KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI COLLEGE OF SCIENCE

DEPARTMENT OF FOOD SCIENCE AND TECHNOLOGY

DETERMINATION OF SOME HERBICIDE RESIDUES IN SWEETPOTATO

BY

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DECLARATION

I hereby declare that this submission is my own work towards the MSc and that, to the best of my knowledge, it contains no material previously published by another person, nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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ABSTRACT

Weeds are undesirable in agriculture activities since they compete with food crops for available soil nutrients, air, water, sunlight and space. Reports indicate that when these herbicides are applied, only about 1% is effective whereas the remaining 99% exist as residues in the surroundings thus posing serious threats to human health, the environment, wildlife and other non-target organisms. The objective of this work was to determine the level of some herbicide residues in sweetpotato. The sweetpotatoes were cultivated in a completely randomized block design (CRBD) with four replications at the Crops Research Institute Agronomy fields, Kwadaso where different treatments made up of combinations of five (5) pre-emergence herbicides (butachlor [50g/L-3L/Ha], imazethapyr [240g/L-3L/Ha], metolachlor [333g/L-4L/Ha], pendimethalin [500g/L-3L/Ha] and terbutryn [167g/L4L/Ha]) and one (1) post-emergence herbicide (propaquizafop [100g/L-1.2L/Ha]) were applied and a control which involved strictly hoeing. After harvest, samples were randomly selected and extracted using a modified QuEChERS extraction method followed by Liquid Chromatography-Mass Spectrometry (LC-MS) to determine the residual levels of the herbicides. The results showed that sweetpotato samples from the control (field work which was strictly hoeing as the method of weed management) had no residues detected. Butachlor, imazethapyr, terbutryn and propaquizafop were also not detected in their respective sweetpotato samples analysed. However, pendimethalin and metolachlor residues were detected at concentrations of 0.0023 µg/g and 0.0029 µg/g, respectively. The findings suggest that herbicide residue levels detected in this study were considerably lower than the maximum acceptable limit (0.05 mg/kg) and thus the dietary exposure could be considered safe to humans.

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OMAFRA	Ontario Ministry of Agriculture, Food and Rural Affairs
USEPA	United States Environmental Protection Agency
MRL	Maximum Residue Limit
CRBD	Completely Randomized Block Design
CR	Crop Research

CHAPTER ONE

INTRODUCTION

1.1 Background

Sweetpotato (*Ipomoea batatas* L.) is a very vital food and industrial crop, cultivated globally with an annual production of over 122 million metric tonnes (Ofori *et al.*, 2009). According to Milind *et al.* (2015), sweetpotato cultivation dates back to the 750 BC, thus one of the oldest vegetables known to mankind. Several species have been commonly used in religious rituals, medicinal and ornamental purposes. It is known to be a staple starchy and tuberous root vegetable and its production is increasing rapidly in many countries in the Sub-Saharan Africa (Korada *et al.*, 2010). According to Amengor *et al.* (2016), SaharanAfrica has about 13.37 million hectares of land cultivated with sweetpotato, thus making it the third most important root crop after cassava and yam. Here in Ghana, sweetpotato is a major non-traditional export crop and in the year 2013, the harvested area was about 74,000 hectares (FAOSTAT, 2015). Odebode *et al.* (2008) attributed the wide spread of sweetpotato in Africa to its ease of cultivation, high ability to tolerate drought and hence its capacity to withstand the rather harsh environmental conditions characteristic of this agro-ecological zone. Other factors that have contributed to the widespread cultivation of this food crop includes the low requirement for fertilizers and the flexible planting and harvesting periods. The white or yellow–fleshed sweetpotato are the commonly grown varieties in most parts of Africa, including Ghana (Kapinga *et al.* 2001). The orange-fleshed cultivars in particular have been reported to possess a high content of naturally bio-available precursors of vitamin A (β-carotene) and its cultivation is therefore encouraged in the developing countries due to their prominence in combating vitamin A deficiency (Laurie *et al.*, 2015). Furthermore, properties such as anti-carcinogenic, cardio-vascular disease-preventing and its high nutrient content has resulted in its recognition as a health food (Njintang *et al.*, 2016). A report by Ofori *et al.* (2009) showed that sweet potato is not usually integrated into the menu of most food service establishments and even in the household menu, and this is probably because more importance and uses are attached to the other roots crops such as cocoyam, cassava and yam (Adu-Kwarteng *et al.*, 2002; Opare-Obisaw *et al.*, 2000)

Degras (2003) reported that, 57% of food crops in some parts of Africa are lost due to the presence of weeds, hence the need to effectively apply herbicides. Weeds influence agricultural activities by competing with crops for available soil nutrients, air, water, sunlight and space, and also harbouring other invasive pests (Wyss and Müller-Schärer, 2001). In modern times, agrochemicals form an integral part of agricultural production systems globally. Herbicides are described as a subtype of pesticides which are applied with the intention of killing, controlling or preventing the excessive growth of weeds or unwanted plants. The control of weeds with herbicides in modern day agriculture has become indispensable due to the acute shortage of farm labourers (Ponnusamy e*t al.*, 2015). Dinham (2003) estimated that about 87% of Ghanaian farmers apply pesticides to control pests, diseases and weeds during the cultivation of fruits and vegetables. Ntow *et al*. (2006) reported that out of the pesticides used in Ghana, herbicides make up 44%, 33% for insecticides and 23% are fungicides. Due to the chemical nature of herbicides, using them excessively and repeatedly may result in serious problems including phytotoxicity to food crops, residual effects on susceptible crops, adverse effects on non-target organisms and ultimately severe health hazards to human and animals due to the accumulation of residues in the crops, soil, surface and ground water (Ponnusamy *et al.*, 2015). Furthermore, upon the realization of the effectiveness of these herbicides, farmers tend to increase application consistently to meet their production targets without taking into consideration the negative aspects associated with these herbicides. According to Das and Mondal (2014), the improper use of these chemicals can injure food crops, severely damage the environment and also pose health threats to the applicator as well as other people exposed to the chemicals.

1.2 Problem Statement

Weeds have been reported to be a very major challenge associated with sweetpotato production and according to Nedunchezhiyan *et al.* (2013), yield reduction of ninety-one (91) % was observed in sweetpotato as a result of weed competition. Moody and Ezumah (1974) also reported yield losses of 22%, 78% and 91% due to the uncontrolled growth of weeds in Hawaii, the West Indies and Nigeria, respectively. Some other reports have indicated that the interference of weeds has resulted in yield reductions which have ranged from 14% to almost 70% in various sweetpotato cultivars (La Bonte *et al.*, 1999). Despite the fact that manual weeding (including hand pulling, slashing and hoeing) is the most common or widespread method of weed control practiced by subsistence farmers in Africa (Chikoye *et al.*, 2002), it has proved to be inefficient because it is tedious, time consuming, labour and cost intensive and expensive (Vissoh *et al.*, 2004; Ekeleme, 2013). Furthermore, the scarcity of labour especially during peak periods of critical competition between weeds and crops make this method quite difficult and uneconomical (V. P. Singh et al., 2016). Therefore, among all the agricultural chemicals, the use of herbicides is becoming popular and imperative for various reasons such as unfavourable climatic conditions for weeding, the non-availability of farm labour and high labour costs (Rao *et al.*, 2012).

Herbicides play a very critical and significant role in modern agriculture since they contribute immensely to food production. According to Grabowski and Jayne (2016), recent evidence suggests that the use of herbicides in some parts of Africa is generally on the increase. It has also been estimated that about 25% of pesticides produced globally are used by farmers in developing countries and the population suffers deaths from pesticides poisoning (WHO, 2008). Herbicides are produced under very strict regulations as a means of reducing their negative impact on human health and on the environment, however, reports indicate that, when these herbicides are applied, only about 1% is effective whereas the remaining 99% exist as residues in the surroundings thus posing serious threats to human health, the environment, wildlife and other non-target organisms (Zhang *et al.*, 2011; Eskenazi *et al.*, 2008). Residue of herbicides found in crops are inevitable even if applied as instructed by the manufacturers; this has therefore attracted attention from the sweetpotato value chain as this could be a great menace to human health and the environment (Darko and Acquaah, 2007; Damalas and Eleftherohorinos, 2011). Farmers are aware of the potential health risks associated with these chemicals, however, some still use these chemicals indiscriminately since they are more concerned about minimizing the destructive effects of weeds on their crops and of course, obtaining optimum yield. Most often, farmers apply herbicides to the target weeds without paying due attention to instructions stated on the labels of the herbicides with respect to the recommended rates of application and the right ways of disposing off excess herbicides after application and this ultimately leads to the presence of more toxic residues (Adomako, 2015).

1.3 Justification

The use of synthetic herbicides for the purposes of controlling weeds is a very common practice in modern agricultural systems (Sanyal and Shrestha, 2008). The application of herbicides has indeed become the main strategy for weed control for both agricultural and non-agricultural purposes in Ghana. More research work has been carried out with emphasis mainly on pesticide residues especially in fruits and vegetables; however, very little has been done with regards to herbicide residues in roots and tubers, especially sweetpotato. There is therefore the need to ascertain the levels of herbicide residues in sweetpotatoes and also adopt appropriate measures for controlling the presence of these residues so as to reduce the health risks posed on consumers.

1.4 Objective

This study aims to determine the levels of some herbicide residues in sweetpotato.

CHAPTER TWO

LITERATURE REVIEW

2.1 Origin and Botany of Sweetpotato

According to Milind *et al.* (2015), the history of sweetpotatoes dates back to 750 B.C. in Peruvian records; these crops were also known in pre-Columbian times in Polynesia as early as 1200 A.D. Being one of the oldest food crops known to mankind, sweetpotato is native to South America where it has been cultivated for over 5000 years (Milind *et al.*, 2015). Also according to history, sweetpotatoes were introduced to Europe by Christopher Columbus after his initial expedition to the New World in 1492. In Spain, sweetpotatoes were cultivated as early as 1500 A.D. and by the 16th century, Spanish explorers took the food crops to the East Indies and the Philippines, from where they spread easily to Africa, China, India, Southern Asia and Indonesia, probably with the help of the Portuguese traders at that time (Milind *et al.,* 2015). Based on the volume of production, sweetpotato ranks as the seventh and fifth most important food crop globally and in developing countries respectively. In recent times, the main commercial producers are China, Vietnam, Indonesia, India, Japan and Uganda (Milind *et al.,* 2015). The sweetpotato was first described by Linnaeus as *Convolvulus batatas* in 1753; Lamarck, in 1791, then classified this species within the genus *Ipomoea* based of the stigma shape and the surface of the pollen grains (Adom, 2016). The name was therefore changed to *Ipomoea batatas* (L.) Lam (Ray and Tomlins, 2010). The systematic classification of the sweetpotato is as follows:

Table 1: Taxonomical Classification of Sweetpotato

Kingdom	Plantae
Sub kingdom	Tracheobionta
Super division	Spermatophyte
Division	Sagnoliophyta
Class	Magnoliopsida
Subclass	Asteridae
Order	Solanales
Family	Convolvulaceae
Genus	*Ipomoea L*
Species	*Ipomoea batatas(L.)*

Source: (Milind *et al.*, 2015)

2.2 Sweetpotato Production

Annual production of sweetpotato in Africa is estimated at over seven (7) million tonnes (Kapinga *et al.*, 2001), and this is known to occupy about sweetpotato 13.37 million hectares of land in the Sub-Saharan Africa (Amengor *et al.* 2016). In Africa, the largest producers are Tanzania followed by Nigeria with record production figures of about 3.6 and 3.3 million tonnes respectively (Amengor *et al.*, 2016). A total land area of about 65, 000 hectares has been reported to produce about 90,000 tonnes of sweetpotato annually in Ghana (Bidzakin *et al.*, 2014) Sweetpotato is a herbaceous perennial crop, however, it is usually domesticated as an annual food crop vegetatively by means of its storage roots or vine (stem) cuttings (Ray and Tomlins, 2010). The prostate vine system of sweetpotato expands very rapidly horizontally on the ground with erect/semi- erect or very spreading growth habit. It is grown widely in the tropics, subtropics and warm temperate regions due to its versatility (Srisuwan *et al.*, 2006). The tubers are harvested 100-180 days after planting the stem cuttings. .The tuberous roots which grow between 15 and 100 centimeters mostly have masses that range between 0.5 and 2.0 kilograms (CSIR-SARI, 2011; Hillocks, 2002). In Ghana, sweetpotato is widely grown on a subsistence scale by small-holder farmers and the notable production areas include the Eastern, Central, Northern, Upper East, and Volta Regions (CSIR-SARI, 2011; Wie and Aidoo, 2017) (Table 2). A report by Kapinga *et al.* (2001), indicates that the white or yellow–fleshed species are the mostly grown varieties in Ghana as these supply substantial amounts of vitamin A when they are incorporated into diets. Odebode *et al.* (2008) attributed the wide spread of sweetpotato in Africa to its ease of cultivation, high ability to tolerate draught and hence its capacity to withstand the rather harsh environmental conditions characteristic of this agro-ecological zone. Low fertilizer requirements, flexibility in planting and harvesting periods are other properties that have probably contributed to the widespread cultivation of sweetpotato in Africa.

