THE EFFECT OF HOG MANURE AND MUNICIPAL BIOSOLIDS ON THE MINERALIZATION AND SORPTION OF PESTICIDES IN SOIL

BY

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ABSTRACT

Reimer, Marguerite. M.Sc., The University of Manitoba, June 2004. <u>The Effect of Hog Manure and Municipal Biosolids on the Mineralization and Sorption of Pesticides in Soil.</u> Major Professor: Annemieke Farenhorst.

The objective of this study was to determine the effects of hog manure and municipal biosolid amendments on the mineralization and sorption of three herbicides: glyphosate, trifluralin and 2,4-dichlorophenoxyacetic acid (2,4-D), in a range of Manitoba soils.

Soil microcosms were assembled to measure herbicide mineralization in soil. Glyphosate and trifluralin mineralization was measured in soils with a history of hog manure application and with fresh hog manure amendments. Fresh manure had no effect on glyphosate or trifluralin mineralization. Increased total glyphosate mineralization was measured in soil with 40 consecutive years of hog manure application, but total trifluralin mineralization was not affected. Soils with 35 (every two years) and 10 (annual) years of hog manure application had no consistent effects on glyphosate or trifluralin mineralization.

2,4-D mineralization was measured in different textured soils, with greatest 2,4-D mineralization in clay loam soil compared to sandy loam, silty loam or sandy clay loam soils. 2,4-D mineralization was greater in soils with lower application rates of fresh hog manure and municipal biosolids than in soil with higher rates of amendment application.

When 2,4-D and biosolids or manure were applied simultaneously, 2,4-D mineralization was greater than when up to 28 days had passed between amendment and 2,4-D applications. Overall, total 2,4-D mineralization in manure-amended soils was equal to or less than 2,4-D mineralization in biosolid-amended soils, and both were often less than non-amended controls.

Batch equilibrium techniques were used to determine soil-water partitioning coefficients (Kd) of glyphosate, trifluralin and 2,4-D and Freundlich distribution coefficients (Kf) of 2,4-D. Fresh manure had no effect on glyphosate and trifluralin Kd values. Glyphosate had higher Kd values in soils without a manure application history, while there was no effect of history on trifluralin sorption. 2,4-D Kd and Kf values were greater in soils treated with lower 2,4-D concentrations and lower manure application rates, relative to soil with higher rates of 2,4-D and manure application rates.

Manitoba producers should be aware of the possible effect a history of manure application may have on decreasing glyphosate persistence, as well as the increased risk of 2,4-D carryover in manure-amended soils.

CHAPTER 1

Extended Introduction and Study Objectives

Pesticides are chemicals used to control insects, diseases and weeds in agricultural crops and urban lawns and gardens. A Parliamentary Report (2000) indicated that over $1.4 billion of pesticides were sold in Canada in 1997, of which herbicides accounted for 85% of sales. While pesticides are applied to control specific target organisms, some chemical may also enter the broader environment during and after application. Therefore, it is important to understand the effects of pesticides on the environment, be it air, water or soil, for protecting our land and water resources and human health. Pesticides applied to or entering the soil react in a variety of ways. Functional groups on the chemical may bind or sorb to soil mineral particles or soil organic matter, or to other ions already sorbed to these soil constituents (Reddy and Gambrell 1987; Senesi 1992). Pesticides may also be degraded or consumed by microorganisms in the soil (Willems et al. 1996).

The objectives of this study were to examine the fate of pesticides in Manitoba soils amended with fresh hog manure, as well as soils with a history of hog manure applications, and municipal biosolids. Previous work has been carried out to study the effect of dairy manure and sewage sludge on the stimulation or inhibition of pesticide mineralization in soil (Doyle et al. 1978; O'Connor et al. 1981; Entry and Emmingham 1995). No studies have reported on the effect of hog manure on pesticide mineralization in soil and there is also a lack of direct comparison between freshly manured soils and soils with manure application histories. Because of the widespread use of hog manure as a soil amendment in Manitoba and the utilization of agricultural land for disposal of municipal biosolids, it is vital that the effects of soil amendments on pesticide mineralization and sorption are investigated.

Hog manure is widely applied onto Manitoba soils, the result of a hog industry producing over 7.3 million hogs annually (MAFRI 2004). It is a valuable soil amendment, adding nutrients and organic matter to the soil and stimulating microbial growth (Lalande et al. 2000). Soils with a manure application history are more likely to be higher in soil organic matter content, microbial biomass and nutrients (Goyal et al. 1993; Hao et al. 2003). These soil characteristics may affect pesticide activity in the soil (Shea 1989; Barriuso et al. 1997; Topp et al. 1997). Producers will not always apply the precise amount of manure necessary to meet the requirements of the following crop, and excess manure may be inadvertently applied as a result of waste disposal. Producers generally do not apply manure and pesticides to soil at the same time, but allow several days or weeks to pass between applications.

The City of Winnipeg utilizes agricultural land to dispose of municipal biosolids, the product of anaerobically digested municipal wastewater and sewage sludge (City of Winnipeg 2001). Biosolids have been shown to increase soil organic matter content and stimulate the soil microbial population (Barriuso et al. 1997). As these factors affect pesticide mineralization and sorption in soil, biosolids were considered to be of great interest and a good contrast to hog manure in this project.

Three herbicides were chosen for use in this study, based on their common use and differences in chemical activities and structures. Glyphosate (the active ingredient in Roundup®) is a non-selective herbicide commonly used in agricultural production, especially since the introduction of glyphosate-tolerant crops. It is frequently used in Manitoba, in part, because more than 45% of the canola grown in western Canada is glyphosate tolerant (Van Acker et al. 2003). Glyphosate is typically rapidly degraded by microbes in the soil (Jacob et al. 1988; Forlani et al. 1999) and has a relatively short half-life of less than 30 days (Smith and Aubin 1993), although a study by Nomura and Hilton (1977) reported glyphosate half-lives in soils up to 22 years. It is not volatile, and is also not likely to leach through the soil profile (Sprankle et al. 1975*a*). Glyphosate is rapidly inactivated in soils due to its sorption onto soil organic matter and mineral particles (Sprankle et al 1975*a*; Torstensson 1985; Piccolo et al. 1996). Additions of phosphorus to soil stimulated glyphosate degradation (Moshier and Penner 1978), perhaps due to lesser sorption and greater availability of the herbicide to soil microorganisms.

Trifluralin (the active ingredient in Treflan®) is a persistent, soil-applied herbicide that is widely used in Manitoba to control grassy and broadleaf weeds in cereal and oilseed crops. Trifluralin has a relatively long half-life of up to 120 days in cool, dry soils (Vencill 2002) due to its resistance to microbial breakdown (Probst et al. 1975). It is persistent in agricultural fields where its soil-residual effects may injure sensitive crops in the year following trifluralin applications (Miller et al. 1975; Gerwing and McKercher 1992). Trifluralin is strongly bound to soil organic matter (Solbakken et al. 1982) and only slowly mineralized by microorganisms in soil (Messersmith et al. 1971; Wheeler et al. 1979). A study showed that the rate of trifluralin mineralization in soil increased when dairy manure was applied at 50 000 and 100 000 kg manure ha^{-1} prior to herbicide applications (Doyle et al. 1978). However, soils amended with 50 000 kg dairy manure ha^{-1} yr^{-1} for 20 years showed similar trifluralin mineralization rates as non-amended soils (Entry and Emmingham 1995).

2,4-Dichlorphenoxyacetic acid (2,4-D) is a broadleaf herbicide. It has a short half-life of 10 days (Vencill 2002) because of its rapid degradation by microbes (Willems et al. 1996). However, it can also cause problems with carryover in crops like peas (Saskatchewan Pulse Growers 2000). 2,4-D is commonly used to control volunteer glyphosate-tolerant canola. Damage to sensitive crops may occur when seeding occurs soon after 2,4-D application (Saskatchewan Pulse Growers 2000). Soil organic matter has been shown to be the most important factor controlling sorption of 2,4-D in soil (Reddy and Gambrell 1987; Hermosin and Cornejo 1991) and 2,4-D sorption increases as soil organic carbon content increases (Ogram et al. 1985; Wu et al 2000).

In this research, glyphosate and trifluralin were applied in laboratory studies to three different soils collected in Manitoba. These soils had varied lengths of histories of hog manure applications. This study examined the impact of a history of hog manure application and fresh hog manure applications on herbicide mineralization and sorption in soil.

Another important issue addressed in this study is the fate of 2,4-D in soils of different textures. 2,4-D was applied to four Manitoba soils with different textures that also received applications of fresh hog manure and municipal biosolids. Soils of different texture contain different amounts of clay and soil organic matter (Brady and Weil 1996), which can affect the sorption of some herbicides (Shea 1989; Coquet 2003). Texture also influences the size and diversity of soil microbial populations (Hassink 1994; Vinther et al. 2001). Studying herbicide mineralization in different soil textures commonly found in Manitoba improves our knowledge of carryover risks, providing producers with more information to make better crop management choices.

It is also important to understand how different rates of manure application may alter the soil's ability to mineralize herbicides. Increasing the rate of manure application may also increase the amount of organic matter and microorganisms applied to soil. Understanding how these increases affect pesticide mineralization and sorption is essential to making wise manure- and pest-management plans that best control pests and protect the environment.

Another area of interest is the effect of increasing the length of time between organic amendments and pesticide applications. Mineralization of biosolid constituents in soil results in changes in the physical and chemical nature of the soil (Sommerfeldt and Chang 1985; Sommerfeldt et al. 1988; Chang et al. 1990), as well as changes in the soil microbial population (Fauci and Dick 1994; Hadas et al. 1996; Lalande et al. 2000; Moorman et al. 2001; Quemada and Menacho 2001). The amount of time between amendment and 2,4-D applications may also affect 2,4-D mineralization rates in soil.

The soil-water partitioning coefficient, Kd, and the Freundlich distribution coefficient, Kf, are values used to establish the relative strength of sorption of a substance to soil and are important parameters in determining pesticide fate in soil. Glyphosate is readily sorbed to soil organic matter (Sprankle et al. 1975*b*), and competition between glyphosate and phosphorus in the soil for binding sites has been observed (Sprankle et al. 1975*b*; de Jonge and de Jonge 1999; de Jonge et al. 2001). In Sprankle et al. (1975*b*), the amount of phosphate in the soil was deemed the most important factor in determining the amount of glyphosate sorbed; as the amount of phosphate in the soil increased, the amount of glyphosate sorbed decreased. The addition of nitrogen fertilizers decreased the mineralization of 2,4-D due to the suppression of enzyme production by specific 2,4-D-degrading organisms (Entry et al. 1993). Organic matter content plays a major role in trifluralin inactivation (Solbakken et al. 1982; Peter and Weber 1985); as organic matter content increased, more trifluralin was sorbed and inactivated (Hollist and Foy 1971). Strong positive correlations between 2,4-D sorption and soil organic carbon content have also been shown (Grover 1973; Ogram et al. 1985; Hermosin and Cornejo 1991; Mallawantri and Mulla 1992; Wu et al. 2000). Because livestock manure is a source of phosphorus (Whalen and Chang 2001) and organic carbon (Sommerfeldt and Chang 1985; Hao et al. 2003), this suggests that the addition of manure and biosolids to soil may influence pesticide sorption. Studies have been conducted to investigate the effect of dairy manure and municipal biosolids on 2,4-D sorption. O'Connor et al. (1981) studied the effect of sewage sludge on 2,4-D sorption in soil and found that aged sludge additions to soil increased 2,4-D sorption compared to non-amended or freshly amended soils. Barriuso et al. (1997) found that 2,4-D sorption was not affected by the addition of composted municipal waste to soil.

Overall, this study will quantify the effects of pesticide fate in Manitoba soils with a history of hog manure application and amended with fresh hog manure and municipal biosolids. By determining the effect that these amendments have on the mineralization and sorption of glyphosate, trifluralin and 2,4-D, practical implications may be passed on to producers in order to promote environmentally and agronomically sound crop protection decisions. From the results of this study, it appears that manure applied at typical field rates will not have a major effect on increasing persistence of glyphosate, trifluralin or 2,4-D. There is an increase in sorption of these herbicides to soil, but this reduces the amount of herbicide present in a plant-available form. Producers need to be aware of and prevent a greater risk of increasing herbicide persistence in soil when amendments are applied at higher rates.

CHAPTER 2

Literature Review

2.1 Fate of Pesticides in the Soil Environment

2.1.1 Pesticide Sorption

Pesticide inactivation in soil can occur by sorption of the chemical to soil mineral particles and organic matter constituents. Sorption plays a major role in determining the amount of pesticide available for degradation or transport, and therefore influences the degree of environmental and agronomic impact the pesticide may have.

2.1.1.1 Pesticide Sorption to Organic Surfaces Organic materials in soil, including decayed plant or animal matter and applied manure and sewage sludge, have properties that may result in increased herbicide sorption (Shea 1989). Sorption reduces the availability of herbicides for plant uptake, thereby reducing the ability of soil-residual herbicides to control weeds. Sorption onto soil organic matter (SOM) is greatest for non-ionizable, hydrophobic herbicides and least for weakly acidic, highly water-soluble chemicals, but all herbicides have some affinity for organic matter (Shea 1989).

