2017). The pyrolysis process catalyses a simultaneous change in the chemical and physical composition of the biomass, thus producing carbon-rich biochar (Jeffery et al., 2011; Kumar et al., 2016). The carbon-rich biochar is composed of highly aromatic structures that make it highly stable and resistant to biological and chemical degradation in soil (Abujabhah et al., 2016; Atkinson et al., 2010). Biochar's production provides a reliable method of recycling agricultural waste and sequestering carbon (Jeffery et al., 2011; Atkinson et al., 2010; Bell & Worrall, 2011). The physicochemical structure of biochar also makes it an ideal material for the amendment of soils (Obia et al., 2016; Abujabhah et al., 2016; Jeffery et al., 2011). Also, several studies have observed biochar to have a high affinity and capacity for absorbing agrochemicals (Beesley et al., 2010; Lohmann et al., 2005). Thus, critical attention has been drawn to the influence of biochar on the persistence and movement of agrochemicals in the soil (Cao et al. 2011; Jones et al. 2011; Spokas et al. 2009; Zheng et al. 2010; Kookana 2010). Overall, the application of biochar is observed to be beneficial to both agricultural production and environmental protection (Zheng et al., 2010; Lehmann, 2007; Beesley et al., 2010; Safaei Khorram et al., 2015).

2.1.1. Biochar for agricultural sustainability

The production of biochar is envisioned as an ideal closed loop for the recycling of agricultural waste biomass. The pyrolysed waste biomass is used to provide bioenergy while the by-product biochar is used for agricultural and environmental purposes. Biochar added to the soil increases soil health and yield. At the same time, it decreases carbon dioxide or greenhouse gas emissions (Zimmerman, 2010). To obtain a closed-loop agricultural system, Figure 2-1 below presents the sustainable biochar concept as adapted by Woolf et al. (2010). Carbon dioxide is removed from the atmosphere through photosynthesis to produce biomass that will be used for the production of biochar. The agricultural waste biomass is then pyrolysed, which prevents this waste from decaying in the open environment. In addition, emissions of methane and nitrous oxides produced from the decay of biomass are reduced because of converting the waste biomass into biochar. The production process produces heat energy and biofuel, which can be used to offset fossil carbon emissions. Furthermore, the biochar can then be used to reduce agrochemical and heavy metal contamination in the soil. The productivity of infertile soils can also be increased, causing a more noteworthy impact on greenhouse gas fluxes by reducing unsustainable practices such as deforestation. Biochar use can, therefore, reduce the impact of agriculture on the natural environment.

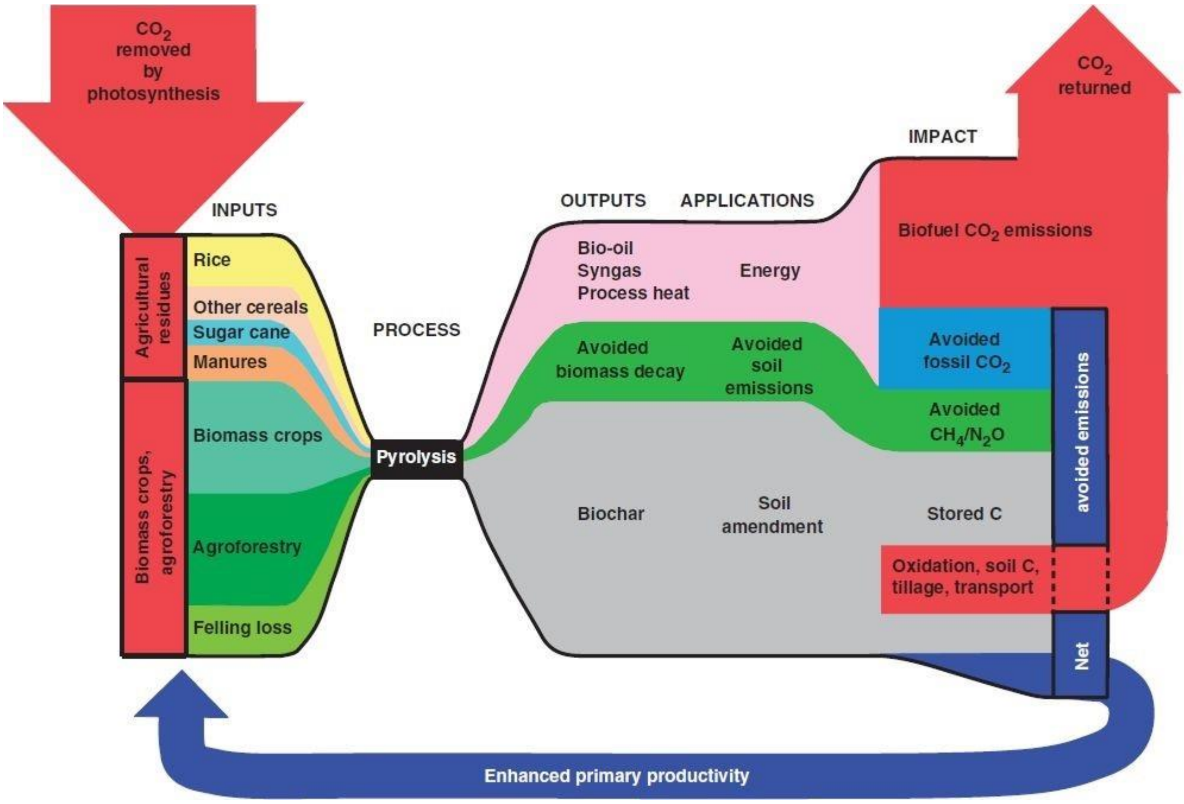

Figure 2-1. Overview of the sustainable biochar concept (Woolf et al., 2010b)

2.1.2. Feedstock and pyrolysis

Biochar can be produced by industrial pyrolysis plants to domestic cookstoves, extending its use from commercial to subsistence farming (Woolf et al., 2010b). Biochar household cookstoves can generate both heat energy and biochar while industrial plants can generate both biofuel and biochar. Biochar production plant systems are classed as pyrolyzers. Pyrolizers can produce biochar, syngas and bio-oil (Scholz et al., 2014; Woolf et al., 2010b). Pyrolysis is in these systems is divided into fast, intermediate and slow pyrolysis, depending on residence time and temperature (Ahmad et al., 2014; Scholz et al., 2014). Fast pyrolysis has a relatively short residence time and produces more of bio-oils, yielding to about 75% bio-oil (Mohan et al., 2006). Intermediate pyrolysis has a residence time of several hours, while slow pyrolysis has a residence time of a few days, both producing more syngas and biochar (25-35%) (See Table 2-1) (IBI, 2015; Ahmad et al., 2014). Unlike a gasification system, a pyrolysis system does not introduce oxygen (Roy & Dias, 2017; Ahmad et al., 2014a; Scholz et al., 2014) therefore producing more biochar than gases. However, gasification systems can be optimized to produce biochar by up to a yield of 30% (Scholz et al., 2014).

Process	Temperature (ºC)	Residence Time	Products			
			Pressure	Liquid (bio-oil) (%)	Solid (biochar) (%)	Gas (syngas) (%)
Fast pyrolysis	300–1000	Short (<2 s)	No	75	12	13
Flash pyrolysis	350–650	Long (5–30 min)	1–3 MPa	50	25	25
Slow pyrolysis	100–1000	Long (5–30 min) to days	No	30	35	35
Gasification	>800	Moderate (10–20 s)	No	5	10	85

Table 2-1. Pyrolysis processes and products distribution (adapted from Mohan et al. 2006; Scholz et al. 2014; Ahmad et al. 2014)

The feedstock properties and pyrolysis conditions are influential in determining the physical and chemical properties of biochar (Kloss et al., 2012; Shackley et al., 2010). Feedstock can be grouped into two categories (i) by-products as waste biomass and (ii) biomass specifically grown for biochar and bioenergy production. Feedstock obtained from waste biomass is the preferred candidate for biochar production due to cost-effectiveness and the recycling of waste biomass (Ahmad et al., 2014a; Brick & Lyutse, 2010). A wide array of feedstock has been used for the production of biochar, these include but are not limited to corn cobs, corn stover, oak wood, orange peel, paper sludge, peanut straw, pine shaving, rice husk, softwood pellets, wheat straw, poultry manure, swine manure, switchgrass, etc. (Ahmad et al., 2014a; Gupta & Kua, 2017). Sustainable biomass feedstock availability can be categorized, as seen in Table 2-2.

Biomass	Availability (maximum sustainable technical potential)
Rice	Globally 890 Tg yr-1 of paddy rice straw are produced. 230 Tg yr-1 is used for animal feed. 86 Tg yr-1 rice hulls are regarded as waste. The total maximum biomass from rice is 746 Tg yr-1.
Sugar cane	Cane production generates 314 Tg yr-1 residues. 50% is bagasse, and 50% is field trash. The amounts of sugar cane biomass range from 196- 275 Tg DM yr-1.
Manure	Cattle, pig and chicken manures are in the order of 470 Tg C, 34 Tg C and 134 Tg; respectively. 25% of cattle manure plus 90% of pig and poultry manure are available.
Biomass crops	100% of the potential production of abandoned, degraded cropland that is not in other use.
Agroforestry	170 Mha of tropical grass pasture converted to silvopasture
Green/wood waste	75% of the low-end estimate of yard trimmings production and wood milling residues, including 40% of waste sawn wood.

Table 2-2. Categorized annual global availability of sustainable biomass feedstock (Adapted from Woolf et al. 2010)

Each biomass produces biochar types with different structures. The chemical composition of the biochar is dependent on feedstock type and pyrolysis conditions (Gupta & Kua, 2017; Hossain et al., 2011; Lehmann, 2007; van Zwieten et al., 2010). The decomposition of cellulose, hemicellulose, lignin and moisture content present in the feedstock determine the physical structure of the biochar because they decompose at different temperatures (Gupta & Kua, 2017; Kloss et al., 2012; Gaunt et al., 2008). Pyrolysis temperature also affects physical phenomena such as the release of volatiles, and carbonization of char skeleton and pore formation. Pyrolysis rate and pressure influence the physical mass transfer of volatiles at specific temperatures (Gupta & Kua, 2017). Volatilization causes mass loss but does not cause much change to the original structure of the feedstock (Kloss et al., 2012). At higher temperatures, biomass goes through a secondary reaction, thereby increasing the yield of gas and liquid and decreasing biochar production, as seen in Table 2-3.

Biomass	**Pyrolysis condition**	**Char yield (%)**
Biomass Pine	*T*: 300°C; slow pyrolysis *T*: 450°C; slow pyrolysis	58 26
Sewage slug	*T*: 350°C; *R*: 30°C/min *T*: 950°C: *R*: 30°C/min	52 39
Corn stover Corn cobs	*T*: 500°C in a fluidized bed	16.80 18.90
Switchgrass (*Panicum virgatum*)	*T*: 600°C; *R*: 6°C/min; 20 min at 600°C	25
Soybean cake	*T*: 550°C; *R*: 300°C/min	21
Rice husk	*T*: 400°C and residence time (*t*) of 5 *s* (at 500°C) *T*: 600°C; *t*: 5 *s* at (500°C)	33 25.50
Hardwood shavings	Fast pyrolysis, residence time <5 *s* and pyrolysis temperature at 500°C	12.70
Douglas fir wood Douglas fir bark Hybrid poplar wood	*T*: 350°C; *R*: 190°C/min	38.30 47.90 31.90
Olive husk	*T*: 200°C (approximately); *R*: 10°C/s *T*: 975°C; *R*: 10°C/*s*	44.50 19.40
Safflower seed press cake	*T*: 400°C; *R*: 10°C/min *T*: 400°C; *R*: 30°C/min *T*: 400°C; *R*: 50°C/min	34.18 30.50 28.70

Table 2-3. Effects of Pyrolysis Condition on Char Yield. N.B Pyrolysis temperature (*T*); Heating rate (*R*) (Adapted from Gupta & Kua 2017)

2.1.3. Physicochemical properties of biochar

Biochar produced by fast pyrolysis differs physically and chemically from that of intermediate and slow pyrolysis (Wang et al., 2015; Jindo et al., 2014). Biochar could intentionally be produced for carbon storage, heavy metal and pesticide adsorption, greenhouse gas sequestration, innovative construction materials and soil amelioration (Wang et al., 2015; Behazin et al., 2016; Jindo et al., 2014; Ajayi & Horn, 2016). The heating rate, final pyrolysis temperature, the flow rate of carbon dioxide, steam, nitrogen and retention time are primary factors that contribute to the physical properties of biochar (Sun et al., 2014; Jindo et al., 2014; Teβin, 2016). The physical structure of biochar is typically amorphous, consisting of a carbon skeleton containing crystalline structures of joint aromatic compounds (Jagtoyen & Derbyshire, 1993). Its porosity can be divided into groups based on diameter. These groups are micropores (diameter of < 2 nm), mesopores (diameter of 2- 49 nm) and macropores (diameter of > 50 nm) (Petter & Madari, 2012; Rouquerol et al., 2014). Micropores are responsible for the sorption of gases and solvents. Mesopores are responsible for liquid-solid adsorption processes. Macropores are responsible for water, gases and root movement within the soil (Mukherjee et al., 2011; Rouquerol et al., 2014). These pore size properties help with the physical protection of microorganisms against predators and desiccation, thereby altering the microbial diversity and taxonomy of the soil (Jindo et al., 2014). As high treatment temperature (HTT) increases, pore pathways appear more defined. The fractions of crystallinity of the biochar increases and a more defined turbostratic layer ordering are formed (Keiluweit et al., 2010), as seen in Figure 2-2. If HTT continuously increases over the order of 2500 ºC, the biomass will then form into graphite-like structures. However, biochar production is usually maintained between 350 ºC to 700 ºC. Plastic deformation, melting, fusion and sintering may occur when biomass is treated under rapid heating rates, long processing time, or in biomass with low mineral content. In such cases, the porous structure is lost and degraded. At lower heating rates, there is an increase in volatile release through biomass pores, thereby retaining the structural complexity of the biochar (Joseph and Lehmann, 2015).

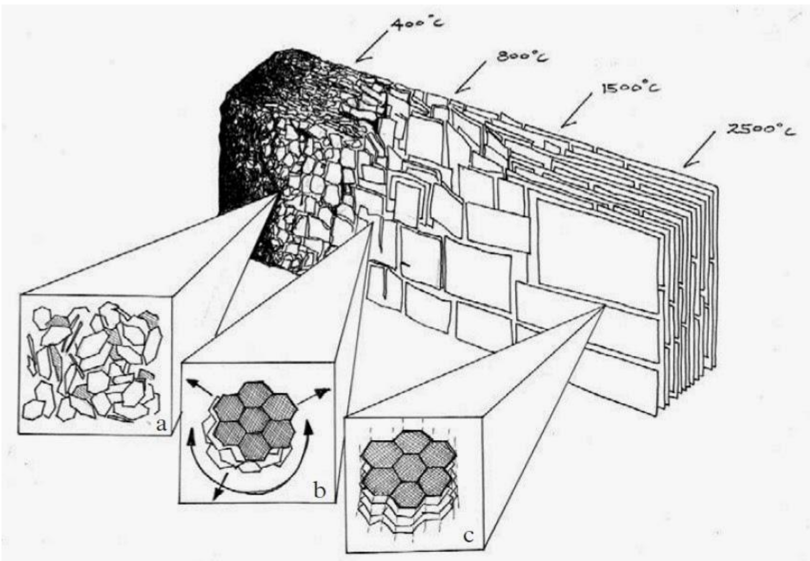

Figure 2-2. Biochar carbon structure relative to HTT. Inset (a) increased degree of aromatic carbon, highly disordered in amorphous mass; Inset (b) growing sheets of turbostratic aromatic carbon; Inset (c): structure becomes graphitic with the order in the third direction (Adopted from Joseph and Lehmann, 2015)

Several alterations occur through the process of pyrolysis. The alterations include C/N, O/C, and H/C ratios, porosity, surface area, cation exchange capacity, crystallinity, and functional groups. The H/O and O/C ratios are reduced due to dehydration and decarboxylation reactions (Behazin et al., 2016; Jindo et al., 2014). Increasing temperatures may increase aromatic carbon-carbon double bonds and decrease O-H and CH_3 (Kloss et al., 2012). The moisture adsorption characteristics of biochar may be influenced by the combined effect of surface area, pore-blocking and oxygenated groups of the biochar. Water molecules bond to surface oxygenated groups via hydrogen bonding (Behazin et al., 2016) and macro or micropores then determine the binding affinity of water molecules to biochar. When biochar is characterized by micropores, the micropores are easily blocked by bridging of water molecules, resulting in a strong binding affinity (Behazin et al., 2016). The ash content of the biochar plays a significant role in the porosity and surface area. Higher ash content tends to fill or block access to micropores, therefore decreasing the surface area of the biochar. High ash content can be found in biochar produced from non-woody feedstock (Behazin et al., 2016; Jindo et al., 2014). Higher ash, N, S, Na, and P concentrations in biochar can be used in soils to correct acidity and regulate C and N dynamics (Domingues et al., 2017). The pH of biochar generally increases with temperature due to its effect on the increase of alkaline cations and non-pyrolysed organic elements already present in the feedstock (Jindo et al., 2014; Wang et al., 2015).

Biochar produced below 500º has a lower capacity to conduct electricity (Behazin et al., 2016), this is because less aromatic structures cause fewer available electrons for electrical conductivity (Keiluweit et al., 2010). The lower capacity to conduct electricity depends on the particle size, surface elements, crystalline structure and available electrons within the biochar structures. Jindo et al. (2014) observed the change in volatile content of woody biochar compared to non-woody biochar. The high volatile-matter was due to the presence of lignin in woody biochar, contributing to its resistance to pyrolytic decomposition (Jindo et al., 2014). The presence of lignin within feedstock played a crucial role in the recalcitrant nature of the produced biochar (Domingues et al., 2017). The recalcitrant nature allowed the biochar to be less prone to biological change due to the amount of aromatic-organic matter, compared to chars produced at lower temperatures (Jindo et al., 2014; Wang et al., 2016, 2015; Domingues et al., 2017). When carbons are assembled into rings, an overlap of p-orbitals occurs. The π electrons become delocalized, thus forming aromatic molecules. The bond between CO and CH aromatic structures determines the stability of the biochar (Petter & Madari, 2012). As studied under Fourier Transform Infrared Spectroscopy, temperature modifies functional groups. Therefore aliphatic carbon groups decrease, but aromatic carbon groups increase (Jindo et al., 2014).

2.1.4. Biochar and soil

Studies focused on *terra preta de Indio* soils in the Amazonian region of Brazil have encouraged and inspired the application of biochar as a soil enhancer promoting carbon storage (Warnock et al., 2007; Joseph, et al., 2010; Lehmann et al., 2011). An important aspect of biochar is its ability to alter soil fertility. Properties that are important to the biochar's capability to modify soils depend on its physical and chemical structure (Shackley et al., 2010; Laghari et al., 2016). The soil conditioning properties of biochar include pore size distribution, water percolation, nutrient leaching and lower bulk density (Rogovska et al., 2014). A larger surface area will allow an increase in air space within the soil (Mccormack et al., 2013), while the micro-, macro-, and mesoporous structure will assist with the retention of water, host-microbial activities. Many studies have observed biochar's ability to alter pH, cation exchange capacity (CEC), electric conductivity (EC), and retain soil nutrients (Shackley et al. 2010; Fungo et al. 2017; Lehmann et al. 2011; Warnock et al. 2007). Work on biochar for heavy metal and pesticide attenuation in the soil has been observed to be dependent largely on biochar's sorption capacity and its ability to modify soil matrices (Liu et al., 2018). Carbonized and non-carbonized organic matter on the biochar's structure, represents a different sorbent capable of absorbing nutrients and agrochemicals such as pesticides and antibiotics (Kumari et al., 2016). The specific surface area, cation exchange capacity, surface group functionality and surface heterogeneity are all factors that determine the biochar's sorption capacity (Kumari et al., 2016; Mukherjee et al., 2016; Larsbo et al., 2013). The nutrients directly available from biochar for the soil is related to the feedstock used (Yuan et al., 2011; Atkinson et al., 2010). Phosphorous is commonly available in ash fractions of biochar, with the presence of chelating substances that control solubilisation (Joseph et al., 2010). Potassium found in biochar is generally available to plants, while nitrogen's availability varies depending on pyrolysis temperature, heating rate, retention rate, and feedstock type (Kamara et al., 2015; Joseph et al., 2010). Due to biochar's surface area, negative surface charge and charge density, biochar allow the soil to retain cations in an exchangeable form (Schmidt et al. 2000), therefore increasing plant nutrient availability and decreasing environmental pollution by nutrients (Lehmann et al., 2011). According to a review by Atkinson et al. (2010), ammonium leaching in greenhouses was reduced by 60%, and nitrous oxide emissions were reduced due to biochar application. Other studies have found that biochar reduced dissolved nitrogen (11%) and dissolved phosphorous leaching (69%) (Laird et al., 2010). However, a great amount of research is needed to ensure that pyrolysis processes and feedstock use are capable of optimizing soil nitrogen for plant availability while minimising leaching (Atkinson et al., 2010). The biochar's capability of modifying pH is another essential characteristic to advocate for biochar as a soil amendment, especially for infertile acidic soils. Biochar is commonly alkaline due to the functional groups such as $–COO^{-}$ ($–COOH$) and $–O^{-}$ ($–OH$) contained within the biochar, which is also responsible for the negative charges in biochar (Yuan et al., 2011). The pH changes are capable of influencing P and N availability since P and N availability are highly dependent on soil pH (Atkinson et al., 2010). The addition of biochar promotes invertebrate diversity and abundance due to fine-scale habitat heterogeneity and nutrient retention (Mccormack et al., 2013). Microfauna (e.g. protozoa and nematodes) and mesofauna (e.g. mites and earthworms) can live within the biochar's porous surface, allowing them to access resources and prevent desiccation (Mccormack et al., 2013; Joseph et al., 2010). Several organisms, such as earthworms and insects, tend to ingest biochar particles, fragmenting the biochar and coating it with organic compounds (Joseph et al., 2010). Fragmentation allows the biochar's surface area to be oxidised and catalyses a reaction with organic matter. Earthworms ingest particles <2 mm and tend to redistribute biochar particles throughout the soil (Joseph et al., 2010). A study conducted by Warnock et al. (2007) found that the addition of biochar increases the abundance of mycorrhizal fungi in the soil, which was associated with biochar's ability to increase the availability of nutrients in the soil. Biochar addition to the soil also altered the activity of other microorganisms (such as Mycorrhization Helper Bacteria) that influence mycorrhizal growth. Biochar addition also increased the signalling dynamics between plants and mycorrhizal fungi or detoxifies allelochemicals, and serves as a refuge for colonizing fungi and bacteria. Steinbeiss et al. (2009) concluded that biochar types affect different microbial activities, e.g., yeast-derived biochar promoted fungal growth, while glucose derived biochar increased gram-negative bacteria. Studies show that biochar is capable of improving soil fertility (Steinbeiss et al., 2009; Shackley et al., 2010; Laghari et al., 2016), thus increasing crop yield. Therefore, there is a need to understand biochar's relationship between crop response and soil health (Chan et al., 2007). Furthermore, research is needed to understand the factors and mechanisms that occur between biochar and soil microbiota, its effect on crop response and climate change (Steinbeiss et al., 2009; Warnock et al., 2007; Mccormack et al., 2013).

2.1.5. Impacts on climate change

The effective role of biochar on its ability to mitigate climate change has been of great interest to current research due to its potential to offset anthropogenic greenhouse gasses by ~12% (Woolf et al., 2010b; Lehmann, 2007). Through pyrolysis, hydrogen and oxygen are eliminated compared to carbon molecules, resulting in biochar mostly consisting of aromatic carbon (C), giving the biochar a recalcitrant nature for hundreds to thousands of years (Keiluweit et al., 2010). The way of which biochar contributes to the mitigation of climate change can be viewed in three ways. Firstly, as waste biomass is being pyrolysed, most of the C that would otherwise occur through natural decay or burning is diverted and modified into a more stable form, therefore, assisting in climate change mitigation (Crombie et al., 2013). Instead of agricultural and forestry waste being combusted in open fields, this available feedstock will be used for biochar production and reused in agricultural soils. Another method for C sequestration is the ability of biochar to increase biomass production through soil modification (Woolf et al., 2010b; Crombie et al., 2013). In addition, biochar amended soils have been capable of suppressing soil greenhouse gas emissions under specific conditions (Fidel et al., 2017; Fan et al., 2017; Crombie et al., 2013). The conditions include the physicochemical characteristics of the biochar and soil. Fan et al. (2017) studied the effect of two distinct feedstock derived biochar unto four different soil types, and found that the attributes of the soil and biochar strongly influenced the level of suppression of gaseous reactive nitrogen emissions of N_2O, NO and NH_3 and crop yield. Biochar-soil interactions must be understood mechanistically to determine how climate, management, soil type, and biochar type affect the impacts of biochar on climate change (Fidel et al., 2017). The use of biochar as an agricultural amendment and climate-change mitigation strategy is anticipated to increase worldwide (Woolf et al., 2010), but field-scale studies must be in place across the globe in order to determine the precise effects of biochar upon climate change (Zhang et al., 2016).

2.2. Implementation of biochar systems

This section explains the frameworks that have been established for the implementation of biochar systems. Though there are sources that assist in understanding the characteristics and effects of biochar for agricultural productivity and environmental soundness, there is limited understanding to promote biochar use on a large scale (Lehmann, 2007). The gap between scientific evidence of biochar benefits and agricultural and environmental stakeholders' acceptability of biochar must first be understood before upscaling the application of biochar.

2.2.1. Biochar system matrix

Many benefits can be obtained from the use of biochar. Some of these benefits, such as carbon sequestration and soil amendment, may be common for all biochars. Systems in place for biochar production include the collection of biomass, the conversion of biomass to biochar, and the application of biochar. The collection and production methods of biochar can also be beneficial to the environment (Roberts et al., 2010). Figure 2-3 shows a brief life cycle assessment of biochar.

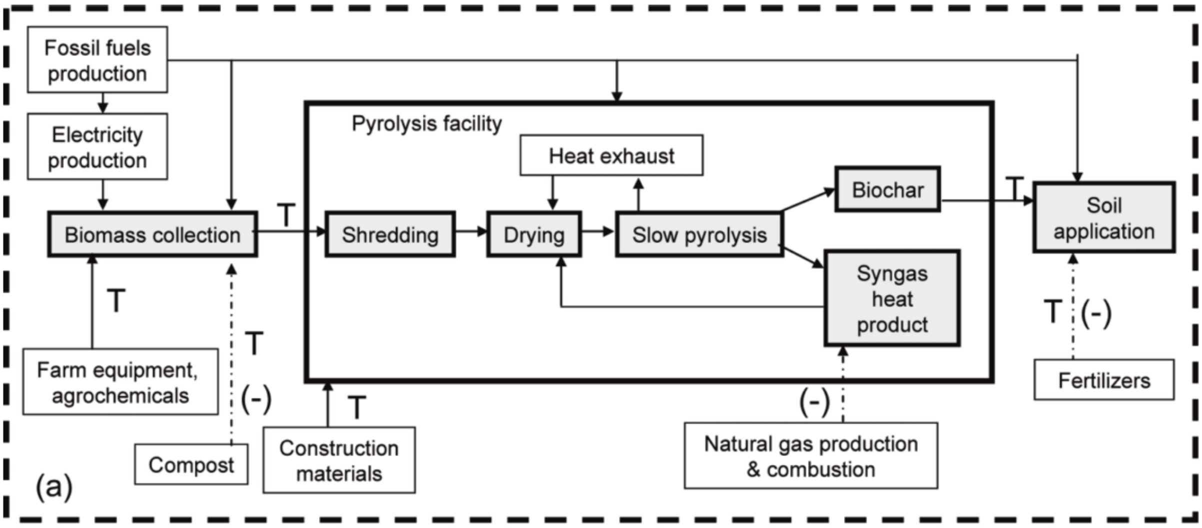

Figure 2-3. (a) Assessment of a biochar system with bioenergy production are shown by the dashed box. Dashed arrows with (-) indicate avoided processes. The "T" represents transportation (Roberts et al., 2010)

The practical and economical method of obtaining biomass is an important aspect that can change the entire biochar process (Shackley et al., 2010). Feedstock must be carefully selected to avoid consequences such as greenhouse gas emissions or using more energy than is generated. The process must ensure economic and environmental sustainability (Roberts et al., 2010). For instance, obtaining virgin feedstock would incorporate biochar systems into already established agricultural or forestry systems, reducing land use and competition of feedstock availability from alternative sources (Smith, 2016). In addition, collecting agricultural, forestry or other wastes would then incorporate biochar systems with waste management systems (Roberts et al., 2010). Legislation can implement a payment scheme for the collection of waste biomass (Woolf et al., 2010a). Conversion of waste biomass offers an alternative for landfill practices. After the feedstock has been identified, the appropriate method for converting biomass into biochar must be selected. Biochar production methods will depend on the intended use of the biochar. Since pyrolysis type and feedstock produce different biochar types, it is essential to examine soil type before the biochar is used to be optimally effective (Joseph et al.

2010). An in-depth understanding of the biochar's characteristics and its effects upon selected soil type must be understood.

2.2.2. Economic benefits of biochar

The cost-benefit assessment of biochar is yet to be definitively established since technological designs and management systems that have not yet been fully developed (Shackley et al., 2010). Some studies have attempted to undertake a full cost-benefit assessment to assume the benefits of biochar in terms of increased crop yield. The net present value for fast pyrolysis is -\$45 t^{-1} feedstock and -\$70t^{-1} feedstock for slow pyrolysis (Shackley et al., 2010). Shackley et al. (2010) discussed that the application of biochar would be more profitable for arable agriculture in East England due to evidence of an increase of 5% wheat and potato yields, 10% reduction of fertiliser use, 3% increase in overall quality and 5% reduction in cultivation costs. The total available cost was reduced and per hectare profitability was increased by £143 ha^{-1} for feed wheat and £545 ha^{-1} for potatoes. Galinato et al. (2011) considered the carbon sequestration and soil amendment benefits of biochar. Biochar application improved yields in a single rotation of winter wheat. Galinato et al. (2011) concluded that with a low biochar cost of \$12 t^{-2} or a greenhouse gas offsetting revenue of \$31 tCO_2e^{-1}, biochar could be economically feasible technology. In a study conducted in the agroforestry system in East Lombok, Indonesia, the addition of biochar was seen to increase monoculture benefits by 21% and intercropping systems by 69% due to its increase in yield effect. Biochar application increased the farmer's income by 25% for monoculture and 21% for mixed cropping systems (Hayashi, 2014). In developed countries, the feedstock is relatively expensive to obtain and are in demand by users for composting, gasification, and anaerobic digestion. Where biochar would be economically feasible is where wastes are treated and converted, incurring high tipping fees to landfills (Shackley et al., 2010). Biochar produced from waste and non-woody feedstock may reduce biochar costs to low levels where farmers can receive an overall benefit from the investment. An introduction of active carbon markets that include biochar deployment for carbon abatement can also add revenue necessary for biochar to become of more value in agricultural systems (Dickinson et al., 2015).

2.2.3. Biochar in developing countries

Agricultural activities are directly affected by changes in climatic conditions. The Stern report (Stern, 2006) depicted that a rise in 2ºC in average temperatures is capable of reducing the world GDP by approximately 1%. Even though it is evident that climate affects agricultural productivity, global agricultural activities are important catalysts for the change in climate with fossil fuel-based inputs and equipment, soil erosion, land conversion and deforestation, and livestock production. Agriculture contributes to over 20% of global anthropogenic greenhouse gas emissions. The contributions are associated with CO_2 (21%-25% of total CO_2 emissions) from fossil fuels used on farms, deforestation and shifting patterns of cultivation CH_4 (55%-60% of total CH_4 emissions) from rice paddies, land-use change, biomass burning and animal wastes; and N_2O (65%-80% of total N_2O emissions) from nitrogenous fertilizers on cultivated soils and animal waste. By 2080, the effect of climate change will ultimately cause a 6% decrease in global agriculture production. A projected decrease of 30% in agricultural output may be observed for developing countries such as Africa and India (Cline, 2008). The need for developing and effectively diffusing innovative agricultural technologies becomes apparent in developing countries. Adaptation and mitigation potential is of high importance for developing countries. Factors include their economy's heavy dependence on agricultural productivity. At present agricultural productivity remains low, food insecurity remains high, and the direct effects of climate change are especially harsh (Lybbert & Sumner, 2012). Agricultural output declines will occur catastrophically in countries that are closer to the equator than countries further from the equator (Cline, 2008).

Since there is a bidirectional relationship between climate change and agricultural productivity, some agricultural technologies have a direct connection to climate change, such as biochar (Lybbert & Sumner, 2012). Biochar research upon crop and plant production, greenhouse gas mitigation, and pollution remediation has increased at a global level. Zhang et al. (2016) conducted a global literature search of 798 publications, composed of 213 fields, 276-greenhouse pot and 335 laboratory studies pertaining to crop/plant productivity, pollutant remediation and greenhouse gases emission, as seen in Figure 2-4.

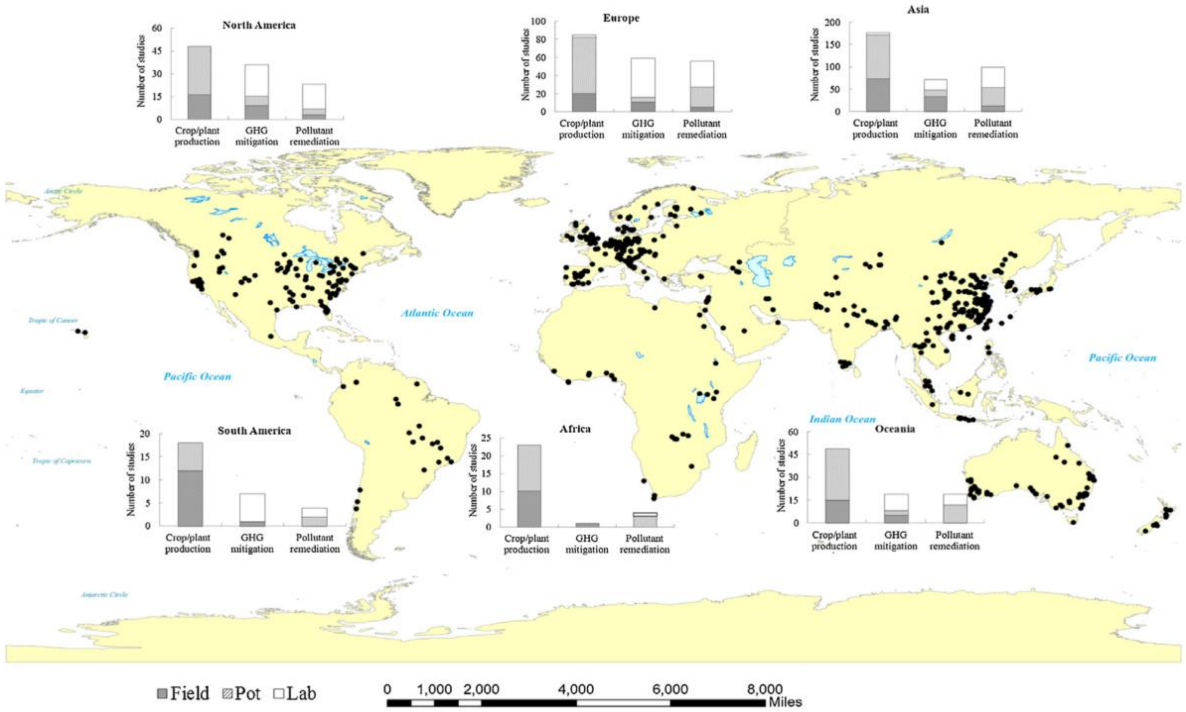

Figure 2-4. Global distribution of biochar-soil amendment studies (continental allocation in terms of laboratory, greenhouse and field studies) (Adapted from Zhang et al. 2016)

Of the 798 publications, most of the studies were conducted in China, EU, USA and Australia. Zhang et al. (2016) suggested that more studies need to be conducted in developing countries to widen the understanding of biochar in an integrated soil-plant system with different soil constraints and biomass availability. The International Biochar Initiative (IBI) has worked with nine developing countries to evaluate cost-effective methods of introducing biochar globally. IBI has introduced small scale pyrolysis units and stoves to produce biochar at a household and village level. Procedures have been developed to analyse biochar and monitor application and plant growth, evaluate production unit performance and assess the economic, environmental, social and cultural cost benefits (IBI, 2018). These countries include Belize, Cameroon, Chile, Costa Rica, Egypt, India, Kenya, Mongolia and Vietnam. Biochar benefits in developing countries can be closely associated with its ability to supply heat energy for cooking, amend infertile soils and reduce deforestation. In developing countries, heat energy for cooking is typically obtained from open burning of biomass. If biochar cookstoves are to be used, fuel gathering pressures for heat energy along with respiratory diseases could be reduced (Figure 2-5). In addition, farmers could also benefit from increased crop yield if the biochar is applied to the soil (Whitman & Lehmann, 2009).

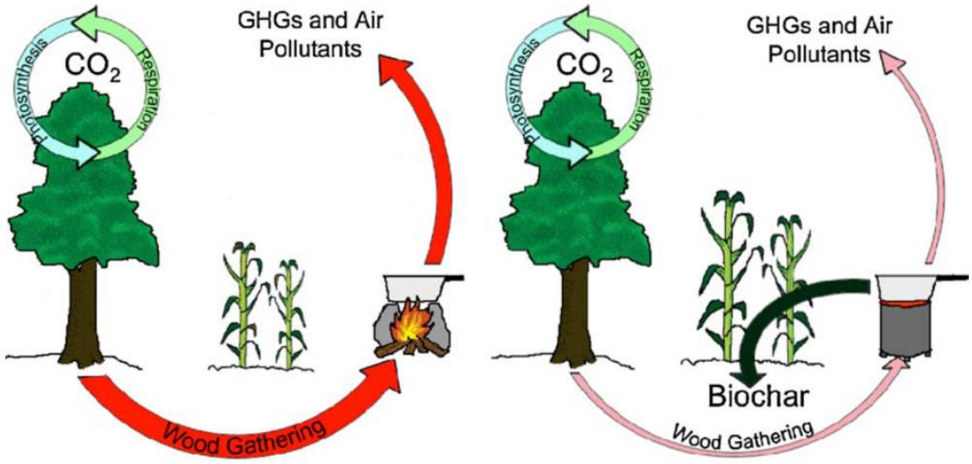

Figure 2-5. Greenhouse gas flows in a traditional cookstove system (left) as compared to a biochar cookstove system (right) (Adopted from Whitman & Lehmann 2009)

A marginal abatement cost curve (MACC) for up to 2030 devised by Pratt & Moran (2010) showed that biochar stove and kiln projects in developing regions (Latin America, Africa and Asia) would be more cost-effective and abate more carbon dioxide than large scale biochar projects in developed. Biochar will simultaneously benefit the agricultural productivity of small farmers by increasing soil fertility. According to Lal (2005), extractive practices by resource-poor farmers in developing countries tend to degrade soil quality and therefore reducing food productivity. It is essential that agricultural practices by resource-poor farmers include land use and management methods that increase and maintain soil productivity, such as biochar implementation. In developing countries, biochar can also be advocated for the removal of contaminants in the soil and water. Large amounts of agricultural waste biomass are being produced in developing countries. The waste biomass produced is ideal for biochar production. In addition, in developing countries, there are limited strategies for the removal of contaminants from soil, water and wastewater. Biochar used for contaminated soil and water treatment can be relatively cheap as compared to advanced methods used in developed countries (Chaukura et al., 2016).

2.2.4. Strategic considerations

Under bioenergy systems, carbon credits could be earned for both cleaner energy and fuels to local people and through the sequestering of carbon. If biochar cookstoves would be implemented by 50% of household fuelwood burning in Africa, approximately 100 Mt of CO_2 could be sequestered on an annual basis, in itself creating over 100M certified emission reductions from biochar carbon sequestration (Whitman & Lehmann, 2009). Putting a price on carbon would create incentives for private research and innovation in agricultural technologies and practices. Difficulty in implementing clean development mechanisms in developing countries such as Africa is the bureaucracy that surrounds the authorization of projects and issuing of credits (Whitman & Lehmann, 2009). The overall rate of project authorization implementation tends to be slow. Strategies for biochar implementation in developing countries must be available for farms that generate substantial surpluses as well as for small farms that sustain themselves and the livelihood of the rural population. A platform for devising solutions can be through understanding the socioeconomic and biophysical factors that drive the needs of farmers in developing countries. Farmers need to have access to markets, inputs, supporting services and information (Sustainable Development Solution Network, 2013) since the production of biochar in developing countries is more likely to be sustainable if produced and applied locally than in a large-scale centralized production, there is a need for production technologies to be available under open knowledge. In addition, all results obtained from applying biochar type in different soil type should be recorded and readily available in order to obtain a standardized guideline for its application (IBI, 2017). Biochar implementation holds two significant aims, (i) benefits to agricultural productivity and (ii) benefits to the environment. Where two aims are devised, one aim usually tends to dominate regardless of its effect upon the other (Pratt & Moran, 2010). For instance, if biochar is realized to be more beneficial in the agricultural sector, dominant agricultural companies will tend to invest on biochar production for agricultural gain and therefore disregarding its effects upon the environment, such as overlooking the potential of biochar upon carbon storage, leading to consequences of greenhouse gas emissions.

2.2.5. Social impacts

The adaptation of appropriate technologies for sustainable farming systems can only be actualized if dissemination of reliable information is efficient. Dissemination of reliable information is preferably facilitated through participatory farmer methods, to reinforce resource planning, and improve research and extension capability (OECD, 2001). Small farmers are often very risk-averse and rely strongly on traditional methods of farming that have been tested over generations. However, traditional practices must be able to adapt to a changing climate in order for food production to be successful (Pratt & Moran, 2010).

Social impacts could occur through the production, handling and effects of improved crop yield. Indoor pollution has been an issue in developing countries, mainly because they depend on combusting raw biomaterials for cooking energy; biochar cookstoves reduce indoor air pollution (Scholz et al., 2014). Apart from biochar cookstoves advertently reducing indoor air pollution, thus decreasing possibilities of respiratory illnesses, increased fuel efficiency is another primary driver for the deployment of biochar cookstoves. The wider feedstock variety reduces required labour for wood collection, and therefore, satisfies on-farm fuel needs. The produced biochar can then either be used in the soil to enhance agricultural production or be used as fuel for further cooking energy (Scholz et al., 2014). On the other hand, potential health risks can be observed in the process of producing, storing, transporting and applying biochar. The leading causes of these concerns are charcoal dust, silicon dust and polycyclic aromatic hydrocarbons, dioxins and furans present in biochar (Shackley et al., 2010). Small particles of less than 10 micrometres are most dangerous to human health (Scholz et al., 2014). Appropriate health and safety precautions must be in action to reduce any harms caused by minute biochar particles. These strategies include keeping biochar covered whilst in storage and transportation and wetting during application to reduce dust formation (Shackley et al., 2010).

2.3. Remediation of Contaminated Soils

This section explains existing approaches to remediate pesticide-contaminated soils. As stated by the European Commission, a contaminated site is defined as: ‘a site where there is a confirmed presence, caused by human activities, of hazardous substances to such a degree that they pose a noteworthy risk to human health or the environment, taking into account land-use’. Due to the physical, chemical and biological complexity of soils, soil attenuation techniques have their own advantages and disadvantages. In this section, recent studies that have been conducted concerning the implementation of biochar as an element for the reduction of pesticide contamination of soils will be discussed.

2.3.1. Techniques for remediation of pesticide-contaminated soils

This section is based on pesticide contamination remediation techniques summarized by Castelo-Grande et al. (2010). Techniques for the remediation of pesticide-polluted soils can be classified as primary action, biological, physicochemical, thermal and other specialized techniques, which are yet at their developmental stage.

The **primary action technique** is the confinement of a contaminated site (Castelo-Grande et al., 2010). The contaminated site becomes surrounded by active or passive barriers that aid in the prevention of contamination to adjacent sites and devoid clean water pathways from entering the isolated contaminated site. These passive or active barriers have a low hydraulic conductivity of approximately 7-10 cm/s. Barriers have been constructed with reactive materials, which directly react and promote the decomposition of the existent contaminant, which requires the drilling of a well of about 15 to 20 meters in depth into the subsoil (Castelo-Grande et al., 2010).

Biological techniques focus on the bioremediation principle whereby natural microbial growth is enhanced to increase the degradation rate of contaminants present in the soil (Castelo-Grande et al., 2010). The microorganisms are supplemented with nutrients, carbon sources or electron donors. Biopiles and land-farming techniques are biological techniques which consist of excavating the contaminated site and thereafter aerating the soil and providing nutrients and controlling the humidity in order to simulate microbial activities (Castelo-Grande et al., 2010). Biopiles technique consists of pipes placed under the biopiles, while agrarian consists of tractors that excavate the soil. This treatment type may be more appropriate for surface soil and unsaturated soils. Other biological techniques consist of composting, bio-air sparging, bio venting, phytoremediation, bio rehabilitation and natural attenuation (Castelo-Grande et al., 2010).

Composting involves mixing the contaminated soils with high organic material thus boosting microbial activities through keeping a constant humidity, pH, oxygen concentration, temperature and carbon/ nitrogen ratio (Castelo-Grande et al., 2010).

Bio-air sparging involves injecting the contaminated soil/groundwater with air, oxygen and nutrients into the saturated zone, thus boosting microbial activities. Rather than pumping air into the saturated zone, *bioventing* pumps air only into the unsaturated zone (Castelo-Grande et al., 2010).

Phytoremediation is an *in situ* technique, which utilizes plant species that are able to degrade certain organic pollutants through extensive biodegradation, phytoaccumulation and phytodegradation (Castelo-Grande et al., 2010).

Natural attenuation is a technique based on leaving the soil to biodegrade its pollutants through natural processes, without the interference of human activities. The disadvantage of this is that decontamination may take longer than the estimated degradation time due to slow processing and degradation kinetics (Castelo-Grande et al., 2010).

Physico-chemical techniques are based on physical and chemical methods of decontaminating soils. The physico-chemical techniques include soil vapour extraction, air sparging, dechlorination, soil flushing, solvent extraction and solidification/stabilization. Soil-vapour extraction technique uses a vacuum, which is inserted to the soil matrix, using a pressure gradient that stimulates air movement in extraction wells. Its primary method is volatilisation removal. Thus, the gaseous phase needs to be further treated before being released into the atmosphere.

Dechlorination is a chemical technique that instigates the loss of halogen atoms from halogenated organic molecules, thus converting these toxic substances into less toxic substances. Soil flushing is a technique that consists of washing of contaminated soil, extracting contaminants by dissolution, suspension, or chemical reaction.

Soil flushing is usually a pre-treatment for reducing contamination of soil before it is treated by another decontamination technology. Solvent extraction, on the other hand, does not eliminate contaminants, but solely separates the contaminants from the soil, thus also being a pre-treatment.

Solidification is a technique that is characterized by the mixing of a reactive material such as concrete with solids, semisolids or sludge in order to contain the contaminants. This technique, therefore, stabilizes the contaminants, limiting its mobility and solubility.

Thermal techniques

Thermal incineration consists of the conversion of contaminants into carbon dioxide and water through high temperature combustion. The main incinerator types are classified as recuperative and regenerative, depending on the energy being recovered. Regenerative systems can recover approximately 90% of combustion energy, but due to this, the higher cost would increase as compared to recuperative systems. The effectiveness of the incinerator depends on temperature, turbulence and residence time, producing fuel gasses, solids from incinerator and water from washing liquids.

Thermal desorption, on the other hand, is a mode of separating the contaminants from the soil but does not allow the contaminants to oxidise. Thermal desorption can be used for soils contaminated with different organic contaminants.

Vitrification consists of converting the contaminated soil into a stabilized, vitreous product. The *in situ* method uses graphite electrodes inserted within the soil, implying high electric current by which the released heat fuses the soil matrix. Pyrolized organic components then move to the vitrification zone where there are thereafter combusted. *Ex vitro*, treatment is similar to *in vitro* treatment, but the main difference is that the soil is excavated and introduced to a vitrification system.

Other techniques include *electro kinetic* technique whereby contaminants are moved within the soil through a low voltage electric current. The effectiveness of this technique is observed with heavy metals, polar organic compounds from low permeability soils, sludge and marine sediments. *Plasma* is another technique that uses heated gas at extreme temperatures to create a plasma. The plasma is then located near the soil where organic compounds are partially broken, and inorganic compounds go through the process of vitrification. The technique is used for different residues, sludge and solids. The plasma technique can be used *in situ*, therefore reducing the transportation cost of toxic materials. *Supercritical extraction methods* use fluid of temperature and pressure above its critical point and extract non-toxic solvents (Castelo-Grande et al., 2010). The technique can rid of a wide array of contaminants without significantly modifying the soil structure and without leaving solvent residues.