Table 2: Sweetpotato Production in Ghana

Region	Area (Ha)	% Contribution	Production (Mt)	% Contribution
Central	371	3.9	6,490	4.9
Volta	880	9.1	15340	11.6
Eastern	1030	10.7	34910	26.4
Greater Accra	38	0.4	640	0.5
Ashanti	37	0.4	620	0.5
Brong-Ahafo	145	1.5	2390	1.8
Northern	414	4.3	6070	4.6
Upper East	5550	57.7	46000	34.9
Upper West	1157	12	19530	14.8
Total	9622	100	131990	100

Source: MoFA Field Survey, 2012

2.3 Sweetpotato and its Potentials

2.3.1 Economical Impact

Root and tuber crops play an extremely important role in the global food system, predominantly in developing countries, where they are considered to be very important staple food crops after cereals (Reddy, 2015; Njintang *et al.*, 2016). These food crops are important sources of carbohydrates and they significantly contribute to the sustainable development, income generation and food security, especially in the tropical areas (Njintang *et al.*, 2016). In terms of the production per unit area, sweetpotato exceeds cereals such as rice, wheat and maize as the world's highest yielding food crop (Reddy, 2015). The increase in sweetpotato cultivation in Africa can also be attributed to the easy planting of the crop, its early maturity and its vast industrial and economic potentials. A research conducted by CORAF/IFPRI (2006) showed that roots and tubers add immensely to agricultural growth in Ghana since these fresh storage tubers are sold in open markets as well as export markets to generate income.

2.3.2 Health Related Impact

Orange-fleshed cultivars in particular have been reported to have a high content of naturally bio-available precursor of vitamin A (β-carotene) and are thus promoted across the developing countries due to their prominence in combating vitamin A deficiency (Laurie *et al.*, 2015). The research findings by Terahara *et al.* (2004) in relation to the antimutagenicity and efficacy of sweetpotato anthocyanins against liver disease revealed that sweetpotato (particularly the purple–fleshed cultivar, Ayamurasaki), which stores high levels of anthocyanin pigments in the storage roots may contribute to maintaining good human health. Sweetpotato contains phenolics, which are found to inhibit the growth of cancer cells in the human colon, and stomach as well as those associated with leukemia (Kurata *et al.*, 2007). These phenolics are known to inhibit growth of fungi and viruses in-vitro (Peterson *et al.*, 2005) and also contribute to the amelioration of diabetes in humans since some studies have shown that they aid in stabilizing blood sugar levels and also reduce the resistance of insulin (Ludvik *et al.*, 2008; Milind *et al.*, 2015). The consumption or processing of sweetpotato with its peels may also enhance its nutraceutical potential due to the higher content of some antioxidants in the peels (Salawu *et al.*, 2015). A study conducted by Tuffour (2013) revealed that sweetpotato starches exhibited properties suitable for use as pharmaceutical excipients in oral tablet dosage forms. His results also showed that sweetpotato starch was more robust as binder and disintegrant compared to the commercially available maize starch. In addition, sweetpotato also contains magnesium which is known to be the key mineral for de-stressing and also promotes artery, muscle, nerve as well as bone health (Milind *et al.*, 2015). The anti-carcinogenic and cardio-vascular disease-preventing properties of sweetpotato coupled with its high nutrient content has resulted in its recognition as a health food (Njintang *et al.*, 2016). The pharmacological activities of sweetpotato are summarized in Table 3 below.

Table 3: Pharmacological Activities of Sweetpotato (*Ipomoea batatas*)

Pharmacological Activities	Plant Parts	Extracts
1. Anti-infective		
i. Anti-fungal	Root	Acetone extract
ii. Anti-viral	Leaf, Root, Peel	Alcoholic and Aqueous extract
iii. Anti-microbial	Leaf	Ethanolic crude leaves extract
2. Anti-cancer		
i. Anti-tumor	Leaf	Aqueous and Alcoholic extract
ii. Anti-proliferative	Leaf, Root	Aqueous extract
iii. Anti-cancer	Leaf	Methanol extract
iv. Colorectal cancer prevention	Root	Sweetpotato protein extract (aqueous, alcoholic)
v. Anti-mutagenic	Leaf, Root	Aqueous extract
3. Inflammatory diseases		
i. Anti-inflammatory	Dried aerial part	Aqueous extract
ii. Anti-ulcer	Root	Butanol extract, sweetpotato flour
iii. Wound healing	Peel, Leaf, Root	Peel extract gel
4. Diabetes		
i. Anti-diabetic	Transgenic sweetpotato whole plant (mainly leaf)	Aqueous and Alcoholic extract
ii. Hypoglycemic	Root	Acetic acid extract of white skinned sweetpotato

5. Atherosclerotic lesions	Purple sweetpotato root	Chloroform, Methanol, Ethyl acetate extract
6. Miscellaneous		
i. Anti-oxidant	Leaf, Root	Methanolic extract
ii. Oxidative stress	Root	Aqueous, Methanol extract
iii. Immunomodulatory	Root	Aqueous extract
iv. Ultra-violet protection	Leaf, Root, Whole plant	Aqueous, Ethanol extract
v. Hepatoprotective	Whole plant	Aqueous extract

Source: (Milind *et al.*, 2015)

2.3.3 Nutritional Impact

Nutritionally, the tubers are known to be well-balanced with a good proportion of protein and calories; due to this fact, sweetpotato, is regarded as a start-up food for infants (Wie and Aidoo, 2017). The tubers also contain several essential vitamins; vitamins B_1, B_5, B_6, niacin, as well as riboflavin which act as co-factors for many enzymes during metabolic processes (Table 4). Vital nutrients including manganese, calcium, potassium and magnesium which are known to play essential roles in carbohydrate and protein metabolism have been reported to be contained in sweetpotato (Njintang *et al.*, 2016). Sweetpotato therefore, outranks many carbohydrate foods in terms of its mineral, vitamins, dietary fibre and protein content (Motsa *et al.*, 2015).

Table 4: Nutritional composition of root tuber of fresh sweetpotato

Nutritional value	Per 100g of sweetpotato tubers
Energy	360 KJ (86 Kcal)
Carbohydrate	20.1 g
Starch	12.7 g
Sugars	4.2 g
Dietary fibre	3.0 g
Fat	0.1 g
Protein	1.6 g
Beta carotene	8.5 mg
Thiamine (vitamin B1)	0.1 mg
Riboflavin (vitamin B2)	0.1 mg
Niacin (vitamin B3)	0.6 mg
Pantothenic acid (vitamin B5)	0.8 mg
Pyridoxine (vitamin B6)	0.2 mg
Folate (vitamin B9)	11.0 µg
Ascorbic acid (vitamin C)	2.4 mg
Vitamin E	0.3 mg
Calcium (Ca)	30.0 mg
Iron (Fe)	0.6 mg
Copper (Cu)	0.2 mg
Magnesium (Mg)	25.0 mg
Phosphorus (P)	47.0 mg
Potassium (K)	337.0 mg
Sodium (Na)	55.0 mg

Zinc (Zn)	0.3 mg

Source: USDA, 2010

In Ghana, the roots of sweetpotato may be deep fried or boiled and eaten as "ampesi" while the leaves are consumed as vegetables and can serve as a substitute for cocoyam leaves locally referred to as "kontomire". The tubers are also used in the preparation of baby weaning foods. However, a study by Ofori *et al.* (2009) indicated that most Ghanaian menus do not contain dishes prepared with sweetpotato. A survey by Baafi *et al.* (2015) indicated that about 39% of the respondents ate sweetpotato two or three days per week; about 28% consumed it at least six days per week and about 12% consume at most only once weekly. This situation needs to be addressed seriously through the rebranding of processed products from sweetpotatoes so as to raise awareness on the great potential of the crop. The use of sweetpotato in several forms in other countries has been reported in literature. In other parts of the world, mostly in the developed countries, sweetpotatoes have been processed into dehydrated forms and purees that are utilized as functional ingredients in several food products (Ray and Tomlins, 2010). According to Njintang *et al.* (2016) about 90% of the starch obtained from sweetpotato in Japan is used in the manufacture of syrups, lactic acid beverages and bread. These can be adopted to boost its production and consumption in

Ghana. Just as "gari" is produced from cassava, other countries have been able to successfully process sweetpotato into a form known as "spari" (coined from "sweetpotato gari") that looks exactly like the local Ghanaian "gari" (Odebode *et al.*, 2008). According to reports, the processes involved are very similar to the processing of cassava into gari. The use of sweetpotato in the confectionary industry for making flour which serves as a supplement to the cereal flour has also been reported. Coloured sweetpotato flour is used in various bakeries and noodles preparations (Ray and Tomlins, 2010). Odebode *et al.* (2008) reported that in other countries such as the USA, sweetpotato tubers, especially the yellowfleshed varieties are cut into large chunks, filled into cans, heated at 85^{0}C and sealed immediately. These are then sold as canned sweetpotatoes. The use of sweetpotato as animal feed has also been reported. The vines as well as the unmarketable and poorly developed tubers can serve as a nutritive and palatable feed for cattle and pigs (Njintang *et al.*, 2016). Processed sweetpotato has the potential of being used as an industrial source of starch, especially the alcoholic industry.

2.4 Sweetpotato Cultivation

2.4.1 Cropping Pattern

Sole cropping is normally practiced in sweetpotato production though it can also be cultivated in intercropping and rotation systems with beans, sorghum, maize and cassava (Davis *et al.*, 1986). Research works on intercropping and crop rotation of sweetpotato with other food crops have revealed that they have the tendency to reduce the infestation of sweetpotato by weevils and ultimately increase crops yields (Mansaray *et al.*, 2013). A typical example is a study conducted in Kerala, India by Pillai *et al.* (1996) which revealed that when sweetpotato was intercropped with colocasia, cowpea or rice, it resulted in tenfold reduction in sweetpotato weevil infestation as compared to mono-cropping. On the contrary, Singh *et al.* (1984) also reported that the yield of sweetpotato grown in the mixed cropping system is generally lower compared to those grown in monoculture. The reason for this observation has been attributed to the shading effect of higher crops on the shorter sweetpotato crops. It has also been reported that the ability of sweetpotato to control weeds has been attributed to the vigorous nature of the vines growth (Brobbey, 2015).

2.4.2 Climate and Soil

Having good adaptability in diverse environmental conditions, warm and humid climates with temperatures between 21 – 26^{o}C have been shown to favour the best growth of sweetpotato. Wide range of soil types have been reported to favour the growth of sweetpotato, however, sandy or sandy loam with adequate drainage, good aeration, porosity and with a reasonable high organic content are ideal for the best growth (Njintang *et al.*, 2016). Ray and Tomlins (2010) reported that sandy soils encourage the development of roots that are long and cylindrical (pencil-like) whereas heavy clay soils restrict or prevent large storage root development due to compactness. Such soils end up producing irregularly sized and shaped storage roots. According to Brobbey (2015), sweetpotato performs best in regions that have a well distributed rainfall of 750 - 1000mm per annum, with about 500mm falling during the growing season. It is able to tolerate drought to some extent but cannot withstand water logging (Obigbesan, 2009). Adequate sunshine is very important for crop development; immoderate shade only leads to reduction in yield (Ray and Tomlins, 2010). Sweetpotato is also known to be acid-tolerant with optimum soil pH within the range 5.5 – 6.5; high soil pH results in pox and scurf diseases whereas low pH causes aluminium toxicity (Nedunchezhiyan and Ray, 2010).