A greater SOM content requires an increase in the herbicide application rate to ensure equivalent efficacy of the herbicide, because SOM has the capacity to make the herbicide unavailable to plants (Upchurch and Mason 1962). Application rate recommendations for pre-emergence herbicides, like trifluralin, depend largely on the amount of SOM present in the soil (Guide to Crop Protection 2000). Upchurch and Mason (1962) found an inverse relation between SOM content and the ability of twelve soil-incorporated herbicides to reduce the growth of weeds, meaning that the herbicides are inactivated or detoxified by the organic matter. The kind and amount of organic matter can have a significant effect on the extent of the detoxification of the herbicide (Doherty and Warren 1969; Barriuso et al. 1997) because organic matter composition determines the type of sorption sites available for pesticides (Shea 1989). The extent of pesticide sorption onto SOM is dependent on the presence of functional groups on the SOM (Torrents et al. 1997), as well as on the pH of the SOM compared to the pKa or pKb of the pesticide (Wu et al. 2000).

2.1.1.2 Pesticide Sorption to Inorganic Surfaces Several factors may be involved in pesticide sorption to inorganic soil surfaces, such as the presence of iron oxides (Madsen et al. 2000). Soil pH affects the amount and type of ions on the surface of the clay mineral. Depending on soil pH, clay minerals can repel the pesticides or form complexes with the pesticides, thus affecting sorption (McConnell and Hossner 1985). Sorption of pesticides can also take place in the interlayer spaces of clay minerals (Glass 1987).

2.1.2 Pesticide Transport

The movement of pesticides after application can result in environmental and agronomic damage. It is essential to understand the potential transport media that may contribute to pesticide contamination of air, soil, surface and groundwater.

2.1.2.1 Pesticide Leaching Leaching of pesticides into the groundwater presents serious environmental concerns. The organic-matter-water distribution coefficient (K_{om}) is an excellent indicator of the likelihood of a pesticide to leach; a two-fold increase in K_{om} correlates to a 10-fold increase in the amount of pesticide leached (Boesten and van der Linden 1991). Pesticides with low water solubilities, strong sorption to soil and relatively long half-lives generally have low mobility in soil and are not readily leached through the soil profile (Elliot et al. 2000). Post-emergence herbicides generally have higher water solubilities and lesser soil sorption than pre-emergence herbicides and are more likely to leach through the soil as a result of a rainfall or irrigation event (Cessna et al. 2001).

Macropore flow of water (i.e. the movement of water through large pores in soil) was found to be a significant route of prochloraz (a fungicide) loss, with 0.2% of the applied chemical being collected in macropore drainage water (Villholth et al. 2000). Conventionally tilled soils experienced less pesticide leaching by preferential flow than no-till soils because of differences in macropore size and distribution between tillage systems (Elliot et al. 2000). Pesticide movement through macropores such as soil cracks and mole drainage in slowly permeable soils will reduce pesticide runoff loss (Brown et al. 1995).

Increased soil aggregate size has been shown to decrease the amount of herbicide sorbed in clay soil, thereby increasing the risk of groundwater contamination by leaching (Novak et al. 2001). An anionic tracer was used in a study by Roulier and Jarvis (2003) to track leaching of MCPA, a phenoxy herbicide, through soils from different slope positions.

Rapid leaching and macropore flow was measured in the fine-textured hilltop soil, while less leaching was measured in the depressional soil that contained more organic matter, sorbed more MCPA and had lesser macropore flow (Roulier and Jarvis 2003).

Pesticide application timing can influence pesticide leaching potential. Greater amounts of herbicides were detected in southern Alberta groundwater when herbicides were applied shortly before heavy rains (Miller et al. 1995*a*), suggesting that, ideally, scheduling of pesticide application should be done around forecasted weather events in order to reduce the likelihood of leaching or runoff of pesticides. A study by Boesten and van der Linden (1991) showed that weakly sorbed pesticides with short half-lives had a higher potential to leach through soils with low SOM content when applied in the autumn versus the spring. The application rate of pesticides has also been shown to affect leaching potential; as pesticide concentration increases, pesticide biodegradation decreased and the ability of pesticides to sorb to soil increased but at a decreasing rate, resulting in a larger risk of pesticide leaching to groundwater (Rao and Davidson 1979).

2.1.2.2 Pesticide Volatilization The loss of pesticides from the soil may occur through the transformation of the chemical into a gaseous state by which it can volatilize into the atmosphere. Burkhard and Guth (1981) found that the rates of volatilization for the pesticides methidathion, diazinon and isazophos (insecticides), metolachlor (herbicide) and metalaxyl (fungicide) increased with increasing pesticide concentration, air temperature, air flow rate, and decreasing SOM content. Another study by Wienhold et al. (1993) found that increasing soil temperature increased volatilization of atrazine and alachlor. Glotfelty et al. (1984) found that moisture played an important role in pesticide volatilization; as moisture content increased in a sandy soil, the volatilization rate of pesticide mixtures containing trifluralin, heptachlor, chlordane, lindane or dacthal also increased.

2.1.2.3 Erosion by Water or Wind Pesticides can be transported during a runoff event, either in solution or attached to eroded sediments. A study by Gouy et al. (1999) determined that the concentration of pesticides in runoff during a simulated rainfall was greatest at the start of the rainfall and decreased as the experiment continued. Pesticides with greater sorption were more likely to be found sorbed to eroded soil particles, while weakly sorbed pesticides were found in greater concentrations in the runoff water (Gouy et al. 1999). Logan et al. (1994) found that the loss of four herbicides from a poorly drained, fine-textured soil was greater in surface runoff than in tile drainage water, with herbicide leaching to tile drains only in the wettest year of the study. Herbicide runoff was greatest for herbicides with longer half-lives, but herbicide runoff was not correlated with herbicide water solubility (Logan et al. 1994).

Wind erosion of pesticides sorbed to soil can be a major loss of applied chemicals, as well as an environmental hazard if pesticides are transported to residential areas or waterways. A study by Clay et al. (2001) found that at one day following application, more than 50% of the surface-applied atrazine, acetochlor and alachlor was present in the wind-erodible fraction of surface soil, but less than 10% was present in the wind-erodible fraction when the pesticides were immediately incorporated after application. Overall, incorporation of the pesticides reduced the erodible-pesticide fraction by 50 to 80% (Clay et al. 2001). Larney et al. (1999) compared the presence of soil-applied and surface-applied herbicides in wind-eroded sediments and also concluded that incorporation of the chemical into soil significantly reduced pesticide transport by wind erosion. The loss of soil-incorporated herbicides was 1.5% of the total chemical applied, while 4.5% of the surface-applied herbicides were lost (Larney et al. 1999).

2.1.3 Pesticide Transformation

After pesticide application, transformation may occur within the soil by biological or chemical means. These mechanisms can significantly affect the efficacy or persistence of the pesticide.

2.1.3.1 Biodegradation Biodegradation of pesticides is the transformation of pesticides by living organisms and is the chief means of pesticide breakdown in soil (Topp et al. 1997). Because microorganisms conduct the biological degradation of pesticides in soil, factors affecting the activity of microorganisms, such as soil moisture and temperature, O_2 and energy sources, generally influence the rate and amount of pesticide biodegradation (Topp et al. 1997). Metabolism of pesticides, where the microorganisms obtain nutritional benefit from the pesticide, is a common method of pesticide degradation in soil (Topp et al. 1997). This often results in complete pesticide mineralization, i.e. the transformation of a pesticide molecule to CO_2, water and inorganic ions (Topp et al. 1997). Cometabolism is the process by which the pesticide is not utilized for microbial nutritional benefit or energy, and can result in the formation of breakdown products that may be degraded further. Pesticides that can support microbial growth by supplying a carbon source may experience accelerated degradation if the microbial population is large at the time of a second pesticide application; however, pesticides that are not utilized as carbon sources for microbial consumption will not experience accelerated degradation (Robertson and Alexander 1994).

Additions of organic matter and fertilizer have been shown to increase pesticide biodegradation, but only when these amendments encourage the growth of microorganisms that can degrade the chemicals (Shea 1989). Soils with a growing crop mineralize herbicides more quickly than bare soils, most likely because of a more active soil microbial population maintained by root exudates (Piutti et al. 2002).

2.1.3.2 Chemical Degradation Chemical degradation is defined as the chemical instability of a pesticide in the soil environment (Topp et al. 1997). A chemical can be transformed by nonbiological processes, such as oxidation-reduction or hydrolysis. Hydrolysis is the main nonbiological process by which pesticides are degraded (Armstrong and Konrad 1974). Organic matter plays a role in the abiotic degradation of herbicides by providing nucleophiles, or an acidic surface for hydrolytic adsorption of the herbicide (Shea 1989). For most pesticides, chemical degradation is much less important than the biological degradation of the chemical.

2.1.3.3 Photodegradation Photodegradation is the breakdown of pesticides caused by exposure to light (Topp et al. 1997). Electromagnetic radiation is absorbed by the chemical which may induce a chemical reaction and alter its structure (Armstrong and Konrad 1974). Photodegradation in soil generally increases as SOM content increases (Konstantinou et al. 2001). Pesticide photodegradation is not an important process contributing to pesticide fate in soil.

2.1.4 Environmental Concerns

A major environmental concern surrounding pesticide use is the occurrence of pesticides in the atmosphere. One study captured urban roof runoff during rainfall and detected several widely used pesticides, such as triazines, acetamides and phenoxy acids (Bucheli et al. 1998). Maximum pesticide concentrations in urban rainwater occurred during and right after agricultural pesticide applications, indicating that pesticides were being washed out of the atmosphere in urban areas, with the potential to enter groundwater (Bucheli et al. 1998). This study is a clear indicator that urban areas are experiencing the effects of agricultural practices, and that consequences of those practices are widespread.

The contamination of groundwater by pesticides is also of concern. A study in Maryland and Virginia by Koterba et al. (1993) found that for 36 pesticides, chemicals were most frequently detected in the shallow depth of the water table. Since most wells derive water from deeper within the water table, this shallow detection was not considered to be a potential health risk to humans (Koterba et al. 1993). However, in Alberta, diclofop, MCPA and bromoxynil were found in groundwater below a manured field, with diclofop and bromoxynil at levels that exceeded the Canadian drinking water guidelines (Miller et al. 1995*b*). Specifically, there is concern that pesticides may leach rapidly through the soil profile by way of macropores, resulting in contaminated groundwater (Miller et al. 1995*b*).

Wetlands in or near cultivated fields may be at risk for pesticide contamination due to pesticide use in agricultural fields. As precipitation increased over a season, the number and concentration of pesticides present in prairie wetlands increased (Donald et al. 1999). Up to 24% of wetlands studied had pesticide concentrations that exceeded the guidelines for protection of aquatic life (Donald et al. 1999). Atmospheric deposition contributes to a continuous low level of pesticide contamination of surface waters, while runoff and erosion contribute to a sporadic but high level of pesticide contamination of surface waters (Raupach et al. 2001).

2.1.5 Agronomic Concerns

It is important to consider what effects pesticides have on the agronomic practices and quality of agricultural land and crops. Bromilow et al. (1996) reported on a study at Rothamsted, England that looked at 20 years of fungicide and herbicide applications and their resulting effects on soil fertility. The pesticides had no detrimental effects on crop productivity and caused no differences in microbial activities or populations, and no pesticide residues (as defined by the extraction methods) were detected 17 to 22 months after the last pesticide application (Bromilow et al. 1996).

Another potential agronomic concern is the ability of plants to absorb herbicide residues that are on the surface of the soil. Al-Khatib et al. (1992) studied the likelihood of herbicide absorption and damage of susceptible crops when leaves came into contact with herbicide residues on the soil surface and found the amount of herbicide absorbed by the plant was very small and that a very large leaf surface would need to come into contact with these residues to cause significant damage.

Pesticide carryover in soil has the potential to harm consecutively planted sensitive crops. Trifluralin has a relatively long persistence in soil that can cause stunting of corn, wheat and barley. Corn stunting due to trifluralin residue was evident in the early part of the growing season, but decreased as the season progressed, with up to 16% yield decrease in plots with an application rate of 4.5 kg trifluralin ha^{-1} the previous year (Hartzler et al. 1989). In another study, wheat plant density and dry matter production were decreased at the beginning of the season as a result of trifluralin residue in soil, but recovered so that a 35% reduction in dry matter production at the beginning of the season resulted in a 10% reduction in seed yield at harvest (Morrison et al. 1989). Increasing the rate of herbicide application also affects carryover and subsequent crop damage. As the imazaquin application rate in a clay soil increased, barley yields decreased (Loux and Reese 1993). Barley yields were reduced in Alberta soils that had received more than 1.4 kg ha^{-1} of trifluralin the previous fall (Darwent et al. 1990), while recommended trifluralin field application rates are around 1.0 kg ha^{-1} (Guide to Crop Protection 2000). Barley yields were lowest in trifluralin-treated soil under moisture stress (Darwent et al. 1990).

Soil texture and pH affect pesticide carryover. A study by Loux and Reese (1993) found that imazethapyr, an imidazolinone herbicide, was more persistent in a clay soil compared to a silty loam, but the persistence in the silty loam increased as pH decreased. Imazaquin, another imidazolinone herbicide, applied to a clay soil caused injury and yield loss in corn, and injury and yield loss increased as soil pH decreased (Loux and Reese 1993).