2.3.2. Pesticide fate in soils

Soil is a foundational resource that is vital for agricultural production. The myriad of naturally occurring chemical, physical and biological interactions occurring within, allow soils to accommodate for biomass production, store carbon and gas balance in the air, regulate the hydrological activity, and host biodiversity (Safaei Khorram et al., 2015). In order for agricultural productivity to sustain an on-growing human population, it is mandatory to maintain good soil health. The dilemma occurs when agricultural productivity cannot satisfy food production needs, thus resorting to the use of agrochemicals. Due to its extensive use, pesticide contamination is now affecting soil health, thus affecting organisms that are dependent upon the soil (Safaei Khorram et al., 2015). Pesticide entry to soil is based on two methods- firstly, direct soil application for pre-emergent weeds, plant pathogens, and soil pathogens (ex. insects and nematodes) control, and secondly, the pesticide is applied via foliar broadcast spray to control post-emergent weed and foliar insects (Racke et al., 1997). When applied to the soil, the pesticide fate is determined by mixing/dissolution in soil water, sorption onto soil particles, microbial degradation, partitioning into gas phase thereby violating into the air, potential surface runoff and groundwater leaching. The environmental factors that affect the fate of pesticides include crop development and properties, soil properties such as hydrology and organic carbon, climate, soil moisture and temperature, and groundwater level (Boesten et al., 2000; Focus, 2012a). The persistence of pesticides within a soil matrix depends on the chemical nature, volatility, solubility, formulation, concentration, application method, time, frequency and amount of the pesticide in combination with several characteristics of the soil, including soil texture (especially clay content), structure, organic matter and humus content, soil moisture, pH and mineral ion content (Arias-Estévez et al., 2008). Other factors of the soil site that determine pesticide persistence include elevation, slope, aspect, geographic location, plant cover, fauna, microbial populations, use of fertilizers, use of other pesticides, tillage, cultivation, drainage, irrigation, burning of crop residues and adjacent environments including field borders and waterbodies (Arias-Estévez et al., 2008).

2.3.3. Pesticides and soil hydrology

Transportation of pesticides through water flow can occur either as a surface water runoff or as downward leaching to groundwater. The amount of pesticide that is lost through surface water runoff is dependent on factors such as the physicochemical nature of the pesticide, application rate, time of application in relation to runoff events, method of application and formulation (Kookana et al., 1998). Pesticide surface runoff is directly dependent on its concentration in the first few centimetres of the soil. Hence, pesticides that are incorporated in the soil or pesticides that highly sorb to the soil are more prone to non-target sites through surface water runoff. However, pesticides with low sorption potential are capable of moving to surface water bodies through subsurface lateral movement (Kookana et al., 1998). As for downward leaching to groundwater, the factors that determine this phenomenon are the physicochemical nature of the pesticide, soil texture, soil structure, preparation of soil surface, the timing of rainfall, irrigation methods, the initial water content of the soil, and formulation and method of pesticide application. Rapid transport of pesticides to groundwater include a combination of preferential flow and co-transport with colloidal matter (Arias-Estévez et al., 2008). Downward leaching is highest for pesticides that are weakly absorbed to the soil matrix. Typically, these are soils of sandy texture and low organic matter in climates with high precipitation and low temperatures, and promote macropore flow (such as heavy loams and clays) (Børgesen et al., 2015). Preferential flow occurs in porous soil systems that have a hierarchical pore composition. These macroporous soils are often characterized by a variety of small scale cracks, structural pores, decayed root channels and macropores and coarse micropores, thus allowing inter aggregate water flow and intra aggregate water flow. Soils with preferential flow patterns can have colloids that can transport pesticides in the soil. Colloid assisted transport occurs when pesticides are strongly sorbed to soil particles such as clay and organic matter colloids. These particles act as vectors for pesticide transportation. The sorption and desorption ratio of pesticides bound to these particles may undergo changes as transportation occurs (Arias-Estévez et al., 2008 and Børgesen et al., 2015).

2.3.4. Types of soil pesticide interactions

The interactions that occur between soil and pesticides are governed by sorption-desorption, volatilization and degradation. Sorption of pesticides within the soil can be classified as reversible or irreversible, both of which are mainly dependent on soil and pesticide characteristics (Gevao et al., 2000). Sorption is based upon chemical bonding and diffusion into the soil structure. Diffusion is a physical process whereby when the pesticide is in its aqueous phase. The pesticide migrates into capillaries and pore spaces, thus allowing itself to be trapped in the soil structure. Diffusion is reversible and can be readily desorbed from the soil structure (Cabrera et al., 2011). Sorption based on the chemical bonding is mainly based on the chemical composition of both the pesticide and soil. Typically, organic acids and phenols are sorbed to positive sites while positive compounds are sorbed to harmful sites of the soil surface. Weak chemical bonds such as hydrogen bonds have electropositive protons that will interact with the electronegative atoms on the soil surface, while stronger bonds such as covalent bonds display an irreversible sorption phenomenon within the soil (Gevao et al., 2000). Pesticide sorption is determined by the soil's moisture, organic matter content, pH, texture and the presence of co-solvents and ions. Pesticides consisting of weak acids or bases are highly influenced by soil pH (Kerle et al. 2007; Kookana et al. 1998). For instance, organo-basic compounds such as s-traizines become cations through protonation as the pH of the soil reaches their pK_a values. Thus, their sorption typically increases as pH decreases (Kookana et al., 1998). Pesticides are easily sorbed by soils with a low moisture content since water typically competes with the pesticide for binding sites within the soil surface. Soil with a high organic matter and clay content tend to have high sorption potential due to their high surface area and chemical activity. Kookana et al., (1998) has observed that the interaction between pesticide and organic matter can have varied interactions depending on the nature of the organic matter. It is therefore essential to understand the pesticide sorption potential, through understanding the type and amount of organic matter present in a given soil (Kookana et al., 1998). Volatilisation occurs when the pesticide is lost from the plant, water or soil as it is converted into vapour. The physicochemical characteristics of the pesticide as well as weather conditions, can determine to what extent volatilisation occurs (Kookana et al. 1998). Volatilisation rate is evidently correlated with the chemical concentration, airflow, temperature, and inherent vapour pressures. The main physical parameter that determines the loss of the pesticide through volatilisation is the pesticide's vapour pressure which is much dependent on temperature (Racke et al., 1997). Degradation can occur through chemical or microbiological processes. Hydrolytic degradation occurs through the interactions associated with the soil pore water, which may be base or acid-catalyzed, or on clay mineral surfaces. A factor that modifies hydrolytic degradation is temperature. Racke et al. 1997 state that pure hydrolysis often increases by a factor of 2X per a 10°C temperature rise. In addition to hydrolytic degradation, oxidation and reduction of pesticides can occur in aerobic and anaerobic soils. Microbial degradation can be in the form of co-metabolic, incidental in nature or linked with energy production and nourishment needs of a given microbiological population (Gevao et al., 2000).. Factors such as compound structure, temperature, soil texture, water content, organic matter, soil microbial biomass, biological diversity, plant coverage and soil depth are all factors that influence pesticide degradation through microbial activities (Cabrera et al., 2011).

2.3.5. Effects of biochar on soil hydrology

Biochar characteristics that will have a direct effect on the hydrological properties of biochar-amended soils are particle shape, size, internal pores, and the surface chemistry of the biochar, inclusive of the ratio of hydrophilic and hydrophobic domains (Lehmann and Joseph, 2015). Due to its porous structure, biochar can modify the size, shape and pore numbers between soil particles. The water flow rate through the soil is greatly influenced by the intra and inter-particle pores within the soil (Sohi et al., 2009). However, the intra-particles in the soil-biochar mixture does not depend on the soil type since the intra-particle size of the biochar does not change with soil type (Lehmann and Joseph, 2015). Furthermore, inter-particle porosity will vary depending on the soil type and biochar. Therefore, the water potential in a soil-biochar matrix is determined by the particle size and texture of the soil and particle size of the biochar. If pore size distribution is fixed, Sohi et al. (2009) state that biochar may increase available moisture in sandy soils and characterize a neutral effect on medium-textured soils. It could negatively affect the available moisture of clayey soils, given that the effect of particle size is short-lived since biochar appears to break down into fine fractions once in the soil (Sohi et al., 2009). In the case of soil hydraulic conductivity, Glab et al. (2016) show that biochar amendment to sandy soils is capable of reducing its hydraulic conductivity. However, since the physical and chemical processes have not yet been clearly understood, it is challenging to generalize if these studies will continually improve or hinder soil water flow (Lehmann and Joseph, 2015). Verheijen et al. (2010) explain that soil water retention is determined by the distribution and connectivity of pores in a soil matrix, soil texture, aggregation and soil organic matter. Lima et al. (2018) showed that coffee ground and coffee husk biochar pyrolysed at 550°C increased the permanent wilting point, field capacity and available water of biochar amended sandy soil. The mechanism of modifying the permanent wilting point, field capacity and available water within the soil due to the biochar's effect on the porous network of the soil, specific surface area, aggregating particles (Głąb et al., 2016; Ulyett et al., 2014), promoting the formation of menisci for more considerable water retention. According to Peake et al. (2014), field capacity is positively influenced by finer particles and available water holding capacity is determined by medium particle sizes. However, Jeffery et al. (2015) reported that biochar with large particle sizes contributed no changes in water retention with soils of high sand content. It is expected that biochar addition to soils is able to affect the water permeability within the soil due to an increase in total porosity, which is responsible for gravitation water movement in the soil. Thus, biochar application can modify soil hydrology, depending on the properties of the biochar, soil texture, (Głąb et al., 2016), climate and soil management combinations (Verheijen et al., 2010).

2.4. Biochar Application for the Reduction of Pesticide Contamination in Agricultural Soils

This section will discuss the effects of biochar-soil-pesticide effects within an agricultural soil scenario.

2.4.1. Biochar physical and chemical characteristics and interactions with soil

Biochar incorporation within the soil can evidently influence soil structure, porosity, texture, particle size distribution and density, thus modifying aeration, soil hydrology, microbial activity and nutritional status of the soil (Joseph et al., 2010). Biochar's potential to modify the physical and chemical properties of the soil depends on the feedstock that has been converted to biochar, oxygen amount and temperature variability whilst in the pyrolysis process, and the nature of the soil in which the biochar is applied (Lehmann, 2007; Verheijen et al., 2010). The surface area in biochar is hugely variable to pore size distribution. Due to the pore size distribution and the low-density nature of biochar, biochar incorporation holds air and water, which then modifies the soil's bulk density. Biochar true bulk density has been found to be between 1.5 to 2.1 g cm^{-3}. Other biochar bulk densities have been found to be between 0.09 to 0.5 g cm^{-3}, which are values a lot lower than most soils (Lehmann et al., 2011). Soil structure and texture vary with different soil types. Sandy soils are limited in specific surface area (sand 0.01 to 0.1 m^2/g) and are not capable of storing large amounts of water as compared to clayey soils with a specific surface area of 5 to 750 m^2g^{-1}, which plays a vital role in the retention of water. Biochar implementation to sandy soils, therefore, increases the overall specific surface area by 4.8 x (Atkinson et al., 2010). Biochar has been observed to improve the water holding capacity and plant available water in loamy and sandy loam soils, increasing the water holding capacity to approximately 11% with an amendment of 9 t ha^{-1} in a silty loam soil (Pandit et al., 2018). In addition to changing the physical structure of soils, the soil chemical properties can also be modified by incorporating biochar. The pH and cation exchange capacity ability of biochar depend on the feedstock type and pyrolysis conditions associated with biochar production (Joseph, Camps-Arbestain, Lin, Munroe, Chia, et al. 2010). Masulili & Utomo 2010 observed that rice husk biochar at 600°C significantly increased the soil pH, soil organic matter, total P, CEC, exchangeable potassium and calcium. Acacia biochar made in earth kilns was also capable of increasing soil organic carbon and cation exchange capacity by 23 -27% and increasing soil pH from 5.0 to 5.6 in nitisol soil types (Agegnehu et al., 2016). The ability for biochar to modify the pH, EC and CEC are much dependent on the pyrolysis temperature. Biochars made at low temperatures are dominated by amorphous C structures, and lower aromaticity compared to high temperature biochar. Biochar comprises of a considerable proportion of aromatic carbon structures, inclusive of fused aromatic carbon structures as compared to other organic matter; this key characteristic determines the stability of biochar within the soil (Lehmann et al., 2011) (*See* Physicochemical properties of biochar in previous section). Since biochar consists of recalcitrant carbon, labile carbon and ash, the recalcitrant carbon nature may be a stable structure that will not cater for the availability of carbon as an energy source for microorganisms, however, depending on the biochar type, a fraction may consist of labile carbon that is readily available for organisms and thus mineralizable (Lehmann et al., 2011). In addition to the mineralizable carbon, the biochar's porous structure is also able to host several microorganisms such as mycorrhizae and bacteria, therefore increasing the microbial community within the soil (Atkinson et al., 2010).

2.4.2. Sorption of pesticides and biochar interactions

As an alternative to different contaminated soil remediation techniques, such as traditional landfilling and dredging, which can be quite costly and sometimes ineffective, there exists the cost-effective *in situ* remediation of contaminated soils through the application of carbonaceous sorbents such as biochar (Patmont et al., 2015). Using biochar as a sorbent amendment technique is based on the basis that pyrogenic carbon-rich materials are able to sorb organic contaminants. Though activated carbon has a high sorption capacity when compared to some biochar types, biochar is preferably used in soils that have very low pyrogenic carbon contents (Oliveira et al., 2001; Johannes Lehmann, 2007). In addition, biochar contains non-carbonized fractions that interact with soil contaminants, specifically oxygen containing carboxyl, hydroxyl and phenolic surface functional groups, which can bind to the soil contaminants (Ulrich et al., 2015; Ahmad et al., 2014b). When an active sorbent is added to the soil, contaminants desorb from weak sorption sites and move toward stronger sorption sites through retarded molecular diffusion or by pore water flow through the soil, and finally, the contaminants are sequestered by the biochar or activated carbon. Table 2-4 below shows contaminant remediation using several different biochar types.

Biochar type	**Contaminant**	**Matrix**	**Biochar rates**	**Effect**	**References**
Wheat straw (550°C)	Bentazone, Tricyclazole	Soil	2% (w/w)	Differences in dissolved organic matter and specific surface area	(García-Jaramillo et al., 2014)
Green waste (450°C)	Atrazine and simazine	Water	100 mg/L	Adsorption and partition	(Zheng et al., 2010)
Woodchips (450 and 850 °C)	Chlorpyrifos and carbofuran	Soil	2 and 5% (w/w)	Adsorption due to high surface area and nano porosity	(Yu et al., 2009)
Cotton straw (450 and 850 °C)	Chlorpyrifos and fipronil	Water and soil	0.1, 0.5 and 1% (w/w)	Absorption due to high surface area and microporosity	(Yang et al., 2010)
Broiler litter (350 and 700 °C)	Deisopropylatrazine	Water	3.3 and 1.7 g/L	Sorption due to high surface area and aromaticity; sorption on a non-carbonized fraction	(Uchimiya et al., 2010)
Bamboo (600 °C)	Pentachlorophenol	Soil	0, 1, 2 and 5% (w/w)	Reduced leaching due to diffusion and partition	(Xu et al., 2012)
Rice straw	Pentachlorophenol	Soil	0.5 to 10.0% (w/w)	Adsorption due to high surface area Water and microporosity	(Lou et al., 2011)
Red gum woodchips (450 and 850 °C)	Pyrimethanil	Soil and water	0.1, 0.2, 0.5, 0.8, 1, 2 and 5% (w/w)	Adsorption due to high surface area and micro-porosity	(Yu et al., 2010)
Hardwood (450 and 600 °C)	Simazine	Soil	5 and 50 g/kg	Sorption due to abundance of micro-pores	(Jones et al., 2011)

Biochar type	Contaminant	Matrix	Biochar rates	Effect	References
Dairy manure (200-350°C)	Atrazine	Water	5 g/L	Sorption and partitioning into the organic phase	(Cao et al., 2009)
Dairy manure (450°C)	Atrazine	Soil	2.5 and 5% (w/w)	Sorption	(Cao et al., 2011)
Mixed sawdust (500°C)	Atrazine and acetochlor	Soil	5% (w/w)	Increase in organic carbon within the soil.	(Spokas et al., 2009)
Birchwood (500°C)	Glyphosate	Soil	0, 10, 20, and 50 Mg/ha	Modification of pH and electrical conductivity	(Kumari et al., 2016)
A mixture of Birchwood (20%) and Norway spruce (80%) (380-430°C)	Diuron and MCPA	Soil	25-200 t/ha	The surface is and degree of carbonization and octanol-water partition	(Cederlund et al., 2017)

Table 2-4. Contaminant remediation using several biochar types

Numerous studies exist by which biochar is used as sorbents for contaminants such as pesticides and heavy metals. Biochar of >500°C has shown to be more effective in absorbing contaminants due to their high surface area and micropore development (Ulrich et al., 2015). Kończak & Oleszczuk (2018) carried out an eighteen-month field experiment using willow biochar produced at 700°C, and results indicated that the biochar type was capable of reducing sewage sludge heavy metal toxicity in addition to reducing the leaching of nutrients. Poplar (*Populus euramericana*) branches were pyrolysed for 350°C showed high sorption affinity to herbicides such as acetochlor and 2, 4-D (Li et al., 2013).

2.4.3. Movement of biochar in soil

Biochar movement within a soil profile and into water resources has not yet been thoroughly understood due to limited long-term standardized methods for monitoring the biochar and understanding its ageing process (Sohi et al., 2009; Verheijen et al., 2009). The potential for biochar movement is mainly due to its application method within a soil type, terrain topography, management practices and climate. For instance, dry biochar applied to clayey soils may move to non-target areas due to wind or air erosion, while biochar applied as a slurry can be transported vertically through the soil profile (Sohi et al., 2009). In addition, in sites where there is plenty of biological activity, biochar particles may also be transported, for example, by anaeic earthworms and arthropods (Lehmann et al., 2011). Major et al. (2010) observed the downward migration of biochar using stable isotope technique and found that over two years, a small amount of soil-applied biochar moved below the 0.1 m application depth into the 0.15-0.3 m sampling depth. 2.2% of biochar applied at 23.2 t BC ha^{-1} was lost by respiration, and approximately 1% was lost through percolating water. Major et al. (2010) also suggested that the larger amount of biochar (20-53%) was assumed to have been lost through surface runoff during intense rain events. Singh et al. (2014) observed that after 10 months of a field trial, 3-4% of the pyrogenic organic matter applied was recovered below the 0-5 cm application depth, suggesting a downward vertical movement. In addition Singh et al. (2015) studied the migration of biochar under different soil types using biochar produced from *Eucalyptus saligna* at an application depth of 0-10 cm and showed that vertical biochar migration was highest for Arenosol (below 50 cm) as compared to the Cambisol and Ferralsol. Singe et al. (2015) suggested that the downward migration could have been caused by the movement of finer biochar particles facilitated by rainfall events (125 mm d^{-1}), and the low concentration of clay within the texture of the Arenosol. These studies suggest that site-specific observations of the target site such as the physical, biological and chemical processes must be taken into consideration in order to optimise the use of biochar for a specific purpose.

2.4.4. Changes of biochar sorption in soil with time

Studies have found that black carbon particles from anthropogenic activities and wildfires show that their stability within the soil ranges from several millennia (Lehmann, 2007). However, biochar's interactions with both the biotic and abiotic soil components have the potential to modify the biochar's characteristics, which in return affects its ability to sorb pesticides. Verheijen et al. (2010) suggest that the fate of biochar within the soil is dependent on solubilisation, translocation and leaching, and oxidation of the biochar that remains within the soil may stimulate the accumulation of carboxylic functionalities of the biochar surface. The interactions with organic and mineral matters may tend to block and deactivate binding sites found on the surface of biochar, thus less of an opportunity for pesticides to sorb to the biochar. Chicken litter biochar made at 450°C and paper-mill and green waste biochar were characterized before application and after 1 and 2 years of application within a Ferrosol. The green waste biochar's surface was observed to be covered with high concentrations of clay minerals consisting of combinations of Al, Si, C, Fe and Ti, and trace Ca, Mg, Mn, K, Na, P, and S. The surface cover of the biochar suggested a decrease in sorption of non-ionic organic compounds (Joseph et al., 2010). In a study conducted by Zhelezova et al. (2017) based on the adsorption and degradation of atrazine and diuron, adsorption of pesticides decreased after 3.5 months of biochar left in the soil. However, degradation rates were not affected by ageing. A suggestion for the decrease of glyphosate sorption was mainly due to the biochar's liming effect within the sandy soil. Trigo et al. (2014) observed that high surface area and porosity in aged one and two years macadamia nut biochar increased indaziflam and fluoroethyldiaminotriazine sorption but decreased terbuthylazine and MCPA sorption. The elimination of the organic film from aged biochar was assumed to increase its specific surface area, exposing underlying micropores. Trigo et al. (2014) observed that even though several pores were filled with organic and mineral matter, the specific surface area was still higher than that of the fresh biochar. Several studies have reported that ageing of char from one to two years does not affect the sorption of pesticides such as diuron and simazine. Zhelezova et al. (2017) suggest that strong sorption tends to restrain microbial degradation of pesticides, thus allowing biochar to age in the soil, therefore, allows an increase in the microbial population within the soil, thereby increasing the degradation of pesticides.

2.5. Pesticide fate modelling

2.5.1. Purpose of Simulation Models

Pesticide fate models grant agricultural and environmental agents the opportunity to forecast the behaviour of a pesticide, thus obtaining solutions to reduce its contamination within the soil. It is common practice that pesticides are being used in agricultural practice. Therefore, recommendations must be devised that will allow the pesticide to fulfil is purpose as a plant protection product and at the same time have a minimal detrimental effect on the environment (Wagenet, 1990). It is in this circumstance where pesticide fate models can effectively be used. These simulation models can identify the best-suited timing and dosage of a pesticide for a specific soil-crop-water combination, thus maximising its role as a plant protection product and minimising its harm toward the environment. To determine the pesticide behaviour in soil, simulation models consider microbial degradation, chemical degradation, pesticide sorption, plant uptake, volatilization and water flow processes.

2.5.2. Types of Groundwater Simulation Models

Varieties of simulation models have been devised to depict the fate of pesticides in the soils. Though they aim to achieve a common objective, simulation models differ in the concept the developer and the degree of complexity of the model. It is therefore essential to identify the processes of the model that will determine a particular outcome that will suit the desired purpose. Failing to identify that different models are suited for different purposes may discredit the models from playing an essential problem-solving role. The European Commission has devised a workgroup entitled the Forum for the Co-ordination of Pesticide Fate Models and their Use (FOCUS) that consists of an established set of simulation models used as tools for review processing of pesticides according to Regulation (EC) No 1107/2009. The FOCUS workgroup consists of a collaboration of scientists of regulatory agencies, academia and industry, along with contributions from the European Food Safety Authority (EFSA, 2018), who is in charge of keeping the models updated and improved. The FOCUS simulation models use environmental data collected throughout the EU as input data to calculate PPP concentrations in ground and surface waters in the EU. Since the FOCUS models have been well-established tools for complying pesticides with regulatory standards, this section discusses several types of groundwater pesticide-fate models being used in the EU. The four main groundwater models developed as risk assessment tools and adopted by FOCUS are PEARL, PELMO, PRZM-GW, MACRO-GW.

MACRO model takes into consideration the rapid preferential flow in soil, consisting of two flow domains that consist of macropore or micropore systems. The boundary between the flow domains is defined by a soil-water pressure head close to saturation and is related to water content and hydraulic conductivity. The Richard's equation is used to determine micropore water flow, and gravity flow is used to determine water flow through macropores. Transportation of solutes in micropores is calculated by the convection-dispersion equation, and a simplified capacitance type approach is used to calculate changes in macropores (Jarvis et al., 2000). MACRO-GW is only used for the Chateaudun groundwater scenario (Boesten et al., 2000).

The Pesticide root zone model (PRZM) consists of hydrologic flow and chemical transport to model runoff, erosion, plant uptake, leaching, decay, foliar wash off and volatilisation. The model also considers advection, dispersion, molecular diffusion and soil sorption. Soil temperature effects, volatilisation and vapour phase transport in soil, irrigation simulation are also included (Focus, 2012b).

PELMO uses capacity based water flow using a daily time step for hydrological processes. Preferential flow and capillary rise are not included. The model also includes pesticide movement using the convection-dispersion equation, crop simulation, soil degradation, pesticide sorption to soil and pesticide volatilization using Frick's and Henry's calculations.

PELMO also takes into consideration runoff, soil temperature, plant-uptake pesticide applications and metabolism (Focus, 2012b).

The pesticide emission assessment at regional and local scales (PEARL) is based on the convection-dispersion equation and Henry’s law, Freundlich sorption model, transformation rate dependent on water content, temperature and depth in the soil and plant uptake. The model also consists of the formation and behaviour of transformation products and models lateral pesticide discharge to drains. As similar to PELMO, PEARL does not include preferential flow (Boesten et al., 2000).

2.5.3. Pesticide Fate Processes

Sorption

Sorption of a pesticide onto soil is one of the essential processes that affect its fate within a soil matrix, thus potentially diverging its pathway from reaching non-target areas. Sorption of pesticides onto soil has been widely known for being affected by the percentage of organic matter or clay content in the soil (Kookana et al., 1998). However, other characteristics such as cation bridging, ion exchange, hydrogen bonding and van der Walls mechanisms play an important role. Along with the characteristics of the soil, sorption is also dependent on the physicochemical composition of the pesticide itself. Pesticide sorption is explained as being partitioned between the aqueous or solid phase of the soil. The relationship between the partition of aqueous and solid phase at a constant pressure after equilibrium can be either linear or non-linear and is typically described by sorption isotherms (Graber and Kookana, 2015).

The ***Linear adsorption*** equation is shown in (1):

$$S = K_d C$$

Where:

$S =$ Sorbate concentration at equilibrium.

$C =$ Non-sorbed molecules in solution at equilibrium.

K_d = Distribution coefficient.

The ***Langmuir absorption*** equation is shown in (2):

$$S = \frac{CbQ}{1 + bQ}$$

Where:

b = The affinity of absorbate for the monolayer surface;

Q = The maximum possible sorption capacity.

The ***Freundlich absorption*** equation is shown in (3):

$$S = K_f C^n$$

Where:

K_f = The Freundlich distribution coefficient;

n = A measure of the intensity of absorption.

The linear equation relates to sorbates that are non-ionic or lack the capacity to interact with specific sorbents, while the Langmuir equation describes sorbate molecules interact with the single-layer surface coverage of the sorbent that has one type of sorption site. The Langmuir equation describes sorbates that once allocated to a sorption site, do not change or affect the absorption structure of adjacent sorbates. The Freundlich equation typically describes adsorbents with high heterogeneous distributions of different site energies, such as that of absorbents that entail a mixture of soil and carbonaceous material.

FOCUS models typically use the soil organic carbon sorption coefficient (K_{OC}) of a pesticide, which is typically calculated by dividing a measured K_d by the soil organic carbon fraction of the soil, as seen in equation (4):

$$K_{OC} = \frac{K_d}{F_{OC}}$$

K_{OC} and F_{OC} are used as input in order to determine the K_d for each soil layer. Therefore, the organic matter in a soil type has been known to be a reliable determinant for pesticide sorption in soil (Focus, 2012b).

Degradation

Pesticide degradation can occur in the soil via microbiological or chemical pathways. Microbial degradation processes tend to occur, particularly near the root zone (Kookana et al., 1998). Microbial processes such as mineralisation and polymerisation along with secondary effects such as a change in pH and redox conditions also affect pesticide fate. Once the pesticide has migrated past the root zone and into the saturated zone, chemical processes such as hydrolysis tend to be predominant (Wagenet, 1990). The chemical properties of a pesticide have a strong influence on the rate at which microbial or chemical degradation may occur. The rate of degradation can be commonly represented by single first-order kinetics, as seen in equation (5):

$$C_t = C_0 e^{-kt}$$

Where:

C_t = Concentration at time t

e = Base e

k = The rate constant of decline 1/days

t = Time

The single first-order kinetics gives a convenient explanation of the rate of degradation using a single parameter, *k*, and the rate of degradation does not depend on the initial concentration of the pesticide. The half-life of a pesticide is described using equation (6):

$$t_{\frac{1}{2}} = natural\ \log(2)/k$$

The half-life describes the time required for the concentration of a pesticide to be reduced by 50% at a certain concentration point in time. It should be noted that laboratory and field values might differ in degradation rates, as field values may be shorter since field conditions consist of diverse soil and environmental conditions (EPA, 2016).

Volatilisation

Pesticides may enter the atmosphere through volatilisation. Volatilisation partitions the pesticide between a liquid and vapour phase. The dominant factors that affect volatilisation are vapour pressure and water solubility, which can be represented by a modified Henry's law constant (H) in the equation (7):

$$H = \left(\frac{C_a}{C_w}\right) RT$$

Where:

C_a = The concentration of pesticide in the air

C_w = The concentration of pesticide in water

R = Gas constant (8·314 Pa/m^3·mol·K)

T = Absolute temperature (K)

The weather conditions and the chemical properties of the pesticide determine the rate at which pesticide volatiles.

Plant uptake

The extent to which plants influence pesticide fate by uptake has not been thoroughly understood due to a lack of quantitative data (Wagenet, 1990). However, plant uptake of a compound can be affected by the chemical properties of the compound, environmental conditions and plant species characteristics (Burken & Schnoor, 1996). The relationship between pesticide fate and plant uptake may be determined by the octanol-water partition coefficient (K_{ow}) of the pesticide (Wagenet, 1990). The effect of plant rhizosphere may also determine the fate of a pesticide in the soil due to the release of exudates that contribute to the presence of microbial organisms. Chemicals that have a K_{ow} of <3 have been commonly accepted as less bio-accumulating substances (Kookana et al., 1998)

Transport process

The transport process of pesticides is based on the physical and chemical processes of solute transport in the soil. Surface runoff and erosion, groundwater leaching and volatilisation drift are the main pathways that influence the transport of pesticides (Kookana et al., 1998). The transport of pesticides depends on the diffusion of pesticide in the gas or aqueous phase along with a solute concentration or gas phase concentration depending on volatilisation, and convection transport of the pesticide (Wagenet, 1990). Water flow in the PEARL model is described by Richard's equation for the change in the hydraulic head by water flow. Richard's equation is described as:

$$C(h) = \frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[k(h)\left(\frac{\partial h}{\partial z} + 1\right)\right] - R_{u,L} - R_{d,L}$$

Where:

$C(h)$ = Differential water capacity (m^{-1})

h = Soil water pressure head (m)

t = Time (d)

z = Depth in soil (m)

$K(h)$ = Unsaturated hydraulic conductivity (m d^{-1})

$R_{u,L}$ = The volumetric volume rate of water uptake (m^3 m^{-3} d^{-1})

$R_{d,L}$ = The volumetric volume rate of lateral drainage (m^3 m^{-3} d^{-1})

The moisture retention function and the hydraulic conductivity function of the soil are required for the simulation of water flow. The Van Genuchten-Maulem parameters can be used to describe hydraulic relationships. The first relationship describes water retention:

$$\theta(h) = \theta_{res} + \frac{\theta_{sat} - \theta_{res}}{[1 + |\propto h|^{n}]^{m}}$$

Where:

$\theta(h)$ = The volume fraction of water (m^3 m^{-3})

θ_{res} = The residual volume fraction of water

θ_{sat} = The saturated volume fraction of water (m^3 m^{-3})

$\propto, n, m$ = Van Genuchten parameters

The value m is calculated by: $m = 1 - \frac{1}{n}$

The second relationship is hydraulic conductivity:

$$K(h) = K_s S_e^{\lambda}\left[1-\left(1-S_e^{\frac{1}{m}}\right)^m\right]^2$$

Where:

K_s = Soil matrix saturated hydraulic conductivity (m d^{-1})

S_e = Relative saturation (-)

λ = Van genuchten parameter (-)

The relative saturation is defined by:

$$S_e = \frac{\theta(h) - \theta_{res}}{\theta_{sat} - \theta_{res}}$$

The hydraulic properties change with depth. Therefore, different horizons can have distinguished hydraulic functions. Pedotransfer functions such as Rosetta can be used to estimate water retention, saturated and unsaturated hydraulic conductivity from primary soil data. Rosetta can be used to estimate water retention parameters according to van Genuchten (1980), saturated hydraulic conductivity and unsaturated hydraulic conductivity parameters according to van Genuchten and Maulem. The model uses soil textural class, sand, silt and clay percentages, bulk density and water retention point at 33 kPa.

2.5.4. Use of Simulation Models

The use of pesticide-fate simulation models has been used as an established tool by regulatory agencies to comply with directives, such as the EU Directive 2009/128/EC (Knäbel et al., 2012). Directives aim to acquire the most sustainable use of pesticide to reduce risk impacts on human health and the environment (Pullan et al., 2016). To comply with directive aims, simulation models evaluate the time it takes for pesticides to dissipate in the soil to a tolerable level before contaminating ground, surface or drinking water. By identifying these processes, guidance is provided to identify remediation techniques that will reduce the contamination of soil and water. Another use of simulation models is to determine the mobility and persistence of new pesticides that will potentially be introduced as a plant protection product. This proactive method screens the candidate pesticide before its application to the soil is realised, thus measuring its potential effects on human health and the environment (Wagenet, 1990). Pesticide fate models can also be used to help farmers to design an effective pesticide management plan. An efficient crop, soil and chemical plan grants farmers to reduce costs by reducing pesticide use at a minimal level that is still able to control pests effectively. Simulation models welcome the opportunity to identify alternative management practices, substitute harmful pesticides to less harmful and potentially cheaper pesticides but still have an equivalent effect on pest management and project best possible water and chemical management systems as knowledge of the physical and chemical properties of the soil is available (Wagenet, 1990). Pesticide-fate simulation models give rise to solutions related to agriculture and the environment, as they may be a fast, cheap and reliable method of synthesising environmental interaction processes that will determine the fate of a pesticide in the soil.

2.5.5. Biochar Application in Model

Since several studies have shown that biochar-amended soil could absorb pesticides and reduce its leaching (Joseph et al., 2010; Tang et al., 2013), a biochar-amended soil would, therefore, influence the predicted environmental concentration of a pesticide in groundwater. Incorporating biochar in a pesticide-fate simulation model would allow us to understand the effects of biochar as a pesticide mitigation strategy. Only a few studies have ventured into integrating mitigation strategies to pesticide-fate simulation models. Oorts et al. (2007) used PASTIS to simulate soil carbon and nitrogen changes in the soil. They used the model to increase water drainage and reduce the total water evaporation of the soil. Aslam et al. (2018) similarly used the PASTIS model to simulate the effects of mulch on the transport and biological processes of pesticides. Marín-Benito et al. (2018) used MACRO as a support simulation model to determine the effects of mulching and intermediate cover crops on pesticide fate. In this study, the mulching soil layer was defined by a specific physical, hydrodynamic and pesticide reactive layer of high organic content and results were compared to field experiment results. The results showed that MACRO reasonably predicted water percolation, soil temperature but was not able to simulate the soil water content. Another study conducted by Queyrel et al. (2016) showed that the incorporation of mulch and catch crop modified the pesticide concentrations resulted from a crop model STICS, thus reducing nitrate and pesticide leaching. Only a few studies have considered mulch to change the pathway of pesticides within the soil using pesticide simulation models. However, no studies have considered incorporating biochar into pesticide fate models, thus determining if biochar will minimize pesticide leaching within the soil profile.

2.6. Conclusions

This literature review consisted of a systematic approach to identify different studies that have been conducted based on the use of biochar for reducing agrochemical leaching. The literature review focused on explaining the fundamentals of biochar and elements related to stakeholders and biochar implementation in agricultural systems. The literature review also focused on studies conducted based on biochar use for pesticide leaching reduction and pesticide fate modelling. Furthermore, this literature review identified that biochar research was needed to address the following: (1) feasibility of implementing biochar in agricultural systems of Belize, (2) biochar use for reducing agrochemical leaching in tropical soils, and (3) the use of pesticide fate models to determine biochar's effects on agrochemical leaching. The following chapters of this thesis explore each of the identified biochar research needs.

Chapter 3. Implementation of Biochar in Agricultural Systems of Belize: Stakeholder Analysis

3.1. Introduction

Agriculture sustains the livelihood of people in many developing countries. In these countries, agriculture accounts for 20-60% of overall gross domestic product and 65% of its labour force (Hoffmann, 2011). The need for agriculture to sustain the livelihood of people faces a major challenge. The challenge is to feed an on-growing human population whilst adjusting to a changing climate. As a result, 27% of the world's tropical forests, 45% of temperate forests, and 70% of natural grassland have been transformed into agricultural land (SDSN, 2013). In addition to deforestation, agrochemicals are continuously being applied to soils to obtain optimum crop yields. If not appropriately managed, deforestation and extensive agrochemical use are able to damage soils, aquatic ecosystems and contribute to climatic changes (Hoffmann, 2011). In 2005, a 10-12% approximation of anthropogenic greenhouse gas emissions were contributed by agriculture (Vermeulen et al., 2012). As observed, the agriculture sector is an interdependent system consisting of increasing food production and protecting the natural environment. Agriculture can transcend between being a solution to food security or a problem to environmental protection (Lybbert & Sumner, 2012). The pressure balance agriculture and environmental protection have been heavily prioritized in developing countries such as Belize, where the economy is based on both agriculture and natural ecosystem services (SIB, 2017).

A strategy to enhance agricultural production and protect the natural environment is to amend agricultural soils with biochar. Biochar is a carbonaceous material produced from waste biomass through the process of pyrolysis (Woolf et al., 2010). Biochar has been used to amend infertile soils, reduce nutrient leaching, combat harmful anthropogenic climatic activities, and reduce agrochemical leaching (Reid et al., 2013). Biochar production is also helpful in managing agricultural waste. Agricultural waste is an ideal feedstock for the production of biochar. In Belize, agricultural wastes include sugar cane bagasse, citrus pulp and peel, residues from logging and commercial sawmilling, forestry residues, waste from shrimp heads, chicken offal, and pig and cattle offal and rejected bananas (BSWMA, 2015). The Toledo Cacao Grower's Association in Belize (IBI, 2018) has produced biochar from cacao pruning for soil amendment. Biochar benefits can increase agricultural productivity while at the same time, minimize damage to the natural environment (Tang et al., 2013).

Even though biochar is available, agricultural stakeholders such as farmers, agricultural suppliers, advisors and policymakers face considerable challenges when adopting a new strategy. The uncertainties derive from the unpredictable effects of the new strategy throughout the agri-food chain and its impacts upon a broad spectrum of associated policies (OECD, 2001). It is essential, therefore, to conduct research that will be able to fill knowledge gaps pertaining to biochar application in agricultural systems. Efficient cooperation amongst different stakeholders is required to achieve the adaptation of a new strategy, an. These stakeholders are affiliated with education, research and development, agricultural-governmental policies, training and advice (World Economic Forum, 2016). Cooperation amongst stakeholders is essential since agriculture is not only based on increasing food production and obtaining profit, but also to focus on achieving aims pertaining to environmental friendliness (OECD, 2001). While the study of biochar is not recent, the only reliable information on biochar trials in Belize has been the International Biochar Initiative (IBI). Although biochar research is continuously expanding in developed countries, Belize remains with limited studies dedicated to the use of biochar (Zhang et al. 2016). In addition, biochar research has limited qualitative studies focusing on agricultural stakeholders' perceptions. Thus, to corroborate biochar as an innovative agro-environmental strategy, it is essential to understand the roles, relationships and insights amongst different agricultural stakeholders in Belize and their ability to further develop and implement biochar within their agricultural systems. Therefore, the objectives of this study were to (1) determine the familiarity with biochar and necessity for its enactment in agricultural systems of Belize; (2) examine the perceptions of different agricultural stakeholders regarding biochar implementation; and (3) gather information about the constraints and present and future opportunities of Biochar in Belize.

3.2. Methodology

3.2.1. Understanding stakeholders' perspectives

The research strategy consisted of inductive, exploratory research, whereby collected data inferred new theories that were based on the understanding of stakeholders' perspectives on biochar implementation. The method was based on Srivastava & Thomson (2009) to evaluate in-depth descriptions of circumstances, interactions, observed behaviours, events, attitudes, thoughts and beliefs and direct quotes from participants. The mixed-methods strategy was used to accumulate both qualitative and quantitative data to identify why the phenomenon occurred as explained by Lieberman (2005). This strategy provided an in-depth understanding of data and allowed the researcher to validate and increase the reliability of findings (Lewis, 2015). The qualitative data collected included textual data (semi-structured interviews and organizational documents) and non-textual data (pictures and audio). The qualitative data consisted of a framework analysis. Data for the framework analysis was collected through semi-structured interviews, focus groups and online surveys (Srivastava & Thomson, 2009; Visser et al., 2000). Furthermore, triangulation was implied to strengthen the validity of results to determine whether qualitative and quantitative data from the semi-structured interviews, online surveys and focus groups corroborated with each other, thus eliminating any potential biases derived from the investigation.

3.2.2. Stakeholder matrix

A matrix of stakeholders was created based on their ability to influence the implementation of biochar in Belize. Similar to the design of Sanye- Mengual et al. (2015), the analysis focused on stakeholders in different stages of biochar implementation. In Table 3-1, the stakeholder types are identified, along with their contributions and values derived from collaboration (World Economic Forum, 2016).

Stakeholder Type	Key Contributions	Value Derived from Collaboration
Government	- Set national goals - Establish an enabling policy environment and invest infrastructure and other public goods and services - Create support for farmers and investors.	- Investment in agriculture, complementing public investment -Contributions to major initiatives
Research and Education/ Extension	- Create research that provides stakeholders with new knowledge - Promote partnership in spheres of influence	-The chance to contribute new ideas -Rich insights from "real world" applications
Farmers	- Influence policy and investment by sharing perspectives and recommendations - Identify needs for organization and training, and invest in implementing new practices	-Access to new technologies, information and markets -Increase yield and income
Agricultural Suppliers	- Invest in value chains, with a long-term view of investment that goes beyond short-term profit and considers the sustainability of the sector - Integrate a partnership approach into a long term business strategy - Introduce new technologies, research or business models	-Establishment of business operations over the long term -Opportunity to innovate with new customers, technologies or business models -Alignment with strategic environmental, social or talent initiatives

Table 3-1. Key stakeholder contributions and value derived from collaboration. (Adapted from World Economic Forum, 2016)

Together, these stakeholders have the potential to develop stronger value chains and systems that lead to improved outcomes at each stage of biochar implementation. The stakeholder types were chosen based on key actors that were associated with the implementation of new agricultural technologies (Figure 3-1) (The World Bank, 2014). Specific stakeholders were identified within the same stakeholder type who might have opposite perceptions as part of our data collection process.

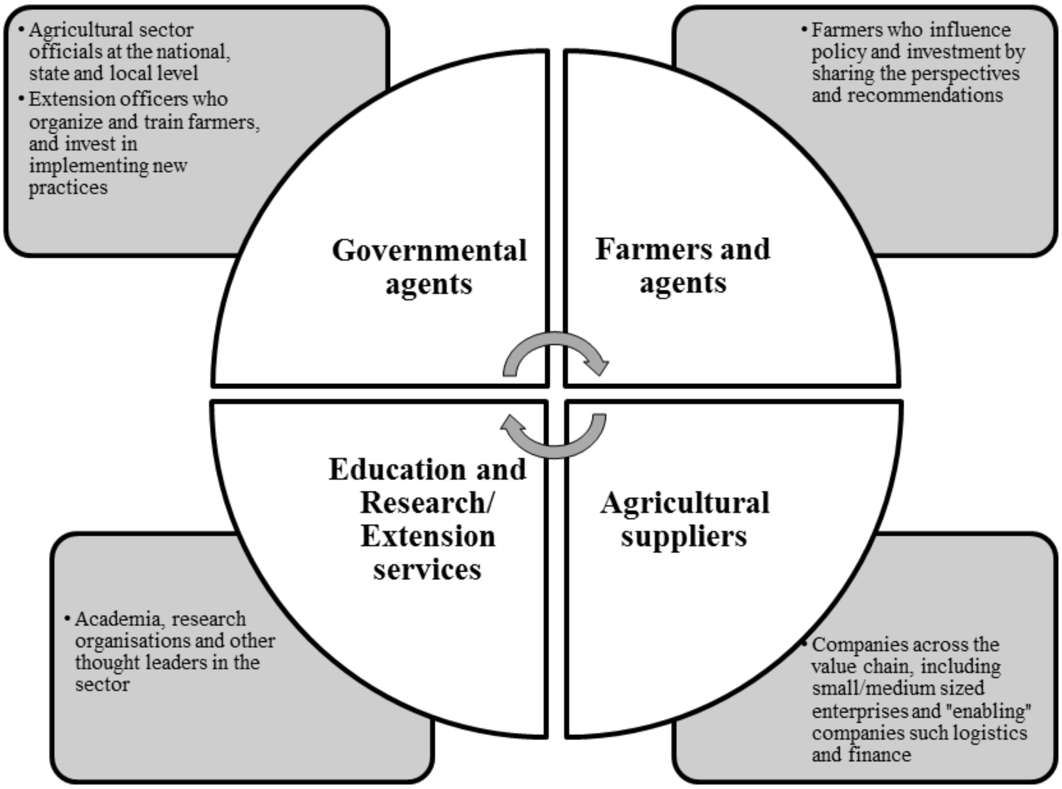

Figure 3-1. Stakeholders identified for the implementation of biochar in Belize

3.2.3. Data collection

To understand the potential of biochar implementation, it was essential to gather perceptions of different stakeholders within Belize. Although governmental agents, education and research, extension services and agricultural supplies were primarily located in urban areas, it was necessary to gather the perspectives of both smallholder and commercial farmers that were not located in urban areas. The stakeholders were gathered by purposive and snowball sampling techniques to increase the sample size (Dragan and Isaic-Maniu, 2013 and Bryman, 2012). Therefore, a combination of both snowball and purposive sampling techniques were used throughout the study for the semi-structured interviews and online surveys. Purposive sampling was used to gather participants for the focus groups. The study reached out to farmers in districts of high agricultural activity, such as Cayo, Stann Creek, Toledo, Corozal and Orange Walk, as seen in Figure 3-2.