2.4.3 Propagation

The propagation of sweetpotato is carried out asexually using either storage roots, vines or stem cuttings (Ray and Tomlins, 2010). Woolfe (1992) has reported that propagation from seed is also possible and is only part of breeding programmes. In the tropical regions, the food crop is usually propagated from vine tip cuttings which are ready to be harvested. Green vines of approximate length 30 cm with at least three leaf nodes are planted either on ridges or mounds which are meant to promote adequate drainage as well as easy harvesting (Low *et al.*, 2009). Planting is also done occasionally on raised beds (wet areas) or even on flat land which is observed in areas where soil is sandier (Obigbesan, 2009).

2.4.4 Land Preparation

The land preparation varies depending on certain factors including soil types, fertility and drainage conditions. Generally, roots and tubers require loose soil in which they can grow with little or no hindrance and the reason for this has been related to the manner in which the roots form and penetrate the soil. Many root and tuber crops initially form relatively thin roots which first penetrate the soil and later grow or enlarge to produce tubers. Land tillage involves three general methods; mounding, ridging and flat planting, which are adopted during the cultivation of sweetpotato (Brobbey, 2015). These tillage operations are necessary since they provide aeration which is very beneficial to the root system.

2.4.4.1 Mounding

Noted to be a common practice in traditional agriculture, mounding involves the gathering of the topsoil into conical heaps known as mounds at various sections using hoes with wide blades. Mound sizes, the mean distance between mounds as well as the number of sweetpotato cuttings planted on each mound vary. Brobbey (2015) is of the opinion that high mounds are more advantageous since they provide more favourable seedbeds for tuber development, larger yields and also the most uniformly shaped roots. The process of mound making ensures the collection of the rich topsoil; the entire depth of the mound also consists of the more fertile topsoil. Furthermore, mounding facilitates easy harvesting. The major disadvantage associated with mounding is the fact that it is an extremely wearisome, time and labour consuming activity which is difficult to mechanize (Onwueme, 1978).

2.4.4.2 Ridging

Planting on ridges has been identified to be the most universally recommended method of growing sweetpotato and it has been observed that the higher the ridge, the more the provision of ample depth of loose and fertile soil for adequate root and tuber development leading to greater yield (Brobbey, 2015). The optimum height of ridges depends on the type of soil and cultivar being planted. According to Loebenstein and Thottappilly (2009), farmers prefer the moulds to the ridges for the reason that it is easy to construct; therefore, such constructions dominate in Uganda and some other countries. However, ridges are the norm when animal traction is employed and their use is on the increase as this is often the approach most extension personnel advocate. However, the disadvantage associated to ridges is that rains tend to wash soil away from the ridge-top, thereby decreasing the height of the ridges (Brobbey, 2015). The washing may be very severe and lead to the exposure of tubers and roots growing within the soil making them unpalatable and susceptible to attacks by rodents and insects.

2.4.4.3 Flat Planting

Flat planting does not involve any mounds or ridges. Before flat planting of sweetpotato is carried out, ploughing and harrowing are typically done to obtain a fine tilt and this is followed by the planting of vines in rows on the flat land (Brobbey, 2015). Planting on flat land also has a number of advantages as planting on ridges. However, the downside here is that, the top soil may be shallow resulting in yield reduction.

2.5 Cultural Practices

2.5.1 Planting

The source of planting material (vines) for most small-holder farmers is their own fields; others acquire vines from other farmers or less commonly, from extension personnel. The best planting materials are apical cuttings obtained from disease-free matured vines (Loebenstein and Thottappilly, 2009). The vine is planted into the soil in such a way that one-half to two-thirds of its length lies beneath the surface of the soil. The vine cuttings are planted at an angle, vertically or horizontally to the surface with at least one-third of the cutting above the soil. Also, this portion should have at least a node on it. In most parts of the tropical regions, planting of vines is done by hand. It is also possible to use mechanical planters which plant vine cuttings horizontally and this has resulted in greater yield according to a research conducted by Chen and Xu (1982). Planting space varies from one country to country but a closer spacing is generally recommended in order to achieve maximum root yield (Nedunchezhiyan *et al.*, 2012a). A plant density of 83,000 per hectare is recommended in India, whereas 25,000 to 125,000 is suggested in Uganda (Adom, 2016). An increase in plant density results in plant vigour and root number increase; however, weevil infestation and root size experience a downslide (Wolfe, 1992). Early planting in the season is also the best as this ensures that the rainy season can be properly utilized since adequate water is very critical in the early stage of plant growth (Brobbey, 2015).

2.5.2 Weeding

Degras (2003) reported that, 57% of food crops in some parts of Africa are lost due to the presence of weeds. According to Milind *et al.* (2015), despite the fact that the growth of the vines is vigorous and causes fast and total ground coverage, weeding is very necessary especially in the early stages of crop growth. The weeds are minimized by a combination of activities including herbicide application, inter-row cultivation and mechanical handweeding by the use of hand tools such as cutlasses, hoes or simple hand pulling (Momanyi *et al.*, 2016). A study was conducted in Kenya by Momanyi *et al.* (2016) with the objective to assess and encourage effective weed management technologies for enhancing the production of sweetpotato. This study involved examining weed control methods including mulching, the application of pre-emergent herbicide and weeding as well as unweeded treatments which served as a control in field trials. It was reported that there was a very high significant ($P < 0.001$) reduction in weed density, dry matter and biomass where weeding, mulching and the use of pre-emergent herbicide was employed as compared to the control unweeded plots. This method of controlling weeds therefore reduced weed density and of course the undesired competition with the sweetpotato crops.

2.5.3 Fertilization

Fertilizers are quite high-priced in recent times and this situation has called for the use of locally available and inexpensive organic sources, such as manures, bio-fertilizers, etc. which are used along with the inorganic ones in a synergistic manner for the maintenance of soil quality and also the encouragement of sustainable crop production (Njintang *et al.*, 2016). . Soil nutrients such as nitrogen (N), phosphorus (P) and potassium (K) are highly required by sweetpotato for good growth and development.

2.5.3.1 Nitrogen

Nitrogen contributes significantly to the yield of storage root and biomass of sweetpotato; however, its excessive application results in the profuse production of leaves at the expense of root yield (Brobbey, 2015; Njintang *et al.*, 2016). Interestingly, a study by Hill *et al.* (1990) revealed that some sweetpotato cultivars have the ability to produce high storage root yields in soils that have low nitrogen content because of the presence of organisms such as Azospirillum which has the capability of fixing nitrogen in the root environment which may result in an increase of storage root yield by 22%.

2.5.3.2 Phosphorus

It has been reported that sweetpotato does not require very large quantities of phosphorus for root development; its response to phosphorus is therefore low as compared to nitrogen and potassium. According to Brobbey (2015), at a soil solution concentration of as low as 0.003 ppm P_2O_5, phosphorus is responsible for 70% of the crop's maximum yield.

2.5.3.3 Potassium

Potassium is a key soil nutrient that is essential for the development of storage roots. According to Brobbey (2015), the presence of high concentrations of potassium in the leaves promotes the synthesis and translocation of carbohydrates from the leaves to the storage roots. Potassium is also known for its immense contribution to early growth, the production of protein as well as improved resistance to diseases (Essilfie, 2015).

2.6 Herbicides

In modern times, agrochemicals form an integral part of agricultural production systems globally. The incorporation of agrochemicals namely pesticides and fertilizers remains a routine agricultural practice especially in tropical countries (Carvalho, 2006). The introduction of agrochemicals in farming not only contributes to the healthy growth of food crops but also the improvement of farm work efficiency as well as stability in the supply of tasty agricultural products (Kughur, 2012). Herbicides are described as a subtype of pesticides which are applied with the intention of killing, controlling or preventing the excessive growth of weeds or unwanted plants. Weeds influence agricultural activities by competing with crops for available soil nutrients, air, water, sunlight and space, and also harbouring other invasive pests (Wyss and Müller-Schärer, 2001). According to Holm and Johnson (2009), the control of weeds is one of the critical agricultural activities that has attracted attention of farmers worldwide. Dinham (2003) estimated that about 87% of Ghanaian farmers, in an attempt to control pests, diseases and weeds during the cultivation of fruits and vegetables, apply chemical pesticides. Furthermore, Ntow *et al.* (2006) agreed to this and estimated that vegetable farms proportionally use about 44% herbicides, 33% insecticides and 23% fungicides. This attention may stem from the fact that weeds have the ability to affect the growth, development and the yield of crops. Sebiomo *et al.* (2011) reported that, over the past four decades, there has been an influx of these herbicides into the worldwide agricultural market space and these are mainly categorized as pre and postemergent herbicides. In most jurisdictions, the sale and usage of herbicides must be approved by an authorized governmental agency; a typical example is the Environmental Protection Agency. The approval process involves studies that must be conducted in order to ascertain whether the herbicide in question is safe and effective against the intended weeds.

2.6.1 The Role of Herbicides in Modern Agriculture

It is an undeniable fact that herbicides play a very essential role in modern agriculture, particularly in the effective control of weeds that attack food crops as well as flower gardens.

It is known that weeds are capable of reducing crop yield and quality and also interfering with cultivation and harvesting operations; therefore, herbicides are undoubtedly very important agricultural chemicals. They can provide cost-effective weed control with the use of minimum labour (Das and Mondal, 2014). There is a high possibility that without these important chemicals, there will be a significant decline in food production; since several food crops especially fruits and vegetables will get affected by pests and diseases and will also be in short supply thereby causing an increase in their prices (Paloma, 2011). Despite the negative impacts of these chemicals especially when they are used indiscriminately, herbicides can be applied safely and effectively. However, if appropriate precautions are not adhered to, herbicides have the tendency to cause some degree of harm to the environment by contaminating surface and groundwater, soil and ultimately killing wildlife (Adomako, 2015).

2.6.2 Effects of Herbicides

These agricultural chemicals have increased crop yield to a large extent by limiting damages caused by pests, the competition for soil nutrients and water from weeds and also by providing adequate amounts of nutrients in forms that are easily available or accessible to plants (Kughur, 2012). Upon the realization of the effectiveness of these herbicides, farmers tend to increase application consistently to meet their production targets without taking into consideration the negative aspects associated with these herbicides. A notable characteristic of herbicides is the fact that their biological activities extend beyond their expected effects on target organisms. They are capable of affecting organisms within in the same ecosystem or in other habitats and this happens when the herbicides are transmitted mainly by wind currents during the process of application or through rain in some other cases. Once applied to fields, these herbicides get translocated sooner or later into the soil According to Kughur (2012), the continuous application of these chemicals can lead to a weighty or severe depletion of soils in the long run; and this is so because the balance of microorganisms in the soils as well as the natural processes of converting organic matter have been disrupted. Ayansina *et al.* (2003) reported that, many concerns have been raised in relation to the excessive application of these herbicides since relevant toxicological amounts may run off into surface water resulting in the potential contamination of surface and ground water as well as other water bodies which when consumed can result in numerous adverse health conditions. These chemicals enter watercourses when they get directly leached from soils or in some other cases, get associated with eroded soil or sediments (Stoate *et al.,* 2001). They can get into contact with surface water through run-off from treated soil as well as plants.

Other entries such as the drains, storm sewers and man-made routes have also been reported (Gavrilescu, 2005). The contamination of water by these chemicals is widespread. When ground water gets polluted with these toxic chemicals, the water quality gets deleteriously affected and it may take several years for the contamination to dissipate. In addition, cleanup or purification procedures may also be very complex and expensive, if not impossible (Aktar *et al.,* 2009). Another potential environmental health risk is the bioaccumulation and biomagnification of the herbicides. Ormerod (1997) described this phenomenon to be an increase in the concentration of compounds as they are moved up to higher natural trophic levels through interactions of the food web**.** A typical example in this case is the possible bioaccumulation in fish tissues of herbicides present in a watercourse. Subsequently, if a human being consumes several of these fishes, he or she will end up ingesting even higher concentrations of these compounds. Damages to the nervous, immune and reproductive systems as well as other vital organs, interference with hormone functions, developmental and behavioral abnormalities, etc. are some of the adverse health effects of herbicides on humans. Furthermore, herbicides are also responsible for gathering fat deposits in the body and these end up causing significant damages (Kughur, 2012). When lactating mothers consume fruits and vegetables that have been sprayed with these chemicals, residues that are usually present find their way into breast milk and by so doing, expose babies to health risks; in a similar fashion, pregnant women can also pass these residues unto their developing fetuses (Jurewicz and Hanke, 2008).