Tillage also influences pesticide carryover. Moldboard and chisel ploughing reduced the concentration of trifluralin in the top 7.5 cm surface soil layer, therefore reducing the extent of corn injury relative to a no-till system (Hartzler et al. 1989). By mixing the soil and redistributing the chemical to greater depths, the chemical was effectively diluted in soil (Hartzler et al. 1989).

Depth of seeding influenced the amount of ethalfluralin-residue damage to wheat; 21% less yield was obtained as seeding depth increased from 4 to 12.5 cm (Darwent et al. 1997).

2.2 Manure

Livestock manure is applied to soil as a means of livestock waste disposal and nutrient and organic matter addition to soil. The addition of nutrients from manure to soil is a major agronomic benefit, but the movement of nutrients to surface water and groundwater can also pose a major environmental risk. Manure can also present a negative effect on the soil microbial community through the addition of toxic amounts of salts and metals.

Application of dairy manure increased extractable and mineralizable NH_4^+ and NO_3^-, extractable P and total N, P and C in pasture soils compared to non-amended soils (Entry and Emmingham 1995). Soil pH decreased and sodium adsorption ratio (Chang et al. 1990) and exchangeable Na, K and Mg increased over time with repeated annual applications of cattle manure (Hao and Chang 2002). Organic carbon (OC) content in soil increased with increasing rates of cattle manure application (Sommerfeldt and Chang 1985). Hao et al. (2003) found that OC and total N contents had increased after 25 years of cattle manure application to soil; however, a study by Sommerfeldt et al. (1988) showed that accumulations of OC and total N increased at a decreasing rate over time because an initial rapid decomposition of manure following application was followed by a slower decomposition over time. Applications of swine manure were found to increase soil P concentrations and ten years of atypically high application rates led to leaching of P to groundwater (Novak et al. 2000). Repeated cattle manure applications to soil also increased total and available soil P levels in other studies (Dormaar and Chang 1995; Whalen and Chang 2001), and lead to increased risk of P leaching to groundwater in clay soils (Whalen and Chang 2001). Irrigation of manured land increased the risk of groundwater contamination by P (Whalen and Chang 2001).

Several studies have demonstrated that manure stimulates N mineralization, suggesting that soil N may be made plant-available more quickly in manure-amended soils. The addition of composted cattle manure to soil resulted in increased net N mineralization, relative to the amount of compost added (Hadas et al. 1996). Liquid hog manure also stimulated N mineralization compared to fertilizer or non-amended soil treatments (Lalande et al. 2000).

The additions of dairy manure amendments (Doyle et al. 1978), farmyard manure (Hadas et al. 1996) and liquid hog manure (Lalande et al. 2000) stimulated soil microbial activity. Other studies also demonstrated that the addition of a fresh energy source with soluble carbon increased microbial growth (Goyal et al. 1993; Fauci and Dick 1994). Entry and Emmingham (1995) found that while dairy manure additions did not influence active bacterial or fungal biomass, higher amounts of total bacterial and fungal biomass were measured after manure addition.

The addition of farmyard manure to previously unmanured and manured soils increased microbial biomass in the first three months after manure application, and biomass and microbial metabolic rate increased with increasing manure application rates (Goyal et al. 1993). Highly-available, soluble organic material in manure was used up during the first four weeks after application, but stimulation of microbial activity continued for up to 33 weeks (Hadas et al. 1996). Increased microbial respiration was measured in manured soils due to the higher levels of accumulated organic carbon (Goyal et al. 1993). Respiratory rates increased at a different rate when manure was applied to either previously manured or unmanured soils, indicating that different types of microbial populations appear in regularly manured soils versus unmanured soils (Goyal et al. 1993). Hadas et al. (1996) found that a history of manure application to soil enhanced the effect of freshly-applied composted cattle manure on increasing microbial activity compared to the addition of cattle manure to soils without a history of manure application. The increase in microbial activity resulted from an increase in the pool of available OC in soil. Fauci and Dick (1994) found that microbial biomass was higher in soils with a long-term history of manure applications compared to unmanured soils.

Manure is also capable of improving soil quality and soil physical conditions. The comparison of several organic amendments found that hog manure, poultry manure and alfalfa hay amendments had a stronger effect on restoring soil productivity than cattle manure, pea hay or barley straw amendments (Larney and Janzen 1996). Moreover, hog and poultry manures were able to restore soil productivity after topsoil removal, whereby the restored soil productivity was similar to soil that did not have topsoil removed (Larney and Janzen 1996). This was thought to be due to the addition of nutrients and organic matter, and the improvement in soil structure suggested that livestock manure is an effective tool in restoring eroded soils (Larney and Janzen 1996). Applications of cattle manure over five or more years resulted in decreased bulk density, with decreasing draft required from tillage equipment with increasing manure application rates (Sommerfeldt and Chang 1985).

Negative consequences of manure application to the soil community include the addition of toxic quantities of salts and metals. When manure is applied on the basis of N fertilization, salts such as K^+ and Na^+ can accumulate in soil, which may affect microbial communities and plant growth if manure is applied at high rates (Eck and Stewart 1995). Applications of 269 and 538 Mg ha^{-1} of cattle feedlot waste were found to depress plant yields due to accumulation of salts and ammonium (Mathers and Stewart 1971). Manure decomposition and nitrification, both microbial processes, were inhibited compared to soils with lower manure application rates (Mathers and Stewart 1971), and indication that excess amounts of manure can have detrimental effects on the microbial community.

2.3 Municipal Biosolids

Municipal biosolids, or sewage sludges, are the anaerobically digested end-product of urban and industrial wastewater and sewage treatment. The organic material from the wastewater treatment is processed and applied to soil in order to prevent pollution by entering waterways or incineration. The digested biosolids are rich in nutrients such as nitrogen, and improve the soil water-holding capacity, making biosolids a valuable by-product of wastewater treatment (City of Winnipeg 2001). However, the application of biosolids to agricultural land is cause for concern because of the metals content that may injure crops, as well as the risk of runoff or leaching of contaminants, including nutrients or pathogens.

Composted municipal waste increased SOM content (Barriuso et al. 1997), as well as SOM mineralization (Perrin-Ganier et al. 2001). When added to soil, composted municipal waste has been shown to stimulate soil microbial population (Barriuso et al. 1997) and soil respiration (Quemada and Menacho 2001), but not in all cases. For example, sludge was found to have greater numbers of protozoa and heterotrophic bacteria than soil, but the addition of sludge to soil did not affect the overall numbers of protozoa and heterotrophic bacteria in soil (Klinge et al. 2001).

Municipal biosolids have been shown to influence the nature and amount of nutrients in soil. Up to 81% of NH_4^+-N from biosolids is lost by volatilization within three weeks of surface application to soil (Robinson and Polglse 2000). Wetting and drying cycles of biosolids in soil stimulated mineralization of organic N, which increased the loss of total N (Robinson and Polglse 2000). He et al. (2000) found that organic N mineralization from biosolids in soil contributed to 48% of the total soil organic N over one year. NH_4^+-N was the most prevalent form of N mineralized in the first six months after biosolids applications to a sandy soil, but NO_3^--N accounted for over 50% of mineral N in the next six months (He et al. 2000).

Biosolids also supply phosphorus, potassium and trace elements (Barbarick et al. 1995; Maguire et al. 2000; Christie et al. 2001). After biosolids had been dewatered and treated to become alkaline, P and K were slowly released from the biosolids and were found to be at least as available as fertilizer P (Christie et al. 2001). Maguire et al. (2000) found that biosolids applied on the basis of N requirements led to an accumulation of P in soils.

2.4 Effects of Organic Amendments on Pesticides

Sludge and manure amendments to soil can stimulate or inhibit pesticide degradation (Doyle et al. 1978; O'Connor et al. 1981; Entry and Emmingham 1995). Increased rates of degradation of a number of unrelated pesticides were measured in soils amended with manure or sludge (Doyle et al. 1978). In soils amended with manure or sludge, several structurally unrelated herbicides have been found to have no inhibitory effect on the overall microbial activity (Doyle et al. 1978).

The addition of easily degradable organic matter to soil can stimulate microbial activity and increase pesticide degradation by increasing the numbers of microbes that degrade pesticides by cometabolism (Entry and Emmingham 1995). Both sludge and manure additions increased the total CO_2 evolution in soil, suggesting that these amendments increased microbial activity (Doyle et al. 1978; O'Connor et al. 1981) because these amendments added microorganisms or nutrients to the soil (Gan et al. 1998).

The influence of manure and biosolids on pesticide fate in soil may vary depending on the amount, composition and timing of amendment application (Doyle et al. 1978; O'Connor et al. 1981; Entry and Emmingham 1995; Barriuso et al. 1997; Celis et al. 1998; Wu et al.

2000; Klinge et al. 2001). The addition of sludge to soil, particularly if supplemented with a concentrated microbial population, was able to increase the rate of degradation of chemicals, providing a potential way to ameliorate environmental contamination (Jacobson et al. 1980). Shea (1989) found that manure was generally more effective than sludge at catalyzing herbicide degradation.

Trifluralin mineralization was greater in manure-amended soil compared to a non-amended control (Doyle et al. 1978), while Moorman et al. (2001) found that amendments such as compost and manure had no effect on trifluralin degradation. Manure addition to soil stimulated microbial activity, but did not cause an increase in specific microbial populations capable of degrading trifluralin (Moorman et al. 2001). Sewage sludge addition to soil did not affect the degradation of the herbicide isoproturon in soil (Perrin-Ganier et al. 2001). 2,4-D efficacy was lower in soils repeatedly amended with sewage sludge compared to non-amended soils due to increased sorption and more rapid degradation of the chemical (O'Connor et al. 1981). Entry and Emmingham (1995) measured increased 2,4-D mineralization in dairy manure-amended pasture soils compared to non-amended soils. In contrast, mineralization rates of various herbicides, including 2,4-D, decreased when applied to composted municipal solid waste or compost-soil mixtures relative to incubations with soil alone (Barriuso et al. 1997). As the rate of composted waste added to soil increased, the total mineralization of these herbicides generally decreased, partly because of increased sorption of the herbicides to the soil-compost matrix (Barriuso et al. 1997).

Sánchez et al. (2003) found that the addition of sewage sludge to soil increased SOC content, which resulted in an increased capacity of the soil to sorb methidathion (an organophosphorus insecticide). The addition of composted municipal waste also increased SOM content, which increased binding of herbicide residues to soil and resulted in an overall decrease in herbicide mineralization, despite the fact that amendments stimulated the microbial population (Barriuso et al. 1997). Other studies also reported increased SOC content and herbicide sorption due to the addition of manure and sewage sludge (O'Connor et al. 1981; Shea 1989; Guo et al. 1993).

Atrazine sorption to different sewage sludge treatments and soil-sludge mixtures was greatest for composted sewage sludge, followed by solid and liquid sludge (Celis et al. 1998). Soil-sludge mixtures resulted in lower atrazine sorption values compared to atrazine in sludge alone due to interactions of soil surfaces with the dissolved organic matter from the sludge, resulting in fewer sites available for herbicide sorption (Celis et al. 1998). Barriuso et al. (1997) found that herbicide sorption to composted sludge was 10 to 20 times greater than to soil alone due to the higher organic matter content of compost. Specifically, 2,4-D sorption rose from 0.4 L kg^{-1} in soil alone to 5.63 L kg^{-1} in composted sludge (Barriuso et al. 1997). However, a study by O'Connor et al. (1981) showed that fresh sludge additions had little effect on 2,4-D sorption, although significantly more 2,4-D sorption occurred in soil pre-conditioned with sludge for two months than in soil alone.

Graber et al. (2001) measured the downward movement of terbuthylazine, atrazine and bromacil in sludge-amended sandy loam soil following an irrigation event. All pesticides experienced increased transport in amended fields compared to the control due to the development of preferential flow pathways around hydrophobic clods of sludge (Graber et al. 2001). Enhanced transport of terbuthylazine and atrazine was also due to the pesticides forming complexes with dissolved, colloidal and suspended organic matter produced during sludge degradation (Graber et al. 2001).

2.5 Herbicides Used in This Study

Three herbicides, glyphosate, trifluralin and 2,4-Dichlorophenoxyacetic acid, were chosen for use in this study, based on their widespread use and varied chemical structures.

2.5.1 Glyphosate

Glyphosate, N-(phosphonomethyl)glycine (Figure 2.1), is a non-selective herbicide used worldwide for the control of weeds. Its mode of action is to inhibit 5-enolpyruvylshikimate-3-phosphate synthase, which results in the depletion of aromatic amino acids necessary for protein synthesis and plant growth (Vencill 2002). It produces one major significant metabolite, aminomethyl-phosphonic acid (AMPA), which degrades more slowly than glyphosate (Rueppel et al. 1977), but is also a short-lived decomposition product (Eberbach 1999). Neither glyphosate nor its metabolites typically persist long in the environment, as shown by Rueppel et al. (1977), who found that over 50% of the ^{14}C-labeled glyphosate added to a sandy loam soil had mineralized after 28 days. Half life of glyphosate ranges from less than 25 days in laboratory experiments to 47 days in the field (Vencill 2002). However, a study by Nomura and Hilton (1977) reported glyphosate half-lives of up to 22 years in soils with pH < 6 and organic matter contents of over 9%, which resulted in increased sorption of glyphosate.