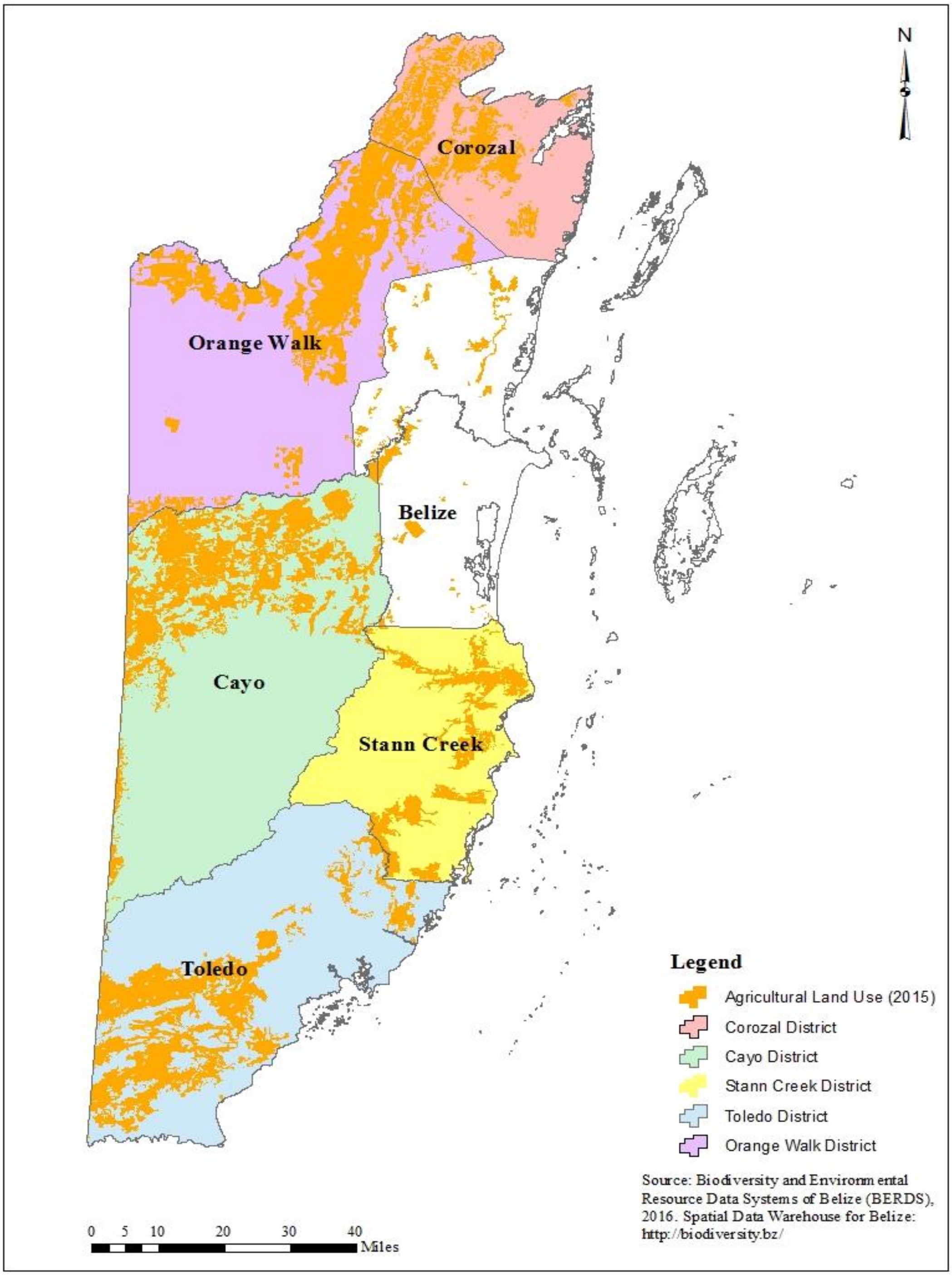

Figure 3-2. Agricultural land use in Belize and study sites

3.2.4. Semi-structured interviews

The semi-structured interviews were conducted between the months of March and April 2017. It consisted of open-ended questions. It held a balance between structured and unstructured discussion to provide a comfortable environment between the interviewer and interviewee (Srivastava & Thomson, 2009). The semi-structured interviews were convenient for directly gathering perceptions of farmers and agricultural suppliers in rural areas where there was a lack of electronic communication. The structure of the semi-structured interview was divided into three major sections. The first section was the general profile that included primary information such as name, title, level of education, level of experience and organization. The second section was context. It included topics related to networking, environmental awareness and protection and concerns to farmers. The third section included perspectives on biochar implementation related to environmentally friendly practices, familiarity with biochar and its use in Belize. It also included topics related to motivation, key barriers, biochar's appeal to different farm types and available information on biochar. Twenty-eight (28) semi-structured interviews were conducted. See appendix A for stakeholder questionnaire.

3.2.5. Online surveys

The online surveys were generated and distributed through the Bristol Online Survey tool between the months of July and August 2017. The online surveys mirrored the structure and themes found in the semi-structured interviews. In addition, it consisted of dichotomous, multiple-choice, rating scale questions and several open-ended questions (Bryman, 2012). The online survey consisted of forty-one (41) participants.

3.2.6. Focus groups

The focus groups sought to engage stakeholders from across the agricultural sector of Belize. Forty-eight (48) participants expressed their perspectives on how to take advantage of opportunities received from using biochar. Participants also expressed their perspectives on how to overcome barriers related to implementing biochar in Belize. The opportunities and barriers discussed in the focus groups were based on results gathered from the previously coordinated semi-structured interviews and online surveys. The activities consisted of two sessions. Session 1 consisted of a presentation based on biochar information and research activities being done locally and internationally. Participants were given post-it in order to write their views/ answers to the proposed question – '*Why do you think biochar may be beneficial?'* They presented their views to the group. Session 2 consisted of a presentation based on the results obtained from the study 'Implementation of Biochar Systems in Belize: Stakeholder Analysis. Participants discussed their views of resolving critical issues derived from the question – '*What can we do to resolve the barriers*?' Participants' seating arrangements were mixed to encourage a free flow of ideas and perspectives. Groups gathered their ideas into common themes and highlighting the top three most pressing issues. Results were presented to the entire focus group. Introductory questions were written on flip charts to help establish the open and participatory style of the event. Their answers were recorded on a post-it and were collected at the end of the event.

3.2.7. Data transcription and analysis

Transcription of textual and audio data gathered from the semi-structured interviews and focus groups was conducted at Newcastle University. It was essential to be concise with judging and interpreting the data presented (Bryman, 2012). Documents were transcribed and translated from either Creole or Spanish into English. Transcriptions against original documents were re-examined to formulate accuracy (Robson, 2011). Transcriptions were written using both Microsoft Excel 2013 and Microsoft Word 2013 to export the data to a qualitative data analysis software, NVivo11- QSR International, to formulate codes in order to accumulate a framework analysis (Srivastava & Thomson, 2009). Descriptive statistics to analyse data from the online surveys were derived using Microsoft Excel 2013 and IBM SPSS Statistics 24.

3.3. Results and Discussion

3.3.1. Distribution of stakeholders

The semi-structured interview and online survey consisted of a total sample size of participants of sixty-nine (n = 69), and the focus groups consisted of a total sample size of forty-eight (n = 48). Participants grouped themselves into five categories: farmers; suppliers; extension services; education and research and governmental agents. As seen in Table 3-2, the semi-structured interviews and online surveys consisted mostly of farmers and extension services while the focus group consisted mostly of participants associated with extension services, research and education.

Stakeholder	Farmers (%)	Agricultural supplies (%)	Extension (%)	Education and research (%)	Government (%)	Other (%)
Semi structured interviews and online surveys	42	4	23	16	10	4
Focus groups	8	2	54	31	4	1

Table 3-2. Distribution of stakeholder participants in the semi-structured interviews, online surveys and focus groups

The categories cast a wide net for understanding the experiences, perspectives and recommendations of stakeholders. Combining perspectives of different stakeholders within the agriculture sector as done by Sanyé-Mengual et al. (2016) validates the need to implement biochar in agricultural systems of Belize. Amongst all the stakeholders, a large number of participants were associated with extension services in the semi-structured interviews, online surveys and focus groups. Extension officers can be viewed as transporters of farmers' experiences, perspectives and recommendations throughout the stakeholder network. An active network can produce several benefits. These benefits include the sharing of financial, human, and technical resources and the availability of new expertise through combined knowledge and experience. The creation of innovative businesses and collaboration methods and the development of institutional strategies, mind-sets and leadership approaches (World Economic Forum, 2016) can also be derived from effective networking. Figure 3-3 depicts the percentage of stakeholders that collaborate with specific organizations in the agriculture sector. Majority of the stakeholders collaborate with the Ministry of Agriculture (MoA), Belize Sugar Industry Research and Development Institute (SIRDI) and the University of Belize (UB). The primary role of MoA is for the development and reinforcement of regulations, while SIRDI and UB are responsible for research and education. These findings suggest that these organizations can systematically influence other stakeholders through regulation, research and education.

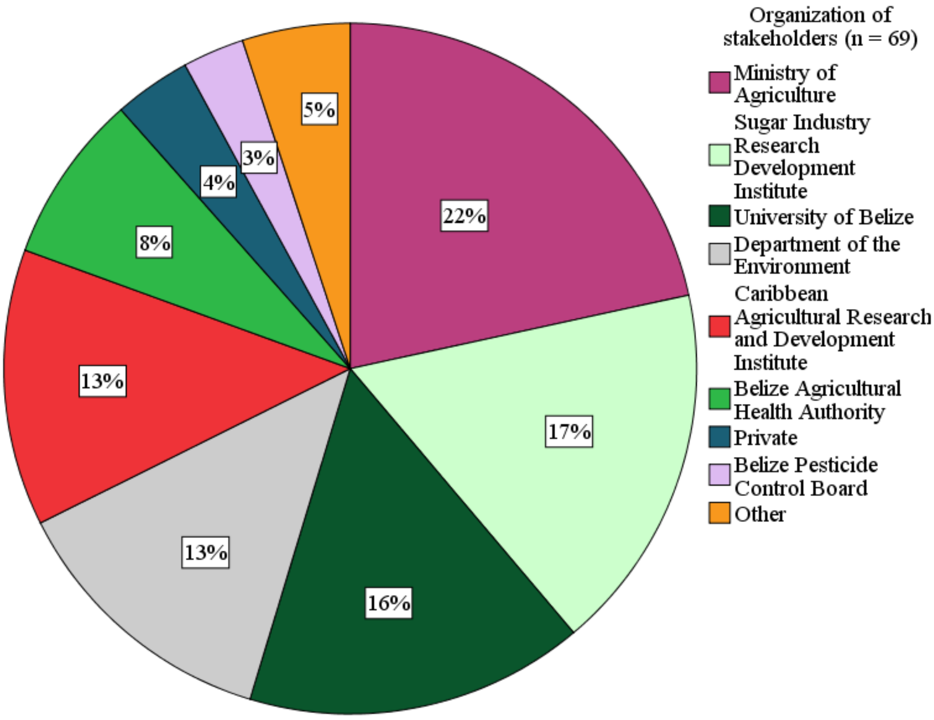

Figure 3-3. Collaboration amongst stakeholders

In a productive networking system, stakeholders must realize that their position within the vast network is essential and that their decisions will affect other stakeholders (Barker & Chapman, 1990). A productive networking system is very important for reinforcing the relationship between farmers and other stakeholders. Farmers are the primary stakeholders that can influence the adaptation of a new practice. Therefore, other stakeholders must collaborate closely with farmers. Figure 3-4 shows the difference in collaboration between farmers and other stakeholders with different organizations. MoA, SIRDI and UB are the principal collaborators. However, less collaboration occurs for farmers as compared to the other stakeholders and this can signify that there may not be enough information being transmitted to farmers due to limited collaboration.

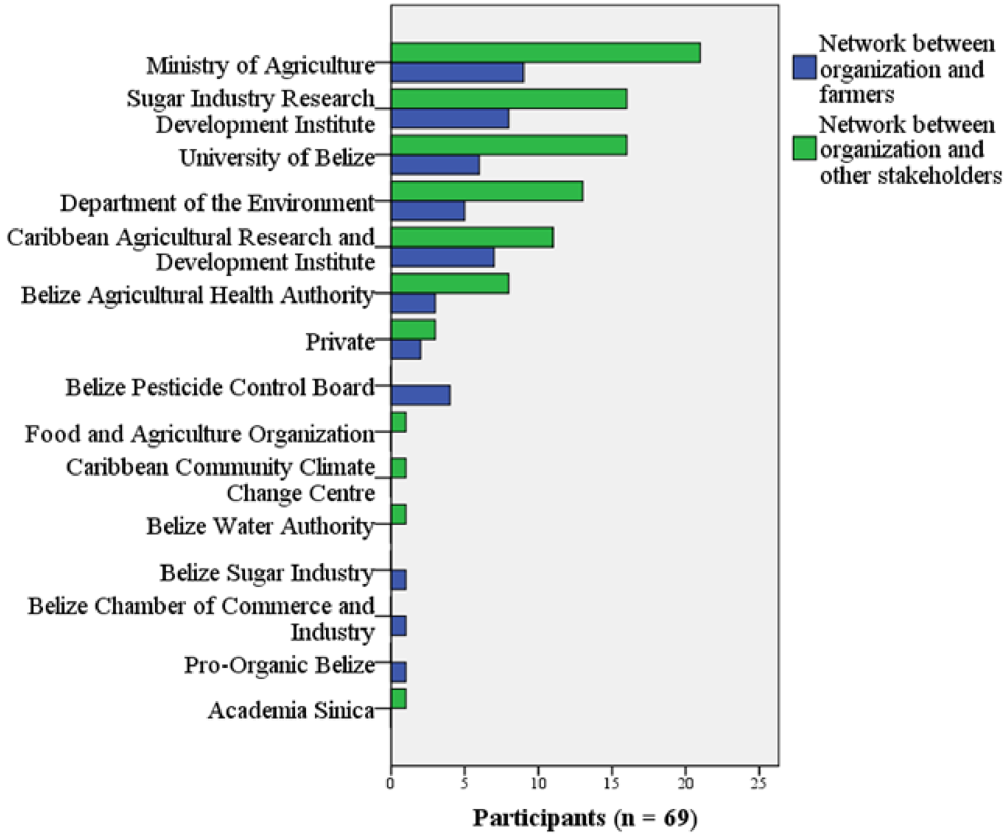

Figure 3-4. Comparison of the collaboration between farmers and other stakeholders

The data also indicates that there is a high degree of collaboration with farmers and organizations associated with research and education. High collaboration occurs between farmers and MoA, SIRDI, Belize Agricultural Health Authority, Belize Pesticide Control Board and Department of the Environment. The high level of collaboration between these stakeholders indicates that biochar benefits associated with an increase in agricultural yield, increase in soil health, increase in carbon storage, and reduction of pesticide contamination can be encouraged. These organizations must have a thorough understanding of biochar benefits and strategies through which these benefits can comply with the goals of the organization. Once this understanding is obtained, the transmission of biochar knowledge between the farmers and these organizations can commence.

3.3.2. Education, research and extension services

A factor that influences the adaptation of any agricultural strategy, such as biochar implementation, in a developing country is the agricultural education systems. Chaudhry and Alhaj (1985) explain that in developing countries, there is a need for the local agricultural education system to be able to identify, and furthermore resolve, the problems being faced in the local agricultural system. Identifying and resolving problems in the Belizean agricultural system is especially necessary since the economy depends greatly on agriculture. By international standards (Maguire, 2000) Belizean universities are very young, dating back to 1970. The University of Belize (UB) is the primary source that generates graduates awarded with an associate's degree in general agriculture (University of Belize, 2012). Although UB has been capable of producing a few graduates with an associate's degree in agricultural studies, most of the Belizeans with higher education in agriculture have obtained studies and training abroad (Serano, 2004). Figure 3-5 presents the different stakeholders and their educational background.

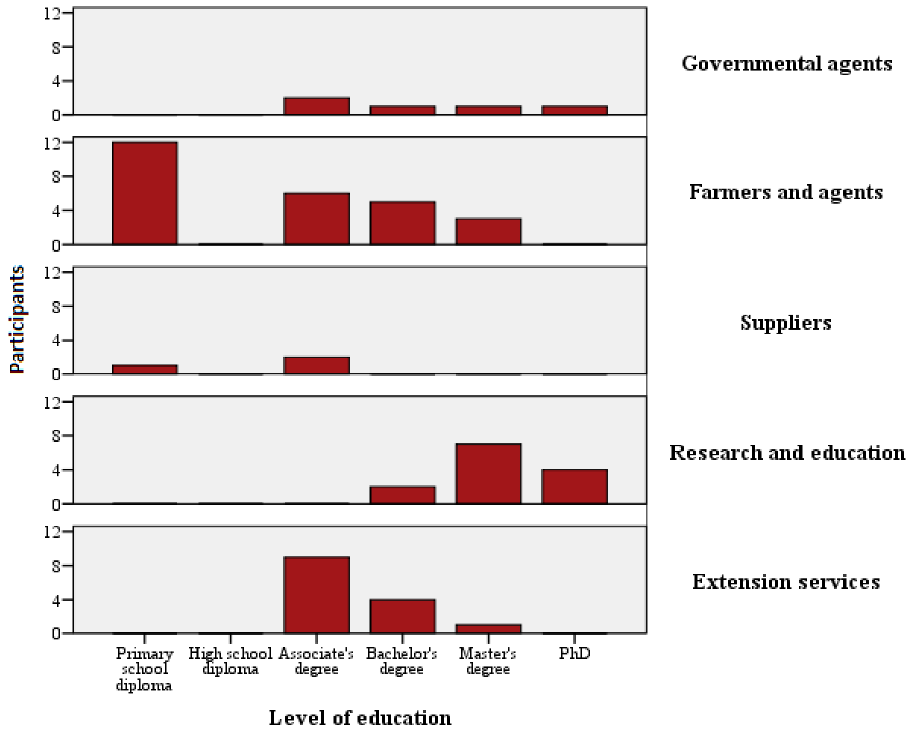

Figure 3-5. Level of education amongst stakeholders

Stakeholders with higher education consisted of governmental agents, research, and education. Most of the participants in extension services had an Associate's degree, while the highest level of education for most farmers was a Primary School diploma. This expresses the importance of transferring new agricultural knowledge from the government, research and education, transferred to extension services and finally received by the farmers. In addition, most farmers were observed to have more than fifteen years of experience in agriculture as compared to the other stakeholders (Figure 3-6). The farmers' years of experience shows that farmers should also transfer their knowledge gathered from experience to stakeholders in extension services, governmental agents, research and education. A well-established interconnection amongst stakeholders is necessary in order to have an efficient and effective exchange of knowledge.

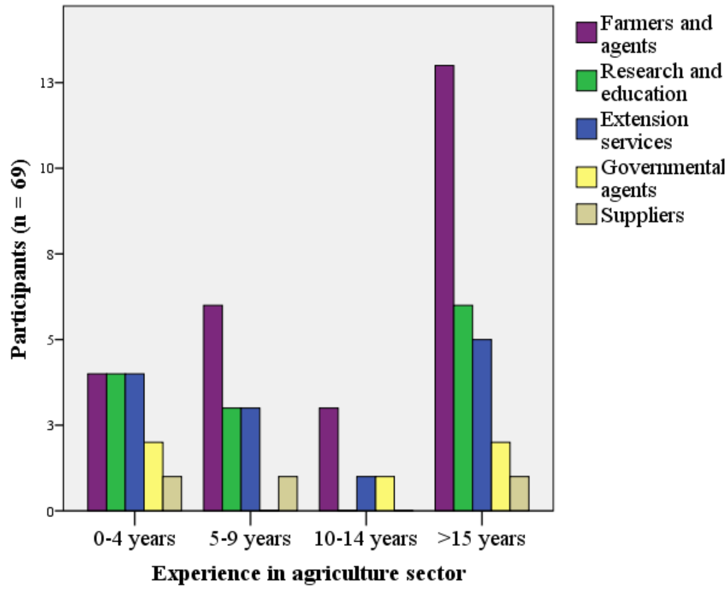

Figure 3-6. Experience in agriculture sector amongst stakeholders

In addition, it is essential that personnel in extension services, research and education are equipped with dealing with agro-environmental issues (Chittoor & Santosh Kumar Mishra, 1998). However, many agricultural personnel in developing countries that have been trained abroad may find it challenging to gain the support necessary to imply the knowledge, training and skills in their local agricultural systems (Saguiguit, 1987). Assisting trained personnel to create positive changes in the local agricultural system is vital for the proper development of the agricultural sector, especially since farmers seek advice primarily from agricultural research, education and extension services.

3.3.3. Farms and supplies

For a farmer, the suitability of applying biochar mainly depends on its already established farm structure. Of the farmers that responded to cultivated land, 36% cultivated more than 200 hectares of land, while another 36% cultivated less than 5 hectares of land (Figure 3-7). The amount of land being cultivated by the farmer indicates the need to sustain soil health for food production. Therefore, biochar could be used for either soil health or pesticide retention or carbon sequestration.

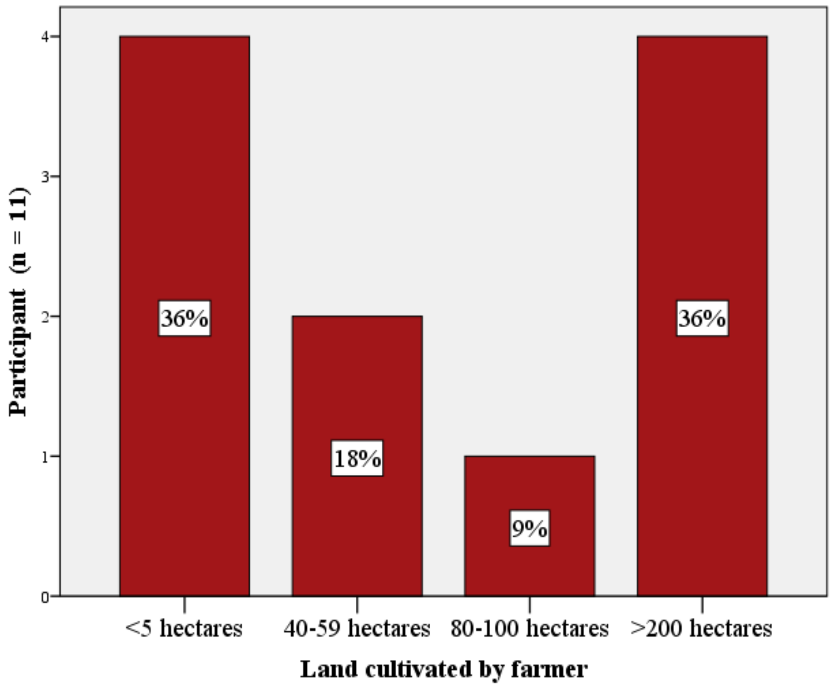

Figure 3-7. Land cultivated by farmers

In this study, 70% of the farmers used their land for plant production, while 10% used their land for animal production. These results indicate that biochar could be used to reduce the contamination of soils and aquatic ecosystems by agrochemicals such as pesticides and antibiotics. When asked about the usual supplies that farmers receive, 33% was fertilisers, 33% seeds and 22% pesticides (Figure 3-8). As observed from the necessities of the farmers, biochar could be used as a soil enhancement to reduce fertilisers, increase germination success, and reduce pesticide pollution.

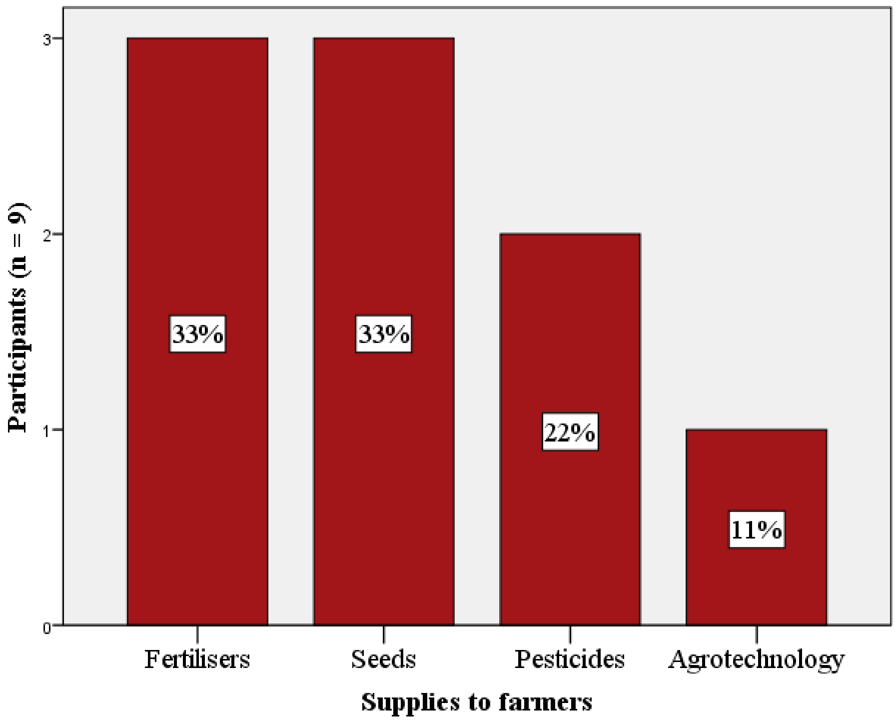

Figure 3-8. Agricultural supplies to farmers

3.3.4. Environmental awareness of farmers and other stakeholders

Farmers were asked about the presence or proximity of any aquatic ecosystems near their farmland. All farmers that responded claimed to have farmland near aquatic ecosystems. Of the farmers that responded, 71% stated that their land was more than twenty meters away from any aquatic ecosystem while 29% of farmers stated that their farmland was twenty metres or less from any aquatic ecosystem (Figure 3-9). Depending on agrochemical management, soil, water, weather and other climatic conditions, aquatic ecosystems in close proximity to agricultural land can be prone to agrochemical contamination. The use of biochar could be used as an absorbent buffer zone to reduce agrochemical leaching and runoff. A strategy such as this could comply with governmental regulations such as the national lands act of Belize. The National Lands Act of Belize – Chapter 191 (2011) states: "Where land approved to the lessee is situate outside a city, town or village and adjoins any running stream, river or open water, a sixty-six feet wide strip of land along such running stream, river or open water shall be left in its natural state unless otherwise approved by the Minister to be used in a specified manner."

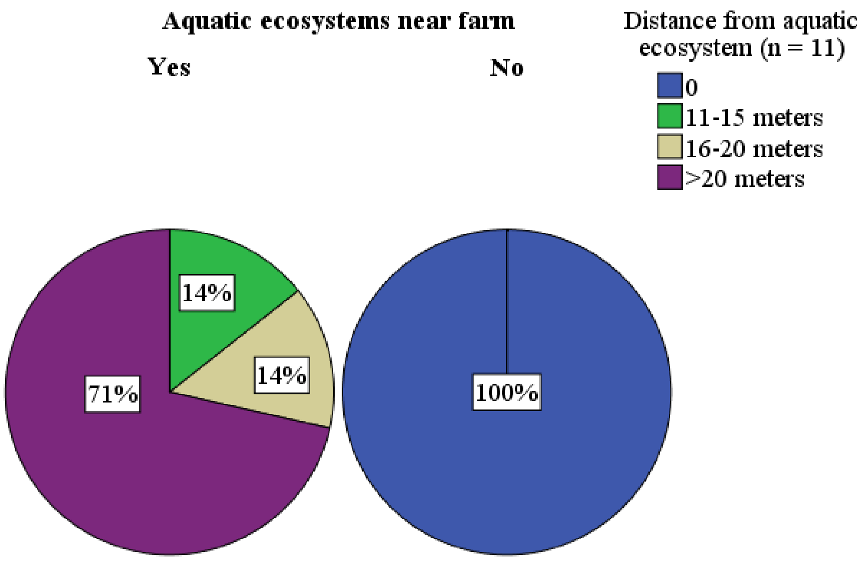

Figure 3-9. Aquatic ecosystems near farmland

Although it was observed that agricultural activity was occurring in very close proximity to aquatic ecosystems, most of the stakeholders emphasized that protecting the environment is essential. Participants (89.9%) understood that it is crucial to protect the environment. 75.4% expressed pesticide pollution as a problem in Belize. 85.5% expressed the need to protect other citizens from being affected by pesticide pollution. 76.8% expressed the need to take safety measures in order to avoid pesticide pollution, as seen in Table 3-3 below.

Theme	**Number of responses (n = 69)**
Environmental protection	62
Pesticide pollution	52
Pesticide pollution effects on other citizens	59
Pesticide pollution safety measures	53

Table 3-3. Environmental awareness amongst stakeholders

Stakeholders expressed that they participated in environmental practices. Figure 3-10 shows that most stakeholders gave high priority to reducing harmful chemicals, educating others about environmental awareness, and practised the concept of reducing, reuse and recycle. These results showed the likelihood of implementing biochar in agricultural systems with pertinence to environmental protection.

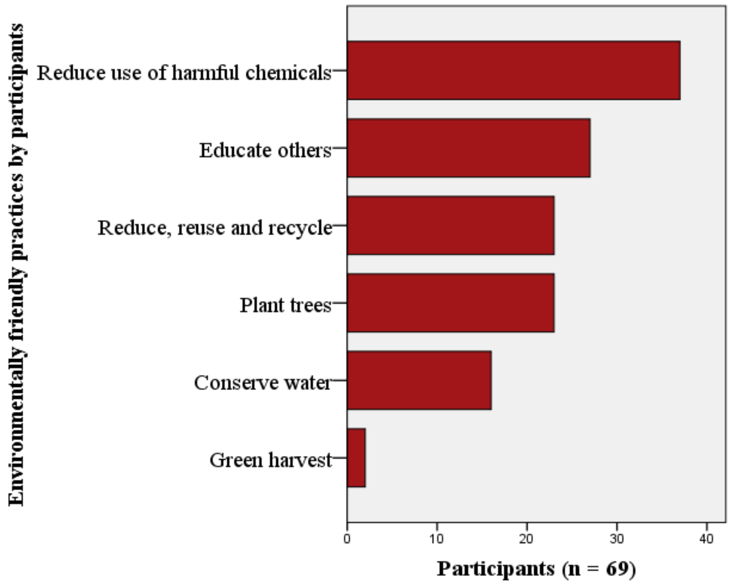

Figure 3-10. Environmentally friendly practices by stakeholders

When asked about reducing pesticide pollution, the stakeholders indicated that educating people is the most effective method. Figure 3-11 compares the perspectives of farmers and other stakeholders. Farmers and other stakeholders agreed that reinforcing sustainable pesticide practices and pollution tax might be solutions to reduce pesticide pollution. Other alternative methods for reducing pesticide pollution included supplying farmers with containers to dispose of smaller pesticide containers, give land tax incentives to those that produce less contamination to virgin land and watersheds, altogether banning harmful pesticides, and firmly implement biological control for pest management.

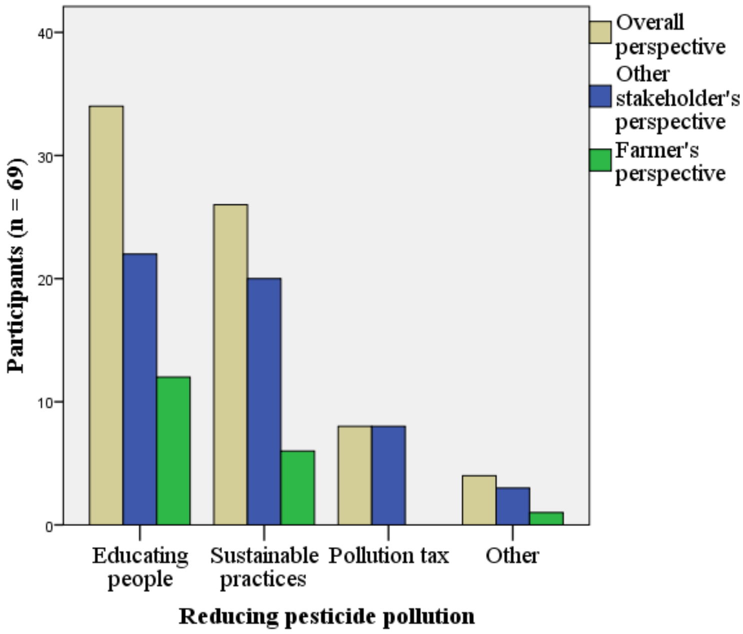

Figure 3-11. Methods of reducing pesticide pollution

3.3.5. Challenges in the agriculture sector of Belize

Climate change was the greatest challenge in the agriculture sector, as expressed by the stakeholders. Climate change was described as drastic changes in temperatures, fluctuations in annual rainfall, and climate extremes such as increased number of hurricane threats, flooding and longer dry seasons. These climatic conditions tend to have a higher impact on tropical and subtropical communities, especially since the economy of these communities have a high dependency on agriculture (Jones & Thornton, 2003). In addition, individuals that have had direct experiences of the adverse effects of climate change are more concerned and thus partake in mitigation strategies (Spence et al., 2011). Directly experiencing the adverse effects of climate change indicate that farmers may be motivated to participate in climate-change mitigation strategies if they understand that agriculture has a high impact on climate change. Stakeholders would also be more willing to use biochar if they understood its climate change mitigation effects (Stavi & Lal, 2013). Biochar in soil could then increase agricultural production. At the same time, it could act as carbon storage in the soil and sequester carbon from the atmosphere for more extended periods (Stavi & Lal, 2013).

In addition to climate change, this study showed that another challenge was the lack of funding and market availability. Funding for irrigation systems, storage centres, packaging and transportation facilities are vital for agricultural production yet limited in developing countries. Thus, stakeholders associated lack both funding and market availability with changes in governmental regulations. Changes in governmental regulations is another challenge faced in

Belize's agriculture, according to stakeholders. The Organization for Economic Cooperation and Development (OECD) use Regulatory Impact Assessments (RIAs) to determine whether regulation may have a positive or negative impact. However, little evidence exists that RIAs are being used in developing countries (Kirkpatrick, 2001). Implying RIAs can contribute to the establishment of an accountable system for policy and governance, which is an essential prerequisite for poverty mitigation and sustainable development (Kirkpatrick, 2001).

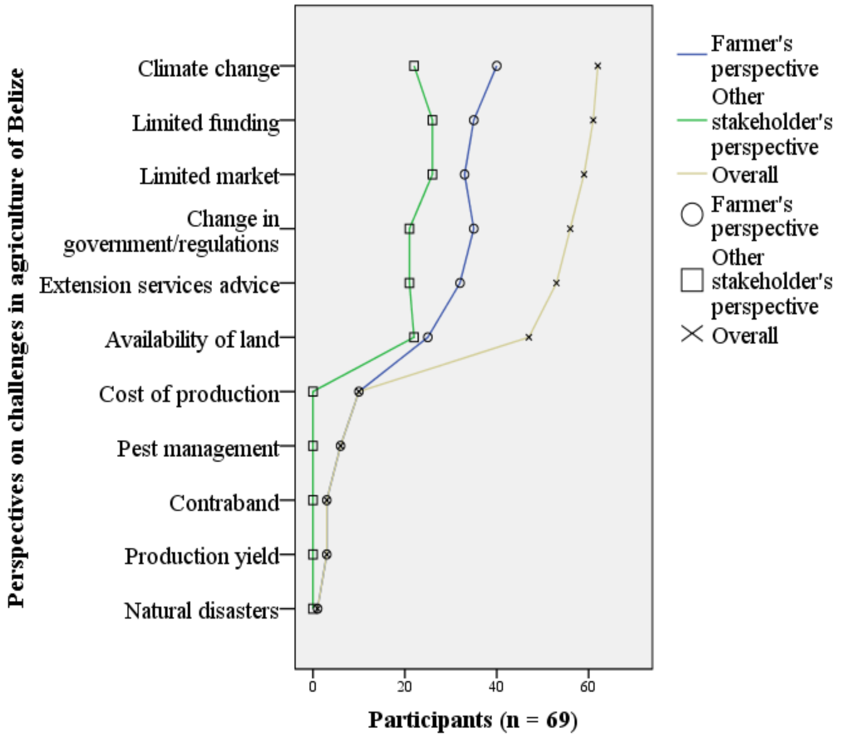

Figure 3-12. Perspectives on challenges faced by stakeholders in the agriculture sector of Belize

The availability of advice from extension officers was another challenge faced in Belizean agriculture. Farmers claimed that they did not receive enough visits from extension services. Extension officers are vital players for transferring and delivering new information and advice from education and research to farmers. In order to obtain positive changes in agriculture, extension services must identify the farmer's existing needs and determine an efficient delivery mechanism that will strengthen the interactions between the extension program and the farmer (Goodwin & Gouldthorpe, 2013).

Land availability for agriculture was another identified challenge. In developing countries, available land is used to cater to growing urbanization caused by rural-urban migration. It is therefore expected that as the population increases, the availability of land decrease (Godfray et al., 2010). However, in 2011 the Ministry of Agriculture and Fisheries of Belize reported that approximately 38% of Belizean total land area is considered suitable for agricultural practices, but only 9.7% is used. Therefore, the problem may not be the availability of land, but rather the policies and regulations that govern the land. Similar to the study of Godfray et al. (2010), this study indicated that resource-deficient farmers that struggle to secure land rights tend to avoid investing capital on land and agricultural management practices.

Other challenges included the cost of production, pest management, contraband, production yield and natural disasters. However, these challenges are interrelated with governmental regulations, funding and climate change. In addition, the perspectives on the significant challenges of farmers slightly differed to the perspectives of other stakeholders. The differences in perspectives infer that there is a gap in communication between farmers and other stakeholders.

Environmental awareness of stakeholders

To determine whether biochar would be accepted as a strategy for environmental protection, the level of environmental awareness of the stakeholders was explored. Results showed that 89.9% of stakeholders emphasized that protecting the natural environment is vital. However, the semi-structured interview showed that the perspectives amongst agricultural stakeholders differed (Table 3-4). The subject of culture, belief and tradition identified in each of these responses corresponds to the study of McFarlane and Boxall (2003). McFarlane and Boxall (2003) explain that the attitude and behaviour of an individual are influenced by the value orientation of an individual. The study also suggests that socialization could shape specific attitudes and behaviours as compared to factual knowledge. Therefore, allowing farmers to commit to an environmental organization network could allow them to be motivated to advance the overall goals of the organization.

Stakeholder category	Organization	Perspective
Smallholder farmer	Subsistence farmer	"The natives have always believed that they have to live in harmony with nature."
Extension officer	Belize Agriculture and Health Authority	"Some farmers consider their environment. The more orthodox are concerned about pests being used. Their belief allows them to use minimal pests and fertilisers."
Researcher	Belize Sugar Industry Research and Development Institute	"Farmers are mainly concerned about yield. Most farmers are still in the milpa system. They practice rotational farming. Even though rotational farming is a tradition, it is not good for the environment since eventually the soil will be used up and not fertile."
Governmental agent	Ministry of Agriculture	"Farmers know that farming practices affect the environment. The awareness is there, but it is not adequately monitored or evaluated."

Table 3-4. Perspectives of different stakeholders on environmental awareness

To understand the need of biochar for agrochemical attenuation, we addressed questions pertaining to pesticide use. As one stakeholder explained: "*Yes, it is a concern, but it is not being dealt with*". Of the 69 stakeholders, 75.4% expressed that pesticide pollution is a problem in Belize and that there is a need to protect other citizens from being affected. 76.8% of the stakeholders expressed that safety measures are needed to avoid pesticide pollution (Table 3-5). Though there exists a high pesticide contamination risk in developing countries, there is a lack of monitoring programmes and management practices (Villamizar & Brown, 2016). In this study, agricultural stakeholders suggested solutions to reduce pesticide pollution. These included educating the unaware about harms of pesticide pollution, reinforcing sustainable pesticide management practices, and possibly implying pesticide pollution tax. Other alternatives for reducing pesticide pollution included supplying farmers with appropriate containers for disposal, land tax incentives to those that produce less contamination, banning of harmful pesticides, and implementing biological control for pest management. Stakeholders realize that pesticide pollution is a problem that can affect the environment. Therefore, attenuation strategies must be introduced.

Theme	Responses (*n* = 69)
Protecting the environment	62
Pesticide pollution as a problem in Belize	52
Minimize pesticide pollution effects on other citizens	59
Safety measures to prevent pesticide pollution	53
Familiarity with biochar	
Adequate Information	9

General familiarity	31
Familiarity with use in Belize	14
Motivations	
Higher yield	64
Improved plant health	56
Improved soil health	55
Environmental protection	46
Ease of handling and application	40
Extension services	43
Barriers	
Scepticism	52
Biochar cost	54
Transportation costs	48
Processing technology	36
Governmental regulations	24
Lack of feedstock	18
Available market	34

Table 3-5. Stakeholders' perspectives on suitability, familiarity, motivations and opportunities of implementing biochar in Belize

These findings explain that stakeholders are willing to prevent pesticide pollution. Due to past experiences, stakeholders understand that natural environmental disasters can affect their agricultural productivity. As Spence et al. (2011) explain, past environmental disaster experiences tend to carve the individual’s fundamental values. The fundamental values are what influence the use of environmentally friendly strategies (Michel-Guillou & Moser, 2006). Therefore, the implementation of biochar as a pro-environmental practice should not only be viewed only to respect the environment, but also to understand that it will assist with the preservation of the stakeholders’ personal, economic and natural resources (Rajapaksa et al., 2018).

3.3.6. Biochar awareness, opportunities and challenges

Biochar research in Belize was initiated in 2011 by the Maya Mountain Research Farm. It was therefore expected that most stakeholders would be unfamiliar with Biochar. However, the results of this study showed that 47% of the participants claimed that they were familiar with biochar, and 20.3% knew about its use in Belize. The results from this study can be compared with the results from Latawiec et al. (2017), where only 27% of Polish farmers were familiar with biochar. However, the study of Latawiec et al. (2017) focused only on farmers. This study focused on a wide range of stakeholders, similar to the study conducted by Bjerregaard and Georg (2011). Delaney (2011) expressed that the lack of implementing biochar was due to lack of knowledge of the technology. The conclusions of Delaney (2011) corresponded with our results that show that only 13.2% of the stakeholders claimed that there was not enough information pertaining to biochar in Belize. However, merely suggesting factual knowledge of biochar to stakeholders may be insufficient to influence the implementation of biochar. As previously discussed, the fundamental values of each stakeholder should coincide with the benefits that biochar can offer. If biochar benefits were realized by all stakeholders, the willingness to implement biochar would be higher (Latawiec et al., 2017). The results showed that 92.8% of stakeholders were motivated by higher yield for biochar use. Farmers were also motivated by biochar's ability to increase soil and plant health (Figure 3-13).

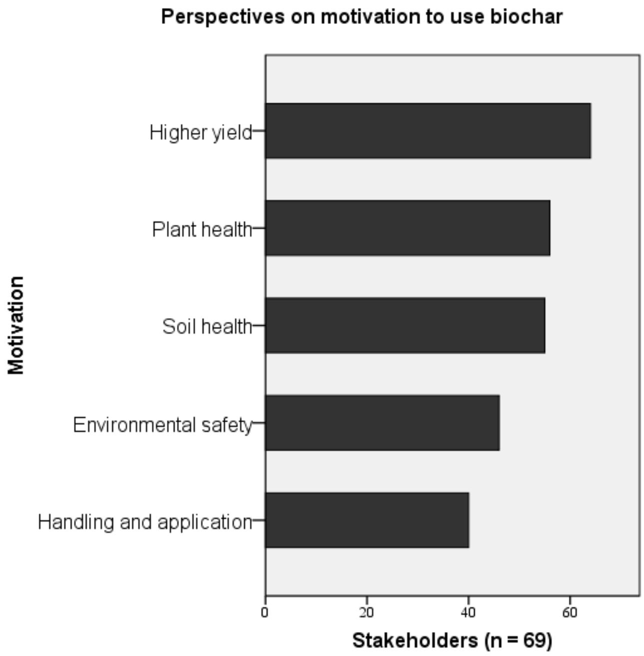

Figure 3-13. Motivation to use biochar

The higher yield and plant health results from this study corresponded to the study of Clare et al. (2014) on Chinese farmers and their acceptance of using commercial biochar. Clare et al. (2014) explained that biochar was only able to succeed if yield rates increased to break even the costs. However, in addition to higher yield, 66.7% of Belizean stakeholders were also motivated by biochar's ability to contribute to environmental safety. The results of this study based on environmental safety also reflected the stakeholder's environmental awareness, similar to the stakeholders in the study of Latawiec et al. (2017).

3.3.7. The future of biochar in Belize

This study found that barriers to implementing biochar were biochar cost, scepticism, transportation cost, processing technology, available market, governmental regulations and lack of feedstock. These barriers arose from the challenges faced in the agriculture sector of Belize. Similar to the results of Latawiec et al. (2017) on Polish farmers and biochar, Belizean farmers that have had a well-established agricultural system find it difficult to adjust to new agricultural strategies. Clare et al. (2014) mentioned that exceptions to avoid new agricultural strategies such as biochar use, would be if biochar was applied to highly degraded soils where high market valued crops would be grown.This study showed that other barriers such as transportation cost, processing technology, available market and governmental regulations stemmed from the overall challenges faced in the agriculture sector of Belize. Regarding available feedstock, 26% of the stakeholders stated that lack of feedstock would be a key barrier faced when implementing biochar. However, the Belize Solid Waste Management Authority has been seeking new strategies for managing agricultural waste. The lack of feedstock availability awareness could be due to the low networking interactions amongst stakeholders. The focus groups of this study suggested that the effective ways in which barriers could be overcome could be through education, training and workshops, conduct field trials and research and stronger collaboration amongst stakeholders (Figure 3-14). The results of Delaney (2011) also suggested that crucial solutions to reinforce biochar implementation amongst Haitian farmers were through research and dissemination of biochar information. In addition, a study conducted by Mehmood et al. (2017) showed that biochar research has been heavily focused on developed countries and not in poor tropical developing countries. Tropical developing countries could benefit greatly from innovative strategies such as biochar implementation. Stakeholders recommended that to overcome biochar implementation barriers, education, research and networking amongst stakeholders are needed. Mehmood et al. (2017) also state that the potential benefits of biochar in poor tropical countries can only be realized if cooperation amongst stakeholders (including knowledge transfer and interdisciplinary research) and investments (such as infrastructure and research equipment) are established. These barriers are also observed in the overall challenges faced by stakeholders in the agriculture sector of Belize. These findings imply that governmental agents, research and education, extension services, farmers and agents need to strengthen their correspondences in order to resolve the overall challenges faced in the agriculture sector of Belize. It is then that biochar will be feasibly implemented in agricultural systems of Belize. See appendix A for further focus group data.

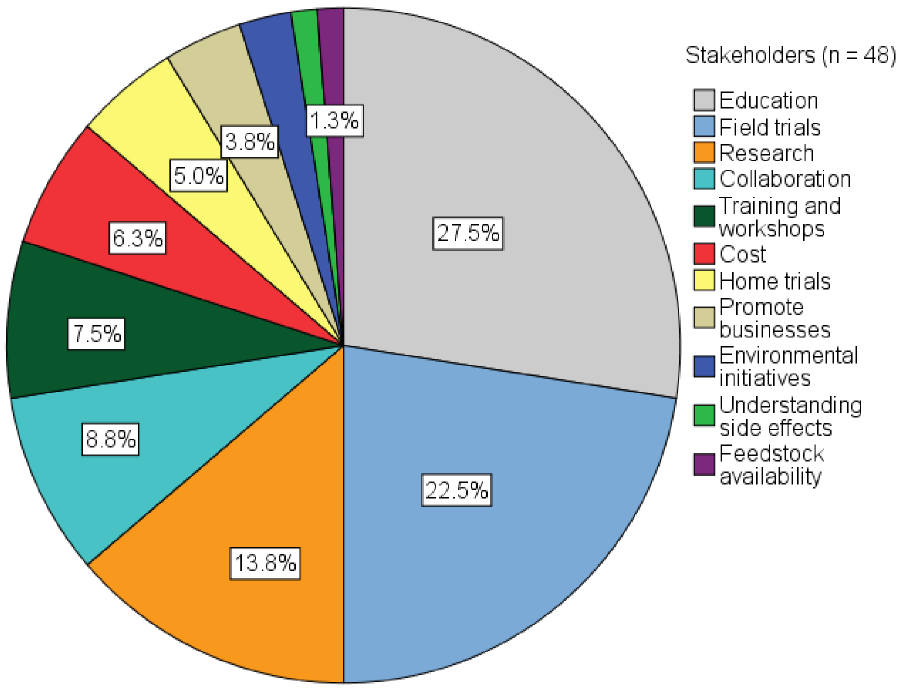

Figure 3-14. Focus groups' perspectives on ways to overcome implementation barriers

3.4. Conclusions

Soil health and restoration, carbon abatement, greenhouse gas mitigation and agricultural waste management are important characteristics that advocate biochar use, acting as a universal tool for synchronizing agricultural production and environmental protection. The need for utilizing these advantages is pronounced in developing countries where the economy is dependent on agriculture and natural ecosystem services. Even though numerous studies have been dedicated to biochar's ability to contribute to agricultural sustainability, research based on the social aspect of implementing biochar has been minimal. This study is the first known study in Belize to collate the attitudes and perspectives of agricultural stakeholders toward biochar implementation in agricultural systems of Belize. The findings suggested that even though biochar research is at its early stages, the majority of the stakeholders were familiar with the definition of biochar. Their knowledge of biochar serves as an excellent platform for its future implementation. It was not surprising that yield increases soil and plant health were the major drivers for implementing biochar. However, climate change was viewed as an important challenge faced in agriculture of Belize, thus using biochar as a potential strategy for carbon abatement. In addition, stakeholders of Belize were found to be highly aware of the importance of protecting the environment, inclusive of reducing pesticide pollution, suggesting that along with increased yield, it is likely that stakeholders would be willing to use biochar as a mitigation strategy for reducing pesticide contamination. This study observed that the overall challenges, i.e. lack of funding, change in governmental regulations, etc. faced in the agricultural sector of Belize directly affected the possibility of implementing biochar. This study suggested that in Belize more research dedicated to biochar must be conducted and the information gathered should then, at best efforts, be efficiently disseminated to all stakeholders. An active collaboration amongst Belizean stakeholders can lead to stronger value chains and systems, leading to improved outcomes when adapting new innovative agricultural strategies such as biochar.