Another concern that has been raised in relation to the leaching of these herbicides into water bodies is the potential adverse implications the compounds may have on the health of aquatic (micro) organisms or ecosystems (Peterson *et al.,* 1994). Also, the excessive use of herbicides can end up eliminating beneficial insects such as aphids, lady bugs, spiders, moths, bees, butterflies, to mention but a few, which play important environmental roles such as the process of plant pollination. Apart from the beneficial insects, Aktar *et al. (*2009) reported that populations of beneficial soil microorganisms can also decline as a result of the excessive treatment of soil with these chemicals and according to Dr. Elaine Ingham, a soil scientist; "the soil easily degrades if we lose both fungi and bacteria''. It is known that plants rely on various microorganisms in the soil to convert atmospheric nitrogen to nitrates which is utilized by the plants; herbicides are able to disrupt this process (Aktar *et al.,* 2009). The spraying of these herbicides can also either directly or indirectly affect non-target organisms by altering the composition of other plants or organisms and also by changing microclimates in a given ecosystem. Another route is when these herbicides volatilize from treated areas and end up contaminating surrounding soil, air and non-target vegetation.

It is therefore prudent to conclude that herbicides are much more than just weed killers. The awareness concerning health hazards associated with herbicides is increasing and consequently, this has resulted in a demand for more stringent regulatory measures with regards to the development of more environmentally safe and effective agricultural chemical formulations. Unfortunately, some farmers still continue to apply these toxic chemicals indiscriminately in order to increase the yield of food crops. Risks form an intrinsic part of existence and therefore, there is the need for risks to be weighed against the possible benefits that are likely to result from any particular activity (Avav and Oluwatayo, 2006).

2.6.3 Types of Herbicides

Herbicides are classified based on the chemical family, time of application, activity, mode of application method of application, mode of action, site of action and selectivity.

2.6.3.1 Classification based on chemical family

Herbicides include a large group of pesticides which are known to have diverse functional groups and structures. Due to this reason, chemical classification is probably more complex and extensive. Herbicides can be grouped into the following families: amino acids and quaternary ammonium salts, aliphatic carboxylic herbicides, benzoic and phthalic herbicides, inorganic herbicides, carbamates and thiocarbamates, pyridines and pyridazines, benzonitriles, cyclohexanediones, halogenated herbicides, triazines, dinitroanilines, imidazolinones, phenols, phenoxy herbicides, ureas and sulfonylureas (Herrera-Herrera *et al.* 2016). Among the commonly applied herbicides, the chloroacetanilide group which is made up of alachlor, butachlor, metolachlor etc. are the most consumed globally (Ramalingam *et al.*, 2015).

2.6.3.2 Classification based on activity

Based on activity, herbicides can be contact, systematic or non-systematic. Herbicides that are extensively translocated through the vascular system of plants alongside water, nutrients and other compounds from absorption sites to sites of action are referred to as systemic herbicides (Vats, 2015). They are completely absorbed through the roots or foliage and are transported through the phloem to other parts. These herbicides are effective against all types of weeds but are especially useful in controlling perennial weeds. Systemic herbicides also require longer time periods to kill weeds unlike fast acting contact herbicides. Examples of systemic herbicides are 2,4-D, dicamba, glyphosate, glufosinate and imazaquin. Contact or non-systemic herbicides only affect the parts of the weeds or undesired plants that are in contact and they are not translocated throughout the plant tissues. Examples include diquat, bentazon, glufosinate and bromoxynil. Generally, contact herbicides are very rapid and effective with regards to the removal of annual weeds. However, due to the capability of perennial weeds to easily regrow using either the rhizomes, tubers or roots, contact herbicides show less effectiveness towards perennial plants. In order to kill regrowth of underground plant parts, there is the need for repeated application of contact herbicides (Vats, 2015).

2.6.3.3 Classification based on time of application

With regards to the time of application, herbicides can be known as either pre-plant, preemergence or post-emergence (Herrera-Herrera *et al.*, 2016). Pre-plant herbicides are generally non-selective herbicides which are applied to soil prior to planting and they get incorporated into the soil mechanically. They are applied months, weeks or days before the crops are planted. Sulfentrazone, atrazine and alachlor are examples of pre-plant herbicides.

Examples of pre-emergence herbicides include pendimethalin, prodiamine and glyphosate and these are applied to the soil after crops have been planted and before weed seedlings begin to emerge through the surface of the soil. When weed seedlings have already germinated or emerged through the surface of the soil, post-emergence herbicides are used. Examples include glyphosate, propaquizafop, paraquat dichloride and fluazifop-p-butyl. Depending on the soil, crop or the climatic conditions, a particular herbicide can be used as both a pre and post–emergence herbicide (Herrera-Herrera *et al.*2016).

2.6.3.4 Classification based on method of application

Herbicides are either soil or foliar applied (Vats, 2015). Soil applied herbicides tend to be used up by the roots / shoots of emerging seedlings and are also used as pre-plant or preemergence treatments. The adsorption of these herbicides to organic matter or soil colloids usually reduces the amounts available for absorption by weeds. Examples of soil applied herbicides include dinitroanilines and thiocarbamates. Portions of plants that are above the ground are best suited for foliar herbicides since the herbicides are absorbed by the exposed tissues. Generally, these can be post-emergence herbicides which are either translocated throughout the plants or remain at specific sites. Examples of foliar applied herbicides are 2,4-D, glyphosate, and dicamba.

2.6.3.5 Classification based on mode of action

Mode of action is a general term referring to all the plant-herbicide interactions with emphasis on the specific plant biological processes with which the herbicides interfere in order to effectively control the weeds (Das and Mondal, 2014). Herbicides such as atrazine and paraquat can inhibit photosynthesis of weeds, produce free radicals, destruct membranes, cause necrosis and desiccation. Furthermore, other herbicides including acifluorfen and diflufenican can also act as inhibitors to the synthesis of pigments, enzymes interference and cause the loss of protection against radicals (Herrera-Herrera *et al.,* 2016). Herbicides such as glyphosate and glufosinate are also known for their ability to avoid the formation of amino acids. Another mode of action involves those herbicides which hinder cell division leading to the inhibition of growth, forming tumours and eliminating translocation and absorption mechanisms.

2.6.3.6 Classification based on site of action

Herbicides are often categorized based on their respective action sites on target weeds. These are specific biochemical sites that get affected by the herbicide in question and this offers a more specific description of the activity of the herbicide. Generally, those that are found in the same site of action class tend to produce related symptoms on susceptible weeds (Miller and Spoolman (2008); Vats, 2015).

2.6.3.7 Classification based on selectivity

It is also possible to distinguish herbicides based on their selectivity for or against the crops of interest. Herbicides that act selectively such as butachlor and metribuzin are more inclined towards specific plants and end up destroying other extraneous weeds (Herrera-Herrera *et al.,* 2016). Non-selective herbicides, e.g. paraquat, glufosinate and glyphosate do not act selectively against certain plant species and therefore destroy any plant materials that they encounter (Vats, 2015). These herbicides are normally applied to soils that are non–cultivated; precautions are taken during their application to avoid contact with crops of concern. These are also used for clearing waste grounds, railway embankments and industrial sites.

Alternatively, herbicides can also be categorized as being either residual or non-residual. Herbicides that are residual live long in the soil and the efficiency of these herbicides depends on how quickly they are broken down either by activity of microbes, sunlight or the chemistry of the soil, and also if the herbicides are leached or volatilized below the upper inch of the soil (Adomako, 2015). On the other hand, non-residual herbicides have very little to no effect with the exception of weeds that are present during the period of application (Holm and Johnson, 2009). Adomako (2015) has also reported that some herbicides are only effective against grasses and in some other cases, only on broadleaf herbs. Those that show various levels of action against both types of vegetation are also available. Residual herbicides usage must be restricted to specific needs since their consistent usage may result in the faster development of bare soil and subsequently causing the tendency of soil erosion and injury to roots. Furthermore, this may encourage the growth of greater weed populations that will be resistant to current herbicide applications (Adomako, 2015).

2.6.3.8 Butachlor

Butachlor (N-butoxymethyl-2-chloro-N-2',6'-diethylacetanilide) with the molecular formula, $C_{17}H_{26}ClNO_2$, is a selective and systemic pre and post-emergence chloroacetanilide herbicide commonly used in Africa and Asia to control a wide diversity of undesirable broadleaf weeds and grasses (Chowdhury and Pal, 2017; Vajargah and Hedayati, 2017; (Senseman *et al.*, 2007). Rao *et al.* (2012) also reported that butachlor is applied as a preemergence herbicide for controlling broad-leaved weeds in rice fields. According to Chiang *et al.* (2001), butachlor and its metabolites have been detected in a number of agricultural soil environments as a result of its extensive application. According to the EU pesticides database, the maximum residue limit (MRL) of butachlor is 0.01 mg/kg (European

Commission, 2016). This herbicide has been reported cause retardation in growth and reproduction in earthworms by specifically damaging epithelial tissues (Muthukaruppan *et al.*, 2005). Butachlor is also genotoxic to cultured mammalian cells by causing strand breaks of DNA as well as micro-nucleus and chromosomal aberration inductions (Panneerselvam *et al.*, 1995). Reports also indicate that butachlor is an indirect mutagen which caused stomach tumors in rats as well as oxidative DNA damage in humans (Coleman *et al.*, 2000; Dwivedi *et al.*, 2012). According to Tilak *et al*. (2007), the prolonged exposure to butachlor was toxic to spotted snakehead fish and has also been found to accumulate through the food chain. Furthermore, Wany *et al*. (1992) conducted a study involving six (6) different species of fish and reported the bio-concentration of butachlor from 2.4 to 220 times the concentrations to which they were initially exposed for 3 to 5 days. As a result of its relatively high stability, butachlor is regarded as a persistent environmental pollutant in agricultural soil (Fang *et al.*, 2009) and this situation poses a potential threat to the agroecosystem and human health through food chains (Yu *et al.*, 2003; Wilson and Takei, 2000). As a consequence, concerns about the potential toxicity and adverse effects of butachlor on the ecosystem have risen and it is therefore imperative to note that the clean-up of butachlor residues from the environment has been of great concern.

2.6.3.9 Metolachlor

Metolachlor (2-chloro-N-(2-ethyl 6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide) is also a common selective chloroacetamide herbicide which is heavily used in China and other countries around the world for effectively controlling broadleaf and annual grassy weeds in a wide variety of crops including corn, soybean, potatoes, corn, tobacco and peanut (Wu *et al.*, 2011). However, the fate of metolachlor has caused great concern due to its relatively long persistence in soil, high water solubility and also its significant toxicological properties (USEPA, 1988). In order to ensure consumer safety in the European Union, the maximum residue limit of 0.05 mg/kg has been established for metolachlor in sweetpotatoes (European Commission, 2016).

2.6.3.10 Imazethapyr

Discovered in the 1980s, imazethapyr [(RS)-5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2imidazolin-2-yl) nicotinic acid], is an imidazolinone herbicide used worldwide to control weeds by inhibiting the activity of acetolactate synthase (ALS) which catalyzes the initial step in the biosynthesis of valine, leucine and isoleucine (Zhao *et al.,* 2016; Maja and Branko, 2011). Imazethapyr is absorbed by both the roots and the shoots and it has been reported to effectively control a wide spectrum of weeds including redroot pigweed (*Amaranthus retroflexus* L.), annual nightshades (*Solanum* spp.), wild mustard (*Sinapis arvensis* L.), lambsquarters (*Chenopodium album* L.), ladysthumb (*Polygonum persicaria* L.), common ragweed (*Ambrosia artemesiifolia* L.) and smartweed (*Polygonum* spp.) (Arnold *et al.,* 1993; Bauer *et al.,* 1995; OMAFRA 2002; Ward and Weaver, 1996). Consequently, phytotoxic effects to some rotational crops have been observed as a result of the presence of imazethapyr residues in soil as well as the development of resistance by weeds to imazethapyr has created a more serious issue that needs to be addressed effectively (Zhou *et al.,* 2009). According to the EU pesticides database, the maximum residue limit (MRL) of imazethapyr is 0.01 mg/kg (European Commission, 2016).

2.6.3.11 Pendimethalin

Pendimethalin (N-(1-ethylopropyl)-3,4-dimethyl-2,6-dinitrobenzenamine) is a preemergence dinitroanaline herbicide which is used to control small-seeded dicots and grasses
(Grey *et al.*, 2000). According to the EU pesticides database, the maximum residue limit (MRL) of pendimethalin in sweetpotatoes is 0.05 mg/kg (European Commission, 2016). This herbicide is among the most water soluble dinitroanaline herbicides and also the least volatile (Wilcut *et al.*, 1988); the main method of dissipation is microbial decomposition (Parochetti and Dec, 1978; Walker and Bond, 1977; Weber, 1990).