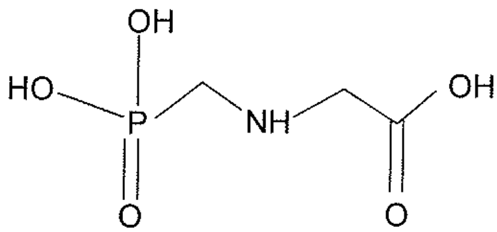

Figure 2.1. Glyphosate molecule.

2.5.1.1 Glyphosate Degradation Abiotic degradation and photodecomposition of glyphosate occur in such small amounts that they are not considered significant causes of degradation; however, degradation of glyphosate occurs readily in the soil because of rapid microbial metabolism (Rueppel et al. 1977). Evidence of the importance of microbial degradation was presented by Moshier and Penner (1978); degradation rates were severely reduced in sterilized soil when compared to non-sterilized soil. Glyphosate was shown to have no negative effects on microbial growth (Haney et al. 2000), and was immediately metabolized by indigenous soil microbes, followed by a slower rate of degradation as the soluble portion of the herbicide was sorbed (Rueppel et al. 1977).

Glyphosate stimulates microbial activity through the addition of readily mineralizable C and N, and increasing glyphosate application rates resulted in increasing C mineralization (Haney et al. 2000). Robertson and Alexander (1994) found that 50% of the initially applied glyphosate was mineralized at 10 days after the first glyphosate application, but 60% of the glyphosate was mineralized at 10 days after the second application to soil. The number of organisms capable of degrading the molecule rose after the first application such that for the second application up to 12% of the initially applied glyphosate ended up in the microbial biomass (Robertson and Alexander 1994). Dick and Quinn (1995) also found higher numbers of microorganisms in glyphosate-treated soil compared to untreated soil, though less diversity of colony types. Slower than average degradation rates are observed in soils that have lower microbial activity or greater tenacity of glyphosate binding (Sprankle et al. 1975*b*). Addition of glucose to soil decreased glyphosate degradation rates as the microbes preferentially consumed the readily available substrate instead of glyphosate (Moshier and Penner 1978).

A wide variety of microbes can metabolize glyphosate (Forlani et al. 1999). The *Pseudomonas* sp. strain LBr is capable of degrading glyphosate, but these microbes cannot degrade glyphosate in the presence of phosphate in the soil. Most likely, the genes responsible for degrading glyphosate are regulated by the presence of phosphate (Jacob et al. 1988). *Pseudomonas* sp. strain PG2982 can use glyphosate as a sole phosphorus source, but only in the absence of any other phosphate source (Fitzgibbon and Braymer 1988). Species of microbes that can degrade glyphosate in the presence of phosphorus include *Streptomycetes* StA and StC, which seem to have a low affinity for inorganic phosphate and thus are able to utilize glyphosate regardless of the presence of phosphate (Obojska et al. 1999). The ability to utilize glyphosate in the presence of phosphate is common to the *Rhizobiaceae* family, particularly *R. meliloti*, and is carried out by the cleavage of the C-P bond in the glyphosate molecule (Liu et al. 1991). *Penicillium chrysogenum* is a fungus that can utilize glyphosate as the sole source of nitrogen, but degradation of glyphosate decreases when other sources of organic N are available and when glyphosate is the only source of phosphorus (Klimek et al. 2001). Several other fungal strains, including some belonging to *Penicillium*, *Sclerotinia*, *Fusarium* and

Trichoderma, are capable of degrading glyphosate when it is used as a sole source of P, and a few species such as *Rhizopus*, *Mucor* and *Neosartorya* can also utilize glyphosate as a sole source of carbon (Krzyśko-Lupicka and Orlik 1997).

While it is useful to know which soil microorganisms can degrade glyphosate in the field, research has also been conducted to remove glyphosate in wastewater effluent from an activated sludge treatment system. Hallas et al. (1992) found that immobilized bacteria (sorbed onto a diatomaceous earth biocarrier) were able to remove glyphosate from the wastewater, providing a cost-effective and reliable method to treat industrial wastewater.

2.5.1.2 Glyphosate Sorption Glyphosate has not been found in runoff water and leachate after application because of its strong sorption and rapid binding to soil (Rueppel et al. 1977). There are several theories which describe the way glyphosate is bound in the soil environment. The chemical itself is a substituted glycine which may be bound to soil in a manner similar to glycine or phosphate (Sprankle et al. 1975*a*). Another study by Sprankle et al. (1975*b*) proposed a few alternate methods of glyphosate binding in the soil, one of which is through the formation of a complex between the carbonyl and phosphonic acid moieties of the glyphosate molecule, which makes the phosphonic acid moiety an important chelating agent for the inactivation of the glyphosate in soil. If the phosphonic acid group does not act as a complexing agent, glyphosate may bind to the soil in a similar process as inorganic phosphorous, with strong sorption to clays saturated with Fe^{3+} and Al^{3+}; as well, glyphosate may be considered an organophosphate herbicide, which indicates that it may be bound to the soil in a manner similar to natural organophosphate compounds (Sprankle et al. 1975*b*).

There has been competition observed between glyphosate and phosphorous in the soil for binding sites (Sprankle et al. 1975*b*; de Jonge and de Jonge 1999; de Jonge et al. 2001). In Sprankle et al. (1975*b*), the amount of phosphate in the soil is the most important factor in determining the amount of glyphosate sorbed; as the amount of phosphate in the soil increased, the amount of glyphosate sorbed decreased. Initial glyphosate binding to soils could be reversed by adding phosphate ions to the soil which compete for the binding sites (Sprankle et al. 1975*a*), resulting in increased glyphosate mobility (Sprankle et al. 1975*b*). Adding phosphoric acid to soil prior to extracting previously applied-glyphosate increased the amount of glyphosate extracted (Roy and Konar 1989), adding further evidence that glyphosate competes for sorption sites with phosphorus.

Humic substances are capable of sorbing high amounts of glyphosate due to their high molecular size and stereochemical flexibility, which results in a high number of hydrogen bonding sites (Piccolo et al. 1996). Soil texture and mineralogy also play important roles in glyphosate sorption. More glyphosate sorption takes place in clay loam soils than in sandy loams (Sprankle et al. 1975*b*; Glass 1987). Glass (1987) found that glyphosate sorption to clay increased from kaolinite < illite < montmorillonite, while Sprankle et al. (1975*b*) found that glyphosate sorption increased from bentonite < illite < kaolinite. The types of cations, as well as the degree of saturation, affect glyphosate sorption onto clays, as cations may form complexes with glyphosate in soil solution (Glass 1987). Glyphosate has been shown to be poorly sorbed in sodium-, calcium- and magnesium-saturated soils compared to aluminium- and iron-saturated soils, but overall sorbs strongly to soil surfaces (Sprankle et al. 1975*b*; Eberbach 1999).

There are conflicting views that soil pH affects the binding or mobility of glyphosate in the soil. Sprankle et al. (1975*b*) showed that soil pH did not affect sorption when glyphosate and phosphorus competed for binding sites. Other studies indicate that as pH increases, glyphosate becomes more negatively charged and is repulsed by negatively charged soil mineral surfaces and so less glyphosate is bound to the soil (Sprankle et al. 1975*a*; McConnel and Hossner 1985; de Jonge and de Jonge 1999). Dissolved organic matter becomes more soluble with increasing pH, possibly reducing sorption of glyphosate onto bulk soil by reducing the amount of sorptive surfaces available (de Jonge and de Jonge 1999). Glyphosate is also less strongly bound in neutral to alkaline soils at lower temperatures and may even experience increased desorption at cool or cold temperatures (Eberbach 1998).

2.5.1.3 Glyphosate Transport Despite the high solubility of glyphosate in water, glyphosate mobility in soil is generally limited, but glyphosate mobility increased as the phosphate level in soil increased (Sprankle et al. 1975*b*). Because glyphosate is strongly sorbed to soil, it did not readily leach through the soil profile and only negligible amounts were found in surface water runoff from glyphosate-applied soil (Rueppel et al. 1977).

2.5.2 Trifluralin

Trifluralin (Figure 2.2) is a nonionic, soil-applied pre-emergence herbicide used to control several grassy and broadleaf weeds (Spencer and Cliath 1974). It is a dinitroaniline herbicide which prevents polymerization of microtubules and disrupts plant cell mitosis (Vencill 2002). Trifluralin has a relatively long half-life of up to 120 days in cool, dry soils (Vencill 2002), but has also been measured as long as 8 to 15 months (Corbin et al. 1994).

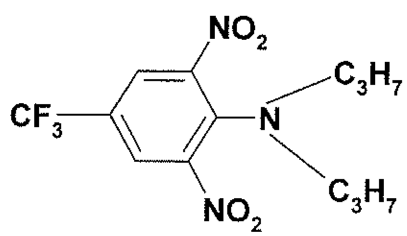

Figure 2.2. Trifluralin molecule.

2.5.2.1 Trifluralin Degradation Trifluralin dissipation as a vapour (Bardsley et al. 1967) and abiotic breakdown of trifluralin are considered to be important pathways for trifluralin loss from soil (Messersmith et al. 1971). Grover et al. (1988) found that 23.7% of the initially applied trifluralin was lost as vapour over the growing season, of which half was lost in the first week after application and incorporation.

2.5.2.1.1 Trifluralin Biodegradation Microbial breakdown of trifluralin is not a major source of degradation. Trifluralin degrades more rapidly in nonsterile soil than in autoclaved soil, but no increase in specific degrading-microorganisms was correlated with increased degradation (Probst et al. 1967). Soil microbial populations do not readily adapt to trifluralin as an energy source, and specific organisms capable of metabolizing trifluralin are inhibited as trifluralin concentration increases in the soil (Messersmith et al. 1971). A study by Doyle et al. (1978) showed that trifluralin had no inhibitory effect on overall microbial activity. Growth of soil organisms increased when exposed to trifluralin and, together with favourable soil moisture contents, increased the rate of trifluralin degradation (Solbakken et al. 1982).

Corbett et al. (1998) found that rainfall and temperature in the first 60 days after application had the most impact on trifluralin persistence, suggesting that controlled laboratory studies may show significantly different mineralization results compared to field studies. Application timing plays a major role in determining trifluralin persistence. When trifluralin was applied in the fall, up to 83% carried over to the next spring and up to 37 % carried over to the second spring, but after a spring application only 33% carried over to the next spring (Smith and Aubin 1994).

Trifluralin degrades more quickly in the first two or three months in soil than in later months (Zimdahl and Gwynn 1977). This is likely due to the initial ease of degradation of soluble and weakly-sorbed herbicide, while the remaining trifluralin is more tightly sorbed and less available for degradation (Zimdahl and Gwynn 1977). Following field application, Savage (1973) observed an initial rapid decline in trifluralin, followed by several months of relatively constant low levels of trifluralin residues. Another study measured almost 70% disappearance of trifluralin from field plots within ten weeks of application, with only 22% of trifluralin being lost over the next ten weeks (Smith 1979). A field experiment by Probst et al. (1967) measured only 10 to 15% trifluralin persisting after 6 to 12 months, while controlled laboratory studies measured slower mineralization. Tiryaki et al. (1997*a*) found that over 97% of applied trifluralin was present in field soil at one month after application, but decreased to 50% at five months. In another study by

Tiryaki et al. (1997*b*), almost 70% of applied trifluralin was present in the field after five months and was mainly found in the zone of incorporation.

Trifluralin is also degraded under anaerobic conditions (Parr and Smith 1973), and more rapid degradation occurs under iron-reducing conditions than in the presence of nitrate or oxygen (Tor et al. 2000). Anaerobic dissipation of trifluralin is more extensive than aerobic dissipation because trifluralin volatilization is inhibited by flooded conditions (Parr and Smith 1973). After 20 days, 99% of trifluralin was lost under moist anaerobic conditions, compared to 15% under moist aerobic conditions (Parr and Smith 1973).

Cropping decisions also affect trifluralin degradation. Trifluralin persistence in field soil was found to be higher in soil cropped to canola compared to fallowed soil (Gerwing and McKercher 1992). However, increased rates of trifluralin disappearance were measured in a growth chamber study when soil was planted to soybeans compared to bare soil (Probst et al. 1967).

2.5.2.2.1 Trifluralin Photodegradation Photodecomposition of trifluralin is likely a minor dissipation pathway under field conditions. Messersmith et al. (1971) found that trifluralin phytotoxicity decreased under exposure to light in laboratory conditions, but this effect was not observed under field conditions. However, another study reasoned that since trifluralin activity is greatly reduced when it is not incorporated into soil following application, UV light from sunlight probably decomposes the chemical left on the soil, in addition to trifluralin losses due to volatilization (Spencer and Cliath 1974).

2.5.2.3 Trifluralin Sorption Trifluralin is more strongly sorbed onto hydrophobic adsorbents like activated charcoal, peat moss and wheat straw than on clay minerals (Grover 1974). Clay contents in soils did not appear to greatly affect trifluralin activity or inactivation (Hollist and Foy 1971; Rahman 1977).

Organic matter content plays a major role in trifluralin inactivation (Solbakken et al. 1982; Peter and Weber 1985); as organic matter content increased, more trifluralin was sorbed and inactivated (Hollist and Foy 1971). High plant-available trifluralin residue levels have been associated with low organic matter levels (Savage 1973), but the retention of trifluralin in plant-available form has also been directly related to the amount of organic matter in the soil (Bardsley et al. 1967). Because trifluralin vaporises rapidly, the presence of organic matter with its increased sorptive capacity is instrumental in retaining trifluralin (Bardsley et al. 1967). Persistence of the chemical was also increased by at least one to two months when organic matter levels were enhanced (Rahman 1977). The strong adherence of trifluralin to organic matter particles is explained by the non-ionic nature of trifluralin which allows it to join easily with organic matter by van der Waals forces (Solbakken et al. 1982).