Chapter 4. Sorption Effects of Biochar on Herbicides and Veterinary Antibiotics in Different Soil Types

4.1. Introduction

Agricultural productivity to present date continues to advance with the assistance of herbicides and veterinary antibiotics. Veterinary antibiotics, for instance, are used to increase livestock production and aquaculture farming (Yao et al., 2013). Herbicides are used to control, eradicate or change the cycle of broadleaf weeds (Castelo-Grande et al., 2010). Although these agrochemicals can be helpful, they can also cause damaging effects to the natural environment if improperly managed. In 2010, approximately 63,000 tons of veterinary antibiotics were used on livestock worldwide. It is predicted to increase to 106,600 tons in 2030 (Pan & Chu, 2017b). Enrofloxacine, oxytetracycline and tetracycline are veterinary antibiotics that have been extensively used to prevent and control diseases whilst promoting growth in livestock (Tasho & Cho, 2016). Their chemotherapeutic efficacy defends against a broad spectrum of gram-positive and gram-negative bacteria. However, environmental contamination of veterinary antibiotics can be derived from intensive use. Tasho and Cho (2016) explain that intensive livestock farming faces waste management issues. When metabolized by animals, approximately 90% of veterinary antibiotics are excreted with urine and 75% of veterinary antibiotics are excreted with faeces (Pan & Chu, 2017b). In addition, most faecal waste from livestock is usually used as fertilizers in arable land (Pan & Chu, 2017a). Consequently, antibiotics and their by-products can leach to surface and ground waters (Carvalho & Santos, 2016). These contamination risks may negatively affect natural ecosystems and human health by contaminating drinking water and producing resistant bacterial strains within the environment (Kemper, 2008).

Herbicides such as diuron and atrazine are used to control a wide variety of annual and perennial broadleaf and grassy weeds (PPDB, 2018). These herbicides enter soil by direct spray, wash off from treated foliage and release from granulates applied to the soil. Its improper management can contaminate drinking, surface and groundwater (Fontecha-Cámara et al., 2007). The risk of contamination to a non-target site is associated with the physicochemical structure of the compound, properties of the soil, climatic conditions, land structure and herbicide management practices (Bedmar et al., 2017; Boesten et al., 2000).

Lal (2005) proposed that an effective way of reducing contaminant leaching is to improve the overall soil quality and health. Some parameter that influences contaminant leaching in soil texture, structure and amount of organic matter. Soils that are prone to contaminant leaching are those that have a relatively depleted soil organic carbon pool and low organic matter levels, such as in tropical soils that have been subject to slash-and-burn farming. Consequently, agronomic production decreases and contaminant leaching increases (Lal, 2009 & Racke et al., 1997). A common strategy for dealing with pesticide-contaminated soils has been to excavate the soil and transfer it to isolated landfills with barriers, thus preventing pollutants from migrating to non-contaminated soils (Castelo-Grande et al., 2010). Though the method may prevent contamination, it is economically unfeasible and yet not able to eradicate the contaminant. Other strategies for the remediation of contaminated soils can be read in Remediation of Contaminated Soils in chapter 2. As opposed to landfills, several countries have now placed efforts in adapting *in situ* techniques for the containment and elimination of contaminants within the soil (Khorram et al., 2015). A distinctive technique for *in situ* amendments of contaminated soils has been to imply carbon-based materials such as biochar within the soil matrix (Joseph et al., 2010 & Khorram et al., 2015). The *in situ* application of biochar is less disruptive to the soil in that the contaminants can be directly absorbed to biochar (Khorram et al., 2015). In addition to reducing the contaminant's movement through the soil-water matrix, the presence of biochar in the soil can simultaneously restore the soil's ecology and aid with plant growth (Khorram et al., 2015).

Furthermore, although the sorption mechanisms of biochar can reduce short term leaching, such as in storm events, in the longer term, the same amount of pollutants will be leached out of the soil, unless absorption is complemented by biodegradation. The main benefit of biochar addition to soil is to retain the pollutants in the bioactive soil horizon for a more extended period, to increase the occurrence of biological removal of contaminants in the soil. It is therefore suggested that the addition of biochar to soils of poor quality may be able to increase its fertility, aggregate stability, biodiversity, (Vermeulen et al., 2012) and at the same time, reduce herbicide and veterinary antibiotic leaching.

The capability of biochar to absorb pesticides from soils has been supported by many studies (Yang et al., 2006; Fontecha-Cámara et al., 2007; Cederlund et al., 2017; Zhelezova et al., 2017). Sorption and column leaching studies have been used to determine the fate of agrochemicals in soil. Sorption isotherms are used to express the relationship between the concentration of an agrochemical between the solid and the aqueous phase at a constant temperature (Grathwohl, 1998). The distribution coefficient (K_d) derived from a sorption isotherm expresses the ratio between the concentration of solute in the aqueous solution and the sorbent. The absorption capacity is indicated by the K_d value (Site, 2000). Therefore the higher K_d, the higher the sorption capacity. Sorption isotherms can be either linear or nonlinear. In the absorption kinetics, absorption is characterized by two sorption stages. Firstly, there is rapid diffusion of the herbicide to the boundary surface of the absorbent; in this case, biochar-amended soil. Secondly, diffusion of the herbicide is much slower since the herbicides are diffused into the mesopores and micropores of the absorbent (Grathwohl, 1998). See Pesticide fate in soils in chapter 2 for further information. In addition to sorption isotherms and sorption kinetics, column leaching breakthrough curves are also used to determine the herbicide fate in a soil matrix.

Given that atrazine and diuron contaminations have been detected in surface and groundwater of American and European countries (Spain at concentrations above 0.1 µg/L (Mandal & Singh, 2017; Fontecha-Cámara et al., 2007)), several studies have focused on the absorption of atrazine and diuron with the use of biochar (Cao et al., 2011, 2009; Mandal & Singh, 2017; Cederlund et al., 2017). With regard to remediation of antibiotic contamination, only a handful of studies have focused on its absorption by biochar or activated carbon (Ahmed et al., 2017; Huang et al., 2017; Yao et al., 2013), yet these studies have not focused explicitly on the sorption of enrofloxacine, oxytetracycline and tetracycline. Therefore, the aims of this study were to determine the most suitable biochar as an absorbing agent for atrazine, diuron, enrofloxacine, oxytetracycline and tetracycline in a temperate oceanic and three tropical soils.

4.2. Methodology

4.2.1. Chemicals

The two herbicides used in this experiment were analytical grade atrazine (1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) of 98.9% purity and diuron (1,1-dimethyl, 3-(3’,4’-dichlorophenyl) urea) of 98% purity both purchased from Sigma-Aldrich Ltd., UK. These herbicides are used to prevent pre– and post– emergence broadleaf weeds in crops such as maize and wheat. The antibiotics used in this experiment were enrofloxacine (1-Cyclopropyl-7-(4-ethyl-1-piperazinyl)-6-fluoro-4-oxo-1,4-dihydro-3-quinolinecarboxylic acid) of HPLC grade 98% purity, oxytetracycline hydrochloride (4S,4aR,5S,5aR,6S,12aS)-4-(dimethylamino)-1,4,4a,5,5a,6,11,12a-octahydro-3,5,6,10,12,12a-hexahydroxy-6-methyl-1,11-dioxo-2-naphthacenecarboxamide hydrochloride) of HPLC grade 95% purity, and tetracycline hydrochloride (6-methyl-1,11-dioxy-2-naphthacenecarboxamide) of 98% purity. Enrofloxacine and oxytetracycline hydrochloride were purchased from Sigma-Aldrich Ltd., UK and tetracycline hydrochloride was purchased from Fluka Analytical, UK. Further characteristics of the chemicals are seen in Table 4-1.

Parameter	Substance				
	Atrazine	**Diuron**	**Enrofloxacine**	**Oxytetracycline**	**Tetracycline**
Physico-Chemical					
Molecular weight (g mol^{-1})	215.68	233.1	359.4	496.9	444.4
Water solubility (mg L^{-1}) at 20°C	35	35.6	130000	1000	1700
Octanol-water partition coefficient at pH 7, 20°C	5.01×10^{02}	7.41×10^{02}	5.01×10^{04}	6.03×10^{-02}	5.01×10^{-02}
Dissociation constant (pKa) at 25°C	1.7	Not applicable	6.21	4.5	3.3
Vapour pressure (mPa) at 20°C	0.039	1.15×10^{-03}	2.53×10^{-08}	1.29×10^{-19}	4.11×10^{-18}
Degradation in soil					
DT_{50} (Typical) (days aerobic)	75	146.6	123	18	30
DT_{50} (lab at 20°C)	66	146.6	297	21	-
Sorption					
K_d	-	12.8	-	698	-
K_{oc}	100	680	392600	52875	40000
K_f	3.2	7.0	-	-	-
K_{foc}	174	757	-	-	-
1/n (-)	1.07	0.75	-	-	-

Table 4-1. Characteristics of different agrochemicals used for batch sorption experiment (Lewis et al., 2016)

4.2.2. Reagents and materials

HPLC-grade methanol was purchased from Scientific Laboratory Supplies Ltd, UK and HPLC-grade acetonitrile was purchased from Sigma-Aldrich Ltd., UK. Calcium chloride dihydrate was purchased from Qmx Laboratories Ltd., UK. HPLC grade water was obtained using the ultrapure water system, Milli-Q Advantage A10 from VWR, UK. The 60 mL amber screw top vials (27.5 mm x 140 mm) and black closed screw caps (24-414 thread with silicone/PTFE liner) were purchased from Chromatography Direct, UK. Thermo syringes 1 mL were purchased from VWR, and syringe filters (13 mm 0.22 µm) were purchased from StratLab Ltd., UK. 2 ml clear robotic 9 mm screw-top vials closed with blue 9 mm white silicone/red PTFE septa screw caps were purchased from Chromatography Direct, UK.

4.2.3. Soil

The clay loam soil was collected in agricultural land of the Corozal district (see Figure 4-1). Land use was characterized by the cultivation of sugarcane for over 35 years. Herbicide previously used was glyphosate. The slope position was footslope, and the relief is characterized as slightly undulating flat land. The soil was classified as vertic gleysol. The loam soil was collected in agricultural land of the Cayo district (see Figure 4-1). Land use was characterized by crop rotation of maize and beans. Herbicides previously used were atrazine and glyphosate. Agricultural activity occurs approximately 36 meters from the Belize River. The slope position is toeslope, and the relief is characterized as a broad floodplain valley with flat land stretching from both sides of the river. The soil was classified as gleyic cambisol. The sandy silt loam soil was collected in agricultural land of the Stann Creek District (see Figure 4-1). Land use was characterized by citrus cultivation for over 30 years. Lime for pH adjustment is used in this soil type. 2, 4-D is the leading herbicide used. The slope position is described as footslope, and the relief is characterized as a broad flood plain valley with flat land stretching from both sides of the river, surrounded by mountainous regions of granite particles. These soil-sampling sites were selected based on the advice from agricultural stakeholders in Belize since they represent the most dominant soil types being used for agriculture in the region. In addition, these soil-sampling sites were located close to natural water bodies.

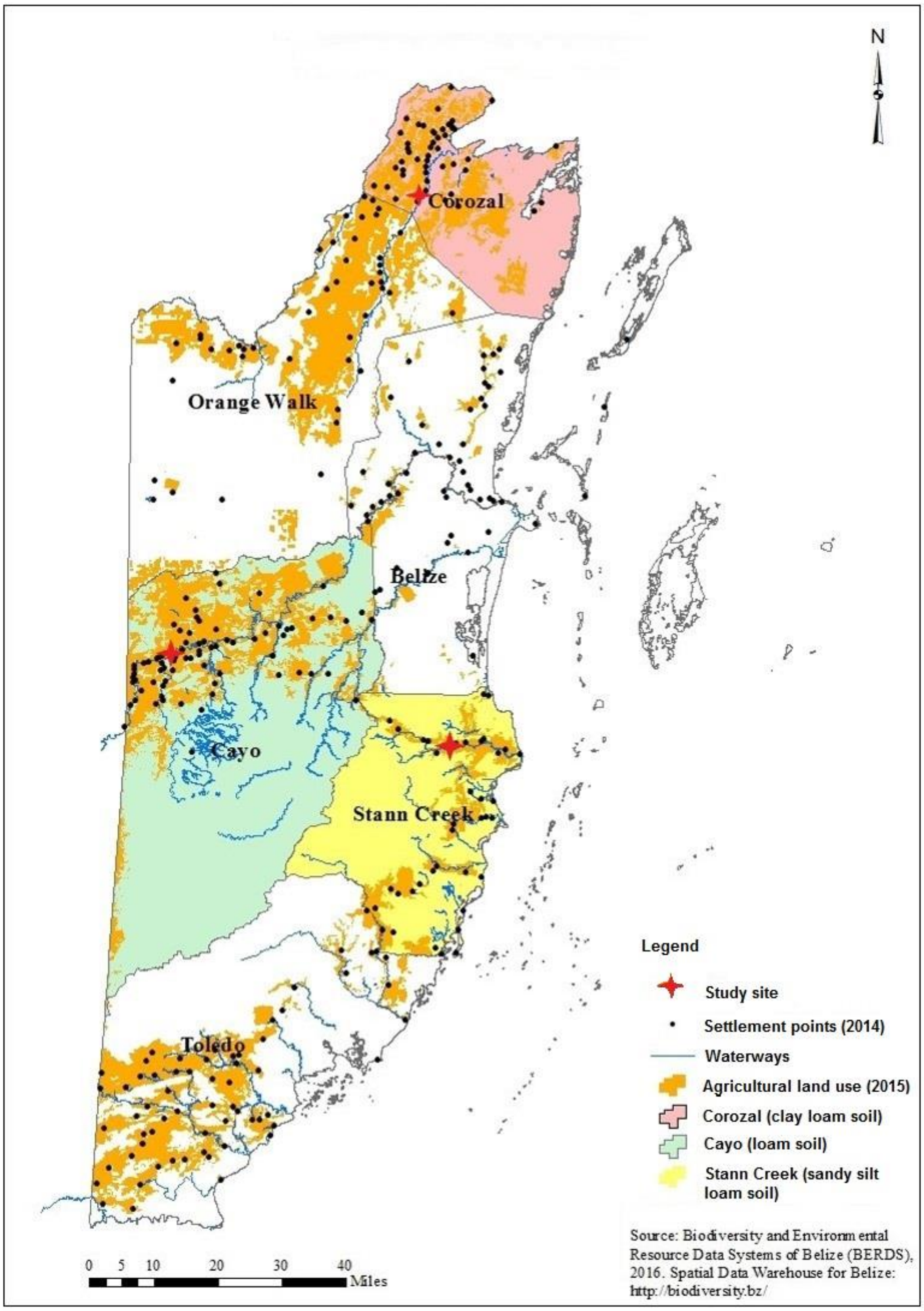

Figure 4-1. Soil sampling location in Belize

The sandy loam soil was collected near the Urban Sciences building in Newcastle University, Newcastle, United Kingdom. Since this soil was not collected in a tropical region, it was used as a reference UK soil to be compared to the tropical soils and was only used for the batch microcosm studies. See Table 4-2 below for further characteristics of all soil types. Further description of soil sampling methods and soil profile description of tropical soils can be seen in Appendix B.

Analysis	Corozal district	Cayo district	Stann Creek district	Newcastle
Soil Class	Clay loam	Loam	Sandy silt loam	Sandy loam
Lime Req. (t/ha)	-	-	5.0	-
pH	8.2	8.1	6.1	7.8
Grid reference	18°13'44.6"N 88°32'07.3"W	17°12'04.4"N 89°00'16.6"W	16°59'40.9"N 88°21'49.0"W	54°58'25.3"N 1°37'34.5"W
C.E.C. (meq/100g)	69.9	27.5	11.4	15.8
Organic matter (%)	5.0	2.9	3.7	8.8
Organic Carbon (%)	2.91	1.68	2.15	5.12
Silt (%)	37.66	41.37	48.02	34.54
Clay (%)	34.93	20.54	15.83	12.11
Sand (%)	27.41	38.09	36.15	53.35
Available water	Medium to high	Medium to high	Low to medium	Low to medium
Drainage rate	Medium to slow	Medium to slow	Rapid	Rapid
Inherent fertility	Medium to high	Medium to high	Low to medium	Low to medium
Potential C.E.C	Medium to high	Medium to high	Low to medium	Low to medium
Leaching risk	Moderate to low	Moderate to low	High to moderate	High to moderate
Warming rate	Medium	Medium	Rapid	Rapid

Table 4-2. Characteristics of soil types

4.2.4. Biochar

The experiment used three types of standard biochars produced and provided by the UK Biochar Research Centre (UKBRC) at the University of Edinburgh (www.biochar.ac.uk). These biochars were produced in stage III pilot-scale pyrolysis unit at 700°C from a feedstock of mixed softwood pellets, rice husk and miscanthus straw pellets. The feedstock type and heat treatment temperature (HTT) are two primary components that influence the physicochemical characteristics of biochar as a product (Yavari et al., 2015). We used biochars produced at a high temperature of 700°C as they have been studied to absorb pollutants more effectively due to their high specific surface area and aromatic carbon content. Biochars produced at low temperatures have been studied to support plant growth due to high levels of volatile matter content (Jindo et al., 2014; Mukherjee et al., 2011; Ahmad et al., 2014; Kookana, 2010). See Sorption of pesticides and biochar interactions in chapter 2 for more information. The physicochemical characteristics of the different biochar types are given in Table 4-3 below.

Source	Unit	Mixed softwood pellets	Rice husk	Miscanthus straw pellets
Temperature	°C	700	700	700
Dry matter	g/kg	990	985	988
Biochar yield	wt % (d.b.)	17.34	32.77	21.07
Moisture	wt % (a.r.)	1.00	1.49	2.23
Total ash	wt % (d.b.)	1.89	47.93	11.55
pH		8.44	9.81	9.72
C_{tot}	wt % (d.b.)	90.21	47.32	79.18
$O:C_{tot}$	Molar ratio	0.05	0.03	0.07
$H:C_{tot}$	Molar ratio	0.24	0.16	0.19
H	wt % (d.b.)	1.83	0.63	1.26
O	wt % (d.b.)	6.02	2.06	6.99
Total N	wt % (d.b.)	<0.1	0.85	1.03
Mineral N	mg/kg (d.b.)	<3	<3	<3
Total P	wt % (d.b.)	0.07	0.16	0.76
Total K	wt % (d.b.)	0.28	0.62	2.60
Total Surface area	m^2/g	162.3	42	37.2
Volatile matter	wt % (d.b.)	6.66	4.99	7.71
Electric conductivity	dS/m	0.16	0.69	1.91
Biochar C stability	% C-basis	97.27	100.18	98.93

Table 4-3. Composition of biochars. Notes: d.b. = dry basis; a.r. = as received. Additional data can be found at the UK Biochar Research Centre website: http://www.biochar.ac.uk/standard_materials.php (Accessed 18/06/2018)

4.2.5. Batch microcosm experiments

Absorption was measured in a batch equilibrium system according to OECD 106 guidelines for testing of chemicals – absorption – using batch equilibrium method (OECD, 2000). The first step consisted of a batch microcosm of only biochar and agrochemicals (herbicides and antibiotics). The experimental design consisted of three factors: biochar type, biochar rate, agrochemical type, with three replicates. Three replicates of each softwood, rice husk and miscanthus straw biochar types were sieved to > 2 mm and separately weighed at 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mg. Each weighed biochar was then placed in a 60 mL amber glass screw top vial closed with a black screw cap threaded with silicone/PTFE liner. The stock solution of the agrochemicals was then prepared. For the preparation of the stock solution, 10 mL of methanol was used as a solubilizing agent for every 1 mg tetracycline, oxytetracycline and diuron; while 10 mL of acetonitrile was used for 1 mg of atrazine, and a mixture of 5 mL methanol and 5 mL acetonitrile was used for enrofloxacine. The stock solution was kept closed in the dark at 4°C. The stock solutions were then mixed into a 1 L amber glass vial where it was then filled to 1 L of HPLC grade water. 50 mL of this mixture was then poured into the 60 mL amber glass screw top vial containing the previously weighed biochars. These were then shaken at 200-rev min^{-1} for 24 hours at room temperature of 20±2°C. The second step was to test the sorption of the agrochemicals by the different soil types. The OECD 106 procedures were repeated for the batch microcosm of only soil and agrochemicals. For this step, 500, 1000, 2000, 5000 and 10,000 g were weighed in triplicate per soil type in the amber glass vials. As per OECD 106, the HPLC grade water was concentrated with 0.01 M calcium chloride dehydrate. 50 mL of this mixture, as previously described, was then poured into the 60 mL amber glass screw top vial containing the weighed soils. The third step was to determine the mixture of biochar and soil absorption of agrochemicals. After having determined which biochar type was the best absorbent of all agrochemicals, the third step was to use this biochar type further investigation. The selected biochar was mixed separately with soil types at rates of 1%, 2.5% and 5% (w/w) per 10,000 g of soil. These application rates were selected as per previous studies biochar (See Sorption of pesticides and biochar interactions in chapter 2 for more information). At this step, liquid samples were extracted at 2, 4, 6 and 24 h for kinetic sorption studies. Liquid samples were then extracted from the amber vials using 1 mL syringes and filtered through sterile, single-use 13 mm syringe filters of 0.22 µm and poured into 2 mL clear robotic screw-top vials closed with blue 9 mm white silicone/red PTFE septa screw caps. In all cases, separate controls consisted of amber glass vials containing deionized water only, deionized water and biochar only, deionized water and soil only and deionized water with agrochemical only. Each control was in triplicate. No adsorption of any of the agrochemicals occurred onto the glass vials.

The sorption data collected from the experiments were described using sorption isotherms (Coquet, 2003). They were either linear or nonlinear. Linear sorption was described using distribution coefficients (K_d), which explained the relationship between the compound concentration being sorbed to the solid phase of the soil and the compound concentration that remained in the aqueous phase of the soil. However, the compounds that expressed non-linear sorption were described using the Freundlich (K_f) or Langmuir (K_L) isotherm models (Wauchope et al., 2002) (see Pesticide Fate Processes in Chapter 2). The data collected from the sorption experiments were fitted to either the linear, Freundlich or Langmuir isotherm models.

4.2.6. Column leaching experiment

Two of the least absorbed agrochemicals in the biochar amended soil matrix, as determined by the batch microcosm experiments, were selected for laboratory column leaching experiments.

The selected agrochemicals were atrazine and diuron. Column leaching experiments followed the OECD 312 guidelines for testing of chemicals – leaching in soil columns (OECD, 2004). Columns were set up to simulate an extreme rainfall-pesticide leaching event that would occur in locations where the tropical soils were collected. These locations were the Corozal, Cayo and Stann Creek districts of Belize. Four Rotaflo Quickfit CR12/30 Pyrex glass columns of 1 cm inner diameter and 30 cm effective height were used for the column leaching experiment. Glass wool was placed inside the bottom of each column to prevent soil loss. Each column was then filled with standard sand (2.54 g/cm^3 solid density) to a height of 5 cm. Two columns were then hand-packed with one soil type, without biochar amendment, to a height of 20 cm. These were labelled as control columns. The other two columns were hand packed with biochar-amended soil at a rate of 2.5% (w/w) to a height of 20 cm. These were labelled as the experimental columns.

Simulated rainfall for each soil was determined by actual rainfall measurements in the Corozal, Cayo and Stann Creek districts. Rainfall data was supplied by the National Meteorological Service of Belize. The extreme monthly rainfall recorded between the years of 1966 to 2018 was selected for the simulation. The actual daily rainfall per district/soil type was calculated using the formula:

$$R_d = \frac{R_m}{D_{dur}}$$

Where:

R_d = Daily rainfall (mm/d)

R_m = Monthly rainfall (mm)

D_{dur} = Duration (days)

After calculating the daily rainfall per soil type, the daily flow of water per soil column was calculated using the formula:

$$R_{df} = \frac{R_d \times 10^2 \times CA_{col}}{10^3}$$

Where:

R_{df} = Daily flow of water in column (mL/d)

CA_{col} = Cross-sectional area of column (cm^2)

The pesticide application in each column was calculated using the formula:

$$P_c = \frac{P_r \times 10^6}{10^8 \times CA_{col}}$$

Where:

P_c = Pesticide application per column (mg)

P_r = Pesticide application rate (kg/ha)

The pesticide concentration in solution was calculated using the formula:

$$P_s = \frac{P_c}{(3 \times R_{df}) \times 1000}$$

Where:

P_s = Pesticide concentration in solution (mg/L)

Table 4-4 below summarizes the parameters used to simulate the rainfall scenario and pesticide concentration for each column experiment.

District	Soil type	Monthly rainfall (mm)	Duration (days)	Daily rainfall (cm/d)	Daily flow of water in column (mL/d)	Pesticide application rate (kg/ha)	Pesticide concentration in solution (mg/L):
Corozal	Clay Loam	525.4	31	1.7	3	2	3.93
Cayo	Loam	714.1	31	2.3	4	2	2.89
Stann Creek	Sandy silt loam	929.20	30	3.1	5	2	2.15

Table 4-4. Simulated scenarios for each soil type in the column leaching experiment

After calculating the simulated rainfall for each soil type, the simulated rainfall solution was prepared using HPLC grade water concentrated with 0.01 M calcium chloride dehydrate. The columns were manually irrigated with the rainfall solution until the soil reached saturation. Once the soil reached saturation, the pesticide in solution was added for three consecutive days. The column was then daily irrigated with simulated rainfall solution until the end of the experiment. Effluents were collected and measured at ten equally distributed time points throughout the experiment. Effluents were stored in 60 mL amber glass vials, in a cold room at 4°C. Liquid samples were then extracted from the amber vials using 1 mL syringes and filtered through sterile, single-use 13 mm syringe filters of 0.22 µm into 2 mL clear robotic screw-top vials closed with blue 9 mm white silicone/red PTFE septa screw caps. These samples were sent for LC-MS-MS analysis after the end of each experiment. Selected soils collected from the columns were sent to Derwentside Environmental Testing Services, UK, for electrical conductivity, pH and organic matter analysis based on the BS 1377: Part 3:1990. One selected soil was sent to RPS Mountainheath Limited, UK, for pesticide analysis. After each column experiment, soils and biochar amended soils were removed from the glass columns. The glass columns were then washed with deionized water and methanol in preparation for the next experiment. The experiments were conducted in consecutive order and lasted 31, 31 and 30 days for Corozal, Cayo and Stann Creek, respectively.

4.2.7. Analysis

Statistical analysis was conducted on sorption data using IBM SPSS Statistics 24. The difference between the measured aqueous concentration in the batch with the absorbent (i.e., soil/biochar/biochar amended soil) and the control batch without the absorbent was statistically determined. The data were evaluated using a Paired Sample t-test ($P < 0.01$). In addition, the difference between the measured aqueous concentration and zero and was statistically determined by calculating the standard error of the mean. When the mean was at least twice as much as the standard error, then the measured aqueous concentration was qualified as statistically significantly different to zero. Only the data points which met both criteria (i.e., statistically significantly different from the control, and statistically significantly different from zero) were used to plot sorption isotherms. Sorption data were fitted to either Linear, Langmuir and Freundlich isotherms using least squares regression. The fittings were calculated using Matlab R2017a. Column breakthrough curves and kinetic absorption were also calculated using Matlab R2017a.

4.3. Results and Discussion

4.3.1. Soil sorption experiments

Atrazine behaved differently in the different soil types. Its measured aqueous concentration in the separate batches containing loam and sandy silt loam soils were not statistically significantly different from the control batch without soil. Therefore, absorption data for loam and sandy silt loam soils were not reported in Table 4-5. However, for the clay loam and sandy loam soils, the measured aqueous concentration in the batch containing these soils was statistically significantly different from the control batch without soils. These analyses meant that atrazine was absorbed by the clay loam and sandy loam soil but not by the loam and sandy silt loam soils. When the atrazine sorption to clay loam and sandy loam experimental data were fitted with the simulated model, the sum of squared residuals (SSR) was least for the Freundlich model. This proved that sorption of atrazine by these soils was best described by the Freundlich isotherm model. The Freundlich exponents (1/n) for clay loam and sandy loam soils were 0.6 and 0.7, respectively (Table 4-5). Usually, 1/n values such as these indicate that when the compound concentration increases, relative absorption decreases due to the saturation of the soil's absorption sites. This indicated that atrazine mobility in the soil could become greater at higher concentrations (Nemeth-Konda et al., 2002; Site, 2000). When compared to atrazine, diuron was absorbed by all the soil types. Although absorption of diuron could be explained by both the Freundlich and Langmuir models, the experimental data were best fitted with the Langmuir model. The Langmuir isotherm parameter $C_{sm,max}$ indicated the maximum absorption capacity of a compound to the soil at high concentrations (Karnitz et al., 2007). In Table 4-5, it was observed that the $C_{sm,max}$ Langmuir parameter was highest for clay loam and sandy loam. However, the sorption between diuron and both loam and sandy silt loam soils was higher than the other two soil types, as observed by the K_L parameter, indicating that diuron had a lower potential to leach in these soils (Inoue et al., 2004)

Chemical	Location	Soil	Linear		Freundlich			Langmuir		
			K_d (m^3/kg)	SSR	(moles/kg)(moles/m^3)$^{-1/n}$	1/n	SSR	K_L (m^3/kg)	$C_{sm,max}$ (moles/kg)	SSR
Atrazine	Corozal	Clay loam	0.0024	1.1e-11	0.0003	0.6	5.3e-12	0.14	0.0172	1.0e-11
	Cayo	Loam	-	-	-	-	-	-	-	-
	Stann Creek	Sandy silt loam	-	-	-	-	-	-	-	-
	Newcastle	Sandy loam	0.0011	2.2e-11	0.0002	0.7	2.0e-11	0.11	0.0095	2.2e-11
Diuron	Corozal	Clay loam	0.0205	4.9e-10	0.0012	0.5	2.1e-11	6.6e+02	7.3e-05	7.6e-12
	Cayo	Loam	0.0031	2.1e-11	0.0004	0.6	1.1e-11	2.0e+08	9.3e-06	7.3e-13
	Stann Creek	Sandy silt loam	0.0026	1.7e-10	0.0001	0.4	9.7e-11	1.2e+10	9.1e-06	6.1e-11
	Newcastle	Sandy loam	0.0088	3.7e-10	0.0002	0.4	5.0e-11	1.1e+03	3.1e-05	3.7e-11
Enrofloxacine	Corozal	Clay loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Cayo	Loam	0.1530	6.7e-08	115.4	1.8	4.84e-08	0.5	0.31	6.76e-08
	Stann Creek	Sandy silt loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Newcastle	Sandy loam	0.1953	1.4e-10	0.42	1.1	5.5e-11	0.73	0.27	1.4e-10
Oxytetracycline	Corozal	Clay loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Cayo	Loam	0.5030	1.60e-09	6.86	1.3	7.1e-10	0.60	0.84	1.7e-09
	Stann Creek	Sandy silt loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Newcastle	Sandy loam	0.4423	3.40e-09	10.8	1.4	1.7e-09	0.5	0.8	3.4e-09
Tetracycline	Corozal	Clay loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Cayo	Loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D

Stann Creek	Sandy silt loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Newcastle	Sandy loam	0.7146	1.0e-08	10.6	1.4	8.8e-09	2.95	0.2420	1.0e-08

Table 4-5. Linear, Freundlich and Langmuir isotherm model fit for compounds onto different soil types. Notes: - = Paired sample t test; $P < 0.05$; N.D = Non detectable; SSR = sum of squared residuals

Studies have shown that factors affecting herbicide absorption by soil are organic matter and clay content (Worrall et al., 1997; Kookana et al., 1998; Naidu & Kim, 2008). As seen in Table 4-2, clay loam and sandy loam soils contained the highest organic matter percentages, i.e. 5 and 8.8 %, respectively. The loam and sandy silt loam organic matter percentages were 2.9 and 3.7%, respectively. It was observed that the higher the organic matter, the more absorption of herbicides occurred (Mudhoo & Garg, 2011). A study conducted by Weber et al., (2004) showed that the absorption of atrazine and diuron were positively correlated to the soil's organic matter and clay content. Several other studies have shown positive correlations between herbicide absorption and organic matter and clay content (Baskaran, 1994; Bedmar et al., 2017; Nemeth-Konda et al., 2002). However, studies have shown that there is a stronger correlation between organic matter and herbicide absorption than clay content (Weber et al., 2004; Kookana et al., 1998). As seen in Table 4-6 , this study showed that the absorption of atrazine had a strong positive correlation with both organic matter and clay content, while the absorption of diuron had a strong positive correlation with only clay content.

Agrochemical	**Soil properties**	
Pearson correlation values[a]	Organic matter (%)	Clay (%)
Atrazine	1.000**	1.000**
	(2)	(2)
Diuron	-0.102	.970*
	(4)	(4)

Table 4-6. Pearson correlation coefficients for Kf values of atrazine and diuron vs. soil properties. N.B: a Significant at the 0.05 (*) or 0.01 (**) level. Number of values correlated are in parentheses. d.b. = dry basis; a.r. = as received.

Enrofloxacine concentration was non-detectable in the aqueous phase of the clay loam and sandy silt loam soils. Oxytetracycine concentration was also non-detectable in the aqueous phase of the clay loam and sandy silt loam soils. Tetracycline was also non-detectable in the aqueous phase of the clay loam, loam and sandy silt loam soils. Non-detection of these compounds in the aqueous phase of the soils could be due to method limitations in the batch experiments whereby the soil to water ratio was inadequate. However, non-detection of these compounds could also be due to high sorption. According to Tolls (2001), the sorption of antibiotics is a surface-related process. Antibiotics have been known to be strongly absorbed due to their monofunctional nature, strong intermolecular attraction and their ability to penetrate into the absorbent layers (Site, 2000). As observed in this study, the antibiotics had higher sorption to the soil than the herbicides. An explanation for this could be that the absorption of both antibiotics and herbicides depend on the organic matter of the soil, there may be competition for surface reactions. The competition for surface reactions can be observed by comparing the Freundlich 1/n parameter. The Freundlich parameter is less than one for the herbicides but more than one for the antibiotics. In addition, active antibiotics in the soil are capable of damaging and reducing the soil microbial population (Kim et al., 2011), therefore preventing herbicides from being degraded by their particular microbes. Therefore, the appropriateness of using a mixture of herbicides and antibiotics was justifiable because the presence of both herbicides and antibiotics in agricultural soils is typically overlapping.

4.3.2. Biochar sorption experiments

The sorption data for the agrochemicals fitted with the Freundlich isotherm model. The Freundlich model fitting demonstrated that the rice husk biochar had the highest absorption affinity for all of the agrochemicals, as compared to softwood and miscanthus biochars (see Table 4-8). Rice husk's ability to have a higher absorption affinity for all of the agrochemicals was primarily influenced by its surface area and H:C molar ratio. As seen in Table 4-7 below, the total surface area and H:C had a strong positive correlation with the absorptions of agrochemicals to biochar.

Agrochemical	**Biochar properties**				
Pearson correlation values[a]	Total ash (wt %; d.b.)	Total surface area (m^2/g)	Total K (wt %; d.b.)	O/C_{tot} (molar ratio)	H/C_{tot} (molar ratio)
Atrazine	-0.538 (3)	0.993 (3)	-0.728 (3)	-0.156 (3)	0.86 (3)
Diuron	-0.763 (3)	0.984 (3)	-0.494 (3)	0.143 (3)	0.972 (3)
Enrofloxacine	-0.871 (3)	0.933 (3)	-0.32 (3)	0.327 (3)	.999* (3)
Oytetracycline	-0.104 (3)	0.833 (3)	-0.958 (3)	-0.581 (3)	0.54 (3)
Tetracycline	-0.667 (3)	.999* (3)	-0.608 (3)	0.006 (3)	0.931 (3)

Table 4-7. Pearson correlation coefficients for Kf values vs. biochar and soil properties for all of the agrochemicals in this study. N.B: a Significant at the 0.05 (*) or 0.01 (**) level. Number of values correlated are in parentheses; d.b. = dry basis; a.r. = a

The biochar molar H/C ratios of ≤0.3 indicate highly condensed aromatic ring systems (Vithanage et al., 2016). The rice husk biochar molar H/C ratio was less than the softwood and miscanthus biochars, indicating a higher degree of carbonization for the rice husk biochar (see Table 4-3). Furthermore, the low H/C ratios of the rice husk biochar as compared to the other biochars showed that rice husk biochar had a higher level of aromaticity, which helped with rice husk biochar's ability to absorb the agrochemicals (Li et al., 2013).

Chemical	Biochar	Linear		Freundlich			Langmuir		
		K_d (m^3/kg)	SSR	(moles/kg)(moles/m^3)$^{-1/n}$	1/n	SSR	K_L (m^3/kg)	$C_{sm,max}$ (moles/kg)	SSR
Atrazine	Rice husk	0.4699	2.2-06	0.005	0.2	5.5e-08	70.9	0.007	1.9-06
	Softwood	0.0363	2.4e-09	0.001	0.4	2.4e-09	49.8	0.0008	2.4e-09
	Miscanthus	0.0251	5.5e-09	0.0002	0.1	3.7e-09	3.1	0.008	5.4e-09
Diuron	Rice husk	1.1261	1.0e-05	0.014	0.3	1.6e-07	93.5	0.014	9.2e-06
	Softwood	0.1006	5.9e-08	0.001	0.3	3.2e-08	0.4770	0.211	5.8e-08
	Miscanthus	0.0859	3.8e-09	0.003	0.4	2.6e-09	19.3	0.005	3.7e-09
Enrofloxacine	Rice husk	0.6979	1.5e-06	0.005	0.3	4.6e-08	1.48	0.473	1.5e-06
	Softwood	0.5153	9.1e-06	0.002	0.2	7.6e-06	0.51	1.007	9.1e-06
	Miscanthus	0.1199	1.6e-09	0.003	0.5	1.2e-09	38.5	0.003	1.5e-09
Oxytetracycline	Rice husk	1.6695	1.7e-06	0.040	0.5	7.7e-08	47.2	0.04	1.6e-07
	Softwood	0.1218	1.6e-07	0.030	0.7	1.6e-07	33.9	0.003	1.6e-07
	Miscanthus	0.1656	2.6e-08	0.016	0.7	2.3e-08	140.1	0.001	2.4e-08
Tetracycline	Rice husk	5.2947	6.8e-07	0.414	0.7	1.7e-07	63.8	0.08	6.4e-07
	Softwood	0.0967	5.5e-08	2.2e-04	0.1	1.1e-08	10.4	0.009	5.4e-08
	Miscanthus	1.0783	6.7e-06	0.003	0.2	6.1e-06	363.7	0.004	6.5e-06

Table 4-8. Linear, Freundlich and Langmuir isotherm model fit for sorption of pesticides and VPs onto different biochar types. Notes: * = No significant difference; N.D = Non detectable

Yavari et al., (2015) explain that when biochars have a low ash content, there is less opportunity for the biochar's surface area to be blocked by the ash. Therefore, the low ash content and high surface area of softwood and miscanthus biochars could be ideal for desorption hysteresis to occur (see Appendix B), hence the reason why softwood and miscanthus biochars could not give a perfect fit for the sorption isotherm models. Agrochemical absorption to rice husk fitted well with the Freundlich isotherm model (see Figure 4-2 to Figure 4-6). However, the Freundlich *n* parameter of $1/n > 1$ showed that as the compound concentration would increase on the rice husk biochar surface, the marginal sorption energy would decrease, which indicated that the mobility of these compounds could become greater at higher concentrations (Nemeth-Konda et al., 2002; Site, 2000). Similar to the soil absorption studies, this sorption experiment used a mixture of herbicides and antibiotics to be absorbed by a single biochar type. A mixture of herbicides and antibiotics represent a typical agrochemical in agricultural soil scenario. Thus, there could be competition amongst the compounds for the biochar sorption sites (Graber et al., 2015). When comparing the results from the soil and biochar sorption studies, it was observed that the application of biochar to soils for the absorption of the antibiotics was not necessarily needed. On the contrary, the application of rice husk biochar in soil for the absorption of atrazine and diuron would be needed. The absorption of atrazine and diuron by the different types of biochar was much higher than the absorption of atrazine and diuron by the different soil types, suggesting that any of the biochar types used in this study could increase pesticide absorption if added to the soil. However, the rice husk biochar proves to be the best absorbent for all of the agrochemicals studied.

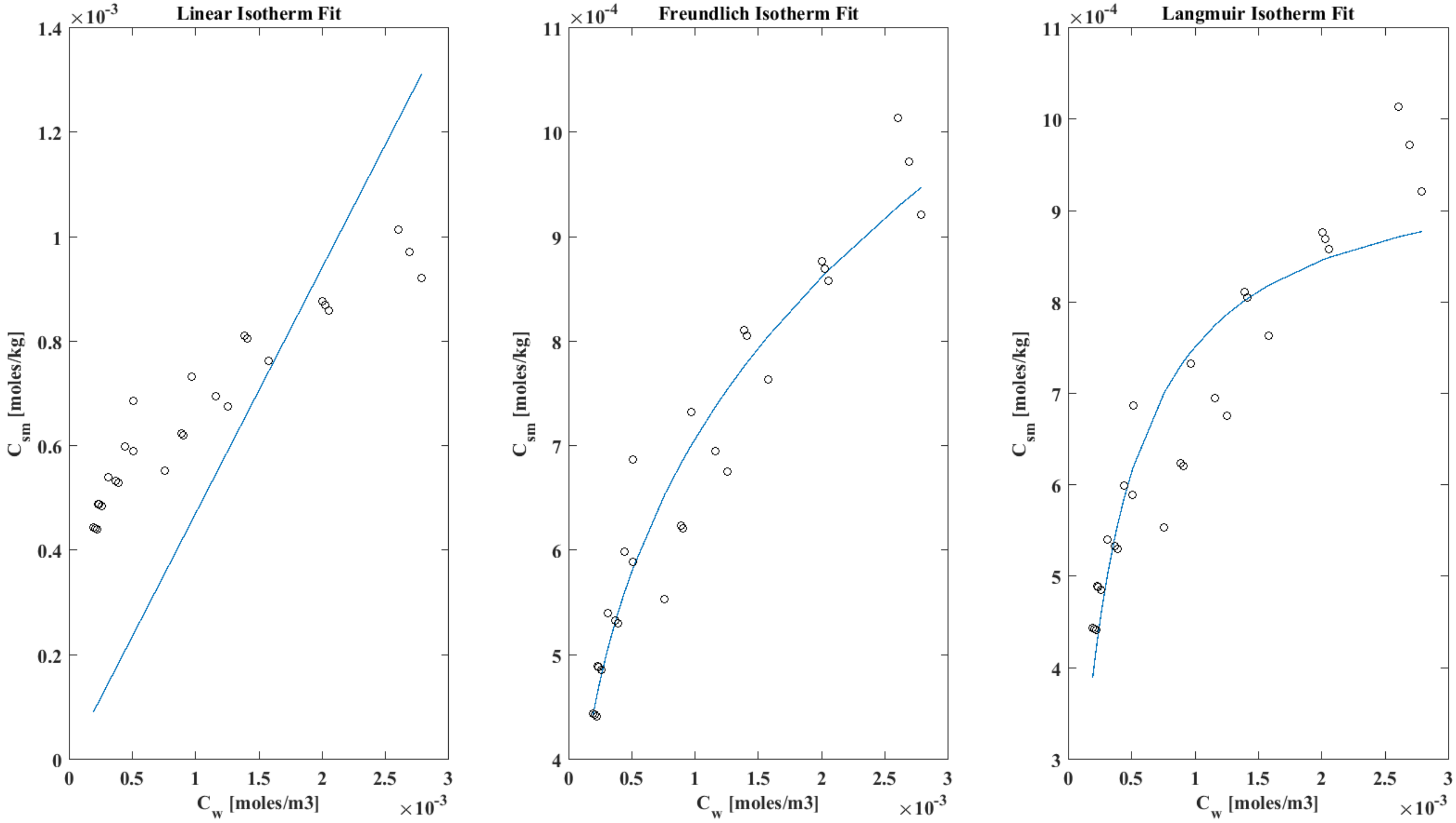

Figure 4-2. Linear, Freundlich and Langmuir isotherm fit for sorption of atrazine onto rice husk biochar

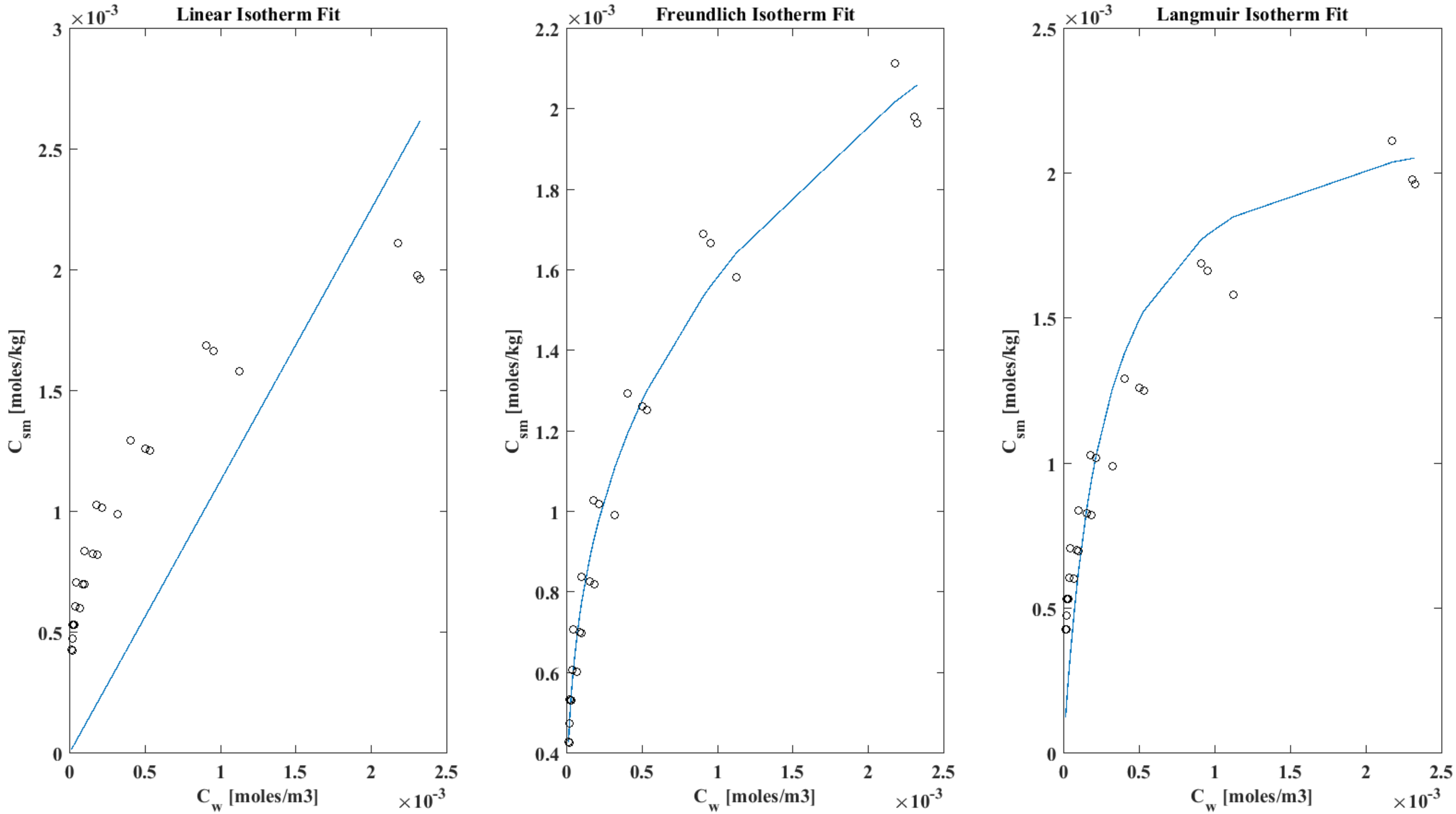

Figure 4-3. Linear, Freundlich and Langmuir isotherm fit for sorption of diuron onto rice husk biochar