2.6.3.12 Propaquizafop

Propaquizafop is a post-emergence aryloxyphenoxypropionate herbicide which is highly active, selective and systemic and is used to combat a broad spectrum of weeds such as bermuda grass, johnson grass and quack grass (Gimenez-Espinosa *et al.*, 1999; Klaus *et al.*, 1991). It is applied to control annual and perennial weeds in potatoes, sugar beets, peanuts, soybeans and vegetables (Ramprakash *et al.*, 2016). These authors further reported that propaquizafop is absorbed from the leaf surface followed by translocation throughout the plant. It then accumulates in the active growing regions of roots and stems. Panda *et al.* (2015) also reported that the post-emergence application of propaquizafop (75g/ha) alone gave effective control of grassy weeds (*Echinochloa colona*, *Dinebra retroflexa* and *Cynodon dactylon*). According to the EU pesticides database, the maximum residue limit (MRL) of propaquizafop in sweetpotatoes is 0.1 mg/kg (European Commission, 2016).

2.6.3.13 Terbutryn

Belonging to substituted symmetrical triazines, terbutryn [2-(t-butylamino)-4-(ethylamino)-

6-(methylthio)-s-triazine] is known to be a widely used selective and systemic pre and postemergence s-triazine carcinogen herbicide which is applied for controlling most annual broadleaf weeds (Riahi *et al.,* 2010). The chemical class triazines constitute a group of similar herbicides which are used worldwide to control most annual grassy and broadleaf weeds in a variety of food crops including potatoes, cereals, legumes and sugarcane (Muir, 1980; Moretti *et al.,* 2002; Arufe *et al.,* 2004). According to the EU pesticides database, the maximum residue limit (MRL) of terbutryn is 0.01 mg/kg (European Commission, 2016). Terbutryn acts as an inhibitor of photosynthesis in the xylem and also accumulates in the apical meristems (Plhalová *et al.,* 2010). Reports also indicate the use of terbutryn as an aquatic herbicide for the control of submerged and free-floating weeds and algae; this practice may end up severely affecting some non-target organisms (Muir, 1980; Roberts *et al.,* 1998; Arufe *et al.,* 2004). The application of terbutryn has been banned for agricultural use since 2003 in the European Union and other countries as a result of its bioaccumulation tendency in organisms; however, it can still be detected in water bodies (Luft *et al.,* 2014; Rioboo *et al.,* 2007). Also, despite the fact that agricultural preparations containing terbutryn have not been registered since 2005, terbutryn still persists and can be detected in the environment (Plhalová *et al.,* 2010).

2.6.4 Mode of Action of Herbicides

A particular herbicide is able to kill weeds in various ways; however, it must meet some requirements in order to be effective (Das and Mondal, 2014). It must first come in contact with the target unwanted plant, be absorbed by it, move to the appropriate site of action in the weed and also accumulate adequate amounts at the site of action so as to suppress or kill the target weed (Beckie *et al.,* 2000). According to Holm and Johnson (2009), the mode of action of herbicides describes the manner in which herbicides control susceptible weeds with particular reference to the biological enzymes or processes in the weeds that get disrupted by the herbicide, thus disturbing the usual growth of the weeds. It must be noted that the terms “site of action” and “mode of action” are interchangeably used during the description of the various groups of herbicides (Adomako, 2015). Understanding each herbicide’s mode of action serves as a very crucial or relevant period in selecting the most effective herbicide for crops, determining herbicide injuries, as well as putting together efficient programs for weed management for agricultural production systems. The dependence on a particular herbicide should not be encouraged since this ends up placing significant pressure on weed populations which may ultimately select for resistant individuals. Over time what happens is that, the resistant weeds multiply and gain dominance in the field, thereby causing a reduction in the effectiveness of the herbicides. Unfortunately, the act of simply rotating the active ingredients of herbicides is not adequate to avert the development of herbicideresistant weeds and as such, this should be done in combination with the rotation of herbicide modes of action plus the application of other weed control methods so as to be able to prevent or delay the development of these herbicide-resistant weed populations. Miller and Spoolman (2008) reported that several weeds have developed some form of cross resistance and are resistant to numerous herbicides found in a single mode of action.

2.6.5 The Fate of Herbicides in Natural Ecosystems

The various mechanisms involved in the fate of herbicides in the environment comprise certain biotic factors (i.e. interactions with living organisms) which include uptake by plants and degradation, or abiotic factors such as volatilization and photochemical degradation (Howell, 2011). These factors and their possible interrelation is illustrated in Figure 1 below.

After application, the fate of herbicides to a large extent depends on the ability of the soil microorganisms to cause the degradation of the herbicides and this is ideally through the complete mineralization of the parent compound into carbon dioxide (CO_2) and also the transfer of the chemicals through some physical processes (Adomako, 2015).

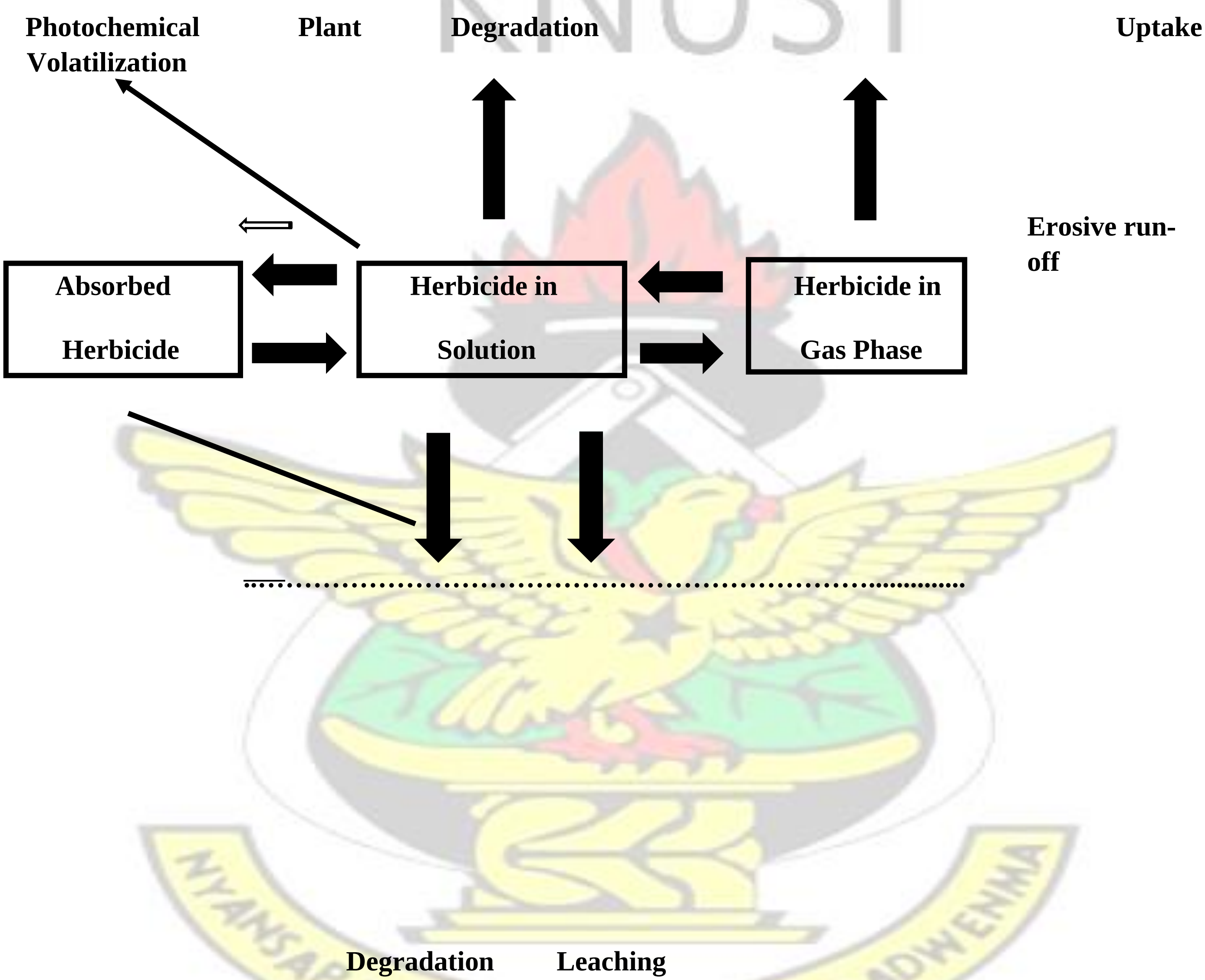

Figure 1: A conceptual diagram of factors that determine the behaviour and fate of herbicides in the environment. (Howell, 2011)

Photochemical degradation presents a major abiotic degradation process and it has been known as "the photochemical transformation of a molecule into lower molecular weight fragments, usually in an oxidation process" (Verhoeven, 1979). Burrows *et al.* (2002) reports that some well-known photodegradation processes are the direct photolysis, photolysis in heterogeneous media and photosensitized photodegradation. A study conducted by these same authors reviewed the potential importance of photodegradation in the remediation of these chemicals and it was noted that many are resistant to photodegradation. This occurrence was attributed to the fact that many pesticides only absorb UV radiations with short wavelengths; and this group embodies only a small percentage of the entire UV radiation that reach the earth's surface. The degree to which these agrochemicals can be photodegraded varies significantly among diverse compounds. A study by Ramezani (2008) revealed that imidazolinone herbicides: imazethapyr, imazaquin and imazapyr significantly degraded faster in light conditions compared to the dark. In the instance of imazaquin, the half-lives recorded were 9.6 months under dark conditions and 9.1 days under light. In a similar fashion, imazethapyr and imazapyr recorded 9.2 months, 9.8 days and 6.5 months, 1.8 days in dark and light conditions respectively. Furthermore, Eyheraguibel, et al. (2009) reported that the herbicides: clopyralid, triclopyr and bentazone are affected by photodegradation in lesser amounts especially when in water; this signifies that the medium of the herbicides also affects their susceptibility to photodegradation. Degradation of triclopyr is the fastest with a recorded half-life of between 12 and 31 h, followed by bentazone which is between 65 and 96 h. With a half-life of 261 days in water, clopyralid has been found to be more persistent. The binding of herbicides to soil and other natural matrices is another observed abiotic feature that can affect their degradation in normal ecosystems (Gevao *et al.*, 2000). According to Howell (2011), soil organic matter is assumed to be the crucial element that is involved in these sorption developments. The binding of these chemicals to soil organic matter occurs through a sequence of different processes including hydrophobic or hydrogen bonding, electrostatic interactions such as charge transfer and ion or ligand exchange. In addition, compounds can also get covalently bonded to the soil matrix (Bollag *et al.,* 1992). According to Gevao et al. (2000), other factors such as the modes of application, concentrations of the compounds applied and the number of times they are applied in a single area, can also affect the binding of pesticides to soils.

The process of biodegradation, which can either be growth-linked or co-metabolic, also plays a very central role in the fate of pesticides within natural ecosystems (Howell, 2011). Biodegradation is termed as growth-linked when an organism breaks down a compound and at the same time, uses it as nitrogen and/or carbon source. As a result of this, degrader organisms get proliferated over the duration that the particular compound exists in the environment. On the other hand, co-metabolic degradation involves the process where an organism uses non-specific enzymes (e.g. mono-oxygenases and dioxygenases) to breakdown a compound (Landa *et al.,* 1994). According to Miller (1996), the process of degradation can either be complete (with the end products being CO_2 and water) or incomplete which is characterized by the formation of secondary metabolites which have the tendency to be toxic to the environment as well. The fate of herbicides after application largely depends on the ability of the microbial population to degrade them and this is ideally by complete mineralization followed by the transfer of the chemical through some physical processes (Adomako, 2015). Mills and Zahm (2001) also reported that the rate of degradation in top soil is not as fast as it can be in sub soil. Abiotic factors are intrinsically linked with biodegradation and bioavailability which has been defined by Anderson *et al.*

(2000) as "a measure of the possibility of a chemical for access into biological receptors and this is specific to the receptor, time of exposure, entry route and the matrix where the contaminant is contained". Bioaccessibility is another concept that is related to bioavailability. Semple *et al.* (2004), defines a bioaccessible compound as a compound which is "available to cross the cellular membrane of an organism from the environment, if the organism has access to the chemical". As illustrated in Figure 2, when the chemicals get bound to the matrix of the soil, there is a reduction in bioavailability and bioaccessibility and subsequently, the probable biodegradation of the compound also experiences the same fate (Howell, 2011). The biodegradation of herbicides involves various microorganisms such as bacteria and fungi which operate under both dynamic aerobic and anaerobic conditions (Larsen and Arildskou, 2002). Also, Adomako (2015) asserts that the biodegradation process of herbicides in soil ecosystems can only occur through the synergistic interactions of a microbial consortium; whose activity is also affected by several soil chemical and physical properties, as well as the nature and degree of contamination of the herbicides. According to Racke *et al.* (1990), a number of herbicides show resistance to microbial biodegradation and as such, they persist in the environment. Furthermore, the development of some biodegradable herbicides and other agrochemicals including fungicides and insecticides in the mid 1970's was prompted by the recognition of the fact that microbial degradation is a primary means of degrading several herbicides in soil ecosystems (Racke *et al.*, 1990).