Soil moisture and temperature also play important roles in trifluralin sorption and degradation. Increased moisture content in the soil resulted in decreased sorption and increased vapour movement of trifluralin (Hollist and Foy 1971). Trifluralin breakdown to carbon dioxide increased with increasing temperature in moist soils (Messersmith et al. 1971). While biodegradation was somewhat slower at lower temperatures, there was no significant difference in herbicide persistence due to temperature differences (Rahman 1977).

2.5.2.4 Trifluralin Transport Trifluralin is a highly volatile herbicide. It will volatilize much more quickly when it is applied onto the surface of the soil than when it is incorporated into the soil. Vapour loss is the major reason for the lack of herbicidal activity when trifluralin is surface applied (Spencer and Cliath 1974). Soil temperature, moisture content and organic matter content all play a role in determining the amount of trifluralin lost to the atmosphere. Trifluralin experiences rapid vapour loss from surface application to moist soils, which is an indication that it should be immediately incorporated to prevent excessive losses (Spencer and Cliath 1974). Spencer and Cliath (1974) also noted that evaporating soil water moves trifluralin up to the soil surface where it volatilizes. Apparent vapour pressure was found to have a positively linear relationship to temperature (Spencer and Cliath 1974). Vapour density decreased as SOM content increased (Spencer and Cliath 1974).

Since trifluralin is strongly sorbed onto SOM, it is not easily leached under field conditions (Smith 1972). Probst et al. (1967) found no evidence of lateral or downward movement of trifluralin. In a Saskatchewan study, less than 0.002% of trifluralin applied was found in drainage water and no traces were found in irrigation runoff water because trifluralin was strongly bound in soil limiting its mobility (Cessna et al. 2001). A study looking at erosion of bare sandy loam soil during a simulated rainfall showed that 90% of trifluralin in the runoff was sorbed to eroded particles (Gouy et al. 1999), indicating that while the trifluralin is inactivated, it can be transported to other areas or water bodies.

2.5.3 2,4-Dichlorophenoxyacetic Acid

2,4-Dichlorophenoxyacetic acid (2,4-D) (Figure 2.3) is a broadleaf herbicide used worldwide. It is a phenoxy acid that was developed in the 1940's and has been extensively used in agricultural and urban settings to control broadleaf weeds. It works as an auxin mimic, causing cell elongation and uncontrolled cell division and growth (Vencill, 2002).

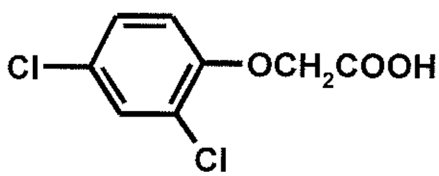

Figure 2.3. 2,4-D molecule.

2.5.3.1 2,4-D Degradation Rapid degradation of 2,4-D is commonly observed and applying 2,4-D at higher concentrations resulted in higher herbicide mineralization (Willems et al. 1996). The addition of 2,4-D had no inhibitory effect on overall soil microbial activity (Doyle et al. 1978). Degradation of 2,4-D is done by specific microbes (O'Connor et al. 1981) and Soulas (1993) found that at least two different populations of microbes are responsible for 2,4-D mineralization. Mycorrhizal and nonmycorrhizal fungi are capable of degrading 2,4-D, mainly by incorporating the carbon from the herbicide into tissue (Donnely et al. 1993). *Phanerochaete chrysosporium* was able to mineralize over 28% of the ^{14}C-carbon in ring-labeled 2,4-D (Donnelly et al. 1993).

2,4-D mineralization rates were fastest shortly following herbicide application and decreased over time to a low constant mineralization rate (Willems et al. 1996). Maximum mineralization rates occurred within the first 20 days of application, which may coincide with maximum amounts of readily-mineralizable 2,4-D metabolites in soil (Willems et al. 1996). The final constant rate is slower due to mineralization of persistent metabolites and decaying microbial biomass (Soulas 1993). Numbers of 2,4-D-degrading organisms increased greatly after the first application of 2,4-D, followed by a decline in microbial populations, which increased again after a second application of 2,4-D (Robertson and Alexander 1994). Mineralization of the first application of 2,4-D began with a lag phase and then increased rapidly, while mineralization after a second application went more quickly without a lag phase (Robertson and Alexander 1994). Not all of the chemical is available for mineralization. Ogram et al. (1985) found that 30% of 2,4-D was not mineralized, due to incorporation of C into microbial biomass or the inhibition of degrading enzymes. Sorption of the chemical removes it from soil solution, thereby protecting it from degradation because bacteria are unable to access 2,4-D held inside the soil matrix (Ogram et al. 1985). Mineralization of sorbed 2,4-D was higher in humic acid than in fresh or partially humified organic matter like wood or straw, because 2,4-D desorbs more easily from an acidic, polar sorbent like humic acid than from more aromatic or hydrophobic sorbents like lignin or straw (Benoit et al. 1999).

2,4-D mineralization was found to be poorly correlated with SOC content and microbial biomass by Willems et al. (1996), but 2,4-D mineralization rates were negatively correlated with SOC content in soil profile studies done by Veeh et al. (1996). Total

2,4-D mineralization was lower at the soil surface than at depths of 150 cm because surface soils contain larger amounts of readily available SOC, which is mineralized by soil microbes in preference to 2,4-D (Veeh et al. 1996; Willems et al. 1996). Adding glucose to soil decreased 2,4-D mineralization rates in incremental soil depths from 0 to 150 cm, but the decrease in 2,4-D mineralization was less when the herbicide and glucose were applied to surface soil samples (Willems et al. 1996).

Veeh et al. (1996) measured decreased mineralization rates with decreasing temperatures. A major drop in mineralization rates occurred below 7°C, and mineralization rates increased by up to two times as temperature increased from 10 to 20°C (Willems et al. 1996). This data has interesting implications for Manitoba producers, as Manitoba soils spend a considerable portion of the year below 20°C.

There is a positive linear correlation between 2,4-D mineralization rates and soil moisture content. Mineralization rates increased 7 to 24 times when soil moisture increased from 15 to 40% of soil moisture holding capacity, because the increased moisture improved microbial mobility, solute diffusion, and chemical availability to soil microbes (Willems et al. 1996).

N additions to pasture soils stimulated microbial biomass but suppressed 2,4-D mineralization; adding 250 and 500 kg N ha^{-1} as fertilizer-N to soil suppressed 2,4-D mineralization by 89 and 30% respectively (Entry et al. 1993). Added N suppressed the enzyme system of specific decomposers capable of degrading the recalcitrant aromatic structures of 2,4-D, although the extent of suppression was not linear over a range of N application rates (Entry et al. 1993). Donnelly et al. (1993) found that as N rates increased, more 2,4-D was incorporated into fungal tissue.

2.5.3.2 2,4-D Sorption Soil organic matter is the single most important factor affecting 2,4-D sorption in soil (Reddy and Gambrell 1987; Hermosin and Cornejo 1991). Ogram et al. (1985) reported that the sorption kinetics of 2,4-D were rapid and controlled by SOC content; as SOC content increased, sorption of 2,4-D increased. Wu et al. (2000) also found strong positive correlations between SOC content and the amount of 2,4-D sorbed by the soil. SOC content was found to be better correlated to K_{oc} (sorptive ability of soil organic matter) than to Kd (sorptive ability of bulk soil) (Rao and Davidson 1979).

Soil pH plays a major role in 2,4-D sorption (Reddy and Gambrell 1987; Wu et al. 2000) because 2,4-D is a weakly acidic organic compound and may exist either in neutral or anionic form (Wu et al. 2000). Low sorption of 2,4-D is related to the anionic form of 2,4-D at soil pH above 7 (Barriuso et al. 1997). Increasing soil pH from 6.3 to 8.3 resulted in decreased 2,4-D sorption (Hermosin and Cornejo 1991). Sannino et al. (1997) found no adsorption of 2,4-D onto clay minerals under neutral pH conditions.

At soil pH < 3, the undissociated form of 2,4-D predominates and sorption occurs through hydrophobic interactions (Wu et al. 2000). At a higher soil pH, 2,4-D exists more in an anionic form and little bonding with soil occurs because of repulsion of the anionic molecule by the negatively charged soil surfaces (Wu et al. 2000). The sorptive ability of SOM (K_{oc}) is less in soils that have a pH less than the pKa of 2,4-D (pKa < 2.7) compared to soils with a pH > 5 (Wu et al. 2000).

2.5.3.3 2,4-D Transport 2,4-D movement in soils was inversely related to 2,4-D sorption, and as little as 7.1 cm of water was needed to leach 2,4-D to 10 cm in an already-saturated soil (Grover 1977). As little as 16 mL water was needed to leach 50% of applied 2,4-D through soil columns, with increasing 2,4-D mobility as soil pH increased and organic matter contents and clay contents decreased (Grover 1977). Increasing 2,4-D application rates also increased 2,4-D mobility in soil (Rao and Davidson 1979).

Fall-applied 2,4-D was lost through surface runoff in snowmelt, and losses were greater from stubble fields compared to fallow fields (Nicholaichuk and Grover 1983). The losses of 2,4-D in snowmelt from the stubble field were similar to those experienced after a severe rainstorm (Nicholaichuk and Grover 1983).

2.6 Summary

Hog manure is a widely used soil amendment throughout Manitoba and the application of municipal biosolids to farmland is increasing. Glyphosate, trifluralin and 2,4-D are commonly used herbicides in Manitoba, as well. Therefore, these particular inputs were chosen for investigation in this study. The decision to include 2,4-D was made after the initial experiments using glyphosate and trifluralin were completed. 2,4-D mineralizes more rapidly than either glyphosate or trifluralin, thus more work could be carried out in the time available, providing more results to the many questions surrounding the issue of pesticide fate in manure and biosolid-amended soils.

CHAPTER 3

Mineralization of Glyphosate and Trifluralin in Soil

3.1 Abstract

Glyphosate and trifluralin total mineralization and mineralization rates (k) were measured using soil microcosms. Manitoba soils were sampled from sites with a history of hog manure application and nearby non-manured soils. Fresh hog manure was applied to these soils or soils were left non-amended as a control. In microcosm studies of $^{14}CO_2$ evolution from ^{14}C-labeled herbicides, glyphosate and trifluralin mineralization data fit closely to the first-order reaction mineralization equation. Glyphosate half-lives were shorter than trifluralin half-lives and total glyphosate mineralization was greater than total trifluralin mineralization, indicating that glyphosate mineralizes more completely and more quickly than trifluralin. Glyphosate half-lives ranged from 18 to 14 days and trifluralin half-lives ranged from 143 to 221 days. Total glyphosate mineralization ranged from 30 to 41% after 332 days and total trifluralin mineralization ranged from 6 to 12% after 430 days. Fresh manure and a history of manure application decreased glyphosate mineralization rates by had no significant effect on trifluralin mineralization rates. The history of manure application had an inconsistent effect on the total mineralization of glyphosate or trifluralin, with no general trend of increased or decreased total herbicide mineralization as a result of manure application history. Fresh manure application also

had no effect on total mineralization of either glyphosate or trifluralin. While fresh manure application and manure application histories may have variable effects on glyphosate and trifluralin mineralization in some soils, there does not appear to be a great impact on the overall persistence of glyphosate and trifluralin in the soils studied.

3.2 Objectives of the Study

Decreased and increased herbicide mineralization rates have been observed in soils amended with dairy and cattle manure (Doyle et al. 1978; Entry and Emmingham 1995; Moorman et al. 2001). The objective of this study was to quantify the effects of long-term liquid hog manure applications and fresh liquid hog manure applications on glyphosate and trifluralin mineralization rates in sandy clay loam and clay loam Manitoba soils.

3.3 Materials and Methods

3.3.1 Analytical methods

Glyphosate stock solutions for experiments were prepared by dissolving phosphonomethyl-labeled ^{14}C-glyphosate (specific activity 0.526 MBq mg^{-1}; Sigma-Aldrich Co., St. Louis, MO) and analytical grade glyphosate (99% purity; Chem Service, West Chester, PA) in deionized water. Trifluralin stock solutions were prepared by dissolving ring-UL-labeled ^{14}C-trifluralin (specific activity 1 855 MBq mg^{-1}; Sigma-Aldrich Co., St. Louis, MO) and commercial grade Treflan (DowAgro Sciences) in methanol. The amounts of radioactivity in herbicide solutions and samples from experiments were determined by Liquid Scintillation Counting (LSC) (LS 7500 Beckman

Instruments, Fullerton, CA) using 10 mL of Scintisafe scintillation cocktail (Fisher Scientific, Fairlawn, NJ).

Soil analyses were determined on air-dried and sieved (<2 mm) samples (Table 3.1). Soil texture was measured using the pipette method (Gee and Bauder 1986). Soil organic carbon and total nitrogen contents were determined by dry combustion of 0.12 g oven-dried soil using a Leco model CHN 600 carbon and nitrogen determinator (Nelson and Sommers 1982). Inorganic carbon was removed prior to dry combustion by digestion with 6 N HCl (Tiessen et al. 1983). Soil pH was determined using 20 mL deionized water and 10 g soil (Hendershot and Lalande 1993). Soil NO_3^--N was extracted with 0.001M $CaCl_2$ and quantified by the automated Cadmium Reduction Method 4500-NO_3^- (Clesceri et al. 1998). Phosphorus in soil was extracted using the modified Kelowna method and quantified by Stanneous Chloride Method 4500-P (Clesceri et al. 1998).