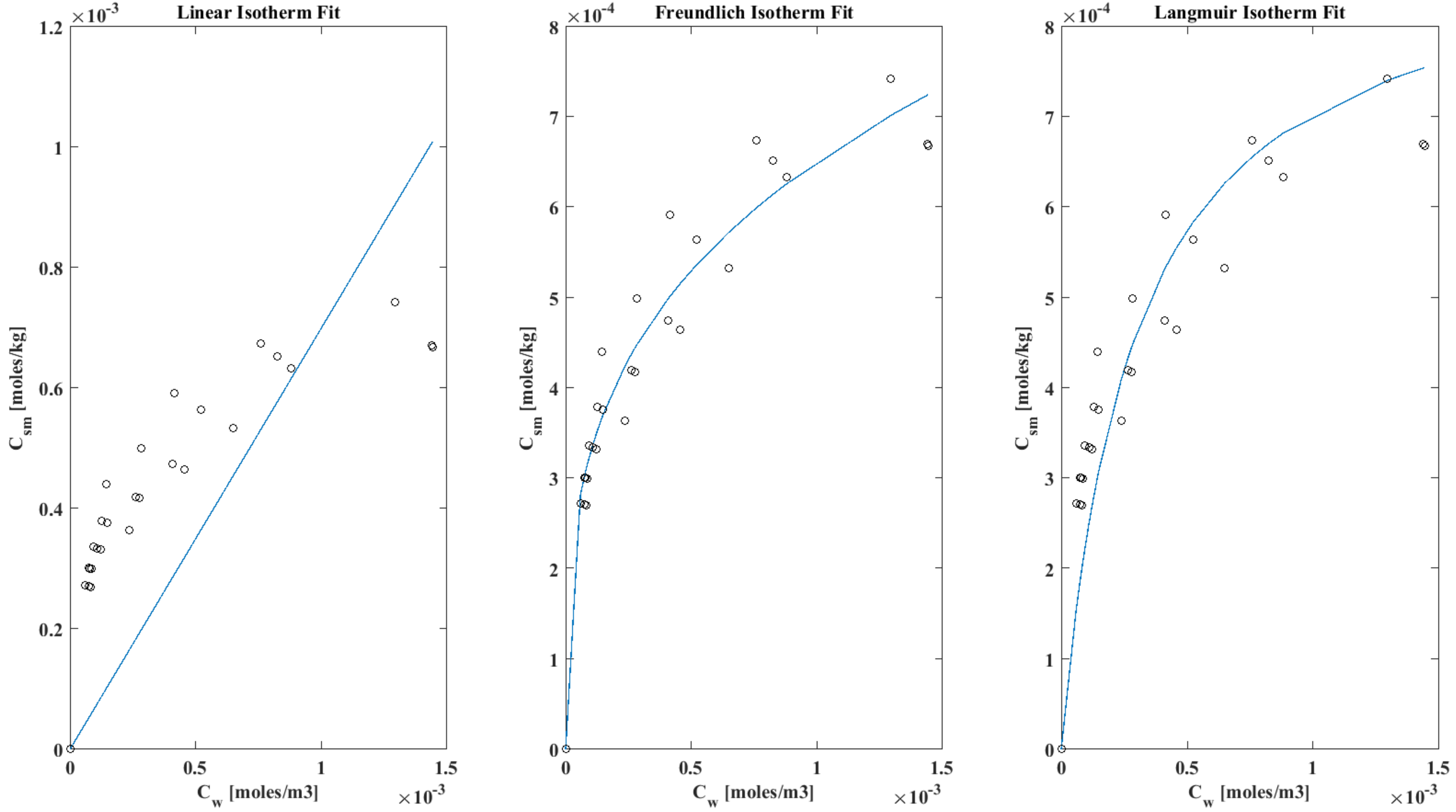

Figure 4-4. Linear, Freundlich and Langmuir isotherm fit for sorption of enrofloxacine onto rice husk biochar

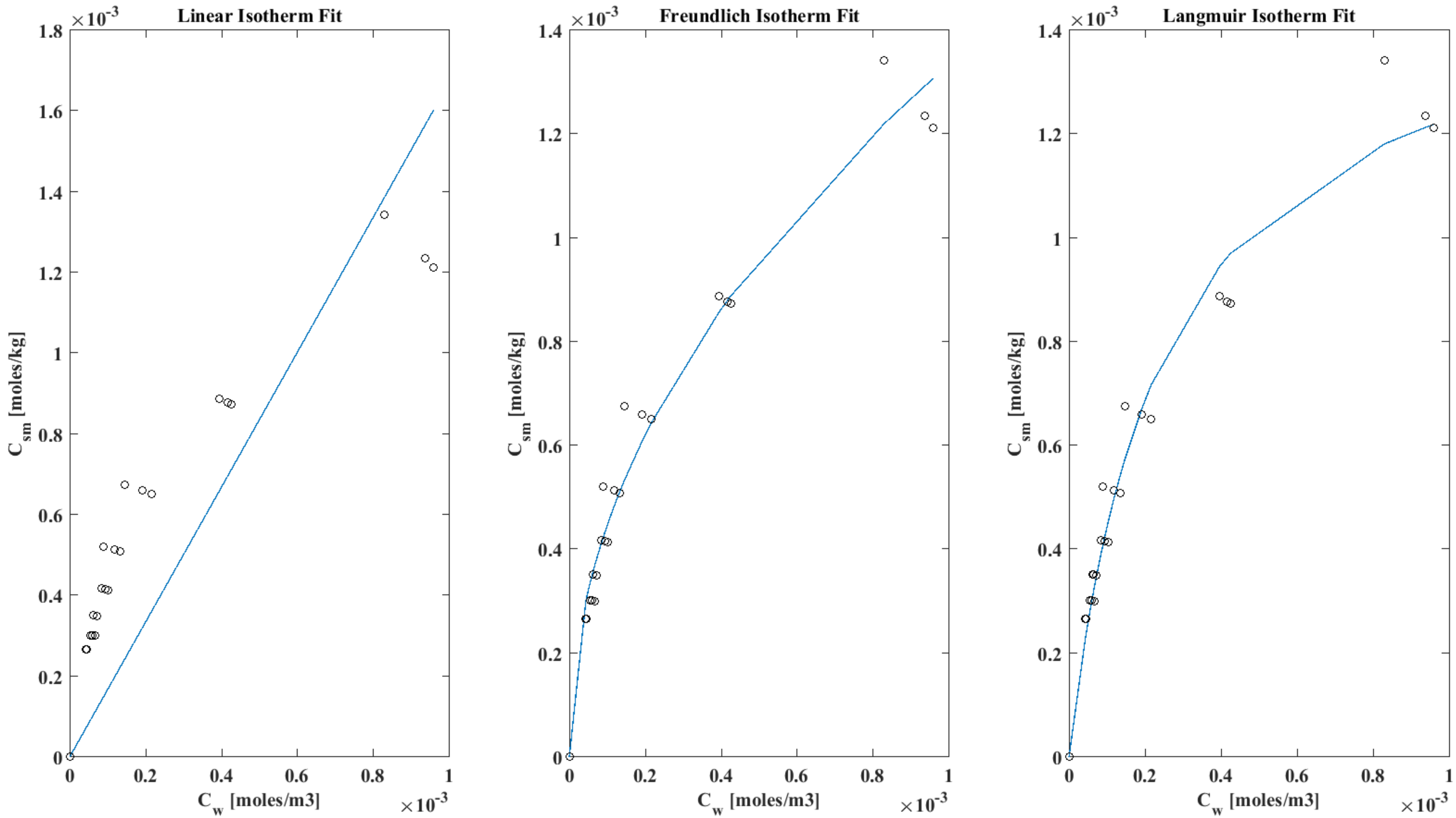

Figure 4-5. Linear, Freundlich and Langmuir isotherm fit for sorption of oxytetracycline onto rice husk biochar

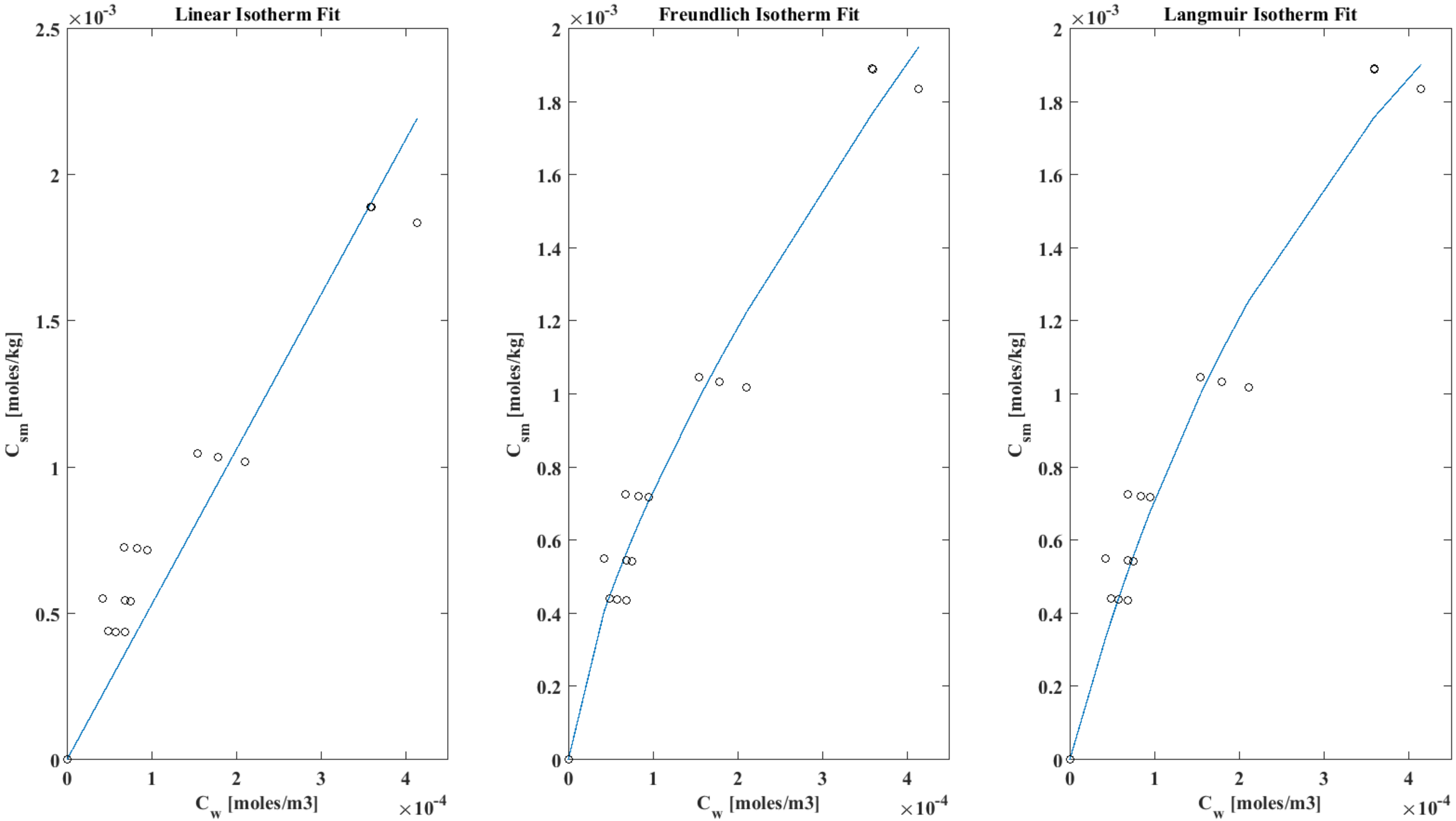

Figure 4-6. Linear, Freundlich and Langmuir isotherm fit for sorption of tetracycline onto rice husk biochar

4.3.3. Biochar amended soil sorption experiment

The results from the previous biochar sorption studies showed that rice husk biochar was the best absorbent for all the agrochemicals. The soils in this study were, therefore amended with rice husk biochar. In the soil sorption studies, the herbicides atrazine and diuron were detectable in the aqueous phase of all soils used in the experiment. As for the antibiotics, enrofloxacine and oxytetracycline were only detectable in the loam and sandy loam soils, while tetracycline was only detectable in the sandy loam soil. In the biochar sorption studies, all of the agrochemicals were detectable in the aqueous phase of all biochars used in the experiment. For this reason, it was necessary to determine the behaviour of all the agrochemicals in a biochar amended soil matrix.

As seen in Table 4-9 below, the antibiotics enrofloxacine, oxytetracycline and tetracycline were non-detectable in the aqueous phase of the biochar amended soil batch microcosm. The antibiotics were non-detectable even at a biochar-soil amendment of 1% (w/w). Although some antibiotics were non-detectable even without biochar amendment, these findings indicated that an amendment of rice husk biochar at 1% (w/w) to soil would be sufficient enough to reduce the risk of antibiotic leaching for those antibiotics that were detectable in the aqueous phase. On the other hand, atrazine was detectable in the aqueous phase of the clay loam and sandy silt loam soils even with 5% (w/w) biochar amendment. However, atrazine was non-detectable in the aqueous phase of the loam and sandy loam soils with 2.5% (w/w) biochar amendment. Diuron, however, was detectable in all of the soils amended with 1% (w/w) biochar but was non-detectable in all of the soils amended with 2.5 and 5% (w/w) biochar amendment (see Appendix B). Furthermore, herbicide absorption was much higher in a biochar-amended soil, even at a minimum soil-biochar amendment of 1% (w/w), as compared to the soil without biochar amendment.

Chemical	Soil	Linear		Freundlich			Langmuir		
		K_d (m^3/kg)	SSR	(moles/kg)(moles/m^3)$^{-1/n}$	1/n	SSR	K_L (m^3/kg)	Csm, max (moles/kg)	SSR
Atrazine	Sandy loam	0.540	3.3e-06	0.0023	0.1	6.6e-07	6.7e+03	0.0013	5.7129e-07
	Sandy silt loam	0.846	9.4e-07	0.0161	0.4	4.3e-08	2.3e+03	0.0016	1.2050e-07
	Clay loam	0.888	1.8e-07	0.1017	0.7	3.3e-08	483.8	0.0031	7.0226e-08
	Loam	1.339	1.2e-06	0.0128	0.3	1.8e-08	2.5e+03	0.0020	2.2488e-07
Diuron	Sandy loam	8.768	0.003	0.0021	0.2	8.5e-05	3.761	2.3317	0.0026
	Sandy silt loam	7.957	4.0e-07	0.0042	0.1	9.5e-09	561.7	0.0162	3.2938e-07
	Clay loam	13.72	1.5e-07	0.0068	0.1	4.8e-09	414.3	0.0351	1.3439e-07
	Loam	16.39	4.3e-07	0.0047	0.1	6.7e-09	588.6	0.0298	3.8024e-07
Enrofloxacine	Sandy loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Sandy silt loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Clay loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Oxytetracycline	Sandy loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Sandy silt loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Clay loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Tetracycline	Sandy loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Sandy silt loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Clay loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Loam	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D

Table 4-9. Linear, Freundlich and Langmuir isotherm model fit for compounds onto rice husk biochar within different soil types. Notes: *= No significant difference; N.D = Non detectable

Similar to the previous experiments, the sorption data best fit with the Freundlich isotherm model. The Freundlich 1/n parameter was much lower than one, meaning that the mobility of these compounds could be much greater at higher concentrations (Site, 2000). Furthermore, biochar amended soil sorption was due to a combination of both biochar and soil sorption mechanisms. However, there are several reasons why atrazine was detected even after 5% (w/w) biochar-soil amendment. Firstly, since all of the antibiotics along with diuron were entirely absorbed by the biochar amended soil at 2.5 and 5% (w/w), there may have been competition between atrazine, diuron and the antibiotics for absorption sites of the biochar amended soil (Graber et al., 2015). This pattern was also seen in the soil and biochar sorption studies. Secondly, since biochar had a higher absorption affinity for the compounds than the soils, the biochar was the dominant absorbent for the compounds. Furthermore, when biochar is mixed with soil, dissolved organic matter from the soil may occupy biochar absorption sites (Ahmad et al., 2014). The dissolved organic matter may act as a coating over the biochar absorption sites, thus blocking the herbicides from binding to the biochar absorption sites. This blocking mechanism also concurred with the results of Cao et al., (2009), where higher dissolved organic matter had reduced atrazine absorption due to pore and absorption site blockage. The atrazine, therefore, had to compete with the antibiotics, diuron and dissolved organic matter for the biochar absorption sites. However, Hale et al., (2015) suggested that the effect of pore blockage could be reduced over time as the compounds could diffuse through the deposits of the dissolved organic matter and onto the absorption sites.

4.3.4. Sorption kinetics experiments

Sorption kinetics of pesticides varies amongst soil types. Thus, the sorption kinetics of atrazine and diuron varied amongst the biochar amended soils. As observed in Figure 4-7 to Figure 4-10, atrazine absorption was fast in the first 6 hours before reaching equilibrium at 24 hours. Fast absorption also occurred for diuron. Inoue et al. (2004) suggest that atrazine and diuron absorption happened at a fast, followed by a slow phase, which was related to the availability of absorption sites and the ability for the herbicides to reach to the absorption sites. As discussed in the biochar amended soil sorption experiments, the main factors that influenced herbicide absorption were the organic matter and clay content of the soil (Kookana, Baskaran, & Naidu, 1998; Weber et al., 2004) and the ash content (Graber & Kookana, 2015) of the biochar. Herbicides, therefore, competed for sorption sites located on the organic matter, clay and ash content of the biochar-amended soil. The Freundlich isotherm showed that in the first 6 hours of atrazine absorption to the biochar-amended soils, atrazine absorption did not reach higher than 1.5 m^3/kg (see Figure 4-7 to Figure 4-10). Even at 24 hours, atrazine concentration remained detectable in the aqueous phase of the biochar amended soil batch microcosm. Unlike atrazine, diuron had a higher absorption of 5 m^3/kg for clay loam and loam and 10 m^3/kg for sandy silt loam in the first 6 hours. For the clay loam and loam soils, diuron absorption was the same at 6 hours as it was 24 hours (Figure 4-7 to Figure 4-10). However, for the sandy silt loam and sandy loam soils, diuron was non-detectable at 24 hours. As discussed in the sorption studies, sorption was described as non-linear, meaning that absorption processes depended on site-specific interactions. These observations clearly showed that diuron and atrazine were in competition between each other and the antibiotics for sorption sites in the biochar amended soil matrix. In addition, other studies have shown that atrazine has a low K_{oc} of 100 as compared to diuron with a K_{oc} of 680 (see Table 4-1), meaning that atrazine is less absorbed than diuron in the organic matter of the soil. Other studies have also shown the competitive nature of atrazine and other organic compounds for sorption sites (Xing et al., 1996). Diuron had higher sorption to the biochar-amended soils than atrazine. These results suggest that atrazine has a higher tendency to leach in soil than diuron. The next section will explain the leaching behaviour of atrazine and diuron in column leaching experiments.

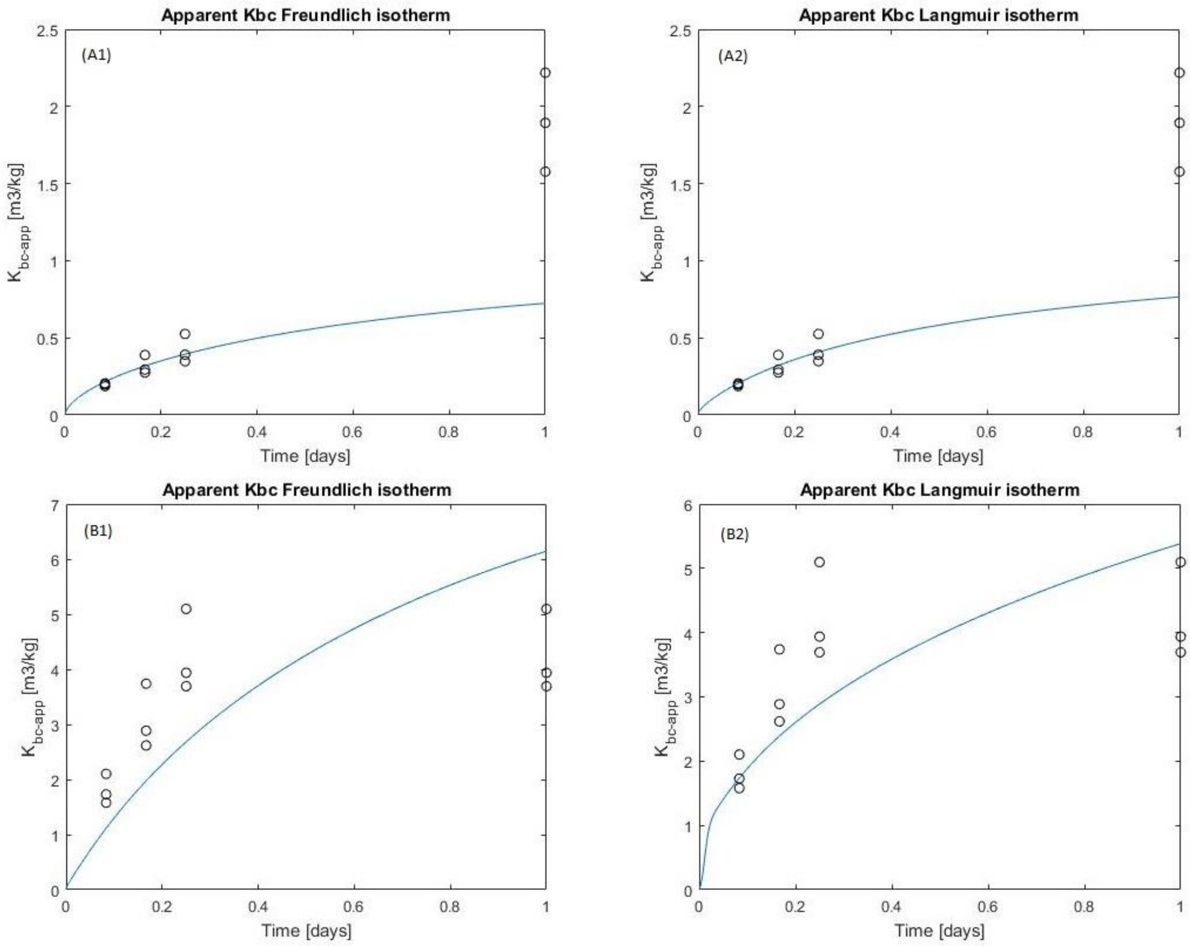

Figure 4-7. Freundlich and Langmuir isotherm absorption kinetics of atrazine (A1 and A2) and diuron (B1 and B2) in a clay loam soil amended with rice husk biochar

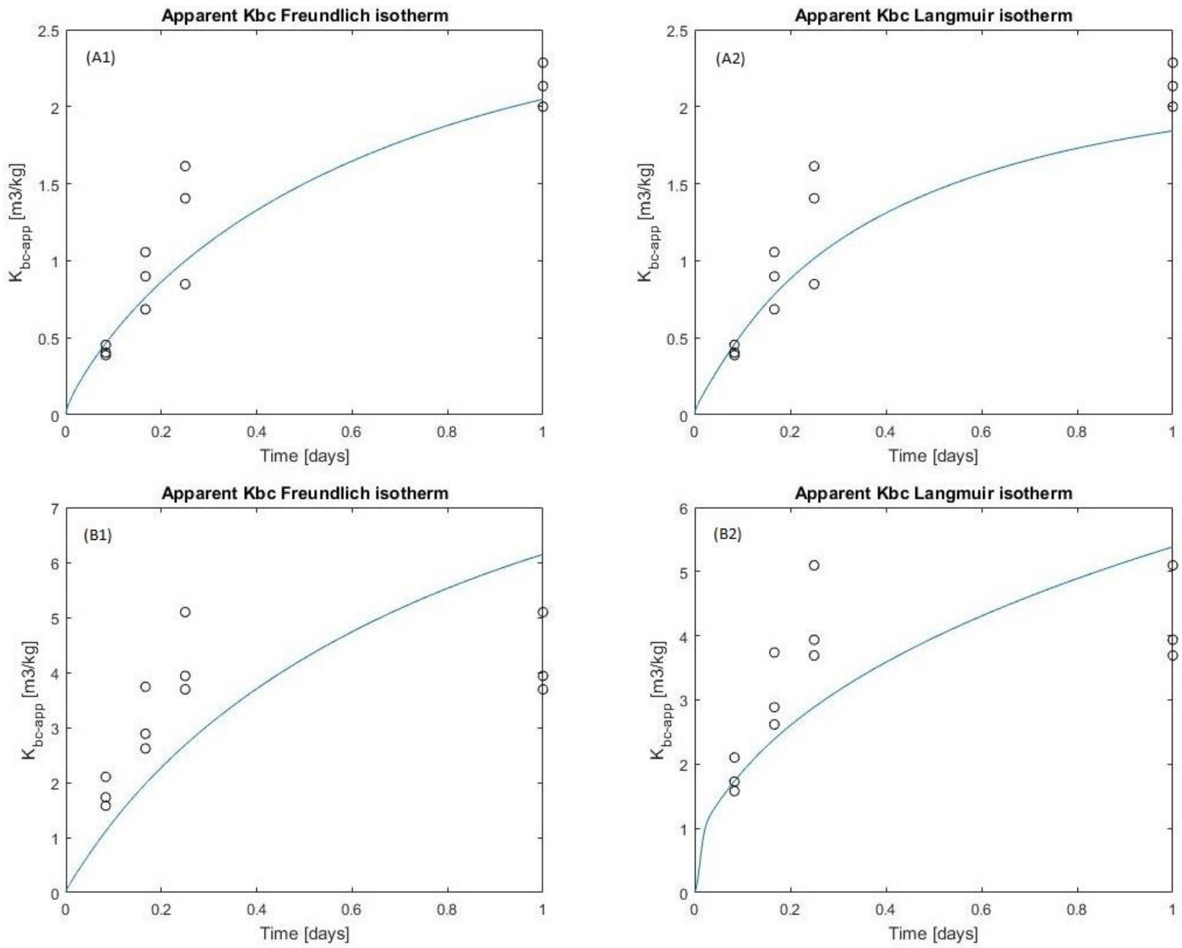

Figure 4-8. Freundlich and Langmuir isotherm absorption kinetics of atrazine (A1 and A2) and diuron (B1 and B2) in a loam soil amended with rice husk biochar

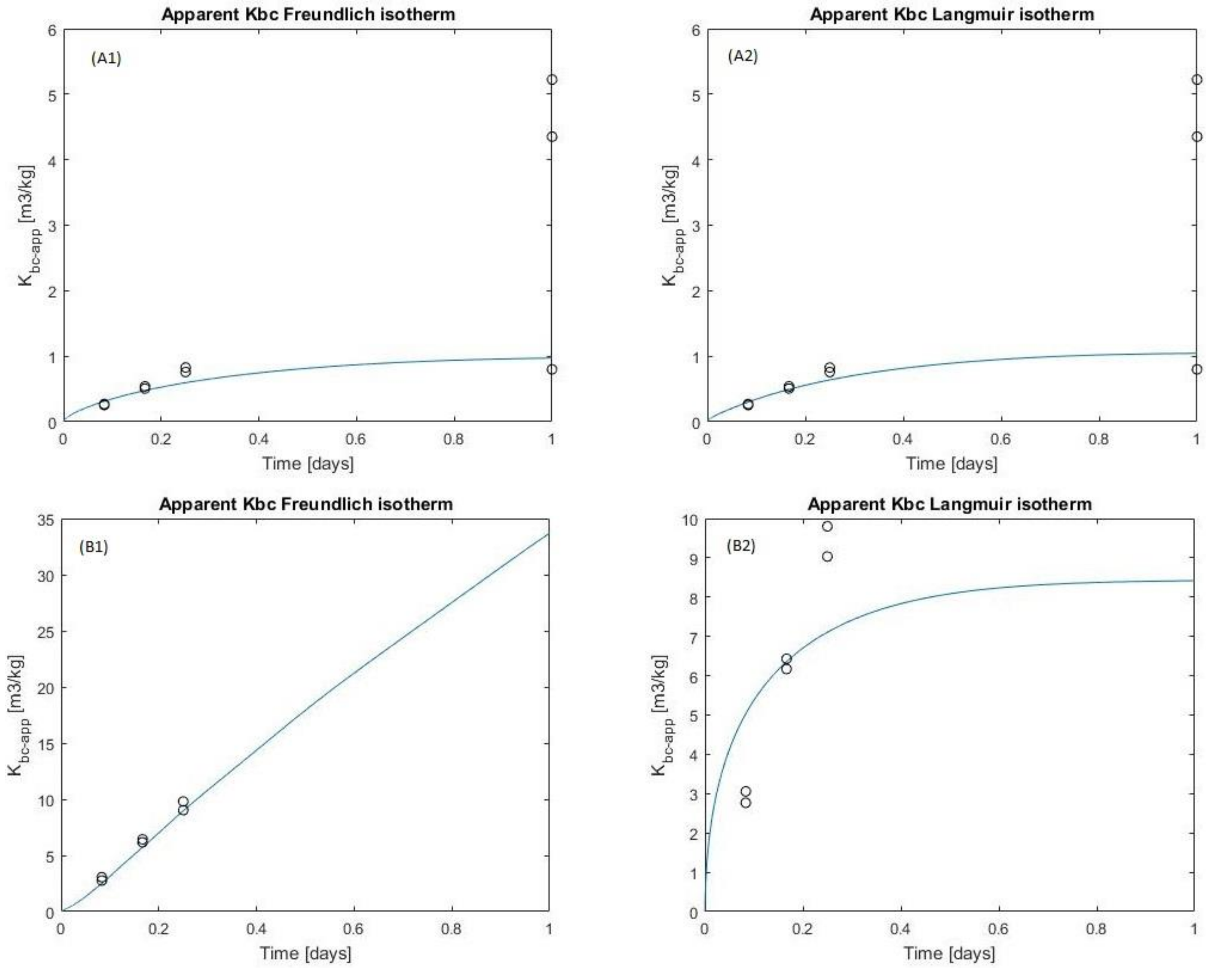

Figure 4-9. Freundlich and Langmuir isotherm absorption kinetics of atrazine (A1 and A2) and diuron (B1 and B2) in a sandy silt loam soil amended with rice husk biochar

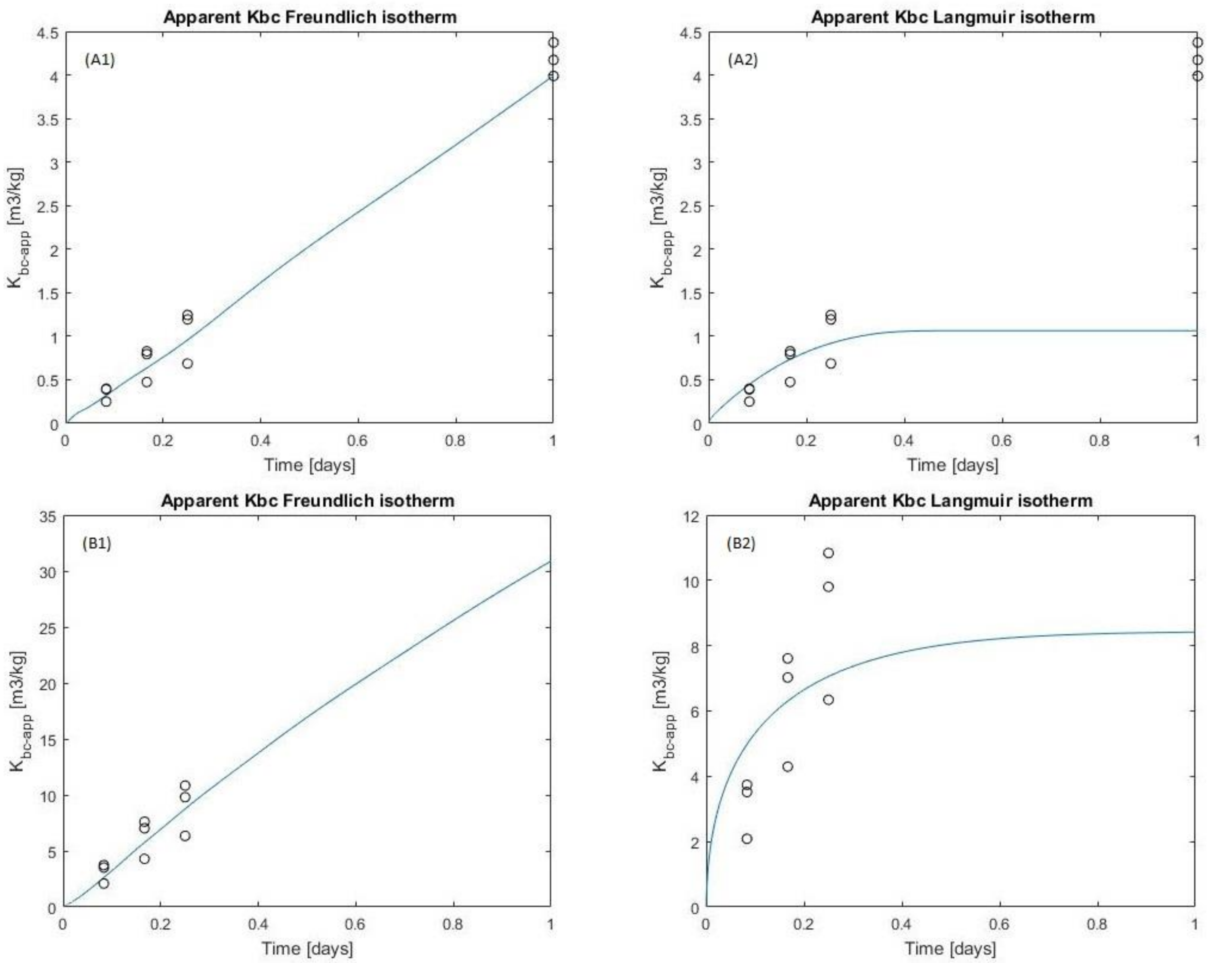

Figure 4-10. Freundlich and Langmuir isotherm absorption kinetics of atrazine (A1 and A2) and diuron (B1 and B2) in a sandy loam soil amended with rice husk biochar

4.3.5. Column leaching experiments

The column leaching experiments showed that the addition of biochar to soil could reduce herbicide leaching. The leaching of atrazine was reduced in the effluents of the biochar-amended loam as compared to the loam without biochar amendment. The leaching of atrazine was also reduced in the effluents of the biochar amended sandy silt loam as compared to the sandy silt loam without biochar amendment. The leaching of diuron was not detected in the biochar-amended loam and the loam without biochar amendment, indicating that the addition of biochar to loam soil was not needed for reducing the leaching of diuron. However, the leaching of diuron was detected in the effluents of the sandy silt loam without biochar amendment but was reduced with biochar amendment. As for the clay loam soil, the water did not leach through the clay loam column with and without biochar amendment. Therefore, no leaching analysis was further conducted for this soil type. However, because water did not leach through the clay loam soil, the leaching of atrazine and diuron in clay loam would not be a problem for groundwater leaching. However, the stagnant water containing atrazine and diuron could be a problem for surface water runoff. The following data compare the leaching of the herbicides in soils with and without biochar amendment. The data also compare the effects of herbicide biodegradation in soils with and without biochar amendment.

The lag time of the model-predicted data of atrazine in loam soil without biochar was much shorter than the experimental data (Figure 4-11 (A1) and (A2)). However, the lag time of the modelled data for atrazine in loam soil with biochar fitted with the experimental data (Figure 4-11 (B1) and (B2)). It was observed that atrazine had a faster breakthrough in loam without biochar amendment as compared to loam with biochar amendment. The effluents of the loam without biochar contained higher concentrations of atrazine as compared to biochar-amended loam, showing that biochar amended loam was able to reduce the leaching of atrazine. As observed in Figure 4-11, the experimental data fit well with the modelled data that considered biodegradation. Figure 4-11 (A1) and (A2) showed that as the breakthrough of atrazine in loam without biochar occurred, it was observed that the atrazine leaching was reduced between 520 to 650 hours. However, after 650 hours, the leaching of atrazine resumed. This phenomenon may have occurred due to atrazine biodegradation by the microbial population in the soil (Bushnaf et al., 2017). Between 520 to 650 hours, biodegradation occurred because the microbial population was high. After 650 hours, the leaching of atrazine resumed because the microbial population started to decrease. As for the atrazine in the biochar-amended loam Figure 4-11 (B1) and (B2), the leaching of atrazine occurred at low concentrations and leaching did not resume once the breakthrough occurred. These results indicated that the application of biochar reduced the leaching of atrazine due to the presence of biochar. Firstly, biochar reduced leaching by absorbing the atrazine. Secondly, the presence of biochar in soil may have stimulated microbial growth, therefore increasing the biodegradation of atrazine in the soil (Qiu et al., 2009; Zhang et al., 2005; Jablonowski et al., 2013). However, some biodegradation uncertainties must be considered since neither the microbial population nor the nutrient concentrations in the soil supplied by biochar were measured.

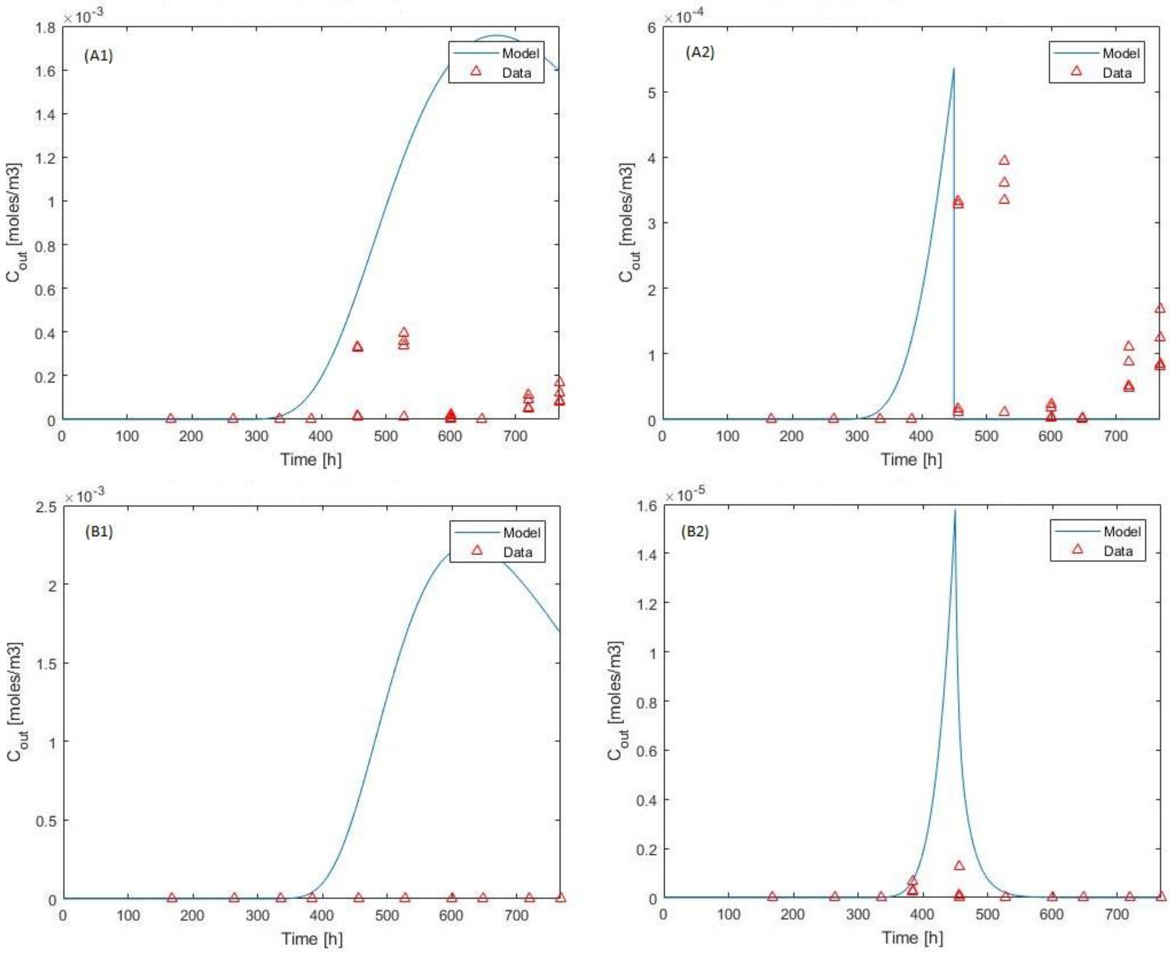

Figure 4-11. Linear isotherm breakthrough curve for atrazine in a loam soil without biochar (A1 and A2) and in loam soil with biochar (B1 and B2). Atrazine in loam soil without biodegradation is shown in (A1) and with biodegradation is shown in (A2). Atrazine in biochar amended loam soil without biodegradation is shown in (B1) and with biodegradation in (B2)

Atrazine in a sandy silt loam soil without biochar behaved differently when compared to atrazine in the loam soil without biochar. In Figure 4-12 (A1 and A2), the experimental data fitted well with the modelled data. As observed in Figure 4-12 (A1 and A2), the breakthrough of atrazine was not completed within the time of the experiment for the sandy silt loam soil without biochar amendment. Atrazine biodegradation was also not observed in the sandy silt loam. These results suggested that that leaching of atrazine would continue even after 700 hrs in the sandy silt loam without biochar amendment. These results concurred with the results found in the batch sorption studies. Atrazine could not be absorbed by the sandy silt loam for reasons as previously discussed. However, when the sandy silt loam soil was amended with biochar, no leaching of atrazine had occurred even at 700 hrs (See Figure 4-12 (B1 and B2)), showing that the fate of atrazine in the sandy silt loam soil was greatly influenced by the presence of biochar due to absorption and biodegradation.

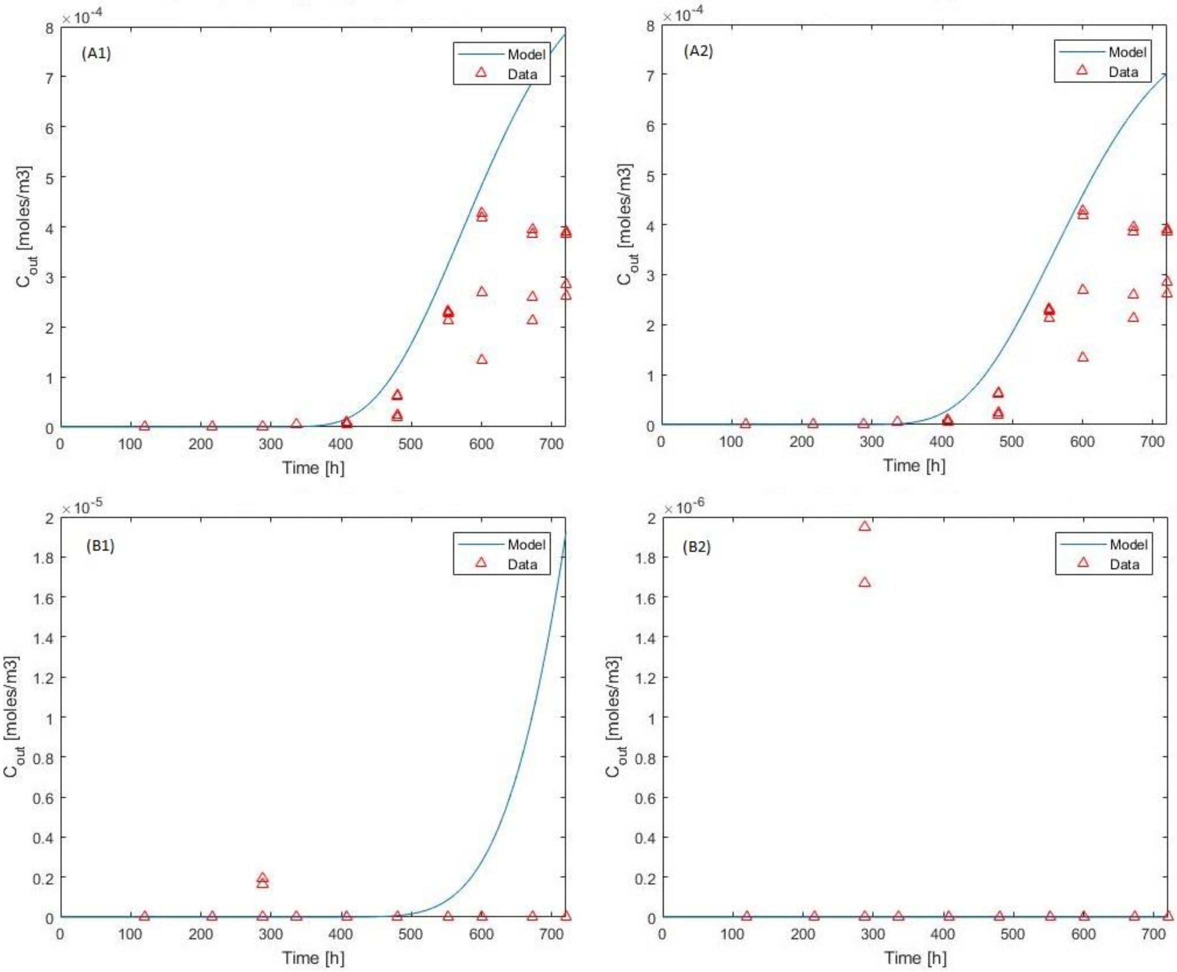

Figure 4-12. Linear isotherm breakthrough curve for atrazine in a sandy silt loam soil without biochar (A1 and A2) and in biochar amended sandy silt loam soil (B1 and B2). Atrazine in sandy silt loam soil without biodegradation is shown in (A1) and with biodegradation is shown in (A2). Atrazine in biochar amended sandy silt loam soil without biodegradation is shown in (B1) and with biodegradation in (B2)

We observed that diuron did not leach in either the loam soil without the biochar amendment or the loam soil with the biochar amendment (Figure 4-13). These results show that diuron may not be a significant threat to groundwater since there is no leaching occurring and that biochar may not be needed to amend loam soil for the leaching of diuron. However, although the vertical leaching of diuron may not have occurred in the loam soil, there could be a threat of diuron contaminating surface water if no biodegradation had occurred. Further, in this discussion, we discuss the possible biodegradation of diuron in the loam soil.

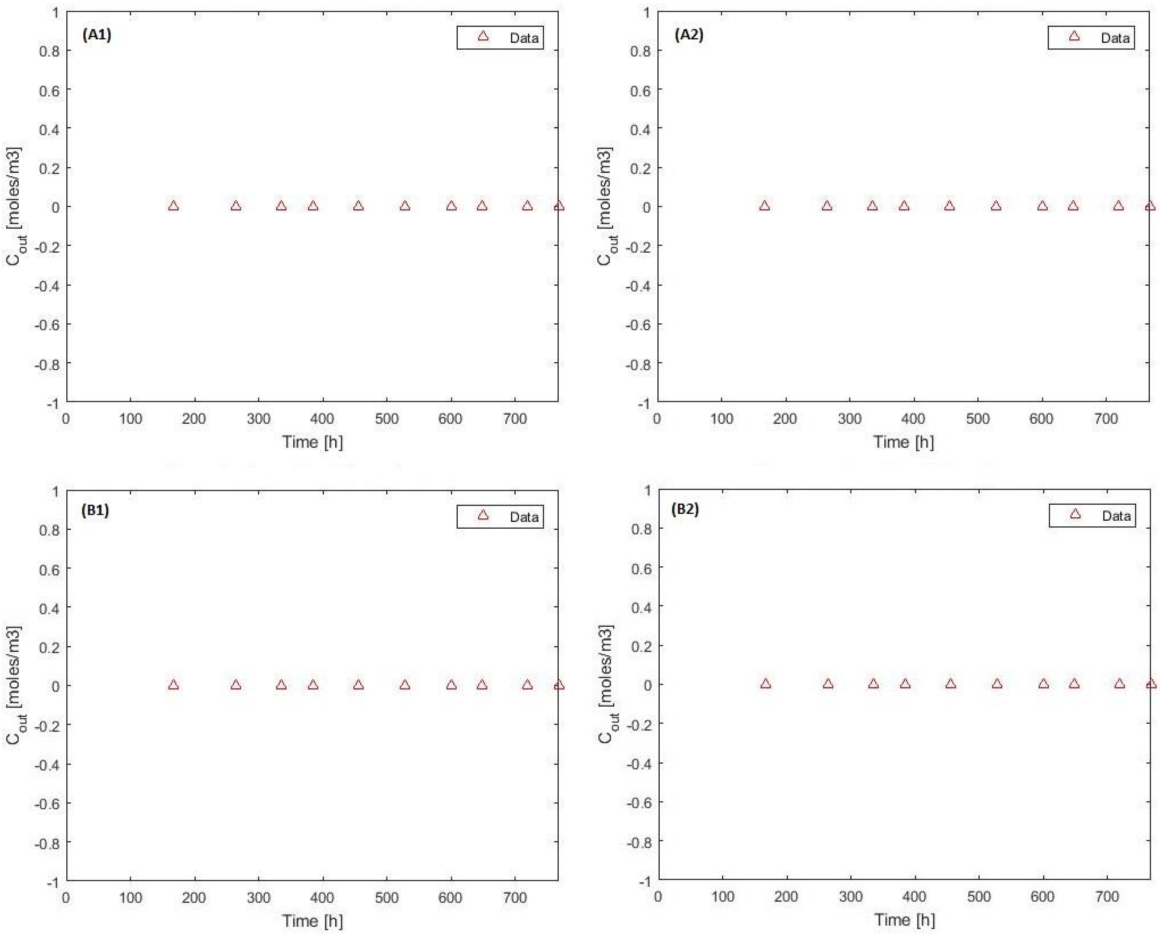

Figure 4-13. Linear isotherm breakthrough curve for diuron in a loam soil without biochar (A1 and A2) and in biochar amended loam soil (B1 and B2). Diuron in loam soil without biodegradation is shown in (A1) and with biodegradation is shown in (A2). Diuron in biochar amended loam soil without biodegradation is shown in (B1) and with biodegradation in (B2)

The model data shows that without biodegradation, the leaching concentrations of diuron would be much higher as compared to when biodegradation was accounted for. When the modelled data accounted for biodegradation, the lag phase was much shorter and the concentration of leached diuron was much lower. In the sandy silt loam without biochar and sandy silt loam amended with biochar, there was a similar pattern in the measured data. However, the overall leaching of diuron was less in the biochar amended sandy silt loam soil than the sandy silt loam soil without biochar amendment (see Figure 4-14).