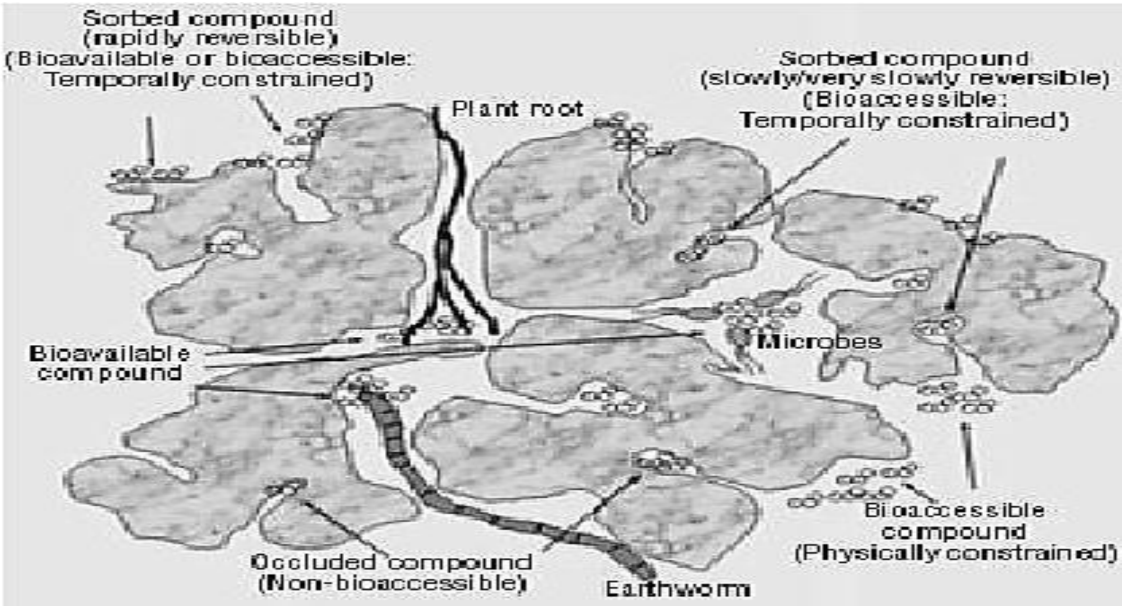

Figure 2: A conceptual diagram depicting how pesticide interactions with the soil matrix can alter compound bioavailability/bioaccessibility.

Source: Semple *et al.*, (2004)

The interactions that occur between the living and biotic constituents of the soil and also the various phases of the soil (i.e. solid, liquid and gaseous) also significantly influence the environmental fate of the herbicides present. Howell, (2011) reported that the factors that affect the volatility of herbicides which include humidity, temperature, vapour pressure, etc. can also influence the rate of biodegradation. This is so because the extent to which the chemicals escape from the soil surfaces or volatilize through the air pockets of the soil greatly affects their concentrations in the soil and consequently, their bioavailability. According to Adawiah (2008), the content of moisture in soil can also influence the volatilization of herbicides and this may be facilitated by a proposed capillary effect, through which compounds that are soluble are more rapidly brought to the soil surface. In effect, soil moisture content has been identified as a key factor that influences the transport of herbicides within the soil.

The erosion of soil by water entails the detachment of soil particles from the surface of the soil and their subsequent movement down slope. Detachment is triggered by the influence of raindrops as well as the abrasive power of surface runoff (Schnürer *et al.,* 2006; Tiryaki *et al.,* 2010). The herbicide is either dissolved in the run-off water or bound to eroding soil. When the field is irrigated faster than it can be absorbed by the soil, run-off can also occur. The amount of herbicides that gets run-off depends on the type of herbicide used, slope of field, soil texture and moisture content as well as the amount and timing of a rain event (Tiryaki *et al.,* 2010; Reichenberger *et al.,* 2007; Kerle *et al.,* 2007). Leaching is said to have occurred when herbicides move downwards in the soil through pores and cracks and this can be influenced by factors including properties of the soil and the herbicides, the rates and methods of application, weather conditions and geography (Adomako, 2015). The soil properties may include the following; soil acidity, soil texture and organic matter content. In the case of the herbicides, the properties may also include adsorption, solubility and persistence. There is the possibility for herbicides that get leached to reach ground water (Toth and Buhler, 2009). According to Tiryaki *et al.* (2010), sunlight is also able to breakdown herbicides through the process of photodegradation and as such, to some degree, all herbicides are susceptible to the process of photodegradation. The rate of photodegradation is affected by the properties of the herbicides as well as the intensity and length of exposure to sunlight. Obviously, herbicides applied to the surface of the soil are more susceptible than those incorporated into the soil. Furthermore, herbicides inside plastic-covered greenhouses may break down faster compared to those inside glass greenhouses, since glass is known to filter out much of the ultraviolet light which is responsible for the degradation of the herbicides (Kerle e*t al.,* 2007; Tiryaki *et al.,* 2010). When herbicides react with other chemicals, water and oxygen in the soil, chemical reactions occur leading to the chemical degradation of the herbicides. Also, as the pH of the soil becomes exceedingly basic or acidic, there is a subsequent reduction in microbial activity. However, rapid chemical degradation can be favoured by these conditions. A report by Kerle *et al.* (2007) indicated that the binding of herbicides to the soil, soil pH and temperature influence the types and rates of chemical reactions that occur.

2.6.6 Determination of Herbicide Residues

Analytical methods for the determination of herbicide residues and their products of degradation share similar characteristics to those of other pesticide residues (Tekel and Kovacicova 1993). The analysis comprises the preparatory steps which are primarily sampling and sample handling techniques, followed by the extraction and clean-up procedures and finally the determination, results and interpretation of the obtained results. Furthermore, the specific steps involved in the analytical method are designed, taking note of the chemical structure of the analyte compounds under study as well as the character of the matrix. In recent times, the trends in analysis of residue development are in the direction of multi-residue methods which allow the simultaneous estimation of herbicides of diverse structural types. Such methods have properties including; good reproducibility, adequate recovery characteristics and low determination limits (Tekel and Kovacicova, 1993). Due to their excellent versatility and separation capacity, a variety of chromatographic and electrochromatographic techniques have experienced growing acceptance and application for the quantitative estimation of herbicide residues in various matrices including soil, food and biological fluids (Cserháti and Forgács, 2001).

Recently, QuEChERS (quick, easy, cheap, effective, rugged and safe) sample preparation approach which was introduced by Anastassiades *et al.* (2003), has emerged as the most universal method of sample preparation. This technique is fast gaining popularity as a result of its simplicity, as well as the use of small volumes of non-chlorinated organic solvents. The QuEChERS method has also been reported to provide high quality results in a quick, easy and an inexpensive approach for the analysis of pesticide residues in water, food as well as soil (Saha *et al*., 2015) . Different methods of chromatography including gas chromatography (GC) *(*Fenoll *et al.,* 2009; Hu *et al.*, 2010), liquid chromatography (LC) (Sondhia, 2010), enzyme-linked immunoassay and capillary electrophoresis Maldaner *et al.* (2008) have been employed till date for the effective determination of several herbicide residues in various matrices. Furthermore, LC hyphenated with tandem mass spectrometry (LC–MS/MS) is a prevailing technique in comparison with the known conventional techniques of GC and LC with respect to the analysis of these chemical residues (Saha *et al.*, 2015).

These same authors developed a rapid and simple method for the simultaneous determination of the residues of some selected herbicides (i.e. imazethapyr, pendimethalin, quizalofop-pethyl and oxyfluorfen) in peanut samples by liquid chromatography-tandem mass spectrometry (LC-MS/MS). Ghoniem *et al.* (2017) also found the QuEChERS sample preparation method followed by LC-MS/MS to be the best combination with regards to the multi-residue determination of herbicides (including triclopyr, 2,4-dichlorophenoxyacetic acid, bromoxynil, fluroxypyr, fluazifop, imazethapyr, ioxynil and bentazone) in fruits and vegetables in terms of short analysis time, safety, high recovery rates and low cost.

Ahmed *et al.* (2014) have also proposed that the QuEChERS method with the quantification method by Gas Chromatography-Flame Photometric Detector (GC-FPD) and Electron Capture Detector (GC-ECD) was the best testing tools in the analysis of pesticide residues in potato tuber samples. Alternatively, Dong *et al.* (2015) developed and validated a quick and sensitive procedure for the estimation of 50 herbicides in cereal grain by ultraperformance liquid chromatography-electrospray ionization-mass spectrometry (UPLC– ESI-MS). This method was also reported to have high sensitivity and precision, satisfactory recovery and finally the multi-class multi-residue analysis at low μg kg^{-1} level for herbicides in cereal grains.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Experimental Site and Duration

A study was conducted at the Crops Research Institute Agronomy fields at Kwadaso in the Ashanti Region during the period from May to August 2016.

3.2 Experimental Layout

The experiment was laid out in a completely randomized block design (CRBD) with four replications. Ridges were spaced 60cm apart. Plots measured 6m x 2.4m were laid out with 1.2m boarder between plots.

3.3 Field Preparation

Field preparation involved ploughing, harrowing to fine tilt and ridging. Pre-emergence treatments were first applied to their respective plots. A week later, healthy vine cuttings were planted, spaced 30cm. Post-emergence treatments were applied four weeks after planting. At maturity, sweetpotato roots were harvested from the two inner rows and bulked on treatment lines. Root samples from each treatment were randomly picked, bagged, labelled and stored in a refrigerator for herbicide residues analyses.

3.4 Treatments

Five treatments were involved in the weed management strategies investigated. Table 5 shows the treatment combinations employed.

Table 5: Experimental Treatments

Acronyms	Treatments
Trt 1	Activus 500 EC [Pendimenthalin (500g/L. -3L/Ha)] + Agil 100 EC [Propaquizafop (100g/L. -1.2L/Ha)]
Trt 2	Terbulor 500 EC [Metolachlor (333g/L) + Terbutryn (167g/L) - (4L/Ha)] + Agil 100 EC [Propaquizafop (100g/L. -1.2L/Ha)]
Trt 3	Butaplus 50 EC [Butachlor (50g/L. -3L/Ha)] + Agil 100 EC [Propaquizafop (100g/L. -1.2L/Ha)]
Trt 4	Vezir 240 SL (Imazethapyr 240g/L. -3L/Ha) + Agil 100 EC [Propaquizafop (100g/L. -1.2L/Ha)]
Trt 5	Hoeing (3 times) (Control)

3.5 Determination of Herbicide Residues

3.5.1 Reference Standards

Butachlor, Imazethapyr, Metolachlor, Pendimethalin, Propaquizafop and Terbutryn herbicide reference standards (purity >94%) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

3.5.2 Reagents and Materials

The following reagents were used; acetonitrile (HPLC grade) and acetic acid (analytical grade). Other chemicals included anhydrous magnesium sulphate ($MgSO_4$), sodium citrate tribasic dehydrate and anhydrous sodium acetate. chloride. Adsorbent C18 (55 mm) and polypropylene centrifuge tubes were also used.

3.5.3 Apparatus

Agilent 1200 series HPLC coupled to an API 4000 Qtrap mass spectrometer equipped with an electrospray ionization interface. The HPLC separation was carried out using an Atlantis dC18 column (100mmx2.1mmx5μm).

3.5.4 Calibration solution

The stock standard solutions containing 1000 mg L^{-1} of the individual target herbicides were prepared in toluene. Working standard mixtures containing 1 mg L^{-1} of each herbicide were also prepared in toluene.