Fresh liquid hog manure was obtained from a hog operation near Fannystelle, MB and stored for one week at 2°C prior to analyses to determine manure characteristics and nutrient contents (Table 3.2). The pH and NO_3^--N content of manure were determined as described for the soil samples. The electrical conductivity (Wolf 2003), total carbon (Nelson and Sommers 1982), P (Kovar 2003), SO_4^{2-}-S (Rasnick and Nakayama 1973), total N (quantified as total kjeldahl nitrogen) (Watson et al. 2003) and NH_4^+-N (Peters et al. 2003) were also determined. Organic N was determined as the difference between total N and NH_4^+-N plus NO_3^--N.

Table 3.1. Selected chemical and historical characteristics of soils used in mineralization study (0-10 cm)

	Birtle		Neepawa		Decker	
	History	Control	History	Control	History	Control
Length of manure application history (years)	40	0	35	0	10	0
Texture	Sandy clay loam		Sandy clay loam		Clay loam	
Clay (%)	29	29	34	34	33	33
Sand (%)	54	54	49	49	36	36
Silt (%)	17	17	17	17	31	31
pH	7.7	6.9	7.8	7.4	7.5	7.9
Organic Carbon (%)	3.91	3.32	4.31	3.74	3.11	2.99
Total N (%)	0.41	0.36	0.42	0.37	0.33	0.33
NO_3^--N ($\mu g\ g^{-1}$)	51	55	7	66	68	19
P ($\mu g\ g^{-1}$)	> 60	56	> 60	40	> 60	24

Table 3.2. Selected chemical characteristics and nutrient contents of fresh liquid hog manure used in mineralization study

pH	EC ($dS\ m^{-1}$)	Moisture (%)	Total C	Total N	NH_4^+-N	Organic N	NO_3^--N	Phosphorus	Sulphate-S
			(kg 1000 L^{-1})						
7.2	12.6	99.3	4.7	1.6	1.3	0.3	< 0.1	0.21	0.10

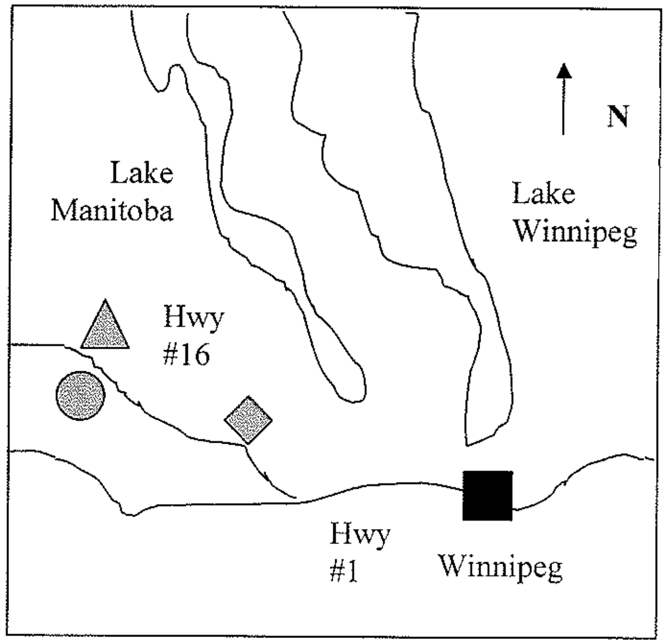

Figure 3.1. Soil sampling sites.

Neepawa

Birtle

Decker

3.3.2 Experimental Design

Surface soils (0-10 cm) of well-drained Orthic Black Chernozems in the Newdale association (Ehrlich et al. 1956; Ehrlich et al. 1957) were collected from three study sites in western Manitoba, identified here by their vicinity to the nearest town: Birtle, Decker and Neepawa (Figure. 3.1). At each study site, representative soil samples were collected from lower slope positions in two adjacent fields: one field with a long-term history of hog manure applications (H: History) and one field that had never received manure because of its proximity to the farm home (NH: No History). The H fields in Birtle and

Decker had received liquid hog manure annually for 40 and 10 years, respectively. The H field in Neepawa had received liquid hog manure every two years during the last 35 years. For all of the H fields and years of application, manure was applied by broadcasting and then incorporated into the soil by a cultivator. Manure application rates varied between sites and years and were not always recorded by the land owners. A typical manure application rate in western Manitoba is 60 000 L ha^{-1}.

Samples from each field (H or NH) were further split into two treatments: one treatment whereby soil was amended with 0.11 L fresh liquid hog manure kg^{-1} soil, and one treatment whereby no amendments were added to soil. The amount of manure applied was equal to an application rate of 90 000 L ha^{-1} (or 112 kg N ha^{-1}) under the assumption that this manure would be incorporated into a top 7.5 cm soil layer with a field bulk density of 1.05 Mg m^{-3}.

3.3.3 Herbicide mineralization

Field moist soils were sieved (< 2 mm) and added (25 g oven-dry basis) to glass beakers in triplicates. Manure was then added to appropriate treatments and thoroughly mixed into soil. Soil water content was brought to 70% field capacity for all soil samples, and samples were placed in microcosms consisting of sealed 1.5 L mason jars (Figure 3.2). Each microcosm also included one vial with 15 mL 1M NaOH to trap CO_2 and one vial with 5 mL acidified water (pH 3) to maintain a humid environment. Prior to herbicide applications, soil/manure microcosms were incubated at 20°C for 12 days to stimulate microbial activity in soil.

Either glyphosate or trifluralin was thoroughly mixed with soil/manure at a rate of 1.82 mg kg^{-1} and 1.22 mg kg^{-1}, respectively. These rates corresponded to recommended field application rates (Guide to Crop Protection 2000) when assuming a field bulk density of 1.3 Mg m^{-3} and a homogenous distribution of the herbicides into the top 7.5 cm soil layer. Microcosms were then incubated at 20°C to monitor $^{14}CO_2$ production using NaOH traps. NaOH traps were replaced every two days from 0 to 18 days, every three days from 18 to 36 days, weekly from 36 to 77 days, biweekly from 77 to 164 days, and then every three weeks until the termination of the experiment at 332 days for glyphosate and 430 days for trifluralin.

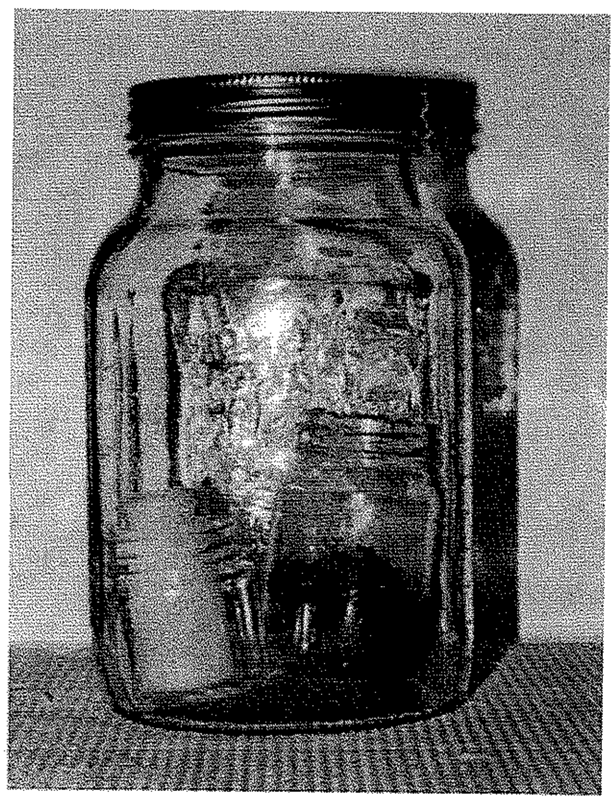

Figure 3.2. Soil microcosm.

Herbicide mineralization rate constants and total mineralization at time infinity were calculated in SigmaPlot 2000 (SPSS Inc.) under the assumption that herbicide mineralization rates were first-order:

$$Mt = M_T(1 - e^{-kt}) \qquad \text{(Equation 3.1)}$$

where Mt = herbicide mineralization at time t, expressed as a percentage of the initially applied radioactivity (%); M_T = total herbicide mineralized at time infinity, expressed as a percentage of the initially applied radioactivity (%); k = first-order mineralization rate constant (day^{-1}); and t = time (day). The time that 50% of the mineralizable portion of the herbicide was mineralized (M½-lives) was calculated by dividing log e^2 by the calculated herbicide mineralization rate constants.

The experimental design was a factorial design (manure history, fresh manure applications) and statistical comparisons were done for each herbicide (i.e. glyphosate and trifluralin) and site (i.e. Birtle, Neepawa or Decker) combination separately. Statistical analyses were performed in SAS 8.2 (SAS Institute Inc. 2001) and included two-way analysis of variance and, if applicable, the Tukey comparison test with the significance level set at $\alpha = 0.05$.

3.4 Results and Discussion

Mineralization ANOVA tables are presented in Appendix IV. For all three sites, H fields showed always greater soil organic carbon and phosphorus contents than adjacent NH fields, but total nitrogen content was not influenced by repeated manure applications onto fields (Table 3.1). It is well known that manure additions to soil may increase soil organic matter levels and promote phosphorus accumulation in fields (Schlegel 1992; Dormaar and Chang 1995; Gao and Chang 1996; Whalen and Chang 2001). For both Birtle and Neepawa, the H fields were more alkaline than the NH fields but for Decker, the H field was less alkaline than the NH field. The impact of long-term manure applications on soil pH appears to be inconsistent, with studies reporting an increase (Eghball 2002) or decrease (Chang et al. 1991) in soil pH following repeated manure additions to fields. NO_3^--N content in soils varied strongly across sites and between fields and was not influenced by previous manure applications. It is unlikely that NO_3^- accumulates in surface soils of fields that receive appropriate manure application rates because NO_3^- is readily taken up by plants and is water-soluble and mobile.

For both glyphosate (Table 3.3) and trifluralin (Table 3.4), the calculated $^{14}CO_2$ mineralization showed an excellent fit to the measured data for all soil samples, with coefficients of determination (r^2) ranging from 0.98 to 0.99. First-order mineralization rate constants varied from 0.0207 to 0.0387 day^{-1} for glyphosate with calculated M½-lives ranging from 34 to 18 days, respectively. Trifluralin mineralization was significantly slower than glyphosate with mineralization rate constants ranging from 0.0031 to 0.0049 day^{-1} corresponding to calculated M½-lives of 221 and 143 days, respectively. Total percent $^{14}CO_2$ evolved ranged from 30 to 41% for soils that received glyphosate and from 6 to 12% for soils that were mixed with trifluralin. Trifluralin mineralization rates were also very low in other studies. For example, when trifluralin was applied at 10 times the recommended field rate only 2.5 to 3.1% mineralized in 83 days of incubation (Wheeler et al. 1979). Doyle et al. (1978) found a maximum trifluralin mineralization of 1.7% at

Table 3.3. First-order mineralization rate constants (k), half-lives (½-lives), total glyphosate mineralized at time infinity (M_T), and coefficients of determination of the mineralization model (r^2) as determined by fitting the evolved ^{14}C-CO_2 in soils to the equation: $Mt = M_T (1 - e^{-kt})$, where t = time (days). Experimental values for total glyphosate mineralization (Exp-M_T) are displayed for comparison with predicted values

	k (day^{-1})	½-lives (day)	M_T (%)	r^2	Exp-M_T (%)
Birtle					
History - fresh manure	0.0227 +/- 0.00* **b****	31 +/- 0.5* **a****	43.0 +/- 0.53* **a****	0.99 +/- 0.00*	40.1 +/- 0.41* **a****
History - control	0.0234 +/- 0.00 **b**	30 +/- 0.4 **a**	40.2 +/- 1.34 **b**	0.99 +/- 0.00	37.7 +/- 1.33 **b**
No History - fresh manure	0.0247 +/- 0.00 **a**	28 +/- 1.4 **b**	32.0 +/- 0.89 **d**	0.98 +/- 0.00	29.7 +/- 0.85 **d**
No History - control	0.0256 +/- 0.00 **a**	27 +/- 0.5 **b**	34.7 +/- 0.92 **c**	0.99 +/- 0.00	32.8 +/- 0.84 **c**
Neepawa					
History - fresh manure	0.0230 +/- 0.00* **b****	30 +/- 0.3* **a****	44.3 +/-1.56* **a****	0.98 +/- 0.00*	41.4 +/- 1.41* **a****
History - control	0.0230 +/- 0.00 **b**	30 +/- 0.8 **a**	43.7 +/- 1.97 **a**	0.98 +/- 0.00	40.6 +/- 1.78 **a**
No History - fresh manure	0.0207 +/- 0.00 **b**	34 +/- 4.6 **a**	43.4 +/- 1.32 **a**	0.99 +/- 0.01	40.1 +/- 0.46 **a**
No History - control	0.0274 +/- 0.00 **a**	25 +/- 0.5 **b**	42.3 +/- 0.25 **a**	0.99 +/- 0.00	40.5+/- 0.31 **a**
Decker					
History - fresh manure	0.0277 +/- 0.00* **c****	22 +/- 0.4* **a****	37.4 +/-1.69* **b****	0.99 +/- 0.00*	35.9 +/- 1.50* **b****
History - control	0.0334 +/- 0.00 **b**	21 +/- 0.3 **b**	38.6 +/- 0.23 **b**	0.99 +/- 0.00	37.4 +/- 0.27 **ab**
No History - fresh manure	0.0340 +/- 0.00 **b**	20 +/- 0.3 **b**	40.0 +/- 0.20 **a**	0.98 +/- 0.00	38.7 +/- 0.23 **a**
No History - control	0.0387 +/- 0.01 **a**	18 +/- 0.5 **c**	38.0 +/- 0.42 **b**	0.98 +/- 0.00	37.0 +/- 0.47 **b**

*Mean of three replicates followed by standard deviation.