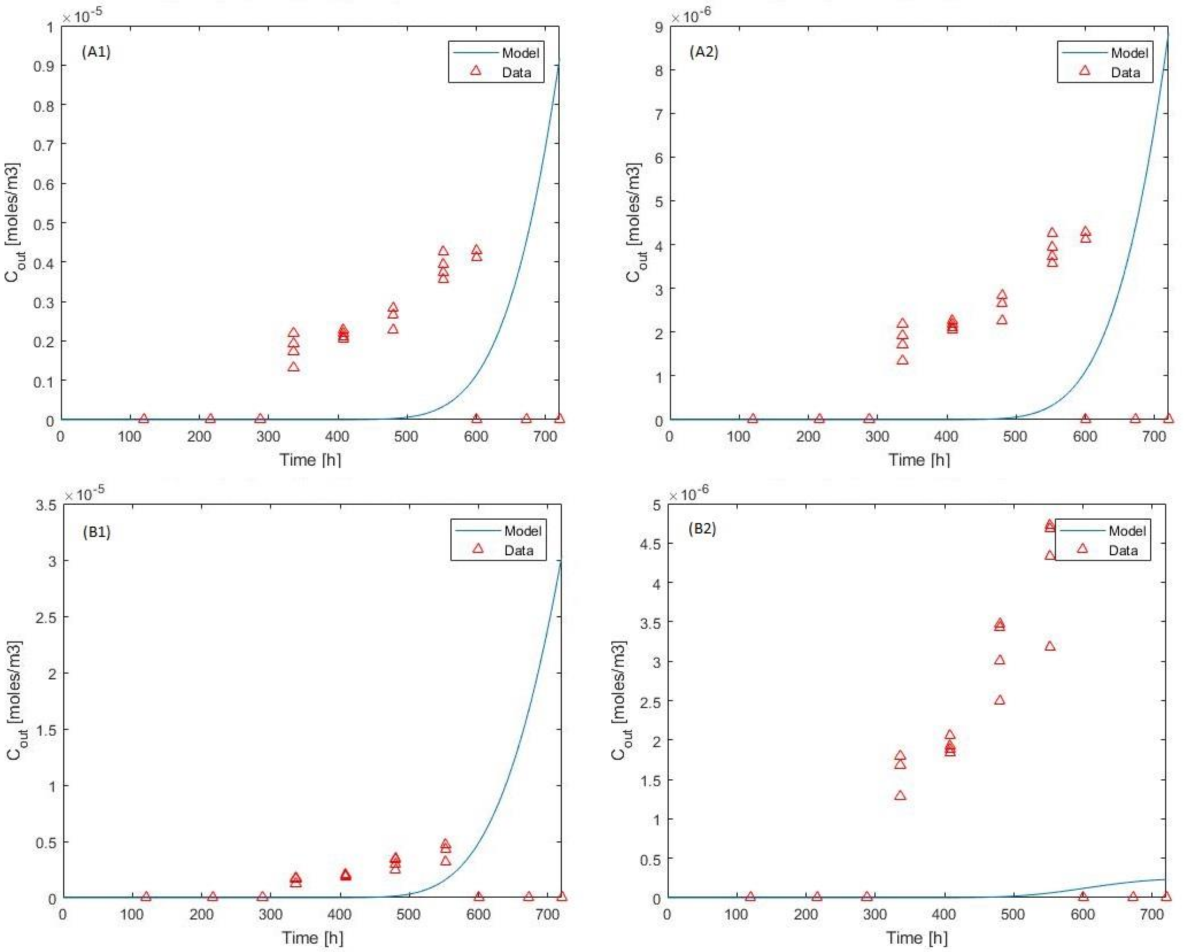

Figure 4-14. Linear isotherm breakthrough curve for diuron in a sandy silt loam soil without biochar (A1 and A2) and in biochar amended sandy silt loam soil (B1 and B2). Diuron in sandy silt loam soil without biodegradation is shown in (A1) and with biodegradation is shown in (A2). Diuron in biochar amended sandy silt loam soil without biodegradation is shown in (B1) and with biodegradation in (B2)

Although the batch sorption experiments showed that biochar-amended sandy silt loam soil proved to be an excellent absorbent for diuron, the batch sorption experiments were conducted for only 24 hours while the column leaching experiments were conducted for 30 days. In Table 4-10 below, the linear K_d of the soil and amended soil mixtures obtained from the batch sorption experiments were compared to the linear K_d of the soil and biochar amended soil mixtures from the soil column leaching experiments. The results showed that the K_d of the batch sorption experiments were much higher than the K_d of the soil column leaching experiments. In the batch sorption experiments, the herbicides had a higher contact time to soil or biochar amended soil mixtures. The soil column leaching experiments were a closer representation of what would occur in an actual environmental scenario, thus catering for preferential flow and other soil hydrological parameters. Table 4-10 shows the K_d comparison between the batch sorption and the soil column leaching experiments.

Soil mixtures	**Batch microcosm linear K_d (m^3/kg)**	**Column leaching linear K_d (m^3/kg)**	
		Soil	*Biochar*
ATR + L	0.0781	0.0045	-
ATR + L + BC	1.3394	0.0045	0.15
ATR + SSL	0.0636	0.008	-
ATR + SSL + BC	0.8455	0.008	0.8
DIU + SSL	0.0000625	0.02	-
DIU + SSL + BC	7.9573	0.02	0.5

Table 4-10. Comparison of linear K_d observed in the batch microcosm and column leaching studies. Note: ATR = atrazine; DIU = diuron; L = loam; SSL = sandy silt loam; BC = biochar

The amount of atrazine and diuron in loam soil and biochar amended loam soil were calculated. The atrazine concentration was much higher in the effluent of the loam soil as compared to the biochar amended loam soil, as seen in Table 4-11. The atrazine mass that remained in the loam soil after irrigation 95.7%. The atrazine mass that has remained in the biochar amended loam soil after irrigation was calculated as 99.7%. These calculations suggested that the biochar amended loam soil retained atrazine more than the loam soil without biochar amendment. Furthermore, the soil analysis concurred that the atrazine mass was less (1.2%) in the loam without biochar than the biochar amended loam soil (12%). Atrazine mass was expected to be less in the loam soil without biochar due to leaching. However, there was a difference between the calculated atrazine concentrations and the atrazine concentrations from the soil analysis. The total unaccounted atrazine mass indicated the possibility of atrazine being biodegraded. Worrall et al., (2001) suggested that although organic matter can absorb pesticides and prevent its leaching, there might be a small risk that the absorbed pesticide may leach later. In this case, however, the pesticides were absorbed, and the presence of biochar may have assisted with the biodegradation process. As previously discussed in the breakthrough curves, there was no evident diuron leaching in the loam and biochar amended loam soil matrices, which implied that biochar would not be needed for reducing the leaching of diuron in the loam soil. Since no leaching of diuron had occurred, it was calculated that the diuron mass in the soil should have remained the same as the pesticide mass initially added to the soil. However, similar to atrazine, there was an amount of unaccounted mass of diuron. The calculated mass of diuron in both the loam and biochar amended loam soil was 100%. However, the soil analysis results indicated that there was only 14.3% of diuron in the loam soil and 8.6% of diuron in the biochar amended loam soil. The unaccounted mass of diuron, similar to atrazine, could be attributed to biodegradation in the soil. These results concur with the previously discussed breakthrough curves.

Mixture	Atrazine					Diuron				
	Pesticide mass in influent (%)	Pesticide mass in effluent (%)	Pesticide mass in soil (calculated) (%)	Pesticide mass in soil (analysis) (%)	Total unaccounted pesticide mass (%)	Pesticide mass in influent (%)	Pesticide mass in effluent (%)	Pesticide mass in soil (calculated) (%)	Pesticide mass in soil (analysis) (%)	Total unaccounted pesticide mass (%)
L + P	100	4.3	95.7	1.2	94.6	100	0	100	14.3	85.7
L + BC + P	100	0.01	99.7	12	87.7	100	0	100	8.6	91.4
L	-	-	-	<0.6	-	-	-	-	<0.3	-

Table 4-11. Soil characteristics and pesticide concentrations of loam soil in top 25 cm of soil column. Note: L = loam; P = pesticide; BC = biochar

4.4. Conclusions

This study determined the effects of rice husk, miscanthus and softwood biochar types upon absorption of atrazine, diuron, enrofloxacine, oxytetracycline and tetracycline. Whilst biochars have been proven to sorb pesticides and pharmaceuticals, sorption varied with biochar, compound and soil type. According to our results, biochars made from miscanthus and softwood did not effectively absorbing these compounds. However, the rice husk biochar was observed to be the best herbicide and antibiotic absorbent. Biochar amended soils had a higher absorption for the antibiotics and herbicides than soils without biochar amendment (2.5% (w/w). Between the herbicides and antibiotics, the antibiotics were most absorbed. The herbicides atrazine and diuron, on the other hand, were least absorbed by the biochar amended soils as compared to the antibiotics. Furthermore, column-leaching studies showed that soils amended with 2.5% (w/w) rice husk biochar, reduced the leaching of both atrazine and diuron. Results also showed that biochar not only aided with the retention of atrazine and diuron, but also was speculated to stimulate biodegradation in the soil matrix. These results suggested that biochar could reduce the leaching of these agrochemicals by absorption and biodegradation.

Chapter 5. Modelling of Pesticide Fate in a Biochar Amended Soil

5.1. Introduction

Although studies have determined the effects of biochar on pesticide fate (Yavari et al., 2015), they have been limited to laboratory and field-based data. Data collection of this type can be time-consuming and costly. Moreover, it is complex to understand the effects of various parameters associated with the fate of pesticides in soil and water. The parameters that influence the fate of a pesticide in the soil are sorption, degradation, plant uptake, volatilization and transport (Queyrel et al., 2016). Pesticide fate models are able to simulate all the necessary parameters that could influence the fate of a pesticide in soil and water. Pesticide fate models vary depending on the developer's representation of the physical processes, programming and intended use. It is essential for the model user to have an in-depth understanding of the model processes to achieve reliable results. Characteristics considered when choosing a model include the availability of data, purpose of the model, parameter estimation and simulation cost. Pesticide fate models have also been used to determine if pesticides comply with environmental regulatory standards. The modelling approach is a cheap and effective method for determining the predicted environmental concentration (PEC) of pesticides in surface and ground waters. Pesticide fate models can vary from simple screening models such as Groundwater Ubiquity Score (GUS) (Pullan et al., 2016) to water transfer models such as PELMO, PRZM and PLM. Other pesticide fate models include PEARL, MACRO and LEACHP (Queyrel et al., 2016).

The EU uses an initiative devised by the European Commission entitled the Forum for the Coordination of Pesticide Fate Models and their Use (FOCUS). The initiative was set up in the late 1990s to develop models to determine the PEC of surface water (PEC_{sw}), groundwater (PEC_{gw}) and soil (PEC_{soil}). These results have been used in EU registration processes for agricultural products under the EU Directive 91/414/EEC framework (Worrall et al., 1998). The EU registration process identified three models that were suitable for the generation of PEC_{gw} for use in regulatory risk assessment. These models were PELMO, PEARL and MACRO. In addition to the models, scenarios were developed based on numerical simulations to represent realistic environmental scenarios. Scenarios were characterized by actual measurements obtained from its respective realistic environmental scenario. The FOCUS groundwater scenarios workgroup developed a set of nine standard scenarios relevant to the potential movement of plant protection products and metabolites to groundwater. The nine standard scenarios collectively represented agriculture in the EU. As selected by FOCUS, these were Sevilla, Porto, Piacenza, Chateaudun, Kremsmunster, Okehampton, Hamburg and

Jokioinen (FOCUS, 2000). These scenarios were developed as input files for FOCUS models such as MACRO, PEARL, PELMO and PRZM.

The scenarios were developed based on several principles (FOCUS, 2000). These included: (1) locations must not exceed ten, (2) realistic combinations of crop, soil, climate and agronomic conditions should be used, (3) scenarios should describe an overall vulnerability approximating the 90th percentile of all possible situations, and (4) the vulnerability should be divided between soil properties and weather. The locations included temperature and rainfall ranges in EU arable agriculture and distributed across the EU with one scenario per member state. Realistic combinations of climatic and soil properties were chosen. Expert judgement selected soil properties to represent the average soil properties in the agricultural region. The representative soils were more vulnerable than the average soil in the region, but not extremely vulnerable as to represent an unrealistic worst-case scenario. Soil vulnerability was defined by chromatographic leaching. As for average rainfall, target values were based on average values of rainfall for each realistic site. These values were used by the weather subgroup to identify appropriate climatic data for a 20-year period. The weather subgroup obtained weather data from the Monitoring Agriculture by Remote Sensing project. Crop parameters were based on the major crops grown in the EU. It must be noted that each scenario is not an equal representation of a specific field in a country in which it represents. The scenarios were developed solely to assist with determining if there exists an ideal and safe scenario where a substance can be used in a region.

The fate of every active substance could be simulated using these standard scenarios and pesticide fate models, fulfilling a standardised Tier 1 assessment of leaching potential. In the EU, the Commission Regulation (EU) No 576/2011 states that no authorisation shall be granted if the concentration of active substances or relevant metabolites in groundwater may be expected to exceed the lower value of 0.1 µg/L. In addition, the Sanco/221/2000 specific guidance document was devised to consider the relevance of metabolites in groundwater. The guidance document states that if metabolites are considered as non-relevant, values of 0.75 µg/L and 10 µg/L apply (FOCUS, 2014). The FOCUS group has provided recommendations for interpreting groundwater scenario results. FOCUS states that if substances exceed 0.1 µg/L in all relevant scenarios, then its inclusion is not possible unless higher tier data is provided. If the substance is less than 0.1 µg/L for all relevant scenarios, then the choice of a realistic worst-case definition gives confidence that the substance is safe to use in a majority of situations in the EU. The scenarios that have given results of less than 0.1 µg/L along with results of existing higher tier studies (such as lysimeter or field leaching studies) help to determine if the substance is safe for use.

These models have been accepted as reliable environmental risk assessment tools. However, they may not consider pesticide mitigation strategies such as applying biochar to a soil top layer. In the PEARL groundwater model, biochar and its effects on soil properties and pesticide fate can be manually incorporated in a scenario. Parameters such as organic carbon, bulk density, texture, hydraulic properties and sorption capacities can be modified when applying biochar to the simulated soil of PEARL, thus changing the result of the PEC_{gw}. The aims of this study were to (1) investigate the effects of biochar associated soil parameters on PEC_{gw}, (2) conduct a sensitivity analysis to examine the different components of biochar and their effects on PEC_{gw}, (3) investigate the effects of differences in substance physicochemical characteristics and biochar mitigation performance.

5.2. Methodology

5.2.1. Model description

The Pesticide Emission Assessment at Regional and Local Scales (PEARL) is a one-dimensional numerical model used at the European Union level for environmental risk assessment and registration (Marín-Benito et al., 2018; FOCUS, 2014). PEARL simulates water flow by using Richard's equation and solute transport by the convection-dispersion equation (Pesticide Fate Processes in chapter 2). PEARL is also able to model the upward flow of water and solutes within the soil. Heat flow is based on the Fourier's law, whilst thermal properties depend on porosity and soil water content, thus depicted as a function of soil depth and time (Marín-Benito *et al.*, 2018). PEARL is also based on the Freundlich sorption model, transformation rate and passive plant uptake rate of the pesticide. For this work, we used the PEARL 4.4.4 version.

5.2.2. Laboratory experiments

To determine the particle size of rice husk biochar 50 g of the unground material was sieved into five sizes: 2000, 1000, 600, 106 and 53 µm. The particle sizes were grouped and classified as sand, silt or clay. Rice-husk biochar particle size resembled a soil texture of 97.6% sand and 2.4% silt, a pH of 9.81 and a bulk density of 120 kg m^{-3}. However, due to the Rosetta pedotransfer function (Pesticide Fate Processes in chapter 2). For estimating soil water retention and hydraulic conductivity, a minimum bulk density of 480 kg m^{-3} was used. These biochar parameters were collected to simulate a biochar layer in PEARL. The biochar absorption parameter used in PEARL was obtained from laboratory experiments (see Chapter 4). The pesticide absorption parameter was essential for determining the effects of biochar effects on pesticide fate in the soil.

5.2.3. The input of pesticide parameters

PEARL was parameterized with pesticide-specific data. Parameters that were not obtained from the laboratory experiments were gathered from published literature, pedotransfer functions, and default values according to the model's user manual. The three herbicides used in the modelling study were atrazine, diuron and glyphosate. Three herbicides were used in this study. The input parameters for each substance were obtained from default FOCUS parameters, the European Food Safety Authority and the Pesticide Properties Database from the University of Hertfordshire. Table 5-1 shows several input parameters used for atrazine, diuron and glyphosate in PEARL. Further detail of other input parameters can be seen in Appendix C.

Parameter	Substance			Data source/remarks
	Atrazine	Diuron	Glyphosate	
Physico-Chemical				
Molecular weight (g mol^{-1})	215.68	233.1	169.1	Lewis et al., 2016
Water solubility (mg L^{-1})	35 at 20 °C	20.8 mg/L at 20°C	10500 at 20 °C	Lewis et al., 2016
Vapour pressure (Pa)	3.9 x 10^{-5} at 20°C	5.98 x 10^{-7} at 20°C	1.31 x 10^{-5} at 20°C	Lewis et al., 2016
Degradation in soil				
DT_{50} soil (d)	75	146.6	15	Lewis et al., 2016
Sorption to soil				
$Kf_{,oc}$ (mL g^{-1})	100	757	16331	Lewis et al., 2016
$Kf_{,om}$ (mL g^{-1})	58	394.43	9472.7	K_{OC} / 1.724
Freundlich exponent 1/n (-)	1.07	0.89	0.86	Lewis et al., 2016
Sorption to biochar				
K_f (L kg^{-1})	5.1	-	-	Measured in laboratory experiments
Freundlich sorption exponent (-)	0.9	-	-	Measured in laboratory experiments

Table 5-1. Several input parameters for different substances used in PEARL

5.2.4. Description of control scenarios

The two scenarios, Sevilla and Thiva, were used as control scenarios to determine the fate of atrazine, glyphosate and diuron in different simulations. The parameters used to create the control Sevilla, and Thiva scenarios remained as initially established by the FOCUS working group and updated as part of EFSA's (2009/2011) review. PEARL simulated PEC_{gw} down to 1-meter depth. Sevilla and Thiva were specifically chosen since their scenario description including rainfall, crops grown, and soil texture were similar to the realistic scenarios from which the soils analysed in the laboratory experiments were collected. A brief description of Sevilla and Thiva scenarios are seen in Table 5-2.

Scenario	Mean annual rainfall (mm)	Organic matter (%)	Texture (USDA)	Crops
Sevilla	493	1.6	Silt Loam	Apples, grass, potatoes, sugar beets, winter cereals, cabbage, citrus, cotton, maize, strawberries, sunflower, tomatoes, vines
Thiva	500	1.3	Loam	Apples, grass, potatoes, sugar beets, winter cereals, beans, cabbage, carrots, citrus, cotton, maize, onions, tobacco, tomatoes, vines

Table 5-2. Description of Sevilla and Thiva used as control scenarios

The herbicides atrazine, diuron and glyphosate were applied to both Sevilla and Thiva. Atrazine is used pre- and post-emergence to control broad-leaved weeds and grasses. Diuron is a pre-emergence herbicide that controls weeds and mosses. Glyphosate is a broad-spectrum herbicide used for broad-spectrum control of weeds and grasses. Application rates of atrazine, diuron and glyphosate were 1.13, 2.0 and 0.51 kg ha^{-1} respectively. A description of the simulated herbicide application is seen in Table 5-3.

Substance	Scenario	Crop	Treatment number	Application rate (g/ha)	First application dates	Data sources
Atrazine	Sevilla Thiva	Maize	1	1130	14 days before emergence	(Hamill and Zhang, 1997)
Diuron	Sevilla Thiva	Maize	1	2000	14 days before emergence	(EFSA, 2005)
Glyphosate	Sevilla Thiva	Maize	1	510	14 days before emergence	(EFSA, 2015)

Table 5-3. Description of crop management and herbicide use in different scenarios

5.2.5. Description of variable scenarios

Control scenarios were modified, and variable scenarios were created to determine the effects of biochar on the PEC_{gw} of atrazine, diuron and glyphosate in PEARL. The PEC_{gw} results of the control scenarios were then compared to the PEC_{gw} of the variable scenarios. The difference between a control and variable scenario was the modification of input parameters. Parameters were modified with guidance obtained from the PEARL user manual. Parameters that were modified included changes in bulk density, organic matter, and thickness of horizon and absorption of pesticides. Each parameter was individually modified to investigate the sensitivity of the PEC_{gw} to each change. When a parameter was modified, the soil hydraulic parameters such as van Genuchten water retention parameters and saturated hydraulic conductivity were simultaneously modified. The hydraulic parameters were estimated using the Rosetta pedotransfer functions (Schaap et al., 2001).

The first modified parameter was the dry bulk density of the first horizon in the soil profile of each scenario. Each dry bulk density modification represented one pesticide fate simulation. Five different dry bulk density simulations were used to investigate the effect of dry bulk density on PEC_{gw} (see Table 5-4). There was an 8.5% difference in dry bulk density for each simulation. These bulk densities were selected based on the range of bulk density that affects the root growth of maize in silt loam and loam soil types (Daddow & Warrington, 1983). Other parameters such as the thickness of horizon, soil type, fraction mineral parts, mass fraction of organic matter and pH remained the same as control.

Simulation ID	**The thickness of Horizon (m)**	**Soil type**	**Fraction mineral parts (kg kg^{-1})**			**Mass fraction of organic matter (kg kg^{-1})**	**pH-H_2O**	**Dry bulk density (kg m^{-3})**
			Sand	Silt	Clay			
Sevilla								
Control	0.1	Silt loam	0.35	0.51	0.14	0.016	7.3	1210
SBD1	0.1	Silt loam	0.35	0.51	0.14	0.016	7.3	1107
SBD2	0.1	Silt loam	0.35	0.51	0.14	0.016	7.3	1313
SBD3	0.1	Silt loam	0.35	0.51	0.14	0.016	7.3	1416
SBD4	0.1	Silt loam	0.35	0.51	0.14	0.016	7.3	1519
SBD5	0.1	Silt loam	0.35	0.51	0.14	0.016	7.3	1622
Thiva								
Control	0.3	Loam	0.319	0.428	0.253	0.0128	7.7	1420
TBD1	0.3	Loam	0.319	0.428	0.253	0.0128	7.7	1299.3
TBD2	0.3	Loam	0.319	0.428	0.253	0.0128	7.7	1540.7
TBD3	0.3	Loam	0.319	0.428	0.253	0.0128	7.7	1661.4
TBD4	0.3	Loam	0.319	0.428	0.253	0.0128	7.7	1782.1
TBD5	0.3	Loam	0.319	0.428	0.253	0.0128	7.7	1902.8

Table 5-4. Modification of dry bulk density in Sevilla and Thiva scenarios. N.B.: S = Sevilla; T = Thiva; BD = Bulk density; C = Control

The second modified parameter was the organic matter of the first horizon in the soil profile of each scenario. Each organic matter represented one pesticide fate simulation. Five different mass fraction of organic matter simulations were used to investigate its effect on PEC_{gw} (see Table 5-5). There was a factor difference of 0.0125 kg kg^{-1} in the mass fraction of organic matter for each simulation. The factor difference was related to the effects of biochar on organic matter in the soil (Nath, 2014; Gamage et al., 2016). The thickness of horizon, soil type, fraction mineral parts, dry bulk density and pH remained the same as control.

Simulation ID	**The thickness of Horizon (m)**	**Soil type**	**Fraction mineral parts (kg kg^{-1})**			**Mass fraction of organic matter (kg kg^{-1})**	**pH-H_2O**	**Dry bulk density (kg m^{-3})**
			Sand	Silt	Clay			
Sevilla								
Control	0.1	Silt loam	0.35	0.51	0.14	0.016	7.3	1210
SOM1	0.1	Silt loam	0.35	0.51	0.14	0.0035	7.3	1210
SOM2	0.1	Silt loam	0.35	0.51	0.14	0.0285	7.3	1210
SOM3	0.1	Silt loam	0.35	0.51	0.14	0.0410	7.3	1210
SOM4	0.1	Silt loam	0.35	0.51	0.14	0.0535	7.3	1210
SOM5	0.1	Silt loam	0.35	0.51	0.14	0.0660	7.3	1210
Thiva								
Control	0.3	Loam	0.319	0.428	0.253	0.0128	7.7	1420
TOM1	0.3	Loam	0.319	0.428	0.253	0.0028	7.7	1420
TOM2	0.3	Loam	0.319	0.428	0.253	0.0228	7.7	1420
TOM3	0.3	Loam	0.319	0.428	0.253	0.0328	7.7	1420
TOM4	0.3	Loam	0.319	0.428	0.253	0.0428	7.7	1420
TOM5	0.3	Loam	0.319	0.428	0.253	0.0528	7.7	1420

Table 5-5. Modification of mass fraction of organic matter in Sevilla and Thiva scenarios. N.B.: S = Sevilla; T = Thiva; OM = Organic matter; C = Control

The effect of thickness of the first horizon on PEC_{gw} first had to be simulated before determining the effects of the thickness of horizon of a biochar-amended soil on PEC_{gw}. Table 5-6 below shows the modification of thickness of the horizon of the first horizon for the two scenarios.

Simulation ID	The thickness of Horizon (m)	Soil type	Fraction mineral parts (kg kg^{-1})			Mass fraction of organic matter (kg kg^{-1})	pH-H_2O	Dry bulk density (kg m^{-3})
			Sand	Silt	Clay			
Sevilla								
Control	0.1	Silt loam	0.35	0.51	0.14	0.016	7.3	1210
SDC1	0.2	Silt loam	0.35	0.51	0.14	0.016	7.3	1210
SDC2	0.3	Silt loam	0.35	0.51	0.14	0.016	7.3	1210
SDC3	0.4	Silt loam	0.35	0.51	0.14	0.016	7.3	1210
Thiva								
Control	0.3	Loam	0.319	0.428	0.253	0.0128	7.7	1420
TDC1	0.1	Loam	0.319	0.428	0.253	0.0128	7.7	1420
TDC2	0.2	Loam	0.319	0.428	0.253	0.0128	7.7	1420
TDC3	0.4	Loam	0.319	0.428	0.253	0.0128	7.7	1420

Table 5-6. Modification of mass fraction of organic matter in Sevilla and Thiva scenarios. N.B.: S = Sevilla; T = Thiva; D = Depth; C = Control

After determining the effects of the thickness of the horizon on PEC_{gw} for each scenario, the effects of biochar amended soil was simulated. Simulations were created based on the realistic effects of biochar on soil and pesticide to determine the effects of biochar amended soil on the PEC_{gw}. Biochar effects on soil and pesticide included changes in dry bulk density, organic matter and pesticide absorption (Gamage et al., 2016). These changes were based on the effects of rice husk biochar on the bulk density of the soil (Gamage et al., 2016). The thickness of the horizon of biochar-amended soil was simulated to determine the practicality of amending soils with biochar with regard to depth (see Table 5-7). Each simulation was created to simulate the effects of biochar amended soil depth on PEC_{gw}.

Simulation ID	The thickness of Horizon (m)	Soil type	Fraction mineral parts (kg kg^{-1})			Mass fraction of organic matter (kg kg^{-1})	pH-H_2O	Dry bulk density (kg m^{-3})
			Sand	Silt	Clay			
Sevilla								
Control	0.1	Silt loam	0.35	0.51	0.14	0.016	7.3	1210
SLD1	0.1	Silt loam	0.35	0.51	0.14	0.0285	7.3	1107
SLD2	0.2	Silt loam	0.35	0.51	0.14	0.0285	7.3	1107
SLD3	0.3	Silt loam	0.35	0.51	0.14	0.0285	7.3	1107
SLD4	0.4	Silt loam	0.35	0.51	0.14	0.0285	7.3	1107
SLD5	0.5	Silt loam	0.35	0.51	0.14	0.0285	7.3	1107
Thiva								
Control	0.3	Loam	0.319	0.428	0.253	0.0128	7.7	1420
TLD1	0.1	Loam	0.319	0.428	0.253	0.0228	7.7	1220
TLD2	0.2	Loam	0.319	0.428	0.253	0.0228	7.7	1220
TLD3	0.3	Loam	0.319	0.428	0.253	0.0228	7.7	1220
TLD4	0.4	Loam	0.319	0.428	0.253	0.0228	7.7	1220
TLD5	0.5	Loam	0.319	0.428	0.253	0.0228	7.7	1220

Table 5-7. Modification of top layer horizon in Sevilla and Thiva scenarios according to rice husk biochar effects. N.B.: S = Sevilla; T = Thiva; LD = Layer depth; C = Control

An additional layer was added to the soil profile of each scenario. The additional layer was parameterized by the actual characteristics of biochar to determine the practicality of using biochar as a layer over a soil profile. Empirical data on the bulk density and fraction mineral parts of the rice husk biochar was obtained in the laboratory and used as input data for simulation. Each simulation consisted of a different biochar layer thickness, as seen in Table 5-8. These simulations were compared to determine the practicality of biochar application – whether biochar is best effective when amended to the soil or as a layer over the soil profile.

Simulation ID	The thickness of Horizon (m)	Soil type	Fraction mineral parts (kg kg^{-1})			Mass fraction of organic matter (kg kg^{-1})	pH-H_2O	Dry bulk density (kg m^{-3})
			Sand	Silt	Clay			
Sevilla								
Control	0.1	Silt loam	0.35	0.51	0.14	0.016	7.3	1210
SBL1	0.1	Sand	0.976	0.024	0	0	9.81	480
SBL2	0.2	Sand	0.976	0.024	0	0	9.81	480
SBL3	0.3	Sand	0.976	0.024	0	0	9.81	480
SBL4	0.4	Sand	0.976	0.024	0	0	9.81	480
SBL5	0.5	Sand	0.976	0.024	0	0	9.81	480
Thiva								
Control	0.3	Loam	0.319	0.428	0.253	0.0128	7.7	1420
TBL1	0.1	Sand	0.976	0.024	0	0	9.81	480
TBL2	0.2	Sand	0.976	0.024	0	0	9.81	480
TBL3	0.3	Sand	0.976	0.024	0	0	9.81	480
TBL4	0.4	Sand	0.976	0.024	0	0	9.81	480
TBL5	0.5	Sand	0.976	0.024	0	0	9.81	480

Table 5-8. Addition of biochar as a top layer over soil profile of Sevilla and Thiva scenarios. N.B.: S = Sevilla; T = Thiva; BL = Biochar layer; C = Control

5.3. Results and Discussion

5.3.1. Effects of bulk density on PEC_{gw}

When running the control simulations for Sevilla and Thiva, the predicted environmental concentrations in groundwater (PEC_{gw}) of diuron and glyphosate were below the 0.1 µg L^{-1} limit (maximum PEC_{gw} of 3 x 10^{-6} µg L^{-1} and 0 µg L^{-1} respectively). The EU Directive 1107/2009 states that active substances and metabolites of plant protection products must not exceed a limit value of 0.1 µg L^{-1}. Therefore, refinement of the soil parameters in line with the addition of biochar would not be required for mitigation of diuron and glyphosate in these scenarios. Atrazine, on the other hand, was above the 0.1 µg L^{-1} limit value for both Sevilla and Thiva scenarios in the control simulations (maximum PEC_{gw} of 14.1 µg L^{-1} and 40.9 µg L^{-1}, respectively). Due to these results, the focus was therefore placed on PEC_{gw} of atrazine in both Sevilla and Thiva scenarios. When the dry bulk density of Sevilla was increased, the atrazine control PEC_{gw} decreased from 14.1 µg L^{-1} to 14.0 µg L^{-1} (Figure 5-1). When the dry bulk density of Thiva was increased, the atrazine control PEC_{gw} of 40.9 µg L^{-1} decreased to 23.9 µg L^{-1}. The increase in dry bulk density was more effective in reducing the atrazine PEC_{gw} in the Thiva scenario than in the Sevilla scenario. In Thiva, a dry bulk density of 1,299 kg m^{-3} resulted in atrazine PEC_{gw} of 41.7 µg L^{-1}. It was reduced to 23.9 µg L^{-1} when the dry bulk density increased to 1,902.8 kg m^{-3} (Figure 5-2).

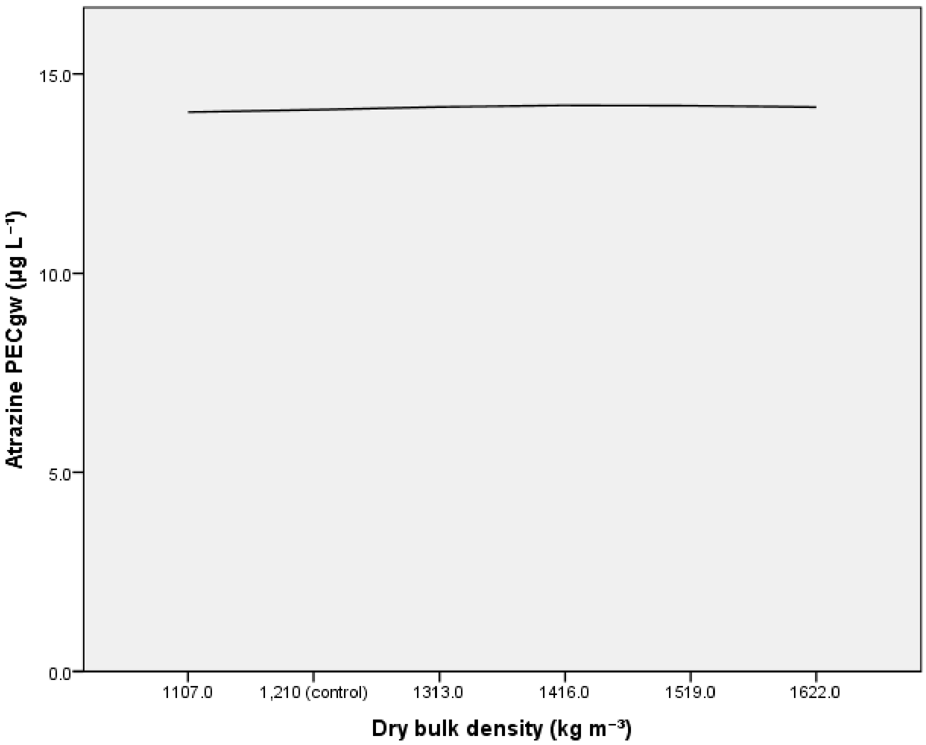

Figure 5-1. The influence of bulk density on PECgw in the Sevilla scenario

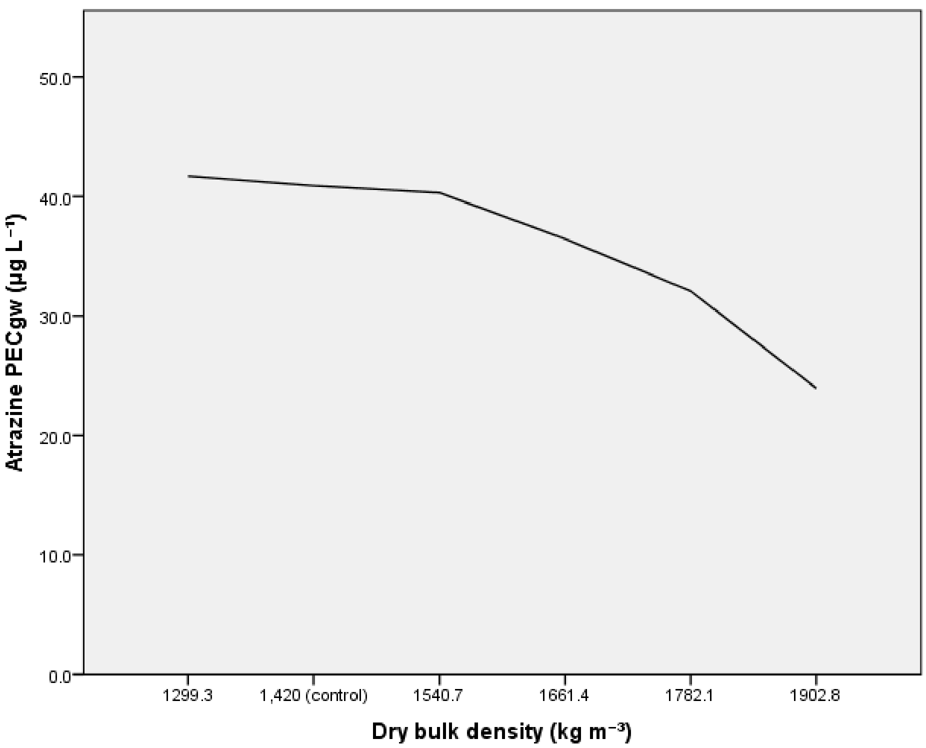

Figure 5-2. The influence of bulk density on PEC_{gw} in Thiva scenario

These results confirm the association between dry bulk density and the predicted environmental concentrations of pesticides in groundwater. When the soil has a low bulk density, the infiltration rate of water increases causing pesticides to leach. When the soil has a high bulk density, the infiltration rate of water decreases, causing increased surface contact between the solid and aqueous phases of the soil. The increased surface contact between the solid and aqueous phase creates an ideal platform for pesticide sorption and diffusion. When comparing the figures above, it is observed that, the decrease in PEC_{gw} was higher for the Thiva scenario than the Sevilla scenario. It must, however, be noted that the bulk density ranges in Thiva were higher (up to 1902 kg m^{-3}) than the bulk density ranges in Sevilla (up to 1622 kg m^{-3}). The difference in bulk density ranges was associated with soil texture and the appropriate bulk density for crop root growth. The soil types in the Sevilla and Thiva scenarios were silt loam and loam, respectively. Soil texture plays a significant role in determining the growth limiting bulk density due to effects on pore size and resistance (Daddow and Warrington, 1983). The ideal bulk density for root growth in silt loam is less than 1300 kg $m^{-3,}$ and in loam, it is less than 1400 kg m^{-3}. The bulk density root-restriction limit for silt loam is less than 1750 kg $m^{-3,}$ and for loam, it is less than 1800 kg m^{-3}. In soils with very high bulk densities, soil water and nutrients may be difficult to access because roots have difficulty in penetrating the soil (Stirzaker et al., 1996). Roots stop growing at a penetration resistance of 689 kPa until they reach the maximum resistance of 2068 kPa (Houlbrooke et al., 1997). These results show that although the PEC_{gw} reduces with an increased dry bulk density, the dry bulk density has to be maintained in a range that is appropriate for plant growth. However, even at unrealistic increases in dry bulk densities, the atrazine PEC_{gw} could not be reduced to below the limit value of 0.1 µg L^{-1}. Therefore, another soil parameter would need to be modified to decrease atrazine PEC_{gw} to below the limit value of 0.1 µg L^{-1}

5.3.2. Effects of organic matter on PEC_{gw}

The results in Figure 5-3 and Figure 5-4 and show the effects of organic matter fractions on the PEC_{gw} of atrazine in Sevilla and Thiva. Although in Sevilla the PEC_{gw} of atrazine decreased from 14.1 µg L^{-1} to 12.8 µg L^{-1}, the decrease in PEC_{gw} was more pronounced in Thiva (from 40.9 µg L^{-1} to 7.1 µg L^{-1}). According to this data, it is observed that PEC_{gw} of atrazine is dominated by the sorption effects of organic matter as compared to the dry bulk density of the soil. The dominant effects of sorption by organic matter can also be explained by the physicochemical characteristic of atrazine. However, even at increases in organic matter, the atrazine PEC_{gw} could not be reduced to below the regulatory standard limit value of 0.1 µg L^{-1}.

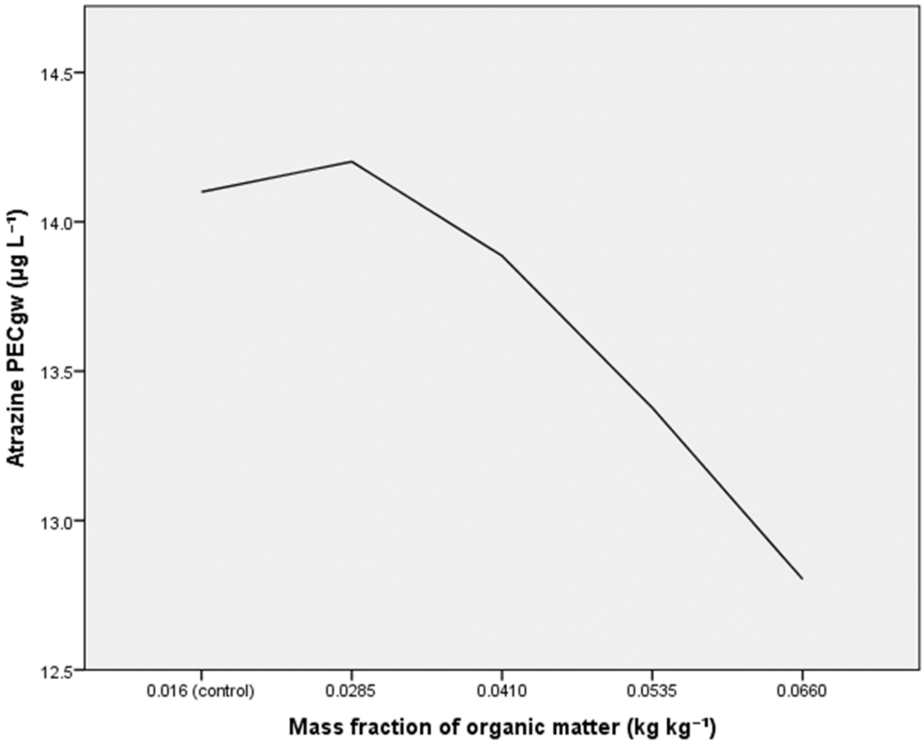

Figure 5-3. The influence of organic matter changes on PECgw of pesticides in Sevilla

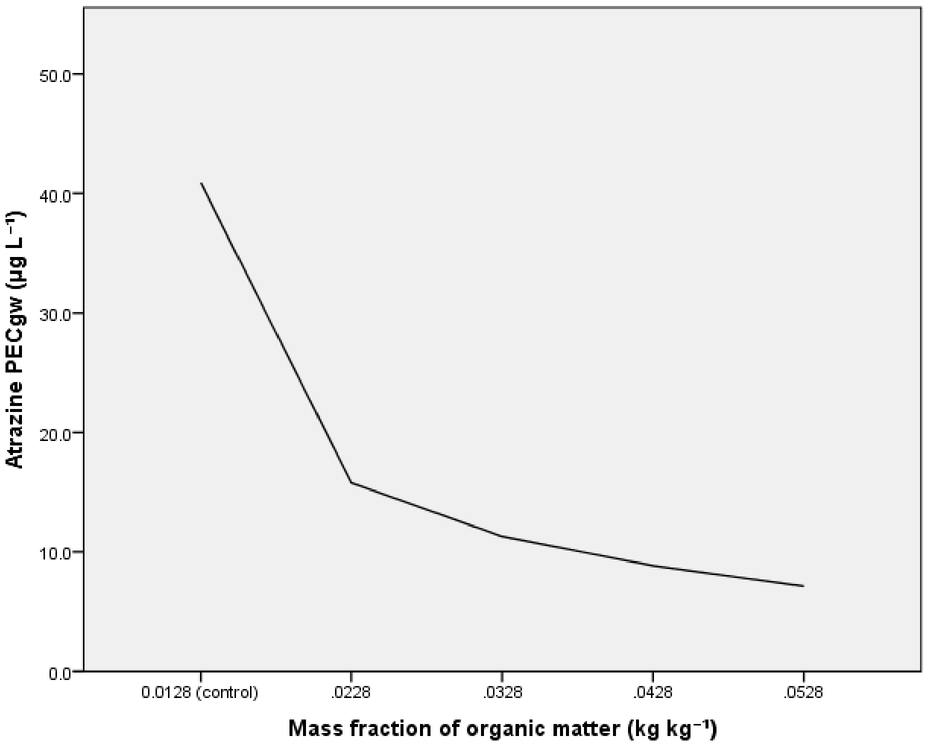

Figure 5-4. The influence of organic matter changes on PECgw of pesticides in Thiva

5.3.3. Effects of biochar amended soils on PEC_{gw}

Before simulating a biochar amended soil effect, the scenarios were tested to determine whether PEC_{gw} of atrazine was affected by an increase in depth of the top layer horizontal of the control soil profile of both scenarios. Figure 5-5 and Figure 5-6 below show that PEC_{gw} of atrazine was affected by increasing the depth of the top layer horizon of the control scenarios. However, a horizontal depth of 0.5 m was not sufficient to reduce the PEC_{gw} to below 10 µg L^{-1}. Changes in horizontal depth show that the increase in depth of the top layer horizon could not be accredited as a parameter that would reduce the PEC_{gw} to below 0.1 µg L^{-1}.