3.5.5 Sample Preparation and Extraction

The sweetpotato samples were placed in well-labelled sample bags and transported on ice to the laboratory for onward processing and subsequent herbicide residue analysis. The samples were washed, peeled and cut into smaller pieces and mixed together. About 100 g of sweetpotatoes per treatment was homogenized in a Binatone blender at high speed with 100 mL of distilled water to give a homogeneous slurry (paste).

A modified approach of the QuEChERS methodology was employed to extract the herbicides from the sweetpotato samples. Respective weights of 10 g per treatment of the homogenized slurry were taken in 50 mL centrifuge tubes. Ten milliliters of acetonitrile, containing 1% ($^{v}/_{v}$) of acetic acid, was added to the sample after which the mixture was handshaken for a minute. 3 g of anhydrous $MgSO_4$ was then added and the tube was immediately hand-shaken for about 20 s. Subsequently, 1.7 g and 1 g of sodium acetate and sodium citrate respectively were added and the tube was hand-shaken for another minute to provide welldefined phase separation after 8 min of centrifugation at 4,000 rpm. 4 mL aliquot of the upper layer was then transferred into a centrifuge tube (15 mL) which contained 0.6 g of anhydrous $MgSO_4$ and 0.5 g of PSA and adsorbent C18. The tube was closed vigorously hand-shaken for a minute after which it was again centrifuged at 4000 rpm for 8 min. An aliquot of the supernatant was finally transferred into an auto-sampler vial prior to its injection into the LC-MS system. For each batch, a matrix blank was also analysed. Figure 3 shows a scheme of the modified QuEChERS method used in this work. Extracts were kept frozen until quantitation was achieved.

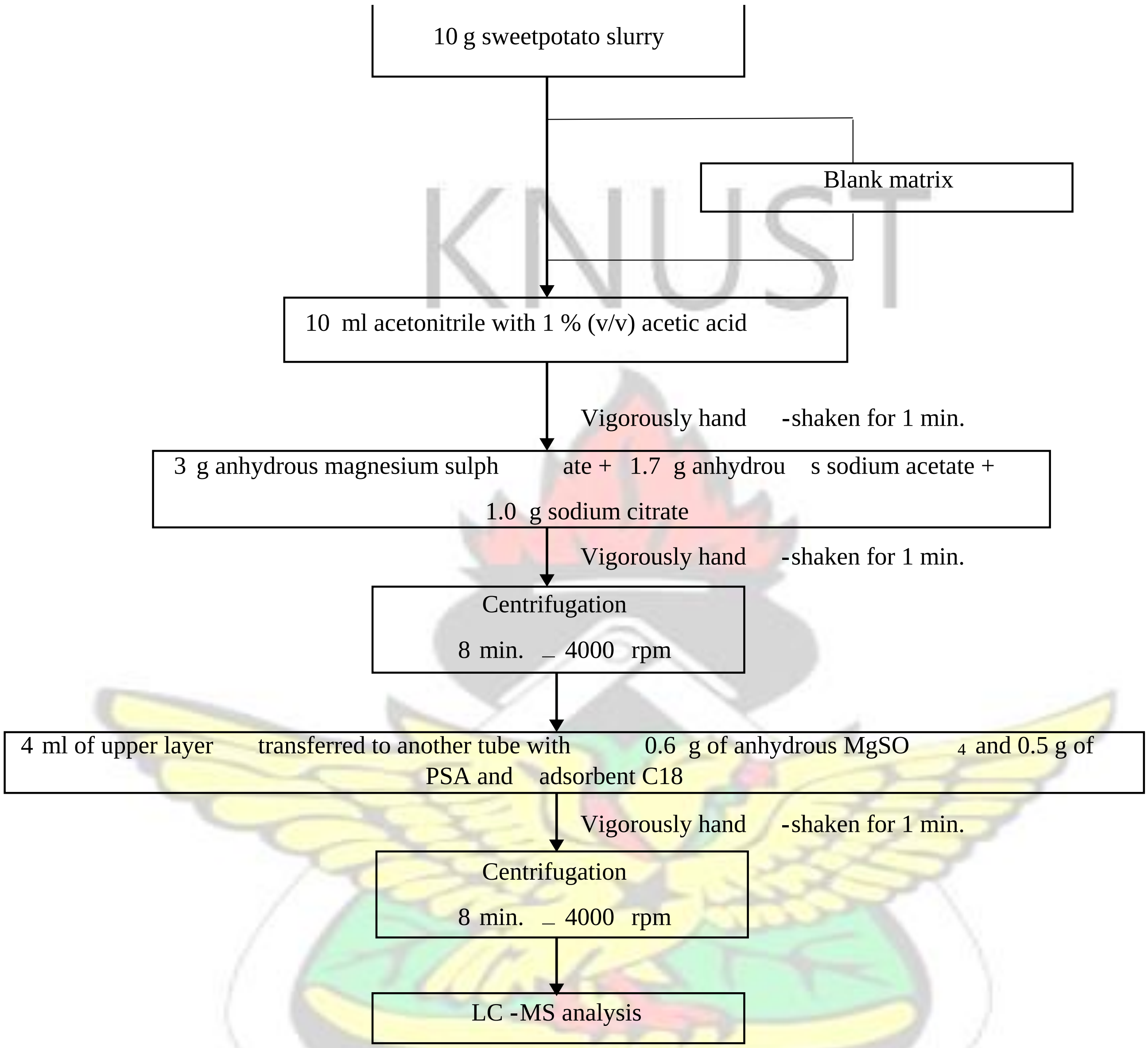

Figure 3. Scheme of the modified QuEChERS method for analysis of herbicide residues in sweetpotato.

3.5.5 Equipment Parameters

The mobile phase used was made up of (A) methanol: water (20:80 $^{v}/_{v}$ with 5 mM ammonium formate and 0.15 % formic acid) and (B) methanol: water (90:10 $^{v}/_{v}$ with 5 mM ammonium formate); with gradient 0 – 0.5min 85% A, 0.5–7min 85 – 2% A, 7 – 15 min 2% A, 15 – 16 min 2 – 85 % A and 16 – 20 min 85 % A. The mobile phase flow rate was 0.3 mL min^{-1} and column temperature was maintained at 35 °C. The source parameters included nebulizer gas 40 psi; heater gas 60 psi; ion source temperature 550 °C; ion spray voltage 5500 V. An aliquot of 10 μL was injected with auto sampler.

3.5.6 Calibration curves and linearity

The evaluation of the calibration curves and linearity were carried out based on injections of the standard solutions prepared at the concentrations of 2.0, 5.0, 10.0, 20.0 and 30.0 ng mL^{-1}. The linearity (R^2 value) obtained was ~ 0.999 for all the standard herbicide compounds analysed.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Level of herbicide residues in sweetpotato

The standard calibration curves used to estimate the target herbicides are shown in Figure 4. The quantitative analysis summary reports are also shown in the Appendix.

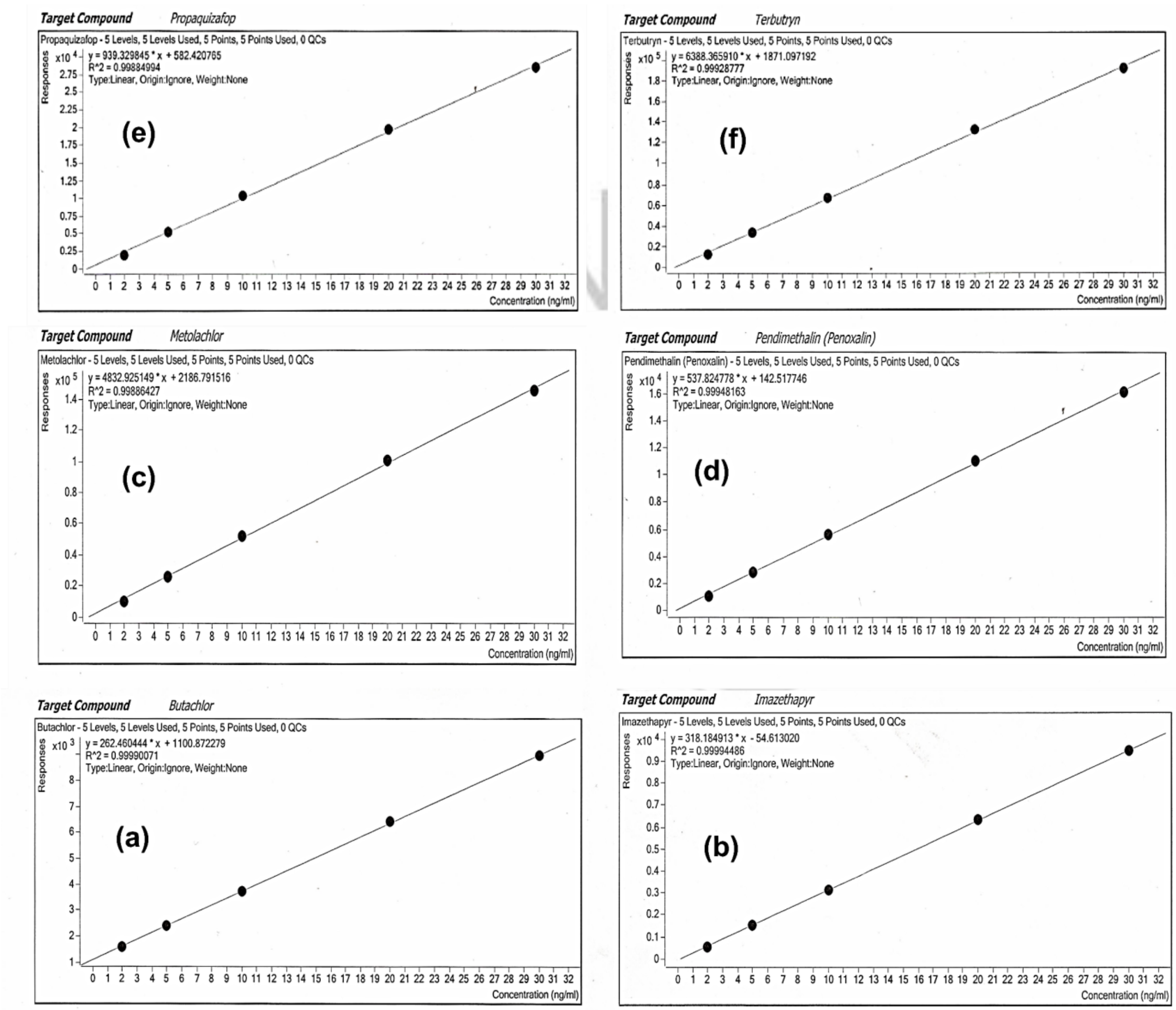

Figure 4: Standard calibration curves for (a) butachlor, (b) imazethapyr, (c) metolachlor, (d) pendimethalin, (e) propaquizafop and (f) terbutryn.

The results obtained after the herbicide residue analysis are presented in Table 6.

Table 6: Herbicide Residues in Sweetpotato samples

Treatments	Herbicide Residues (µg/g)					
	Butachlor	Imazethapyr	Metolachlor	Pendimethalin	Terbutryn	Propaquizafop
1 (CR5)	ND	ND	ND	0.0023□0.00	ND	ND

2 (CR6)	ND	ND	0.0029□0.00	ND	ND	ND
3 (CR7)	ND	ND	ND	ND	ND	ND
4 (CR8)	ND	ND	ND	ND	ND	ND
5 (CR9) (Control)	ND	ND	ND	ND	ND	ND

ND – Not Detected; Limit of Detection (LOD) = 1 ppb (0.001 µg/g)

The LC-MS results indicated the detection of pre-emergence herbicides; pendimethalin and metolachlor residues in treatments 1 (CR5) and 2 (CR6) samples at concentrations 0.0023 µg/g and 0.0029 µg/g, respectively. All other treatments showed no herbicide residues i.e., butachlor, imazethapyr, terbutryn and propaquizafop (which was applied post-emergence throughout all the treatments except the control). It is possible that these herbicide compounds got degraded to undetectable levels by the time the sweetpotatoes were harvested. According to Howell (2011), biotic and abiotic factors make up the various mechanisms involved in the fate of herbicides in the environment. The biotic factors are basically the interactions with living organisms which include uptake by plants and degradation by microorganisms, whereas the abiotic factors include volatilization and photochemical degradation. Adomako (2015) further explained that after application, the fate of herbicides to a large extent depends on the ability of the soil microorganisms to cause the degradation of the herbicides and this is ideally through the complete mineralization of the parent compounds into carbon dioxide (CO_2) and also the transfer of the chemicals through some other physical processes. As expected, the control also recorded no herbicide residues since the method of weed management employed was strictly hoeing. The concentrations of pendimethalin and metolachlor applied were 500g/L (3L/Ha) and 333g/L

(4L/Ha) respectively. Imazethapyr, terbutryn, butachlor and propaquizafop concentrations were also 240g/L (3L/Ha), 167g/L (4L/Ha), 50g/L (3L/Ha) and 100g/L (1.2L/Ha) respectively. This indicates that the concentrations of pendimethalin and metolachlor applied were higher compared to the other herbicides used and this may have contributed to the presence of their residues in the sweetpotato samples post-harvest. This could also signify that the quantities applied with respect to the remaining four herbicides were just right to avoid the persistence of their residues in the sweetpotatoes. Furthermore, this phenomenon may also be attributed to their short duration nature of persistence in plants.