**Means followed by same letters are not significantly different at $P < 0.05$ (Two-way ANOVA followed by Tukey's test for comparison).

Table 3.4. First-order mineralization rate constants (k), half-lives (½-lives), total trifluralin mineralized at time infinity (M_T), and coefficients of determination of the mineralization model (r^2) as determined by fitting the evolved ^{14}C-CO_2 in soil to the equation: $Mt = M_T (1 - e^{-kt})$, where t = time (days). Experimental values for total trifluralin mineralization (Exp-M_T) are displayed for comparison with predicted values

Birtle

	k (day^{-1})	½-lives (day)	M_T (%)	r^2	Exp-M_T (%)
History - fresh manure	0.0042 +/- 0.00* **a****	165 +/- 7.9* **c****	10.0 +/-0.41* **ab****	0.99 +/- 0.00*	8.0 +/- 0.21* **b****
History - control	0.0043 +/- 0.00 **a**	161 +/- 3.8 **c**	10.6 +/- 0.25 **a**	0.99 +/- 0.00	8.4 +/- 0.26 **a**
No History - fresh manure	0.0037 +/- 0.00 **b**	189 +/- 8.0 **b**	9.4 +/- 0.17 **c**	0.99 +/- 0.00	7.0 +/- 0.06 **c**
No History - control	0.0031 +/- 0.01 **c**	221 +/- 8.3 **a**	9.6 +/- 0.22 **bc**	0.99 +/- 0.00	6.7 +/- 0.06 **d**

Neepawa

	k (day^{-1})	½-lives (day)	M_T (%)	r^2	Exp-M_T (%)
History - fresh manure	0.0046 +/- 0.00* **a****	152+/- 11.9* **b****	7.5 +/- 0.33* **d****	0.99 +/- 0.00*	6.2 +/- 0.10* **d****
History - control	0.0037 +/- 0.00 **b**	187 +/- 20.0 **a**	8.9 +/- 0.52 **c**	0.99 +/- 0.00	6.7 +/- 0.20 **c**
No History - fresh manure	0.0047 +/- 0.00 **a**	147 +/- 9.7 **b**	12.8 +/- 0.39 **b**	0.99 +/- 0.00	10.6 +/- 0.21 **b**
No History - control	0.0049 +/- 0.00 **a**	143 +/- 6.0 **b**	15.0 +/- 0.08 **a**	0.99 +/- 0.00	12.3 +/- 0.25 **a**

Decker

	k (day^{-1})	½-lives (day)	M_T (%)	r^2	Exp-M_T (%)
History - fresh manure	0.0039 +/- 0.00***ab****	176 +/- 6.8* **a****	10.0 +/- 0.84* **c****	0.99 +/- 0.00*	7.7 +/- 0.76* **c****
History - control	0.0034 +/- 0.00 **ab**	202 +/- 13.1 **a**	13.1 +/- 0.60 **b**	0.98 +/- 0.00	9.4 +/- 0.23 **b**
No History - fresh manure	0.0040 +/- 0.00 **a**	175 +/- 10.6 **a**	13.1 +/- 0.27 **b**	0.99 +/- 0.00	9.9 +/- 0.32 **ab**
No History - control	0.0033 +/- 0.00 **b**	215 +/- 44.3 **a**	15.3 +/- 0.47 **a**	0.98 +/- 0.00	10.5 +/- 0.76 **a**

*Mean of three replicates followed by standard deviation.

**Means followed by same letters are not significantly different at $P < 0.05$ (Two-way ANOVA followed by Tukey's test for comparison).

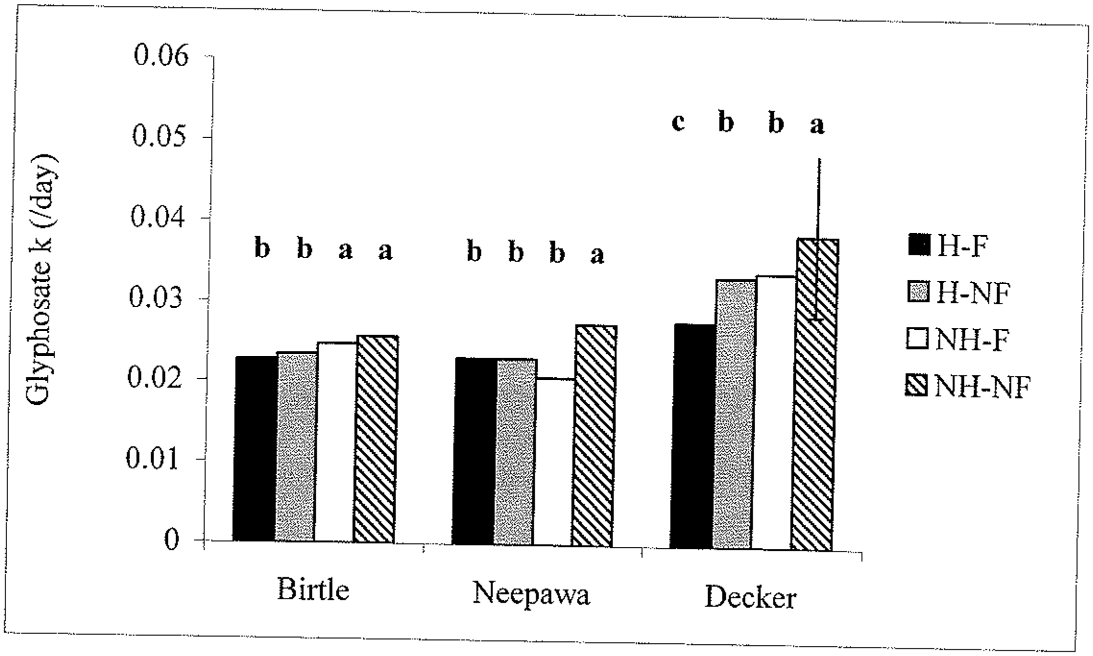

Figure 3.3. Glyphosate mineralization rate (k) (day^{-1}) in three amended soils.

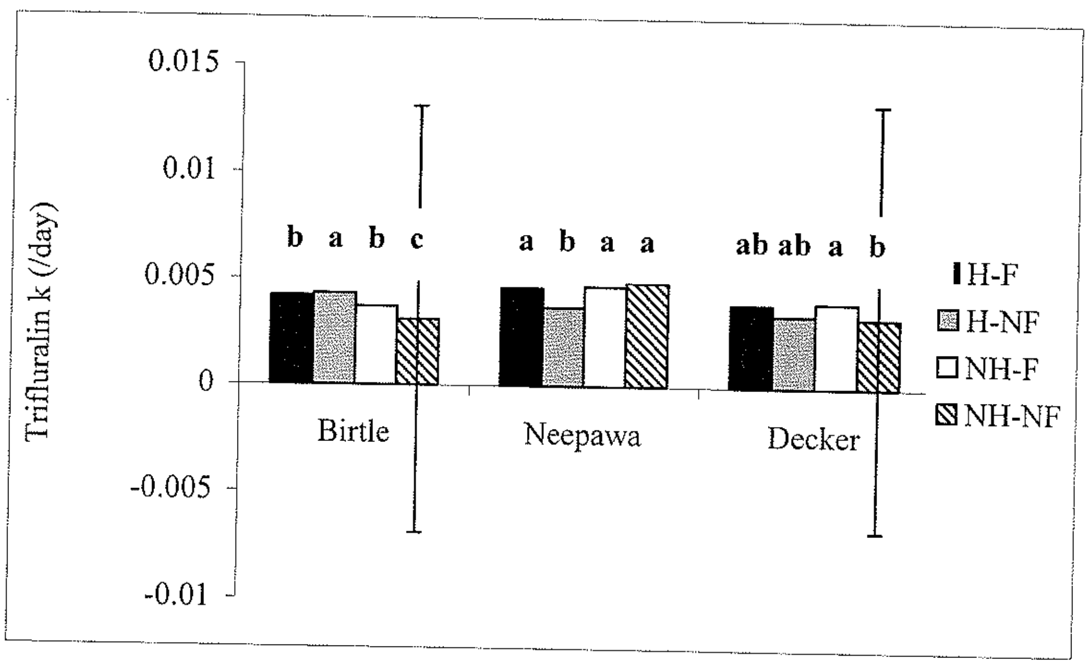

Figure 3.4. Trifluralin mineralization rate (k) (day^{-1}) in three amended soils.

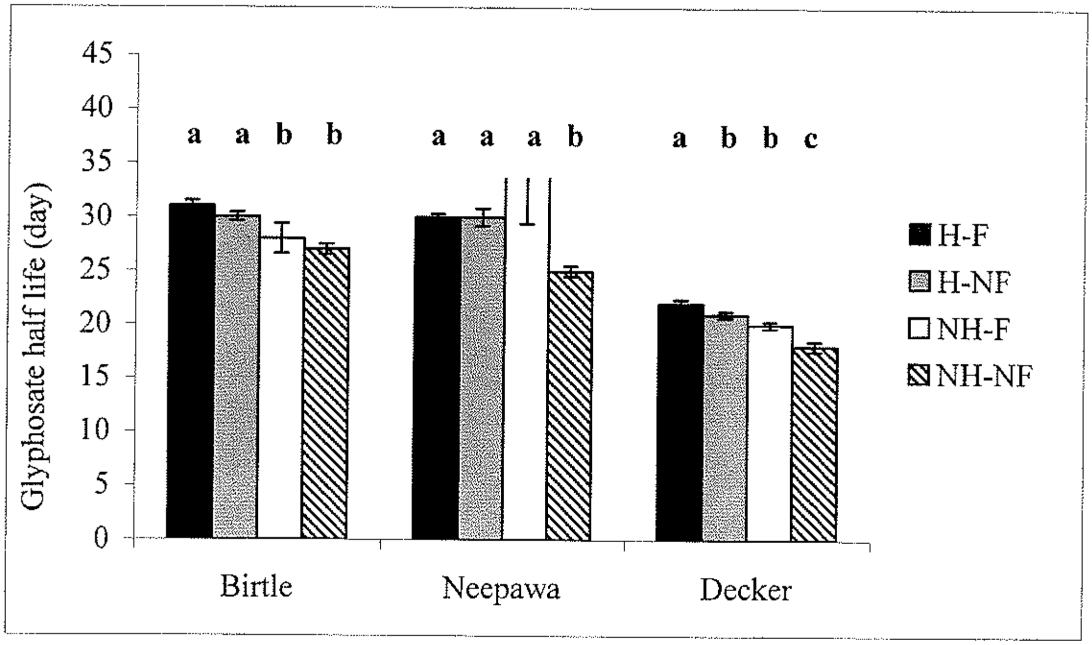

Figure 3.5. Glyphosate half life (days) in three amended soils.

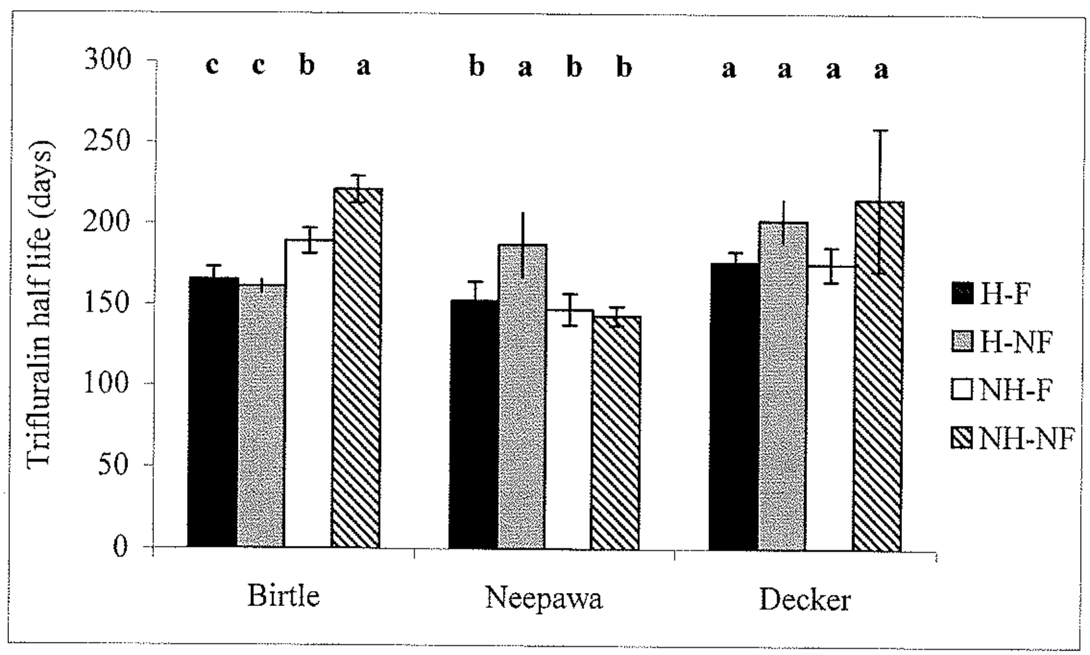

Figure 3.6. Trifluralin half life (days) in three amended soils.