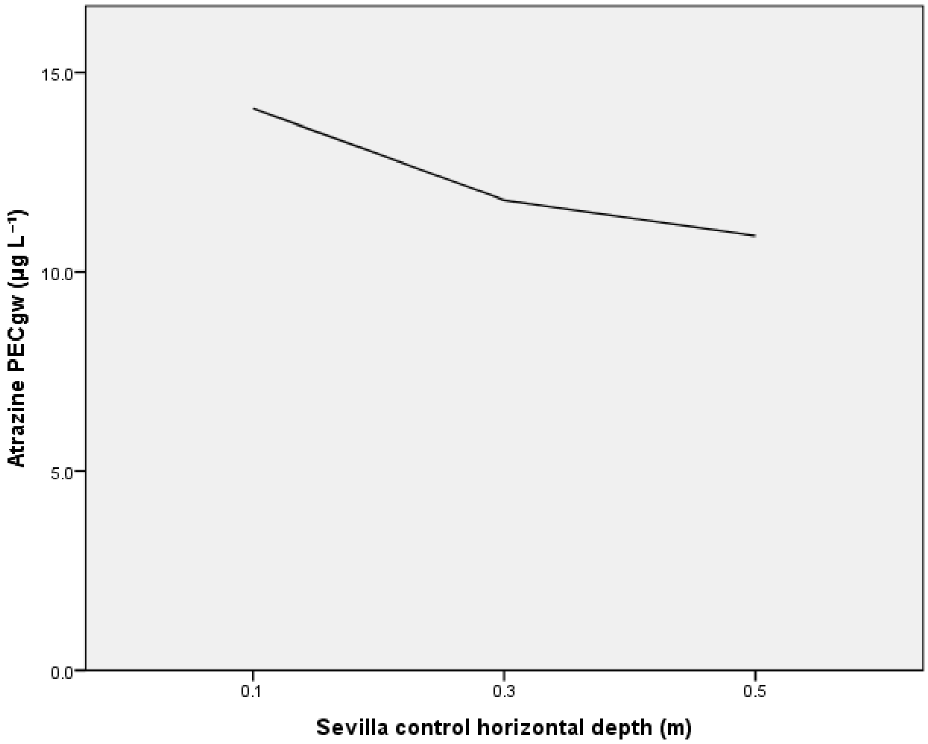

Figure 5-5. Modification of the depth of the top layer horizon in the Sevilla control scenario

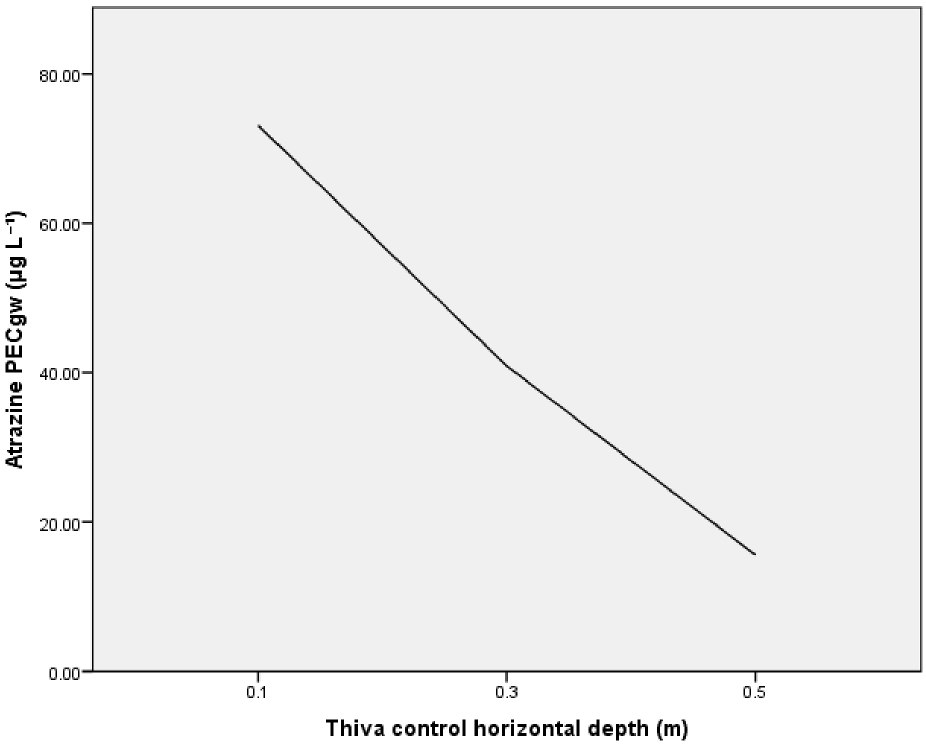

Figure 5-6. Modification of the depth of the top layer horizon in the Thiva control scenario

Since the changes in horizontal depth did not have a noteworthy effect on PEC_{gw} of atrazine, the effects of biochar to soil were simulated at different depths. With this said, the dry bulk density of biochar is much lower than mineral soils. Thus when homogeneously mixed with the soil, biochar is able to decrease soil bulk density (Verheijen et al., 2009). By decreasing the bulk density of the soil, biochar presents several of its benefits to the soil (see Sorption of pesticides and biochar interactions in chapter 2). As concluded in Chapter 4, biochar was absorbed atrazine. The simulated biochar effects on soil dry bulk density and organic matter were, therefore, in accordance with studies that have shown biochar's effects to soils (Blanco-Canqui, 2017). Biochar's absorption effects on atrazine were also included in these simulations. It was observed that the biochar absorption effects immediately decreased the atrazine PEC_{gw} to below the regulatory standard limit value of 0.1 µg L^{-1} in both the Sevilla and Thiva scenarios (Figure 5-7 and Figure 5-8). The sorption effects of biochar on atrazine were observed starting at the 0.1 m depth of amending the soils with biochar. This observation shows that a biochar amendment of 0.1 m in the soil is suitable enough for reducing the PEC_{gw} of atrazine in both Sevilla and Thiva scenarios.

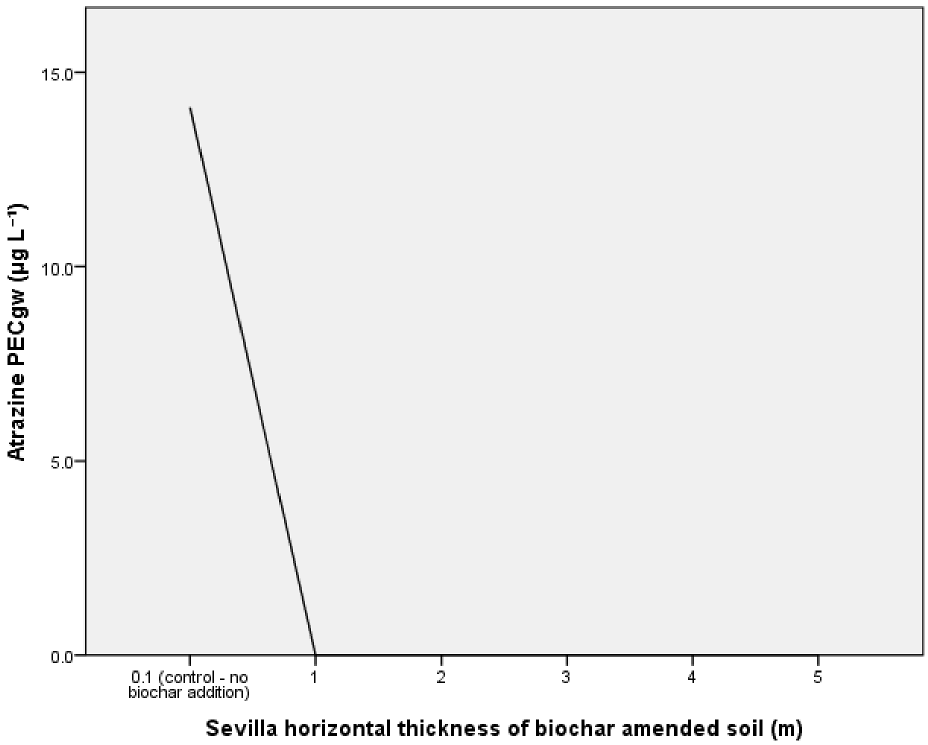

Figure 5-7. Biochar amended soil on PECgw of atrazine in the Sevilla scenario

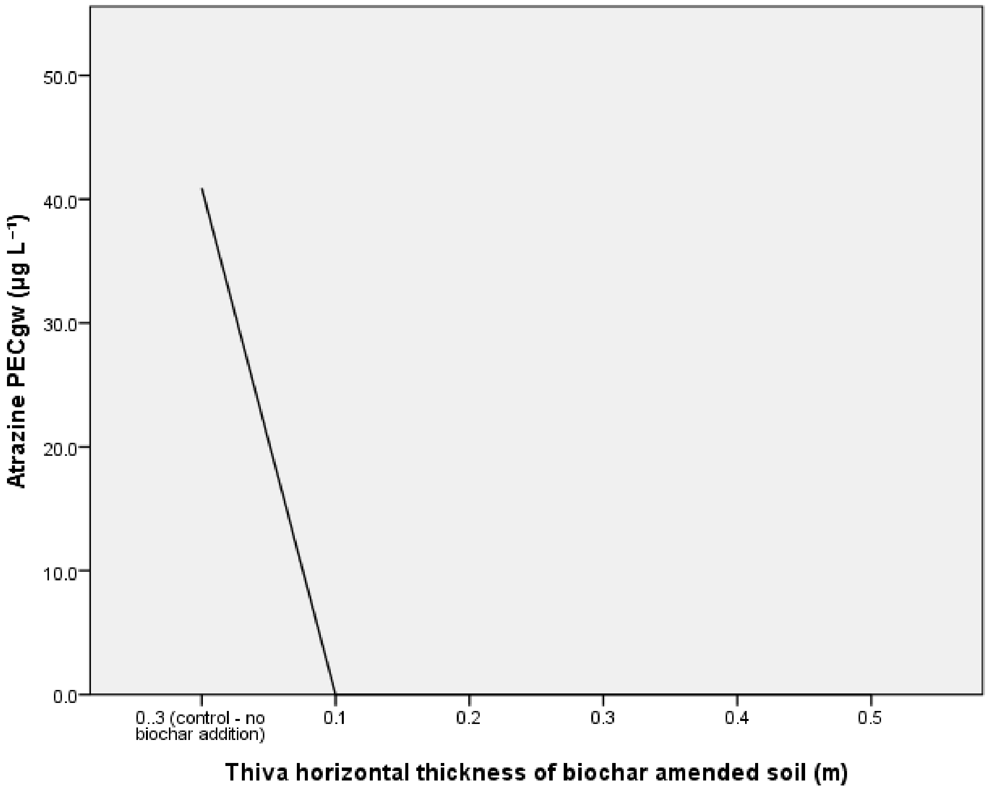

Figure 5-8. Biochar amended soil on PECgw of atrazine in the Thiva scenario

5.3.4. Effects of biochar as a layer on PEC_{gw}

As observed in laboratory studies, the unground rice husk biochar had a dry bulk density of 120 kg m^{-3}. The particle size distribution of the rice husk biochar mimicked a 97.6% sand and 2.4% silt. The effects of biochar as a layer over the soil profile were simulated for the Sevilla and Thiva scenarios. The soil profile below the biochar layer remained the same as the control scenarios. It was observed that when biochar was added as a layer over the soil profile of both Sevilla and Thiva, its effects immediately decreased the atrazine PEC_{gw} to below the regulatory standard limit value of 0.1 µg L^{-1}. A biochar layer thickness of 0.1 m was sufficient to reduce the PEC_{gw} regulatory standard limit value (see Figure 5-9 and Figure 5-10).

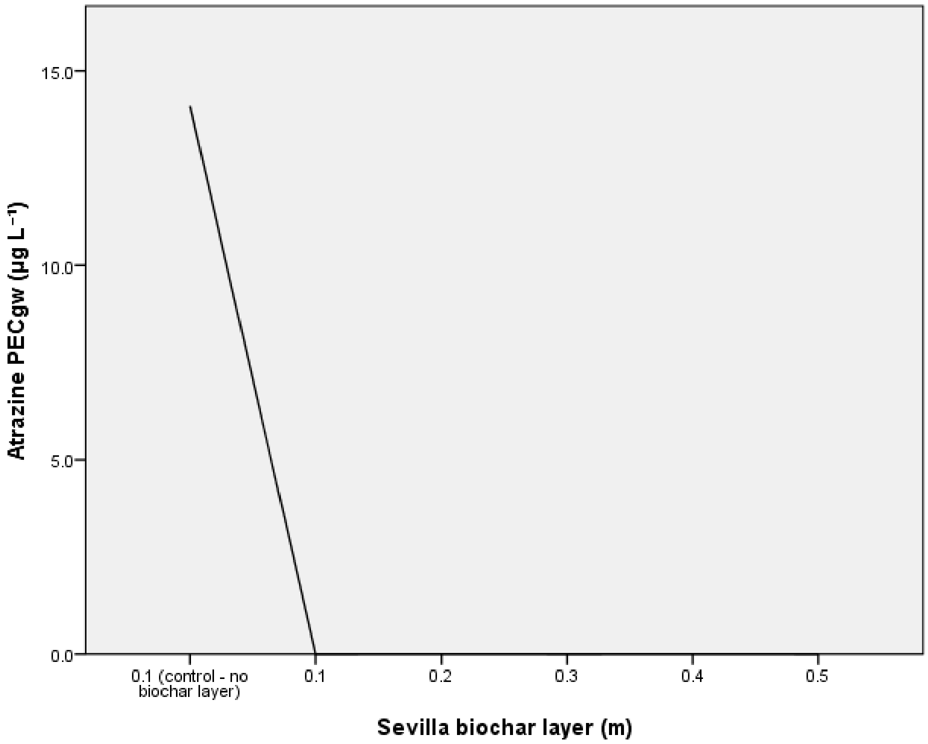

Figure 5-9. Application of biochar as a layer over the Sevilla soil profile

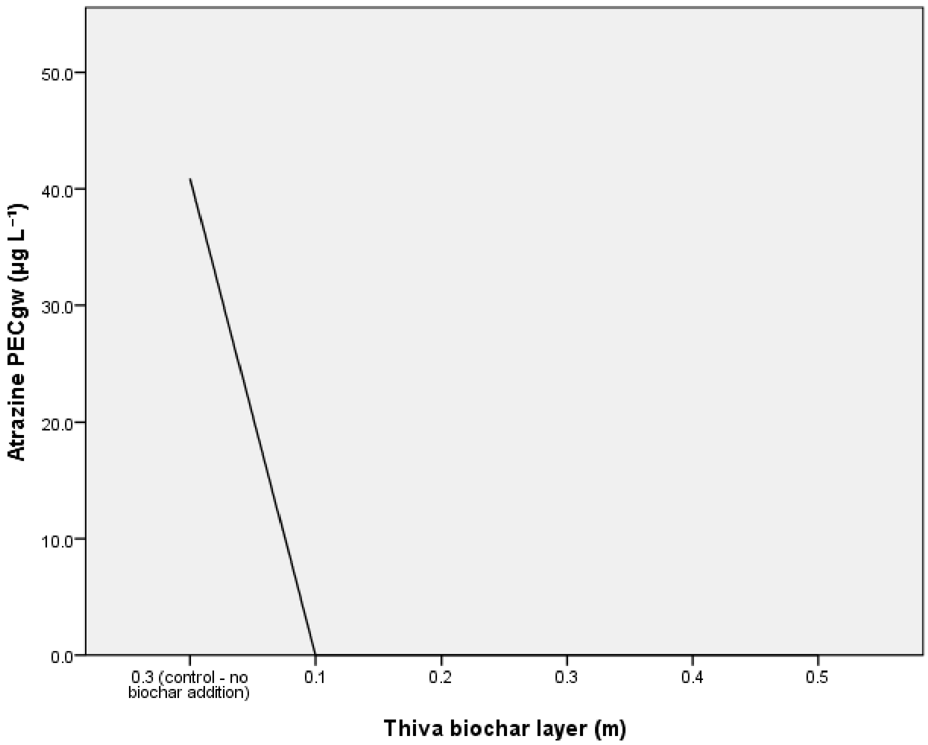

Figure 5-10. Application of biochar as a layer over the Thiva soil profile

The application of rice husk biochar was, therefore, capable of reducing the leaching of atrazine below the limit value of 0.1µg L^{-1} for both Sevilla and Thiva scenarios due to its absorption capacity. These results are consistent with laboratory data in Chapter 4, where atrazine was reduced in a rice husk biochar amended soil.

5.4. Conclusions

The influence of biochar on soil parameters (i.e., dry bulk density, organic matter, absorption, biochar application depth and biochar as a layer) on PEC_{gw} were investigated. The results showed that diuron and glyphosate PEC_{gw} levels were below the EU Directive 1107/2009 framework limit value of 0.1µg/L in both Sevilla and Thiva. Therefore, biochar mitigation strategies were not necessary for diuron and glyphosate in these scenarios. However, atrazine remained above the limit value in the controlled scenarios of both Sevilla and Thiva. Changes in dry bulk density and organic matter in the soil prove to influence the PEC_{gw} of atrazine. However, changes in bulk density and organic matter were not able to reduce atrazine to below the limit value. The PEC_{gw} of atrazine was only reduced to below the 0.1µg/L when biochar's absorption mechanism was taken into consideration. Biochar amended to soil and biochar as a layer over the soil profile proved to reduce the PEC_{gw} of atrazine to below the 0.1µg/L. Given that atrazine is banned in the EU but still used in agricultural soils of countries such as Belize, biochar can be used as a useful tool to reduce the predicted environmental concentrations of atrazine in groundwater. Applying biochar as a layer over the soil or mixing biochar with the soil can both be practical ways that can be adapted as a mitigation strategy to comply with regulatory standards. These results indicated that PEARL was a useful pesticide-fate simulation model to determine the effects of biochar on pesticide fate in a European scenario. The results gathered from the PEARL simulations were validated by the results obtained in Chapter 4. However, to use PEARL to determine pesticide fate in tropical soils, new tropical scenarios with parameters such as rainfall, temperature, soil properties, etc., would need to be developed and implemented in the model. The development of tropical scenarios for the determination of pesticide fate in tropical region poses to be an excellent opportunity for future research. Overall, the use of PEARL to determine the fate of pesticides in biochar amended soils offers a cheap and effective way of estimating the predicted environmental concentrations of pesticides in groundwater.

Chapter 6. General Discussion

6.1. Implementation of Biochar in Agricultural Systems of Belize: Stakeholder Analysis

Biochar use can be a suitable tool to intertwine both agricultural production and environmental protection. Several benefits can be reaped with biochar in agricultural soils. These benefits include reducing the agrochemical contamination of soil and water, improving soil health and quality, combating climate change, producing energy and managing agricultural waste. Making use of these benefits can be advantageous, especially for developing, tropical countries such as Belize that much depend on both agriculture and natural ecosystem services. It is therefore essential to make utmost efforts to create a balance between agricultural production and environmental protection. However, the implementation of biochar depends on the efforts of agricultural stakeholders. Stakeholders in Belize face several challenges in the agriculture sector. These challenges cause a trickle-down effect that can either encourage or hinder the implementation of biochar. The greatest challenge faced in Belize's agriculture, according to the stakeholders interviewed in this study, was climate change. Therefore, any issues associated with climate and the environment have been understood to affect agricultural productivity directly and indirectly. Because the stakeholders understood the importance of making efforts to mitigate climate change and protect the environment, they were motivated to use biochar for its positive effects on agricultural yield, soil health and environmental protection. Stakeholders were also intrigued that soils amended with biochar could reduce agrochemical contamination. However, stakeholders found that barriers such as scepticism, biochar and transportation costs and processing technology would need to be overcome. These barriers could be overcome through education, training and workshops; research on biochar benefits, and create stronger collaboration chains amongst stakeholders. It is through these steps that biochar could act as an ideal solution to balance both agricultural production and environmental protection in Belize.

6.2. Sorption effects of biochar on herbicides and veterinary antibiotics in different tropical soil types

The use of biochar to reduce agrochemical contamination in the soil was of interest for the agricultural stakeholders of Belize. The results of Chapter 3 mentioned that further research is needed to determine the effectiveness of biochar for reducing agrochemical contamination in tropical soils. In addition, tropical soil types of poor quality and health can be prone to agrochemical leaching. These findings were further justification for conducting this study. It was observed that the absorption capacity of a biochar amended soil matrix was determined by a combination of physicochemical properties of the biochar, soil and agrochemical. From the three-biochar types – produced from miscanthus straw pellets, mixed softwood pellets and rice husk – the rice husk biochar had the highest absorption distribution coefficient for the atrazine and diuron and the antibiotics enrofloxacine, oxytetracycline and tetracycline. In the column leaching studies, it was observed that rice husk biochar amended tropical soils, at depths of 25 cm, were able to reduce the leaching of atrazine and diuron as compared to the control soils that did not have any biochar addition. In addition, compared to the batch sorption studies, the column leaching studies yielded lesser absorption distribution coefficients. This was due to contact time of the herbicide and biochar amended soils. The herbicides in the column leaching studies had less of contact time to interact with the biochar amended soil matrix as compared to the batch sorption studies. Furthermore, the column-leaching model also speculated that the addition of biochar could encourage biodegradation of herbicide in a soil. This speculation could be essential to advocate for biochar to be added to the soil for the mitigation of herbicide contamination in soil. This study suggests that the addition of rice husk biochar at 2.5% (w/w) to tropical soils was proven an effective strategy for reducing agrochemical contamination in tropical soils. Further field studies should be conducted in Belize to determine the effects of biochar-amended soils on the fate of herbicides. Further studies could also be conducted to determine biochar's effects on crop yield.

6.3. Modelling of Pesticide Fate in a Biochar Amended Soil

Findings in chapter 4 have suggested that biochar can be an effective strategy for reducing agrochemical contamination of soils. However, laboratory experiments, such as those found in the previous chapter, could be time-consuming and costly. In this chapter, the predicted environmental concentrations of pesticides in groundwater of biochar-amended soils were further investigated with the use of pesticide fate models. The pesticides used in this study were atrazine, diuron and glyphosate. The modelling approach is not costly but yet effective in determining the predicted environmental concentrations of pesticides in groundwater. For this, the PEARL pesticide-fate model was adapted from the initiative entitled Forum for the Coordination of Pesticide Fate Models and their Use (FOCUS). Results obtained from FOCUS have been used in European Union registration processes of plant protection products under the EU Directive 91/414/EEC framework. The PEARL model was identified as the most suitable model for implementing and simulating the effects of biochar amended soil on the predicted environmental concentrations of pesticides in groundwater. In addition, scenarios had to be used as input files for the PEARL model. Scenarios are numerical simulations developed to represent realistic agriculture scenarios in the EU. Of nine standard scenarios, two standard scenarios were selected from the FOCUS groundwater scenarios. Their parameters were then modified to represent the effects of biochar on the soil. The model simulated the effects of biochar on bulk density, organic matter, and hydrology of the soil, absorption of pesticides and depth of the top horizon of the soil profile. The model predicted that even without biochar addition, which were the control scenarios, diuron and glyphosate, complied with EU Directive 1107/2009 regulatory standards. The EU Directive 1107/2009 suggest that predicted environmental concentrations of pesticides in groundwater should not exceed a limit value of 0.1 µg L^{-1}. Therefore, changes in soil parameters based on the effects of biochar addition to soil were not required for the mitigation of these pesticides. However, atrazine exceeded the limit value in both Sevilla and Thiva scenarios. Therefore, it was necessary to simulate the effects of a biochar-amended soil on the predicted environmental concentrations of atrazine. Further changes in bulk density, organic matter and horizontal depth of the soil reduced the predicted environmental concentrations of atrazine in groundwater. However, these changes did not reduce the atrazine to a level where it was able to comply with the EU regulatory standards. However, when the effects of 2.5% (w/w) amendment of biochar to the soil were considered in the model, the predicted environmental concentrations of atrazine in groundwater was reduced to below limit value of 0.1 µg L^{-1}. The effects of biochar were simulated as a 0.1 m of biochar amendment to soil and a 0.1 m of biochar as a layer over soil profile. Both simulations yielded the same results, complying with the EU regulatory standards. The results of the model also reflected that of the results gathered from Chapter 4. These results suggest that in relation to the needs of the stakeholders as observed in Chapter 3, the PEARL model could be used as a useful tool to determine the effects of biochar on the predicted environmental concentrations of pesticides. These results also suggest that biochar-amended soil at 2.5% (w/w) and a depth of 0.1 m or biochar as a layer of 0.1 m over a soil profile could be an effective and practical strategy for reducing the predicted environmental concentrations of pesticides in groundwater.

6.4. Implications

This study has analysed the agricultural stakeholders' perceptions on the constraints, present and future opportunities of implementing biochar in the agricultural systems of Belize. This research has demonstrated that biochar addition to soil is able to reduce agrochemical contamination of soil and water.

Not only does the study analyse the perceptions of implementing biochar, but also it also holistically identifies important challenges that are being faced by stakeholders in the agricultural sector of Belize. A study such as this is novel to Belize. The challenges being faced in the agricultural sector of Belize could either hinder or encourage the implementation of biochar. Through this, it was identified that stakeholders could be motivated to use biochar for both agricultural and environmental purposes once biochar research is established in Belize. It is only by understanding these factors that biochar can be successfully implemented in agricultural systems of Belize.

The agricultural stakeholders proposed that they could use biochar in their agricultural soils once biochar research has been conducted in Belizean soils. The recommendations from stakeholders led to laboratory experiments based on soils collected in Belize, biochar that could potentially be used in Belize and agrochemicals that are typically used in Belizean agriculture. Soils collected in Belize were ideal for this study because Belize is a developing country that is characterised by tropical soils. In addition, due to agricultural practices, tropical soils may be prone to agrochemical leaching. This study, therefore, identified the use of biochar as an effective means to reduce agrochemical contamination in tropical soil and water. The use of biochar could be used in tropical soils of similar characteristics as this study. Furthermore, it was discovered that biochars produced at one standard temperature of 700°C but from the different feedstock, could have different absorption capacities for different types of agrochemicals. It is, therefore essential to understand the effects of different biochar types to optimise their effectiveness.

To understand the effects of biochar amended soils on pesticides, several elements of the PEARL pesticide-fate model and the FOCUS groundwater scenarios were successfully modified. Modifications of the model and the groundwater scenarios to simulate the effects of biochar-amended soils on pesticides have not been observed in any previous study. Given that PEARL has been used as a tool for registration processes of plant protection products based on the EU Directive 91.414/EEC framework, results obtained from this model are validated. In this research field, this study has, for the first time, demonstrated that pesticide fate models could be used as tools to simulate the effects of biochar on pesticide fate. It has also for the first time demonstrated that biochar application to soil could be a feasible and practical method for reducing pesticide leaching in the soil. It has demonstrated that biochar can act as an effective risk mitigation strategy for the reduction of pesticide contamination to groundwater.

6.5. Future work

Although this study has presented several novel findings, further analysis, adaptations, and experiments were left unexplored due to time and resources. However, the unexplored elements of this study have created opportunities for future work. The following paragraphs explain the prioritised vital areas for future research.

The perspectives of stakeholders with regard to the implementation of biochar in agricultural systems of Belize were analysed. As a result, stakeholders suggested research and education related to biochar must take place before it is implemented in agricultural soils, which can be achieved by reinforcing network and collaboration amongst stakeholders. A collaboration amongst farmers, extension officers, researchers and academics and governmental agents, could facilitate biochar field trials. Although stakeholders expressed interest in using biochar for reducing agrochemical contamination, they also expressed interest in using biochar for soil health, quality and crop yield. Field trials based on this would be feasible. In addition, stakeholders were keen to understand the methods of producing biochar. Thus, future research could venture into designing biochar production systems that could suit smallholder and commercial farmers. Unsurprisingly, smallholder farmers were very interested in designing cheap biochar cook stoves for the production of biochar. In addition, stakeholders were also very interested in determining a cost-benefit analysis to evaluate the feasibility of implementing biochar in Belize.

Although in this study miscanthus straw pellets, softwood pellets and rice husk biochar were used, further studies could extend to using different biochar types. Experiments could extend to biochars produced from feedstock that is most commonly considered agricultural waste in tropical regions. In addition, experiments could consider the effects of biochar produced from local biochar cook stoves. Using biochar produced from cook stoves for the absorption of agrochemicals would be the practical scenario, especially for smallholder farmers. In addition, due to time constraints associated with obtaining permission from the university to use certain substances, the herbicide glyphosate could be an ideal substance to include in future experiments. Glyphosate is commonly used in tropical regions and in different parts of the world. Furthermore, batch sorption experiments could further explore the effects of specific biochar characteristics on the fate of agrochemicals and soils, such as biochar particle size, application rate, ageing effects of biochar, effects of biochar on soil pH, organic matter, electrical conductivity and hydrology. The effects of biochar could further be compared to the effects of activated carbon on agrochemical sorption. The effects of biochar on biodegradation of the agrochemicals would also be necessary for further studies. In addition, column-leaching studies could consider the effects of different depths of biochar amendment in soil, and further investigate the effects of different application rates.

Future work could be conducted on modelling the effects of biochar-amended soils on the predicted environmental concentrations of pesticides in groundwater. The FOCUS scenarios used in the PEARL model were based on a collective representation of agriculture in the EU. However, since developing countries such as Belize do not have initiatives such as the FOCUS workgroup, there are no representative environmental scenario files, that could be used as input for the PEARL model. Furthermore, in Belize, limited data is available based on soil types and other environmental parameters that are associated with the fate of pesticides. It is, therefore, essential to create tropical scenarios. This study focused on the contamination of groundwater. However, further modelling should be conducted to explore the effects of biochar on surface water contamination. This is especially important for agrochemicals that do not leach down the soil profile, remain in the top layer of the soil profile, and do not biodegrade.

Field experiments based on biochar as a buffer zone over a soil profile or as a buffer zone between agricultural land and aquatic ecosystems should be carried out to determine its effects under field conditions. It would be essential to determine whether biochar sorption effects reduces over time. It would also be essential to determine the extent to which biochar promotes biodegradation of agrochemicals in the soil. In addition, an understanding of whether biochar particles can migrate through the soil, and if these particles could act as agrochemical carriers that could possibly cause further agrochemical pollution. Further research is needed, especially in biochar-amended soil where the biochar could potentially deactivate the effects of pesticides applied to plants.

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Appendix A.

Appendix A.1. Stakeholder analysis questionnaire

Implementation of Biochar Systems in Belize: Stakeholder Analysis

June 2017

Consent to Participate in Questionnaire

Research Project: 'Feasibility of Implementing Biochar Systems in Agricultural Soils of Belize'

You have been asked to participate in a questionnaire conducted by Mr. Gerardo Ofelio Aldana from the School of Agriculture, Food and Rural Development at Newcastle University. Funding for this study comes from the Commonwealth Scholarship Council, UK, and Newcastle University. The purpose of this study is to assess stakeholder perceptions around biochar systems in the country of Belize. You were selected as a possible participant in this study because of your particular knowledge and/or experience in the agricultural sector of Belize. You should understand well the information below, and ask questions about anything you do not understand before deciding whether or not to participate.

1. This questionnaire is voluntary. You have the right to not answer any question. We expect that the questionnaire will take fifteen minutes.
2. You will not be compensated for filling this questionnaire.
3. Unless you give us permission to use your name, title, and/or quote you in any publications that may result from this research, the information you tell us will be confidential.
4. This project will be completed by 2019. All questionnaires will be stored in a secured space in a computer (locked through a password) until the end of 2019.

I have been given a copy of this form.

(*Please check all that apply*)

- ☐ I give permission for the following information to be included in publications resulting from this study:
- ☐ My name
- ☐ My title
- ☐ Organization
- ☐ Direct quotes from this interview
- ☐ I want feedback/results after this study has been completed

First Name: ___________________________________

Last Name:

Signature of Subject: ___________________________________

Date: ___________________________________

Please contact Mr. Gerardo Ofelio Aldana at g.o.aldana2@newcastle.ac.uk if any questions or concerns arise.

Questionnaire: Feasibility of Implementing Biochar Systems in Agricultural Soils of Belize

Profile

1. For how long have you worked in the agriculture sector?

2. How many farms do you advise? What types of farms do you advice? (Conventional, Organic, Integrated, etc.)

3. What is your highest graduated level of education?

4. Is it in your line of duty to be associated with related agricultural stakeholders, i.e. Belize Water Authority (BWS), Department of the Environment, Caribbean Agricultural Research and Development Institute (CARDI), Belize Sugar Industry Research and Development Institute (SIRDI), University of Belize (UB), etc.?

Context

1. What do you think are currently the main concerns of farmers?

2. What is the driving change in farming currently? (Positive/Negative)

3. What are the main views of farmers toward the environment?

4. Is pesticide pollution concern in your area? Is this being addressed in your work?

5. How concerned are farmers in regards to pesticide pollution? Do they take measures to reduce pesticide pollution? (What do they do and why?)

6. Do farmers view the issue of pesticide pollution from a citizen standpoint of view? (E.g. Concern about the cost of remediation, pollution of rivers, destruction of coral reefs, etc.)

Awareness of Biochar

The answers from the following questions are dependable on the different levels of knowledge about biochar. Therefore a general explanation of biochar must be presented.

1. Are you involved in any environmentally friendly agricultural practices?

2. What are the best alternative methods for reducing pesticide pollution in water? (Ex. Pesticide tax, education to improve targeting of pesticide application, etc.)

3. Are you familiar with biochar systems? (Pesticide remediation, soil conditioner, carbon negative, water and nutrient retention, etc.)

4. Do you think that biochar systems would be easily adaptable by farmers?

5. What do you think would motivate farmers the most to adopt innovative biochar systems? (Five [5] being most motivational)

	5	4	3	2	1	I don't know
Higher Yield	☐	☐	☐	☐	☐	☐
Better Plant Quality	☐	☐	☐	☐	☐	☐
Environmental Safety	☐	☐	☐	☐	☐	☐
Ease of Handling and Application	☐	☐	☐	☐	☐	☐

6. To which types of farmers would biochar mostly appeal to?

7. Which key barriers would be encountered in regards to biochar implementation? (Five [5] being most motivational)

	5	4	3	2	1	I don't know
Scepticism	☐	☐	☐	☐	☐	☐
Near Retirement	☐	☐	☐	☐	☐	☐
Cost	☐	☐	☐	☐	☐	☐

	5	4	3	2	1	I don't know
Processing Technology	☐	☐	☐	☐	☐	☐

8. In which ways would it be possible to overcome these barriers?

9. Do you think there is adequate information on biochar technology?

10. Forward: Thinking about this topic, do you have any other comments you would like to share?

Appendix A.2. Focus group transcriptions

Name	Position	Organization	Comments
Luciano Chi	Researcher	SIRDI	- SIRDI implements best management practices in sugarcane production with small farmers. It is geared toward the reduction of contamination of the environment and to increase yield. - Biochar technology can be included inside the research activity at SIRDI where it can be evaluated at field level. - Collaboration amongst stakeholders in the sugar industry can assist in resolving key obstacles. - We need sensitization and research.
-	Extension	SIRDI	- Biochar has the potential once research has been conducted, which may take years to obtain accurate data and validate its use/ effectiveness, especially in Northern Belize where soils are alkaline.
-	Extension/Farmer	SIRDI	- To take advantage of biochar in the sugar industry could be to reduce pesticide contamination and therefore protect the environment. - Farmers need more information
-	Extension	SIRDI	- We can use biochar in organic farms, and also to improve soils such as nutrient retention, increase soil pH. Can also be used in sugar cane industry due to the high use of pesticides. - Trials must be done for farmers to adopt biochar and increase production.
-	Extension officer/Organic farmer	BSCFA	- Use to reduce inorganic fertilizer and stop causing synthetic fertilizer pollution. - More training and information is needed.
-	Extension	SIRDI	- By educating farmers and finding reliable resources to assist farmers in practising 'biochar' for betterment of their soil. - Farm visit and educational sessions with farmers, and educational sessions with field officers are needed to broaden biochar knowledge. - Encourage farmers through experiments.
-	Extension	SIRDI	- SIRDI will produce *Metarhizium* (a natural fungus) for the pest mitigation in sugar cane and can be complemented with biochar. - SIRDI has fertilizer applicators. Biochar produced to a required grain or particle size can be incorporated on the roots of sugar cane. - We have low fertility soils. According to research, we need four bags of fertilizers for keeping soils where fertile. - We must conduct trials with biochar so as to see the benefits.
	Extension	SIRDI	- Organic farmers who worked in the Corozal area would be interested in trials. - We can take advantage of biochar since it is a natural product. It is environmentally friendly. It will also make the soil fertile or have longer soil life. - We can resolve key obstacles by having more research on Biochar, especially in Northern Belize, and having trials with small scale farmers and then promote it if it works.
-	Extension	SIRDI	- Start to do more investigation on biochar in different areas.

			- Do demonstration plot evaluation - See results on demonstration plots and compare data.
Felipa Moralez	Extension	BSCFA	- Inform farmers about biochar - Have workshops with farmers to resolve critical obstacles.
	Extension	BSCFA	- Use biochar on the areas which need the most. Soil which has low nutrients. - We can resolve these obstacles with more information and research on biochar. - Do experiments on the type of soil and effects biochar have directly to the environment
	Extension	-	- Drying coconut waste after taking out the water for charcoal. Use biochar for cooking. - We can sell biochar to farmers and for gardens to improve the soil. - We can mix with soil in nurseries. - Awareness of biochar to help resolve critical obstacles.
	Extension		- Putting into practice biochar to reduce contamination and increase the use of organic waste - Obstacles can be minimized by providing information to farmers. Have trials for the association and farmers.
	Extension		- Biochar is beneficial since it can increase the availability of soil nutrients. - Obstacles can be minimized by demonstrating the benefits.
	Extension		- It is beneficial because we can make good use of waste materials in our homes. - We can overcome barriers by making small trials by incorporating it into the soil to reduce contamination of pesticides and determine the cost-effectiveness.
	Extension		- Few farmers work with biochar without knowing it is biochar. Farmers in Hill Bank carry out biochar practices. - We can overcome obstacles through the dissemination of information and involving farmers to participate in trials. - Obstacles will always exist. It can be overcome with the persistence of field experimentation. We can gather groups of farmers and practice with them. - Relate biochar with other farming practices.
	Extension		- As far as I am aware, cacao growers in Toledo are doing biochar. Biochar benefits the environment. It helps to mitigate climate change and contributes to alternative options for sustainable agriculture.
	Extension		- Awareness to the farmers. - Determine the cost-benefit analysis. - More information on the biochar used in Belize
	Extension		- In the sugar industry in Northern Belize. Take advantage through capacity building, the establishment of trials and training of farmers. - We can resolve key obstacles by resolving stakeholder issues and collaboration of stakeholders by addressing climate change issues, food production and other social issues.
	Extension		- Transfer of information through different mediums. Small scale business improves production. Increase nutrients in soil. - We can overcome barriers through demonstration, experiments and research.
	Extension		- Provide information to farmers - Recycle waste material that is non-toxic

		- Educating us and also farmers about what biochar is about.
Extension		- I can make trials with different farmers only for vegetable and fruit farming at small scale since I need to make my own conclusions on biochar with my own experience and results. Biochar can be used as an air filter inclusive.
Extension		- Biochar can be beneficial only for small producer/farmer with the affordability of implementing it.
Extension	BSCFA	- Only some farmers are using organic material from home waste management to their field.
Extension		- Farmers who have the resources to use biochar and find it beneficial to their agricultural practices. - As a farmer, the cost of producing cane will be less because by using biochar, they will be able to spend less on fertilizers.
Extension		- Capacitate farmers about biochar because of some lack of information. - Tell them about the benefits of biochar.

Comments from organizations

Benefits	Obstacles
SIRDI - It is cheap - Reduces contamination - Helps retain nutrients and minerals of soil. - Increases yield production. - Climate change - It may be beneficial	- Cost-benefit analysis for small scale farmers - Sustainability of raw material - Further research on soil impact in Belize (Alkaline soils in the North) - General farmer sensitization in Belize - In need of cost-benefit analysis in Belize
- Reduce pesticide contamination - Irrational use of pesticides - Can serve as a pesticide runoff buffer of contaminants - Prevents the spreading of pesticides in our soil - Better alkaline soils - Inexpensive compared to the damages created by pesticide	
- It is good because farmers tend to burn a lot. - By using biochar, it can help with the retention of nutrients and water. - There is a lot of waste that can be used to do biochar. - It can help with the division of garbage waste into organic and non-organic. It will help clean up the environment.	- We have to be conscious of the side effects which are air pollution and deforestation
- Beneficial to the south of Belize because the soil has a lower pH. - It can be economical for everyone in Belize - It uses agricultural waste which reduces the level of pollution. - It lowers the risk of contamination of water sources.	-

- It is beneficial because it is suitable for soil fertility, carbon sequestration and regulates soil pH - Sable solid rich in carbon - Climate change mitigation potential - Increases agricultural production - Affordable for small farmers	-
PCB	
- Excellent when combined with other organic substrates (Compost), especially considering nutrition composition. - Yield. Health.	- Benefits are influenced by the scale of operation - Government ministries of agriculture, natural resources, energy, public health, research institutions such as CARDI, CREI, SIRDI, universities (UB, Galen) - We can resolve critical issues by published research, farm/plot demonstrations, and farmer education.
- Increase the carbon content of the soil - Organic amendment - Reduction of environmental contamination - Increase in soil micro-organisms and production of healthier plants - Remediate adverse effects of misuse of pesticides in the agriculture sector	- Extension department, extension services and farmers associations can make it work. - Consider field trials at the farmer level, setting up trials at home. - Research unit can conduct field days to introduce to small farmers. - We can lobby government ministries to include in annual work-plan of agriculture. - We can resolve obstacles by education/testimonials. - Top-level of ministry, farmers. - Include biochar in experimental trials. - Include biochar potential in the production of vegetable crops.
Yaxche	
- Can work in poor soils - Using cutting from Inga alley cropping - Absorb waste for those still using chemicals (conventional farmers) - Maximise our compost application and build poor soil to be more productive in smaller places.	- Trial plot to see the benefits in crop production - More research and explanation on how it works - Table of recommendations on the use of biochar and source of biochar. - Small home trials. - More training and how it works. Working with farmers and seeing which farm needs to get more knowledge of it. - A deeper understanding of usage and application. How long, how much and what is used? - More research and explanation. How to apply it. How it could be applicable to plots. - A guideline on its application.
- Crop residue can be given a higher purpose - Carbon sequestration in soils - Increase production and increase income - Soil remediation of pesticides - Possible business venture for farmers (kilns, finished biochar) - Increase soil health and properties	- Is it scalable, cost-effective - Adoptability may be slow - It could compliment initiatives aimed at identifying risks and developing risk management strategies for pesticides. - Entrepreneurial efforts. Someone will need to venture into promoting, educating and selling.

	- Conducting local research to generate data for decision making and promotion - Linking biochar benefits with climate and smart agriculture - Networking opportunities. - Research, generate info and dissemination. Government inclusion for policymaking. Public-private partnership. - Get growers to try and get it working for themselves
- It can be done - Good for reforestation - Enhancing soil as It relates to the inga alley cropping byproduct	- More research needs to be done in Belize - Get soil data - Trials in back garden/small scale garden

Appendix B.

Appendix B.1. Characteristics of soil types

Analysis	Cayo district	Stann Creek district	Corozal district	Newcastle
Soil Class	Loam	Sandy silt loam	Clay loam	Sandy loam
Grid reference	17°12'04.4"N 89°00'16.6"W	16°59'40.9"N 88°21'49.0"W	18°13'44.6"N 88°32'07.3"W	54°58'25.3"N 1°37'34.5"W
pH	8.1	6.1	8.2	7.8
Lime Req. (t/ha)	-	5.0	-	-
Phosphorus (ppm)	22	5	320	24
Potassium (ppm)	272	153	704	227
Magnesium (ppm)	265	247	655	149
Calcium (ppm)	5899	1318	14065	3396
Sulphur (ppm)	3	3	30	111
Manganese (ppm)	101	12	86	42
Copper (ppm)	6.7	5.2	5.3	27.2
Boron (ppm)	1.21	0.60	1.74	1.78
Zinc (ppm)	5.5	3.8	1.4	75.3
Molybdenum (ppm)	0.54	0.11	0.39	0.10
Iron (ppm)	174	506	54	542
Sodium (ppm)	17	28	243	100
C.E.C. (meq/100g)	27.5	11.4	69.9	15.8
Organic matter (%)	2.9	3.7	5.0	8.8
Organic Carbon (%)	1.68	2.15	2.91	5.12
Silt (%)	41.37	48.02	37.66	34.54
Clay (%)	20.54	15.83	34.93	12.11
Sand (%)	38.09	36.15	27.41	53.35

Appendix B.2. Sampling Methodology

Soil samples were collected only from the A horizon up to a maximum depth of 20 cm, due to the specific objective of using the soil samples for batch adsorption-desorption using a batch equilibrium method, as instructed by the OECD 106 Guideline for the Testing of Chemicals. Eight soil samples were analysed in a 15-meter diagonal pattern across the border of the agricultural field where a biochar buffer strip could be ideally installed. Once soils were observed to be similar in analysis, 3 kg of soil at one sampling area was collected. After work had been completed, any areas in which the ground had been disturbed was at its best returned to a state which rendered the site safe for continued use. A GPS system was used to locate and fix grid points within the sample area. Bulk density samples were collected in each site using hand tools. Field samples were transferred to a plastic tray for air drying. Samples were labelled correctly to avoid identification errors during transfer. Plantlant residues were removed. Field samples were sieved through a 2 mm sieve. Clods passing through the sieve were carefully crushed and re-sieved. After sieving, each soil sample was placed in a labelled polythene sample bag. The bags were transferred to boxes.

Appendix B.3. Site and Soil Profile Description

Profile No.: **BZCY**

District: Cayo

Soil Classification: Gleyic cambisol

Location: 11 km NW of San Ignacio Town, Cayo District, Belize, Central America.

Grid Reference: 17°12'04.4"N 89°00'16.6"W

Described by: G. O. Aldana *Date:* 16/01/2018

Elevation: -30 m

Relief: Broad flood plain valley with flat land stretching from both sides of the river.

Slope: 3° *Slope Form:* Linear *Slope Shape:* CL *Aspect:* 8186 km W

Slope Position: Toeslope

Parent Material: River alluvium in the floodplain with underlying Cretaceous limestone.

Soil Surface: Presence of leaf litter, earthworm casts.

Erosion/Deposition: None evident.

Rock Outcrops: None

Land Use/Vegetation: Rotation cropping of maize and beans. Herbicides previously used are known to be atrazine and glyphosate (Helosate). Presently, the herbicides being used are pendimethalin (Prowl H2O), 2, 4-D, and Nicosulfuron (Primero). Beans and Maize rotation have been used for three years, but before then, only corn and sorghum were planted in rotation. No irrigation system is installed. Agricultural activity occurs 36 meters from the Belize River. Ecosystems that surround the district consists of Sub montane broad-leaved moist and wet forest, lowland broad-leaved moist scrub forest, and lowland broad-leaved moist scrub forest.

Soil Drainage Class: Poorly drained

Horizons:

0-24 cm Ap

Very dark greyish brown (2.5Y 4/2) moist loam; moderately developed medium sub-angular blocky structure; friable; slightly hard when dry; moderately sticky and moderately plastic when wet; many fine fibrous roots.

24-56 cm Bg

Dark greyish brown (10YR 4/2) moist silty clay loam with 1% reddish-yellow mottles (5 YR 7/8); moderately developed fine sub-angular blocky structure; firm; soft when dry; very sticky and moderately plastic when wet.

56-81 cm Bg2

Dark yellowish brown (10YR 5/2) moist silty clay loam with 1% reddish-yellow mottles (5 YR 7/8); moderately developed fine sub-angular blocky structure; firm; soft when dry; very sticky and moderately plastic when wet.

***Profile No.:* BZCZ**

District: Corozal

Soil Classification: Vertic gleysol

Location: 16.17 NNW of Orange Walk Town, Orange Walk District, Belize, Central America

Grid Reference: 18°13'44.6"N 88°32'07.3"W

Described by: G. O. Aldana *Date:* 16/01/2018

Elevation: -44 m

Relief: Slightly undulating flat land

Slope: 5° *Slope Form:* Linear *Slope Shape:* CL *Aspect:* 8173 km W

Slope Position: Footslope

Parent Material: Light to dark grey silty and sandy shale with occasional dolomite

Soil Surface: Capped

*Erosion/Deposition: G*ranular structure.

Rock Outcrops: None evident.

Land Use/Vegetation: Sugar cane has been cultivated for over 35 years. The parcel is used as a cane variety trial to evaluate variety adaptation to this soil type. Mechanical weed control has been used as the first approach; minimal weed control has been used, except for weed control in the fire lines around the perimeter of the cane parcel. Glyphosate is the primary herbicide being used — ecosystems that surround the sampling site consist of lowland broad-leaved moist forest, and submontane pine forests.

Soil Drainage Class: Imperfectly drained

Horizons:

0-24 cm Ap

Black (gley 1 2.5/N), moist clay loam; moderately developed medium angular blocky structure; common fine calcium carbonate nodules; hard when dry; moderately sticky and moderately plastic when wet, firm; fine fibrous roots, common medium angular stones.

24-56 cm Bv

Black (gley 1 2.5/N), moist clay, course blocky structure; hard when dry; very sticky and very plastic when wet; extremely firm.

56-81 cm Bg

Bluish grey (Gley 2 5/5B), moist clay, structureless; hard when dry; very sticky and very plastic when wet; extremely firm; no roots.

81-100 cm+ Cgk

Bluish grey (Gley 2 6/5B), moist clay, structureless; hard when dry; very sticky and very plastic when wet; extremely firm; pale yellow subangular calcium carbonate nodules (2.5Y_/2/9.5); no roots.

Profile No.: **BZSC**

District: Stann Creek

Soil Classification: Gleyic acrisol

Location: 14.9 km NNW of Dangriga Town, Stann Creek District, Belize, Central America

Grid Reference: 16°59'40.9"N 88°21'49.0"W

Described by: G. O. Aldana *Date:* 16/01/2018

Elevation: -15 m

Relief: Broad flood plain valley with flat land stretching from both sides of the river, surrounded by mountainous region formed from granite particles.

Slope: 2° *Slope Form:* Linear *Slope Shape:* CL *Aspect:* 8186 km W

Slope Position: Footslope

Parent Material: Colluvial deposits derived from granite upslope.

Soil Surface: Flat

Erosion/Deposition: None evident

Rock Outcrops: None

Land Use/Vegetation: Citrus cultivation for over 30 years. Nutri-cal is used as fertilizer and applied once a year. 2, 4-D is used as a herbicide. Ecosystems that surround the sampling site include submontane broad-leaved moist forests, submontane broad-leaved steep moist forests, and submontane pine forests.

Soil Drainage Class: Imperfectly drained.