According to the EU pesticides database, the maximum residue limits of both pendimethalin and metolachlor in sweetpotatoes is 0.05 mg/kg. It is evident that the residues detected in this study are lower and this therefore signifies that the risk associated with the dietary exposure of these herbicides in sweetpotatoes is considered safe to humans and will therefore pose no adverse health effects as far as food safety is concerned.

Saha *et al.* (2015) also cultivated peanut samples (*Arachis hypogaea* L.) in experimental fields and reported that at harvest time, no herbicide residues were detected in peanut kernel for pendimethalin and imazethapyr after treatments. This therefore indicated that the residue levels of the selected herbicides were below the maximum residue limits prescribed by European Union as well as other international organizations. A similar study carried out by Sireesha *et al.* (2011) revealed that the detected residues of pendimethalin in radish tubers were below the maximum residue limit at harvest. Alternatively, Sondhia and Dubey (2006) reported the detection of 0.007 µg/g residues of pendimethalin in green onion at 1.0 kg/ha application rate. Comparatively, the amount of pendimethalin applied in this study was twice that used in the sweetpotato research and that explains why the concentration of residues detected was also higher. Furthermore, Sondhia (2013) conducted a field study and analysed the residual effects of pendimethalin applied as pre-emergence at 1.0 kg/ha in cauliflower, radishes and tomato. At harvest, 0.001 µg/g, 0.014 µg/g and 0.008 µg/g residues of pendimethalin were detected in cauliflower, radishes and tomato respectively. In another research by Sondhia (2008), which involved the application of 100 g/ha imazethapyr, the residues detected in soybean grains, straw and soil were 0.102 µg/g, 0.301 µg/g and 0.008 µg/g respectively. Despite the fact that the application rate in this research was lower, higher concentrations were detected. This could probably mean that the rate of degradation of the herbicide was low hence the persistence of the residues in the crops and soil. The concentration of the residues in the soil was the least in this case and this could be attributed to the degradation by microorganisms in the soil. A recent study by Poonia *et al.* (2017) also reported that imazethapyr residues in soil were detected below the limit of quantification; however, in the plants, residues persisted to the levels of 0.015 µg/g at harvest of the groundnut samples. The concentration of the residues detected were far below the tolerance limits approved by European Union standards as well as the Indian Food Safety and Standards Authority and hence, risks associated with dietary exposure of these herbicides were considered safe for human consumption. The authors also reported that the short duration nature of persistence of the herbicides in soil and plants also confirmed that the herbicides were safe for the environment as well as for rotational crops.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The residual levels of five (5) different pre-emergence herbicides (butachlor, imazethapyr, metolachlor, pendimethalin and terbutryn) and one (1) post-emergence herbicide (propaquizafop) in sweetpotato samples were investigated.

The samples from the control (field work which was strictly hoeing as the method of weed management) had no residues detected. Butachlor, imazethapyr, terbutryn and propaquizafop were also not detected in their respective sweetpotato samples analysed. However, pendimethalin and metolachlor residues in treatments 1 (CR5) and 2 (CR6) samples were detected at concentrations of 0.0023 µg/g and 0.0029 µg/g, respectively.

The findings suggest that residues detected in this study were lower than the maximum acceptable limit (0.05 mg/kg) and thus the dietary exposure could be considered safe to humans.

5.2 Recommendations

The following are recommended:

- Lower concentrations of pendimethalin and metolachlor should be applied during the weed management of sweetpotato or should be avoided altogether.
- Further studies to ascertain the effect of herbicide concentration as well as different geographical locations or soil environment on the residue levels in sweetpotato.
- Further studies involving other food crops as applicable.

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APPENDIX

Appendix 1: Quantitative Analysis Summery Report

Quantitative Analysis Summary Report

Batch Data Path	D:\MassHunter\Data\RAY\Ray_work\QuantResults\Raywork.batch.bin		
Analysis Time	6/30/2017 4:22 PM	**Analyst Name**	LCMSMSD-PC\Admin
Report Time	6/30/2017 4:24 PM	**Reporter Name**	LCMSMSD-PC\Admin
Last Calib Update	6/30/2017 4:22 PM	**Batch State**	Processed
Quant Batch Version	B.07.01	**Quant Report Version**	B.07.01

Sequence Table

Data File	Acq Method File	Sample Name	Sample Type	Position	Volume	Level
Ray1.d	Raymix.m	Raymix_2ppb	Calibration	Vial 21	-1.00	1
Ray2.d	Raymix.m	Raymix_5ppb	Calibration	Vial 22	-1.00	2
Ray3.d	Raymix.m	Raymix_10ppb	Calibration	Vial 23	-1.00	3
Ray4.d	Raymix.m	Raymix_20ppb	Calibration	Vial 24	-1.00	4
Ray5.d	Raymix.m	Raymix_30ppb	Calibration	Vial 25	-1.00	5
Ray6.d	Raymix.m	CR_5	Sample	Vial 26	-1.00	
Ray7.d	Raymix.m	CR_6	Sample	Vial 27	-1.00	
Ray8.d	Raymix.m	CR_7	Sample	Vial 28	-1.00	
Ray9.d	Raymix.m	CR_8	Sample	Vial 29	-1.00	
Ray10.d	Raymix.m	CR_9	Sample	Vial 30	-1.00	
Ray11.d	Raymix.m	blank	Sample	Vial 31	-1.00	

Quantitation Results

Target Compound *Imazethapyr*

Data File	Compound	Sample Type	Response	Final Conc	Exp Conc	Accuracy
Ray1.d	Imazethapyr	Calibration	568	1.9572	2.0000	97.86
Ray2.d	Imazethapyr	Calibration	1514	4.9311	5.0000	98.62
Ray3.d	Imazethapyr	Calibration	3162	10.1079	10.0000	101.08
Ray4.d	Imazethapyr	Calibration	6333	20.0763	20.0000	100.38
Ray5.d	Imazethapyr	Calibration	9468	29.9275	30.0000	99.76
Ray6.d	Imazethapyr	Sample	17	0.2263		
Ray7.d	Imazethapyr	Sample	26	0.2518		
Ray8.d	Imazethapyr	Sample	16	0.2221		
Ray9.d	Imazethapyr	Sample	24	0.2478		
Ray10.d	Imazethapyr	Sample	15	0.2174		
Ray11.d	Imazethapyr	Sample	14	0.2171		

Target Compound *Terbutryn*

Data File	Compound	Sample Type	Response	Final Conc	Exp Conc	Accuracy
Ray1.d	Terbutryn	Calibration	13143	1.7643	2.0000	88.22
Ray2.d	Terbutryn	Calibration	33330	4.9245	5.0000	98.49
Ray3.d	Terbutryn	Calibration	67157	10.2195	10.0000	102.19
Ray4.d	Terbutryn	Calibration	132257	20.4099	20.0000	102.05
Ray5.d	Terbutryn	Calibration	191490	29.6819	30.0000	98.94
Ray6.d	Terbutryn	Sample	129	0.0000		
Ray7.d	Terbutryn	Sample	913	0.0000		
Ray8.d	Terbutryn	Sample	249	0.0000		
Ray9.d	Terbutryn	Sample	1421	0.0000		
Ray10.d	Terbutryn	Sample	778	0.0000		
Ray11.d	Terbutryn	Sample	35	0.0000		

Target Compound *Metolachlor*

Data File	Compound	Sample Type	Response	Final Conc	Exp Conc	Accuracy
Ray1.d	Metolachlor	Calibration	10266	1.6758	2.0000	83.79
Ray2.d	Metolachlor	Calibration	25885	4.9035	5.0000	98.07
Ray3.d	Metolachlor	Calibration	52153	10.3385	10.0000	103.39
Ray4.d	Metolachlor	Calibration	101127	20.4721	20.0000	102.36
Ray5.d	Metolachlor	Calibration	145290	29.6101	30.0000	98.70
Ray6.d	Metolachlor	Sample	230	0.0000		
Ray7.d	Metolachlor	Sample	15964	2.8508		
Ray8.d	Metolachlor	Sample	261	0.0000		
Ray9.d	Metolachlor	Sample	2518	0.0685		
Ray10.d	Metolachlor	Sample	1958	0.0000		

Quantitative Analysis Summary Report

Data File	Compound	Sample Type	Response	Final Conc	Exp Conc	Accuracy
Ray11.d	Metolachlor	Sample	504	0.0000		

Target Compound *Propaquizafop*

Data File	Compound	Sample Type	Response	Final Conc	Exp Conc	Accuracy
Ray1.d	Propaquizafop	Calibration	2055	1.5675	2.0000	78.38
Ray2.d	Propaquizafop	Calibration	5283	5.0042	5.0000	100.08
Ray3.d	Propaquizafop	Calibration	10375	10.4246	10.0000	104.25
Ray4.d	Propaquizafop	Calibration	19699	20.3513	20.0000	101.76
Ray5.d	Propaquizafop	Calibration	28436	29.6534	30.0000	98.84
Ray6.d	Propaquizafop	Sample	23	0.0000		
Ray7.d	Propaquizafop	Sample	33	0.0000		
Ray8.d	Propaquizafop	Sample	8	0.0000		
Ray9.d	Propaquizafop	Sample	3	0.0000		
Ray10.d	Propaquizafop	Sample	57	0.0000		
Ray11.d	Propaquizafop	Sample	2	0.0000		

Target Compound *Butachlor*

Data File	Compound	Sample Type	Response	Final Conc	Exp Conc	Accuracy
Ray1.d	Butachlor	Calibration	1633	1.9784	2.0000	98.92
Ray2.d	Butachlor	Calibration	2486	4.9722	5.0000	99.44
Ray3.d	Butachlor	Calibration	3718	9.9708	10.0000	99.71
Ray4.d	Butachlor	Calibration	6481	20.1941	20.0000	100.97
Ray5.d	Butachlor	Calibration	8945	29.8865	30.0000	99.62
Ray6.d	Butachlor	Sample	871	0.0000		
Ray7.d	Butachlor	Sample	1064	0.0000		
Ray8.d	Butachlor	Sample	685	0.0000		
Ray9.d	Butachlor	Sample	972	0.0000		
Ray10.d	Butachlor	Sample	976	0.0000		
Ray11.d	Butachlor	Sample	783	0.0000		

Target Compound *Pendimethalin (Penoxalin)*

Data File	Compound	Sample Type	Response	Final Conc	Exp Conc	Accuracy
Ray1.d	Pendimethalin (Penoxalin)	Calibration	1095	1.7710	2.0000	88.55
Ray2.d	Pendimethalin (Penoxalin)	Calibration	2604	4.9408	5.0000	98.98
Ray3.d	Pendimethalin (Penoxalin)	Calibration	5642	10.2262	10.0000	102.26
Ray4.d	Pendimethalin (Penoxalin)	Calibration	[illegible]	[illegible]	20.0000	101.58
Ray5.d	Pendimethalin (Penoxalin)	Calibration	16136	29.7373	30.0000	99.12
Ray6.d	Pendimethalin (Penoxalin)	Sample	50	0.0000		
Ray7.d	Pendimethalin (Penoxalin)	Sample	558	0.7729		
Ray8.d	Pendimethalin (Penoxalin)	Sample	135	0.0000		
Ray9.d	Pendimethalin (Penoxalin)	Sample	646	0.9355		
Ray10.d	Pendimethalin (Penoxalin)	Sample	1374	2.2891		
Ray11.d	Pendimethalin (Penoxalin)	Sample	4	0.0000		