Horizons:

0-24 cm Ap

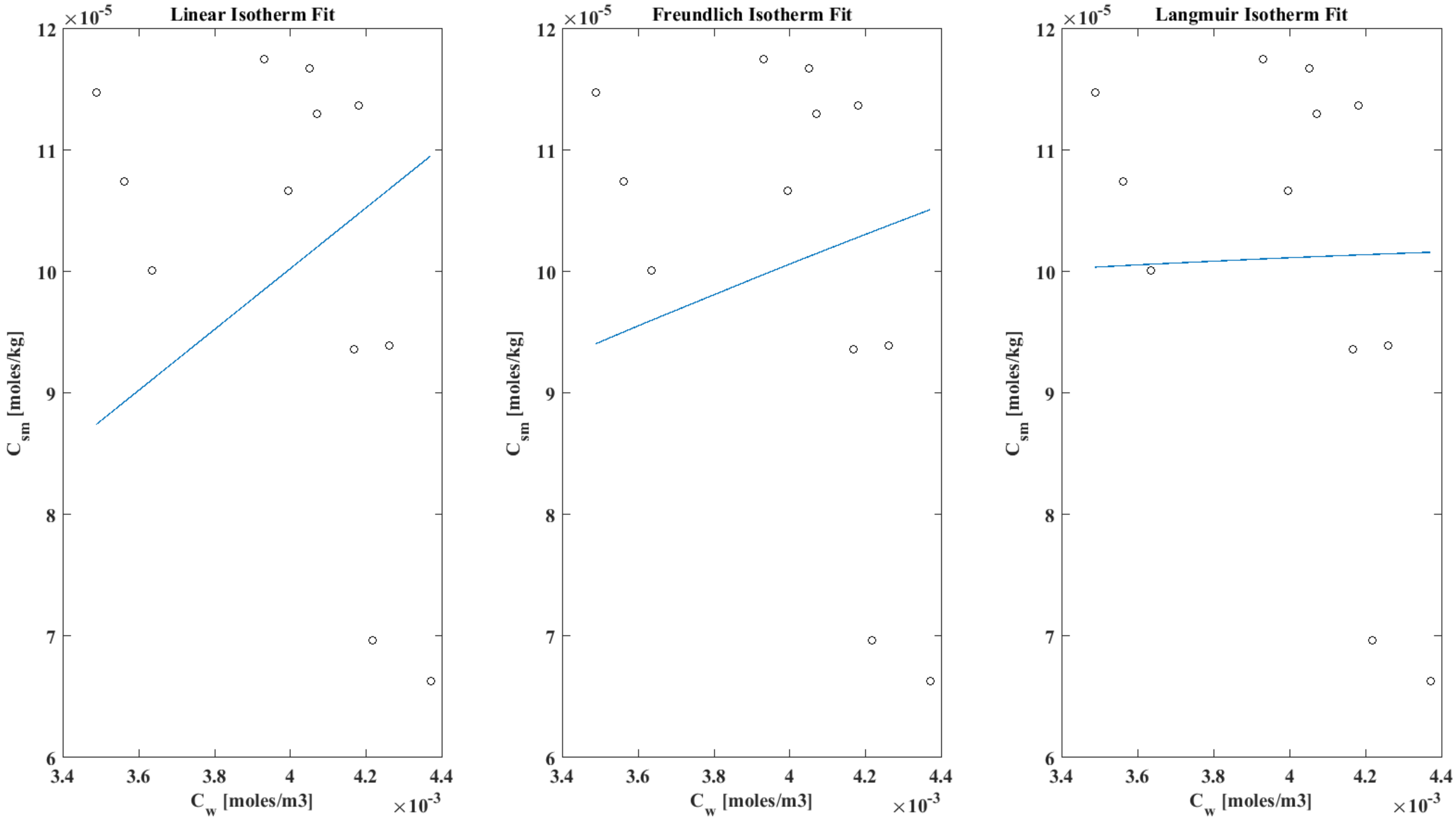
Dark yellowish brown (10 YR 3/6) moist sandy silt loam; weakly developed medium granular structure; soft when dry; slightly sticky and slightly plastic when wet; friable; medium fibrous roots.

24-56 cm Eb

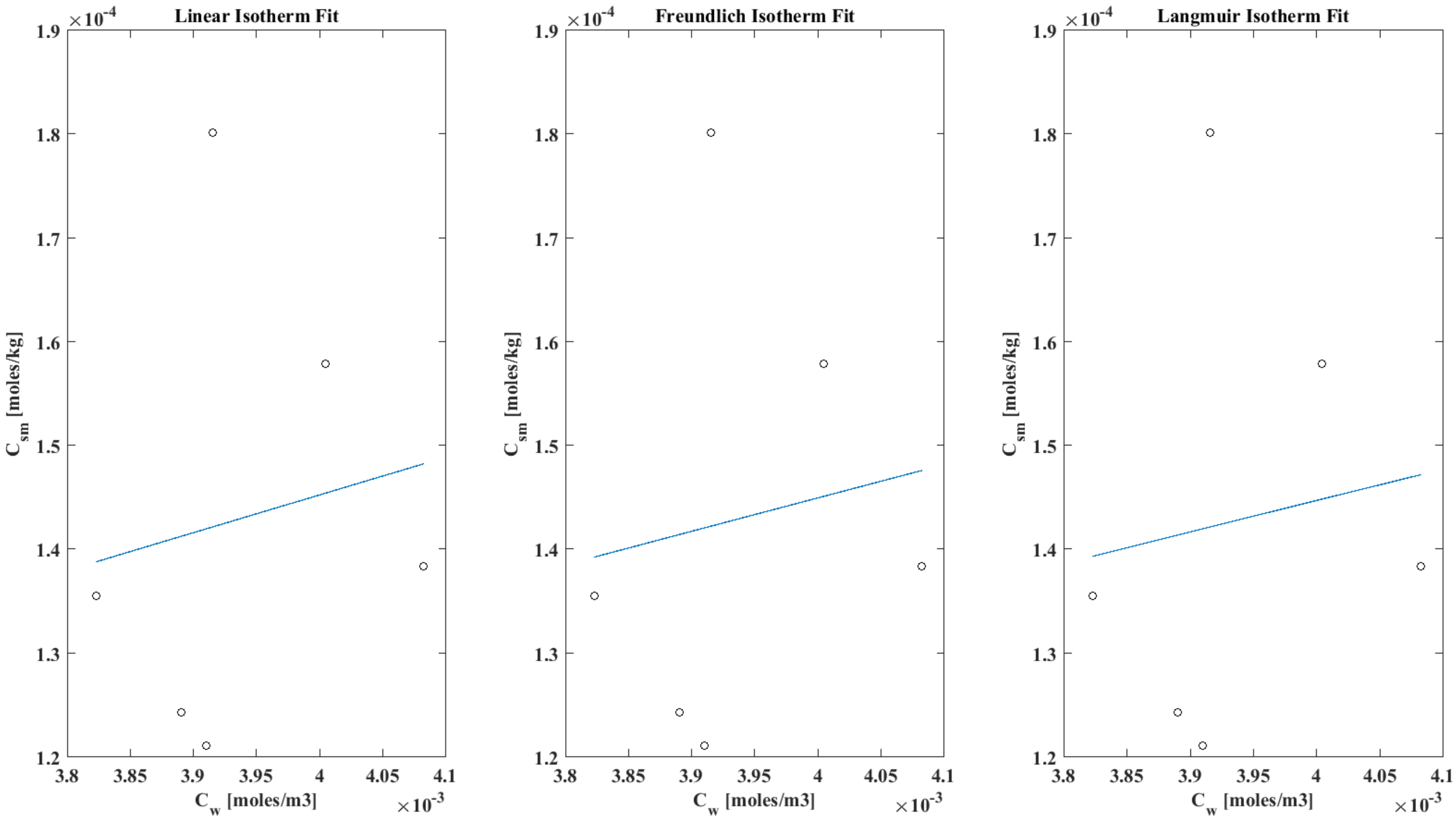
Yellowish-brown (10 YR 5/6) moist sandy silt loam; weakly developed medium granular structure with a light red (10 R 6/8) mottles; soft when dry; slightly sticky and slightly plastic when wet; friable; coarse woody roots.

56-81 cm Bg

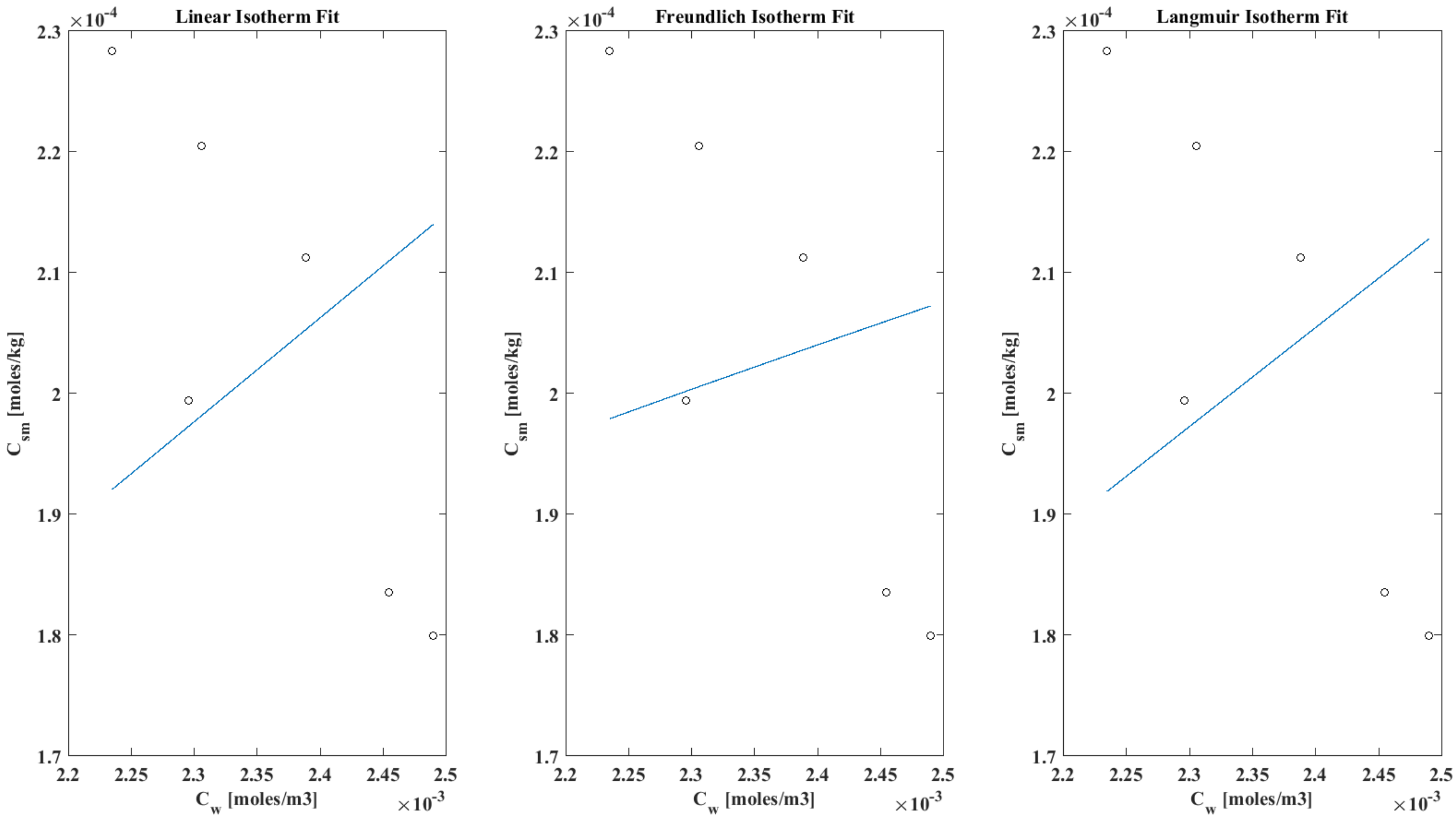
Yellowish-brown (10 YR 5/8) moist sandy silt loam; weakly developed medium granular structure with a light red (10 R 6/8) mottles; soft when dry; slightly sticky and slightly plastic when wet; friable; coarse woody roots.



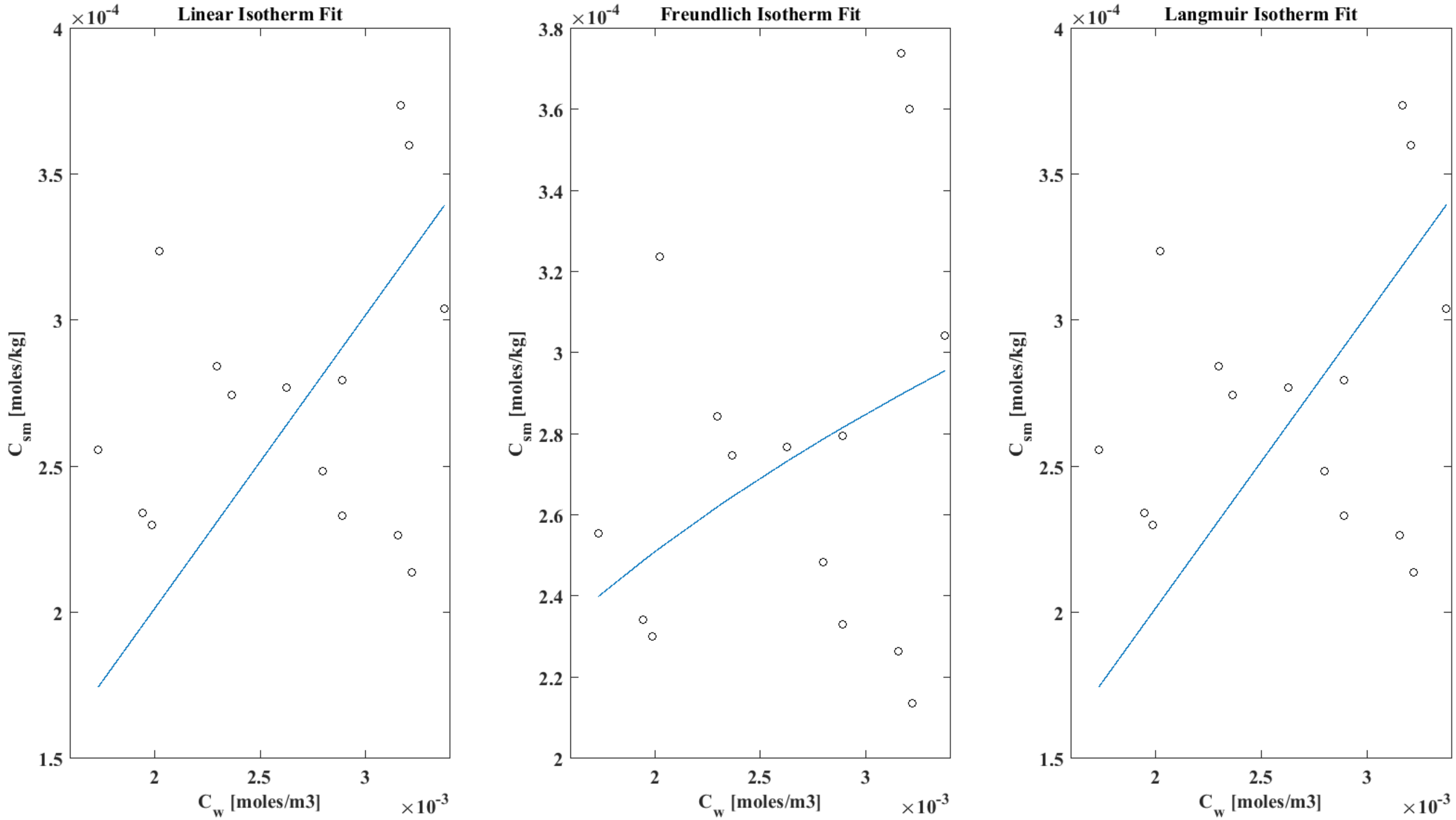
Appendix B.4. Linear, Freundlich and Langmuir isotherm fit for sorption of atrazine onto miscanthus biochar



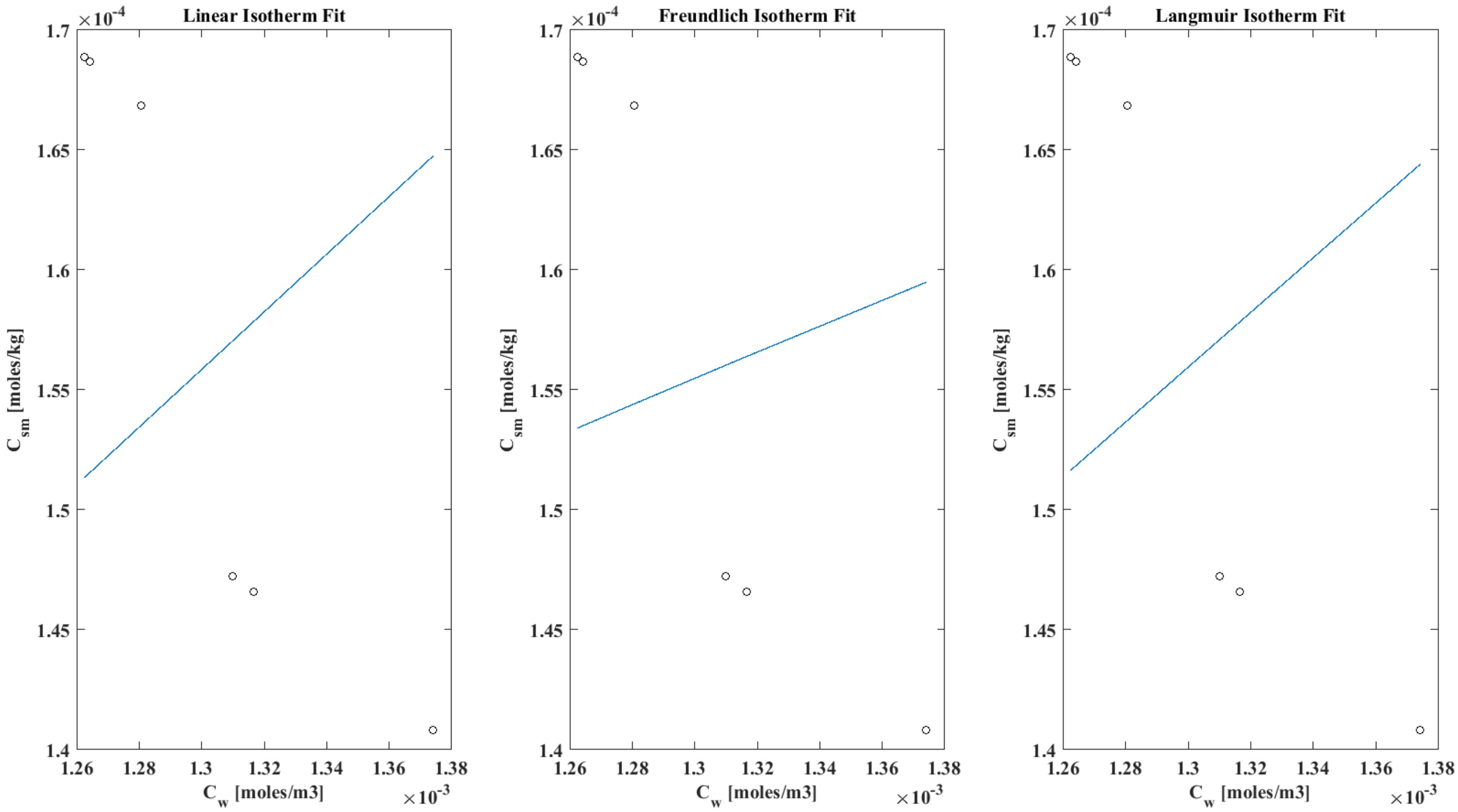
Appendix B.5. Linear, Freundlich and Langmuir isotherm fit for sorption of atrazine onto softwood biochar



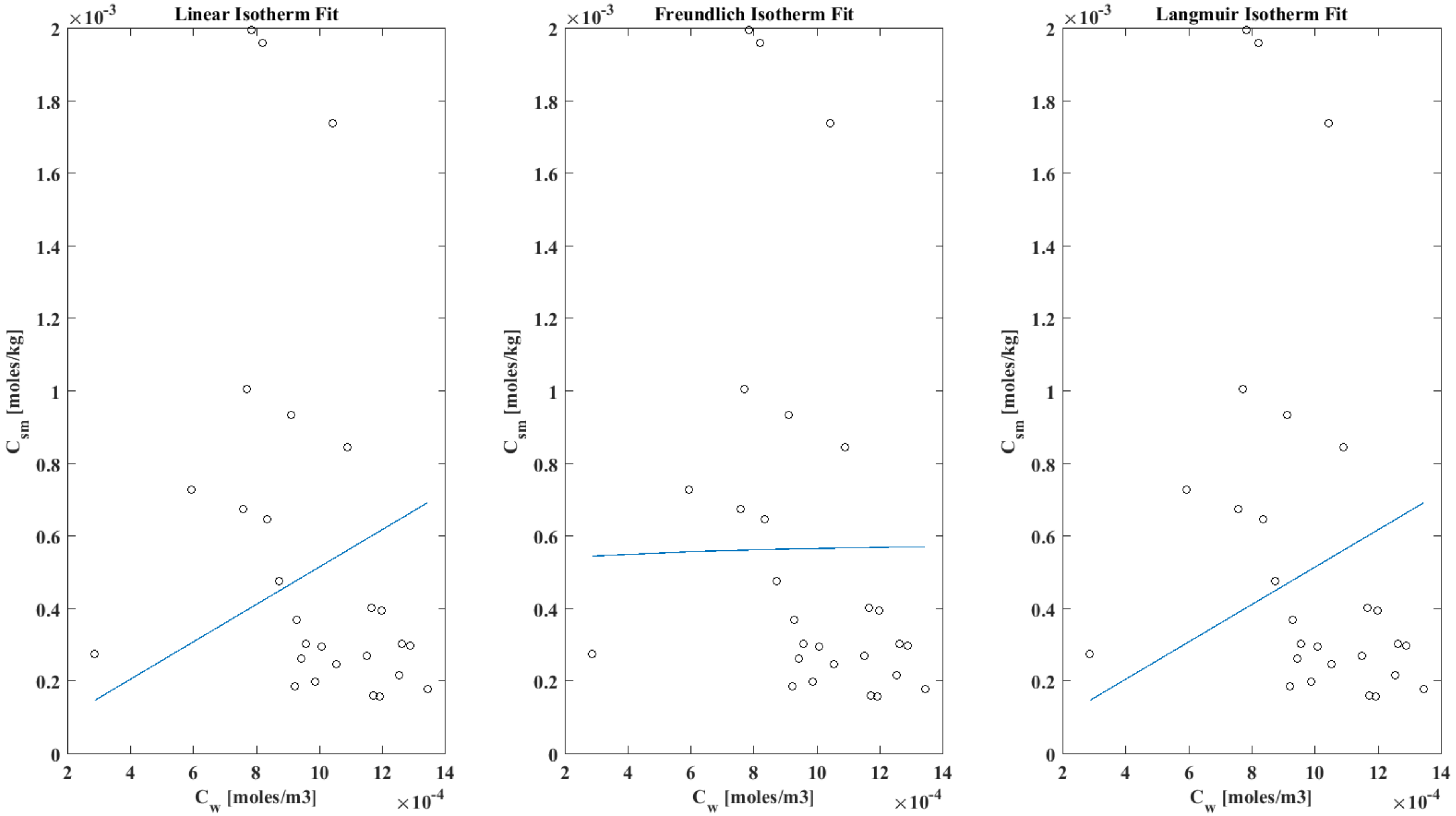
Appendix B.6. Linear, Freundlich and Langmuir isotherm fit for sorption of diuron onto miscanthus biochar



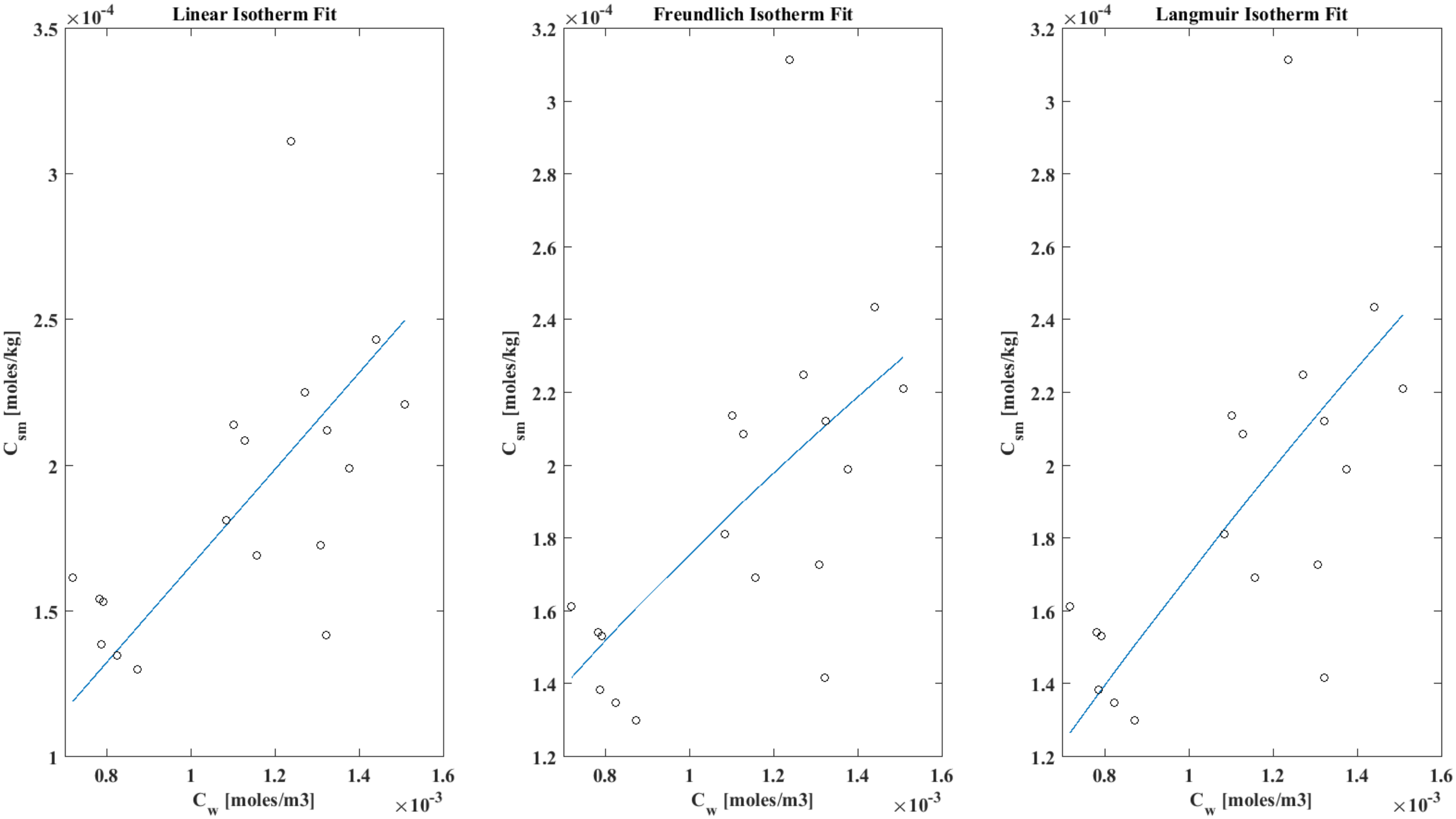
Appendix B.7. Linear, Freundlich and Langmuir isotherm fit for sorption of diuron onto softwood biochar



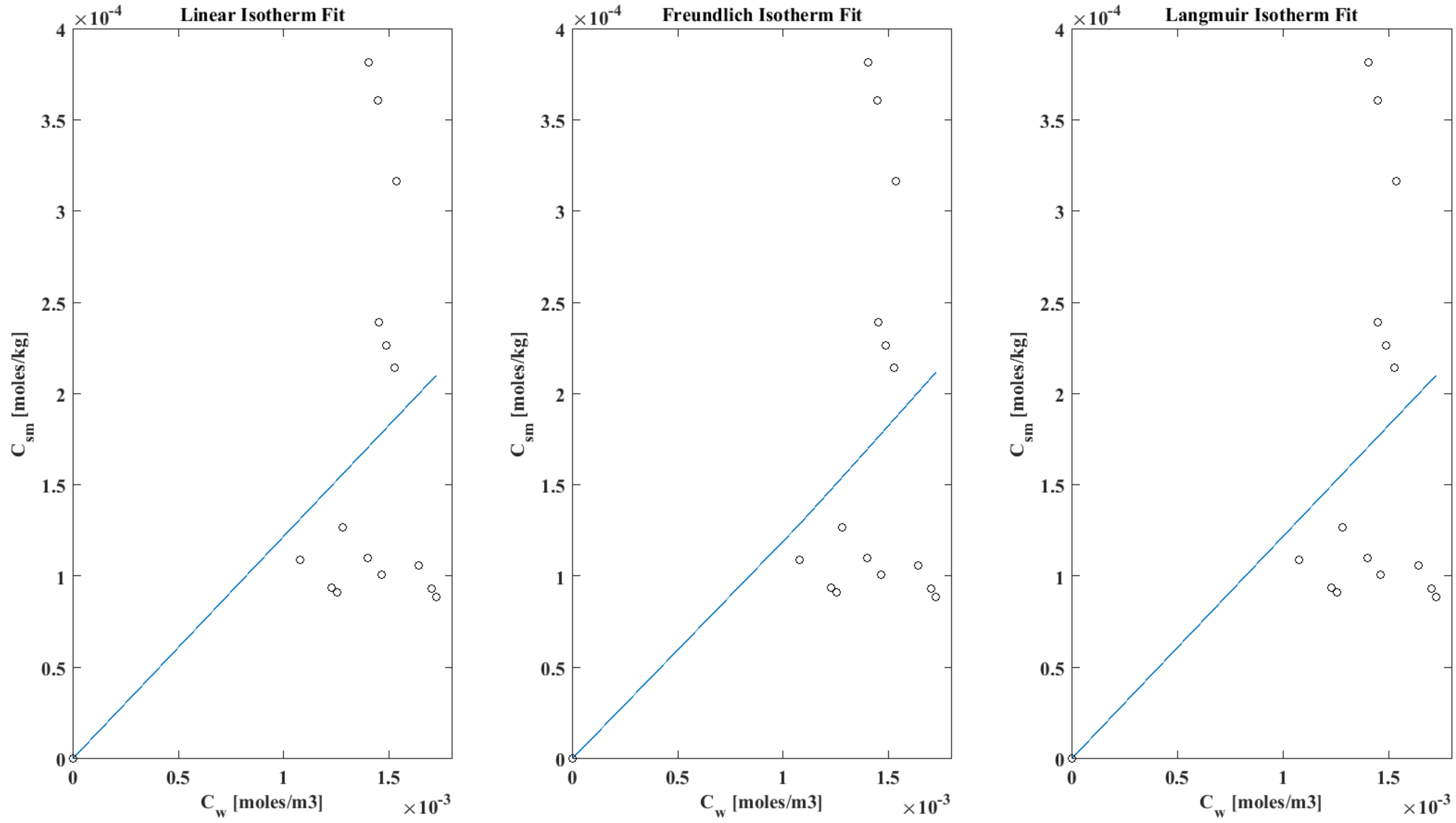
Appendix B.8. Linear, Freundlich and Langmuir isotherm fit for sorption of enrofloxacine onto miscanthus biochar



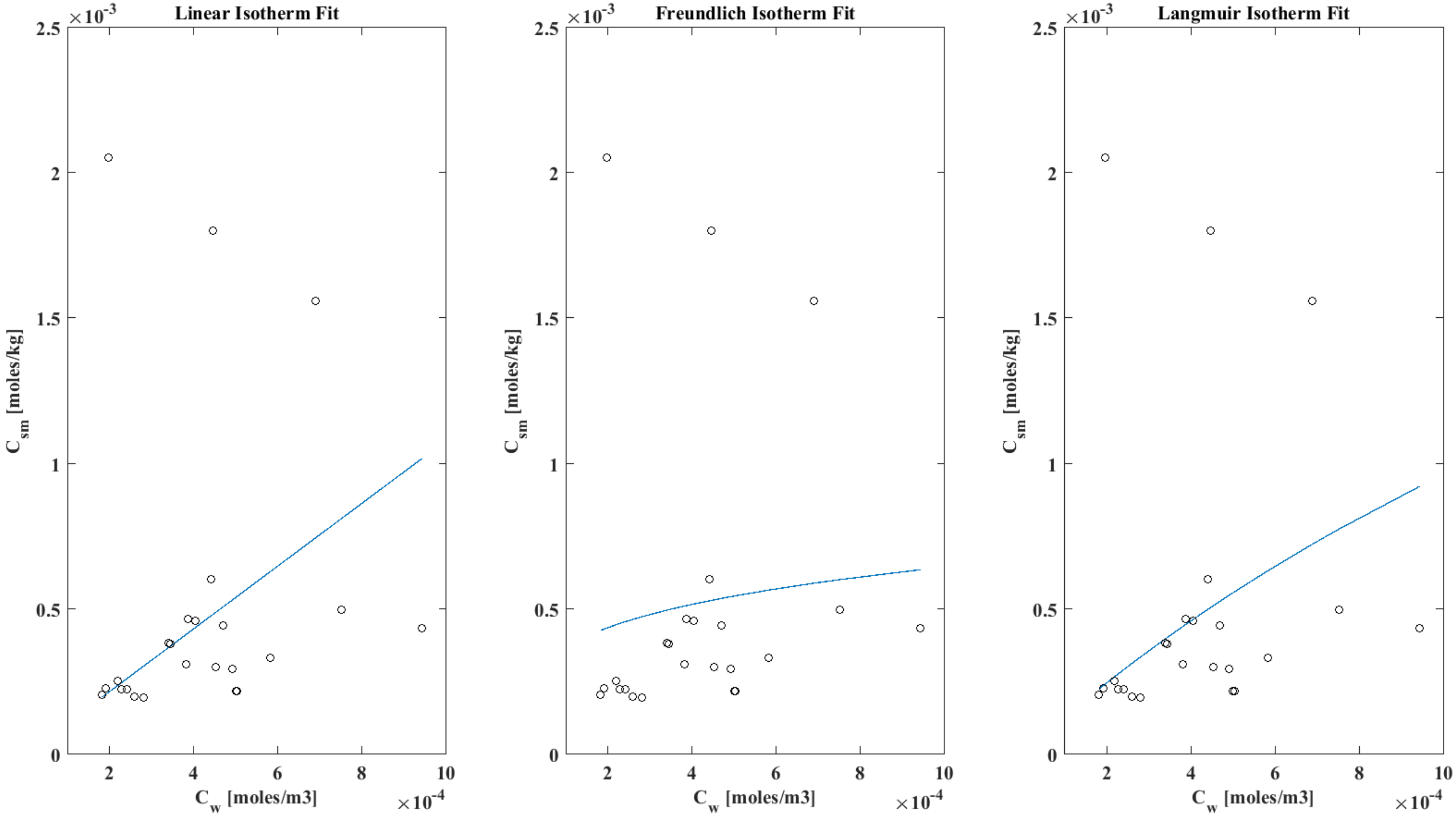
Appendix B.9. Linear, Freundlich and Langmuir isotherm fit for sorption of enrofloxacine onto softwood biochar



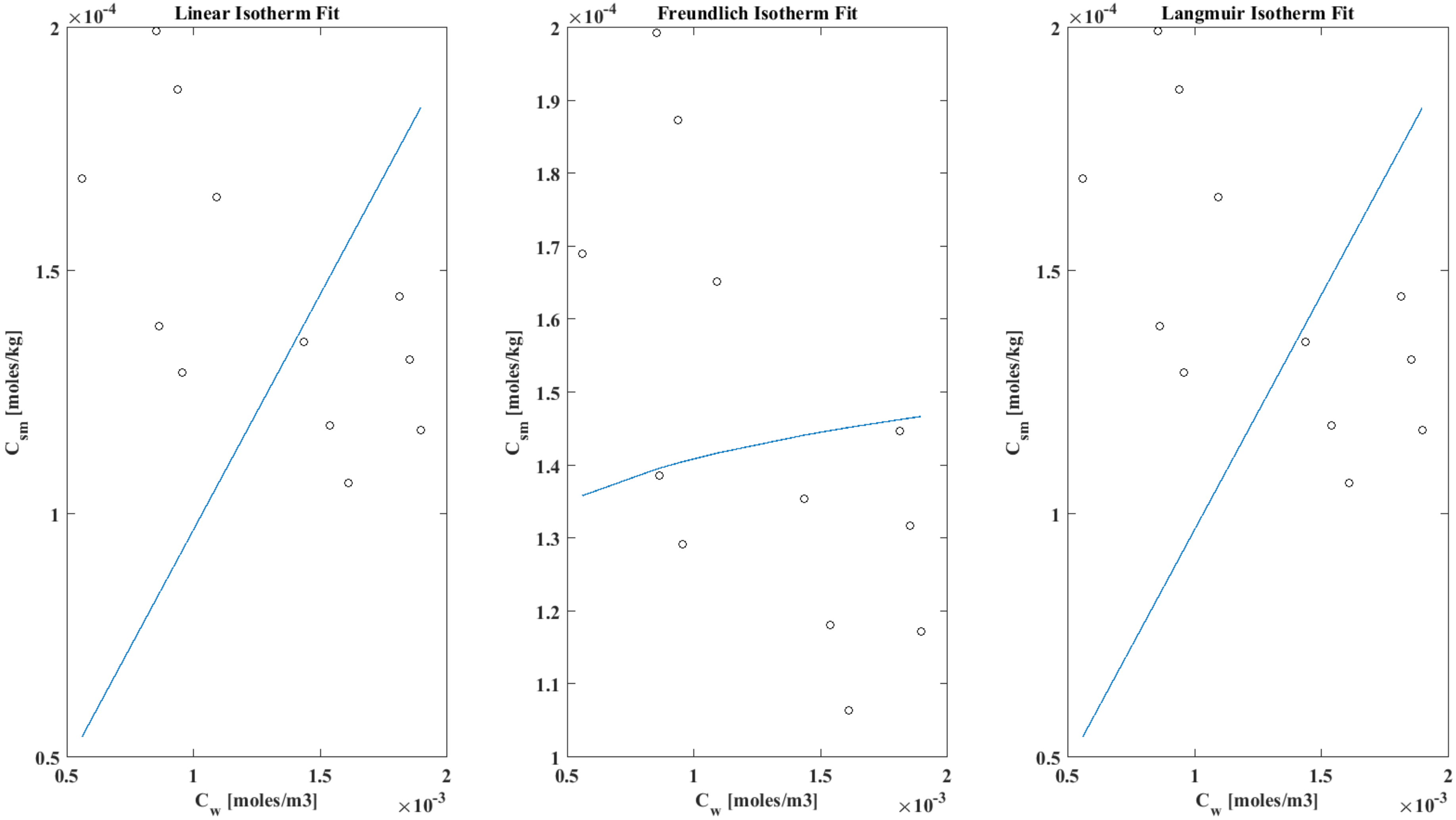
Appendix B.10. Linear, Freundlich and Langmuir isotherm fit for sorption of oxytetracycline onto miscanthus biochar



Appendix B.11. Linear, Freundlich and Langmuir isotherm fit for sorption of oxytetracycline onto softwood biochar



Appendix B.12. Linear, Freundlich and Langmuir isotherm fit for sorption of tetracycline onto miscanthus biochar



Appendix B.13. Linear, Freundlich and Langmuir isotherm fit for sorption of tetracycline onto softwood biochar

Appendix B.14. Linear, Freundlich and Langmuir isotherm model fit for sorption of different compounds onto biochar at 2mm

Chemical	Biochar	Linear		Freundlich			Langmuir		
		K_d (m^3/kg)	SSR	K_f (m^3/kg)	n	SSR	K_L (m^3/kg)	$C_{sm,max}$ (moles/kg)	SSR
Atrazine	Rice husk	7.2503	2.8635e-08	0.0041	5.3133	1.3040e-09	861.6384	0.0091	2.4852e-08
	Softwood	0.0109	1.1089e-08	2.1101e-04	3.6002	9.5469e-09	1.1769e+07	4.6417e-05	8.9675e-09
	Miscanthus	0.1317	6.5061e-08	6.0173e-04	8.7158	4.2727e-09	1.4092e+05	2.9531e-04	1.9469e-09
Diuron	Rice husk	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Softwood	0.2773	3.7574e-07	6.5399e-04	13.0609	1.0048e-08	187.3910	0.0019	3.0225e-07
	Miscanthus	2.6054	4.9277e-07	0.0018	7.3731	8.1846e-09	83.8214	0.0314	4.8776e-07
Enrofloxacine	Rice husk	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Softwood	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Miscanthus	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Oxytetracycline	Rice husk	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Softwood	0.1744	1.6960e-08	0.0013	3.3544	6.0330e-09	1.2446e+04	1.6925e-04	4.9213e-09
	Miscanthus	1.3328	1.9167e-11	0.0097	2.4191	4.3946e-12	1.1870	1.1231	1.9157e-11
Tetracycline	Rice husk	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Softwood	0.4034	2.4758e-08	0.0019	3.4845	4.3645e-09	4.6560e+03	3.1223e-04	4.0619e-09
	Miscanthus	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D

*= No significant difference
N.D = Non detectable

Appendix B.15. Atrazine and Diuron Kinetics

Chemical	Soil	VW	Lin. Tort	Lin. SSR	F. Tort.	F. SSR	F. MB	L. Tort	L. SSR	L. MB
Atrazine	Sandy loam	4.4907e-05	0.2821	2.7537	0.4759	1.8164	1.0000	0.5786	1.1926	1.0000
	Sandy silt loam	4.4907e-05	0.4112	3.6808	0.6154	3.5669	1.0000	0.6712	3.8217	1.0000
	Clay loam	4.4907e-05	1.1839	6.3615	1.0454	3.5380	1.0000	1.0604	3.3540	1.0000
	Loam	4.4907e-05	0.3480	9.5994	0.6171	10.1465	1.0000	0.5843	9.5983	1.0000
Diuron	Sandy loam	-			-	-	-	-	-	-
	Sandy silt loam	4.4907e-05	0.0376	21.6967	0.2662	0.0984	1.0000	0.0945	0.5924	1.0000
	Clay loam	4.4907e-05	0.7732	0.1626	0.4474	0.3775	1.0000	0.8040	0.4075	1.0000
	Loam	4.4907e-05	0.1599	0.2684	0.2525	0.0402	1.0000	0.1621	0.2573	1.0000

Appendix C.

Appendix C.1. Input parameters for atrazine used in PEARL

Parameter	Value	Data source / Remarks
Physico-Chemical parameters		
Molecular weight (g mol^{-1})	215.68	Lewis et al., 2016
Water solubility (mg L^{-1})	35 at 20 °C 42.2 at 25°C	Lewis et al., 2016
Molar enthalpy of dissolution (kJ mol^{-1})	27	Default, FOCUS (2001, 2015)
Vapour pressure (Pa)	3.9×10^{-5} at 20°C	Lewis et al., 2016
Molar enthalpy of vaporization (kJ mol^{-1})	95	Default, FOCUS (2001, 2015)
Diffusion coefficient in water (m^2 d^{-1})	4.3×10^{-5}	Default, FOCUS (2001, 2015)
Diffusion coefficient in gas (m^2 d^{-1})	0.43	Default, FOCUS (2001, 2015)
Degradation in soil		
DT_{50} soil (d)	75	(at 20C in Lab; field study DT_{50} = 29 d) Lewis et al., 2016
Temperature correction function		Default, FOCUS (2001, 2015)
Reference temperature (°C)	20	Default, FOCUS (2001, 2015)
Temperature exponent: (K^{-1})	0.095	Default, FOCUS (2001, 2015)
Q10 (-)	2.58	
Activation energy (kJ mol^{-1})	65.4	Default, FOCUS (2001, 2015)
Moisture correction function		Default, FOCUS (2001, 2015)
Reference moisture (-)	pF2	
Moisture exponent MACRO (-)	0.49	Default, FOCUS (2015)
Moisture exponent PRZM (-)	0.7	Default, FOCUS (2001, 2015)
Sorption to soil		
$Kf_{,oc}$ (mL g^{-1})	100	Lewis et al., 2016
$Kf_{,om}$ (mL g^{-1})	58	K_{OC} / 1.724
Freundlich exponent 1/n (-)	1.07	Lewis et al., 2016
Crop/ Management related parameters		
Wash-off factor from crop		
MACRO (m^{-1})	1	Default, FOCUS (2015)
PRZM (cm^{-1})	0.01	Default, FOCUS (2015)
DT_{50} crop (d)	10	Default, FOCUS (2001, 2015)
Crop uptake factor (-)	0	Worst case

Appendix C.2. Input parameters for diuron used in PEARL

Parameter	Value	Data source / Remarks
Physico-Chemical parameters		
Molecular weight (g mol^{-1})	233.1	EFSA, 2006
Water solubility (mg L^{-1})	35.6 mg/L at 35°C 20.8 mg/L at 20°C	EFSA, 2006
Molar enthalpy of dissolution (kJ mol^{-1})	27	Default, FOCUS (2001, 2015)
Vapour pressure (Pa)	1.15×10^{-6} at 25°C 5.98×10^{-7} at 20°C	EFSA, 2006
Molar enthalpy of vaporization (kJ mol^{-1})	95	Default, FOCUS (2001, 2015)
Diffusion coefficient in water (m^2 d^{-1})	4.3×10^{-5}	Default, FOCUS (2001, 2015)
Diffusion coefficient in gas (m^2 d^{-1})	0.43	Default, FOCUS (2001, 2015)
Degradation in soil		
DT_{50} soil (d)	146.6	(20 – 119d, n = 5) EFSA, 2006
Temperature correction function		Default, FOCUS (2001, 2015)
Reference temperature (°C)	20	Default, FOCUS (2001, 2015)
Temperature exponent: (K^{-1})	0.095	Default, FOCUS (2001, 2015)
Q10 (-)	2.58	
Activation energy (kJ mol^{-1})	65.4	Default, FOCUS (2001, 2015)
Moisture correction function		Default, FOCUS (2001, 2015)
Reference moisture (-)	pF2	
Moisture exponent MACRO (-)	0.49	Default, FOCUS (2015)
Moisture exponent PRZM (-)	0.7	Default, FOCUS (2001, 2015)
Sorption to soil		
Kf_{oc} (mL g^{-1})	757	(EU dossier Kd range 3.5-15.6 mL/g, Koc range 498-1358 m L/g) EFSA, 2006
Kf_{om} (mL g^{-1})	394.43	K_{OC} / 1.724
Freundlich exponent 1/n (-)	0.89	EFSA, 2006
Crop/ Management related parameters		
Wash-off factor from crop		
MACRO (m^{-1})	1	Default, FOCUS (2015)
PRZM (cm^{-1})	0.01	Default, FOCUS (2015)
DT_{50} crop (d)	10	Default, FOCUS (2001, 2015)
Crop uptake factor (-)	0	Worst case

Appendix C.3. Input parameters for glyphosate used in PEARL

Parameter	Value	Data source / Remarks
Physico-Chemical parameters		
Molecular weight (g mol^{-1})	169.1	Lewis et al., 2016
Water solubility (mg L^{-1})	10500 at 20 °C	Lewis et al., 2016
Molar enthalpy of dissolution (kJ mol^{-1})	27	Default, FOCUS (2001, 2015)
Vapour pressure (Pa)	1.31 x 10^{-5} at 20°C	Lewis et al., 2016
Molar enthalpy of vaporization (kJ mol^{-1})	95	Default, FOCUS (2001, 2015)
Diffusion coefficient in water (m^2 d^{-1})	4.3 x 10^{-5}	Default, FOCUS (2001, 2015)
Diffusion coefficient in gas (m^2 d^{-1})	0.43	Default, FOCUS (2001, 2015)
Degradation in soil		
DT_{50} soil (d)	15	(at 20C in Lab; field study DT_{50} = 23.79 d) Lewis et al., 2016
Temperature correction function		Default, FOCUS (2001, 2015)
Reference temperature (°C)	20	Default, FOCUS (2001, 2015)
Temperature exponent: (K^{-1})	0.095	
Q10 (-)	2.58	Default, FOCUS (2001, 2015)
Activation energy (kJ mol^{-1})	65.4	Default, FOCUS (2001, 2015)
Moisture correction function		Default, FOCUS (2001, 2015)
Reference moisture (-)	pF2	
Moisture exponent MACRO (-)	0.49	Default, FOCUS (2015)
Moisture exponent PRZM (-)	0.7	Default, FOCUS (2001, 2015)
Sorption to soil		
Kf,oc (mL g^{-1})	16331	Lewis et al., 2016
Kf,om (mL g^{-1})	9472.7	K_{OC} / 1.724
Freundlich exponent 1/n (-)	0.86	Lewis et al., 2016
Crop/ Management related parameters		
Wash-off factor from crop		
MACRO (m^{-1})	1	Default, FOCUS (2015)
PRZM (cm^{-1})	0.01	Default, FOCUS (2015)
DT_{50} crop (d)	10	Default, FOCUS (2001, 2015)
Crop uptake factor (-)	0	Worst case