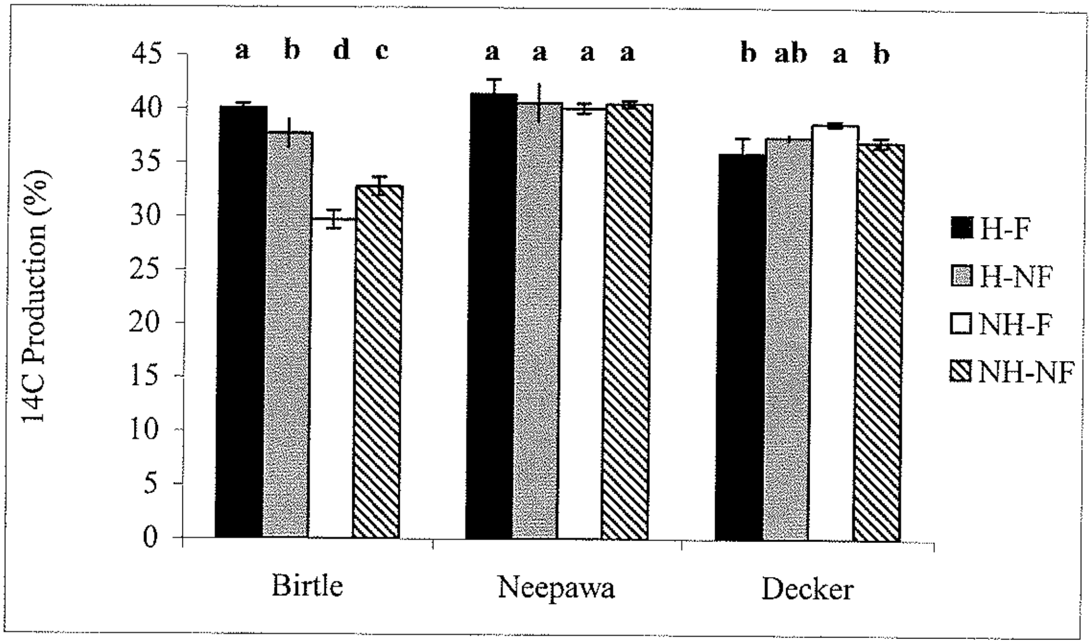

Figure 3.7. Total glyphosate mineralization (% ^{14}C production) in three amended soils.

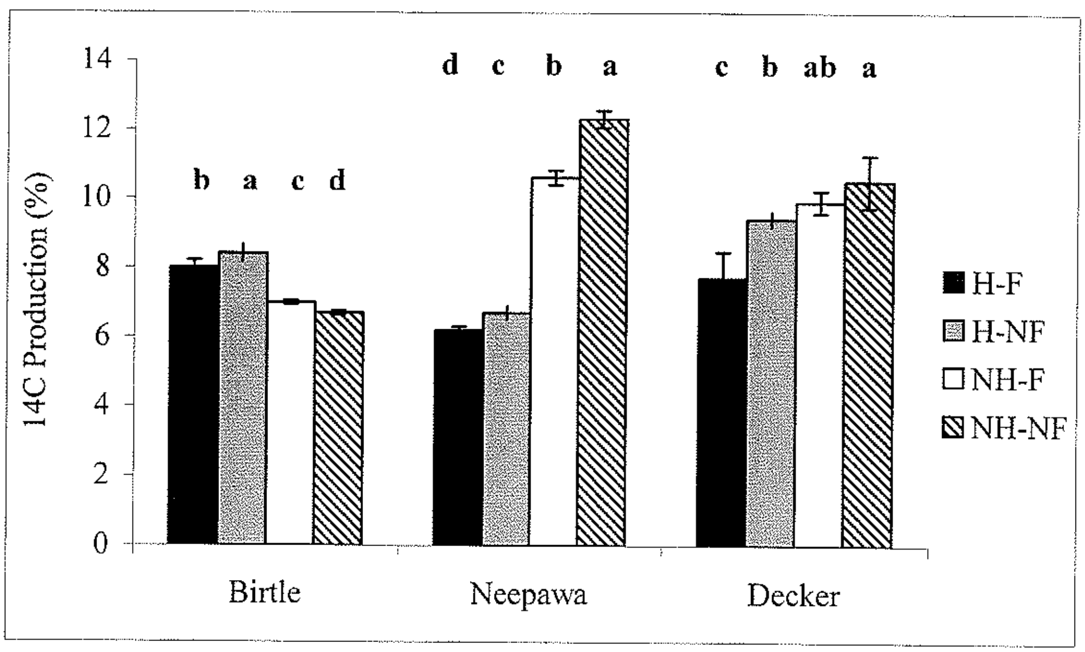

Figure 3.8. Total trifluralin mineralization (% ^{14}C production) in three amended soils.

60 days. However, 46% of the initially applied trifluralin mineralized after 6 months of incubation in another study by Zimdahl and Gwynn (1977). Total glyphosate mineralization is reported to range from 35% after 28 days (Sprankle et al. 1975*b*) to 50% after 26 days (von Wirén-Lehr et al. 1997).

For both Neepawa and Decker, glyphosate mineralization rates were significantly greater in soils that were free of manure applications relative to soils with a history of manure applications, or onto which fresh manure was applied (Table 3.3). For Birtle, glyphosate mineralization rates were significantly greater in the NH field compared to the H field, but fresh manure application to either NH or H fields had no significant impact on glyphosate mineralization rates in soils (Fig. 3.3). Although these results indicate that manure applications to fields will generally decrease glyphosate mineralization rates in soil, the difference in M½-lives between treatments was always less than 10 days.

The manure history at Birtle had a stronger effect on total glyphosate mineralization than fresh manure applications (Table 3.3). At Birtle, the total amount mineralized was approximately 10% higher in the H field than in the adjacent NH field (Fig. 3.7). In contrast, fresh manure applications to the H field significantly increased total glyphosate mineralization by only 3%, while fresh manure applications to the NH field significantly decreased total glyphosate mineralization, but by only 2%. Fresh manure applications to the NH field at Decker significantly increased total glyphosate mineralization, relative to the other treatments but, again, the actual difference in total glyphosate mineralization among treatments was less than 3% (Fig. 3.7). Total glyphosate mineralization at

Neepawa, where it was greatest of all soils tested, was not influenced by either a manure application history or fresh manure applications (Fig. 3.7).

Manure had a stronger significant effect on trifluralin mineralization rates (Table 3.4) than on glyphosate mineralization rates (Table 3.3). For Birtle, the H field had a significantly greater trifluralin mineralization rate than the adjacent NH field (Fig. 3.4), with a 24-day difference in M½-lives between amended (fresh manure) H and amended NH soils, and a 60-day difference in M½-lives between non-amended (no fresh manure) H and non-amended NH soils (Fig. 3.6). In contrast, for the Neepawa site, the trifluralin mineralization rate was significantly lower for the H field than the adjacent NH field (Fig. 3.4), with differences in M½-lives ranging from 5 to 44 days between amended H and amended NH soils and between non-amended H and non-amended NH soils, respectively (Fig. 3.6). For Decker, long-term manure applications did not influence trifluralin mineralization rates in soil.

For both Birtle and Decker, fresh manure applications to NH soils significantly increased trifluralin mineralization rates in soil, but the addition of fresh manure had no significant effect on trifluralin mineralization rates in the NH field at Neepawa (Table 3.4). In contrast, applications of fresh manure to the H field significantly increased trifluralin mineralization rates at Neepawa, but fresh manure applications to H fields had no influence on trifluralin mineralization rates at Birtle and Decker (Fig. 3.4).

The total amount of trifluralin mineralized in Birtle, Neepawa and Decker soils was significantly influenced by either a history of manure applications or fresh manure amendments, or both (Table 3.4). For Neepawa, total trifluralin mineralization in soil significantly increased from amended H soils < non-amended H soils < amended NH soils < non-amended NH soils, with a two-fold increase in total mineralization between the amended H and non-amended NH treatments (Fig. 3.8). This agrees well with the results for the Decker soils because total trifluralin mineralization was significantly smaller for the amended H treatment, and significantly larger for the non-amended NH treatment, relative to the other treatments (Fig. 3.8). For Birtle, actual differences between treatments were always less than 2% but the non-amended H soil showed significantly greater total trifluralin mineralization than the non-amended NH soil, and the amended H soil showed significantly greater total trifluralin mineralization than the amended NH soil (Fig. 3.8). Therefore, although fresh manure had no effect, a history of manure application increased trifluralin mineralization, in contrast to the other two sites.

The effects of manure applications on herbicide mineralization in soil varied among soil sites and with the type of herbicide applied (Table 3.5). For Birtle, both glyphosate and trifluralin mineralization in soil was more strongly influenced by a history of manure applications in the field than by the applications of fresh manure to soil in the laboratory. Since the interaction between the two factors (i.e. manure history and fresh manure applications) was also significant, particularly for trifluralin, the effect of fresh manure applications on herbicide mineralization in soil was dependent on whether or not manure had been previously applied in the field.

For Neepawa, total glyphosate mineralization in soil was not influenced by fresh manure applications in the laboratory or by a history of manure applications in the field (Table

Table 3.5. Factors influencing glyphosate and trifluralin mineralization in soil. The history factor compared herbicide mineralization in soils with and without a history of manure applications in the field. The fresh factor compared herbicide mineralization in soil with and without fresh manure additions in the laboratory. First-order mineralization rate constants (k) and half-lives (½-lives) were calculated assuming that mineralization was first-order. Exp-M_T refers to experimental values for total herbicide mineralization at 332 days for glyphosate and 430 days for trifluralin

	Glyphosate			Trifluralin		
	k (day^{-1})	½-lives (day)	Exp-M_T (%)	k (day^{-1})	½-lives (day)	Exp-M_T (%)
	Birtle – 40 year history of manure applications (applied annually)					
History	P<0.001	P<0.001	P<0.001	P<0.001	P<0.001	P<0.001
Fresh	-*	-	-	-	P<0.01	-
History x Fresh	-	-	P<0.001	P<0.001	P<0.01	P<0.01
	Neepawa - 35 year history of manure applications (applied every two years)					
History	-	-	-	P<0.01	P<0.05	P<0.001
Fresh	P<0.001	P<0.05	-	-	-	P<0.001
History x Fresh	P<0.001	-	-	P<0.05	P<0.05	P<0.001
	Decker – 10 year history of manure applications (applied annually)					
History	P<0.001	P<0.001	P<0.05	-	-	P<0.001
Fresh	P<0.001	P<0.001	-	P<0.05	P<0.05	P<0.01
History x Fresh	-	P<0.01	P<0.01	-	-	-

* Not significant at $P<0.05$.

3.5). In contrast, trifluralin mineralization was reduced by a history of manure applications in the field than by fresh manure applications in the laboratory. The interaction between the two factors (i.e. manure history and fresh manure applications) was also significant, particularly for trifluralin.

For Decker, glyphosate mineralization rate was equally influenced by both a history of manure applications in the field and fresh manure applications in the laboratory (Table 3.5). However, trifluralin mineralization rate was more influenced by fresh manure applications in the laboratory than a history of manure applications in the field. The interaction between the two factors (i.e. manure history and fresh manure applications) was only significant for total glyphosate mineralization and half-lives.

The increased microbial growth expected with the addition of fresh manure did not stimulate glyphosate or trifluralin mineralization to the extent expected, with only slight increases in glyphosate and trifluralin k and total mineralization compared to soils with no fresh manure added. However, dairy manure added to soil at rates of 50 and 100 T ha^{-1} increased trifluralin mineralization by 183 and 283%, respectively (Doyle et al. 1978), while Moorman et al. (2001) found that aged cattle manure had no effect on trifluralin mineralization.

3.5 Summary and Conclusions

Glyphosate and trifluralin mineralization rates fit closely to the first-order reaction model. Both the rate and extent of mineralization were much greater for glyphosate than trifluralin. Glyphosate mineralization rate was greater in soils without a history of manure application and without fresh manure added, relative to soils that had received manure. Generally, fresh or historical manure applications tended to slow the rate of glyphosate mineralization, but had no effect on the total mineralization. Rates were highest in the no history controls for all soils. Fresh manure application had little effect on the total mineralization of glyphosate. Trifluralin mineralization rates were not consistently increased as a result of a history of manure application or fresh manure application. Fresh or historical manure application decreased the total mineralization of trifluralin in the Neepawa and Decker soils, but in the Birtle soil that had the longest exposure to manure application, the history of manure application increased both the rate and the total trifluralin mineralization. The effect of fresh manure and manure application histories does not appear to have a great impact on the persistence of glyphosate and trifluralin in these soils.

CHAPTER 4

Mineralization and Sorption of Glyphosate and Trifluralin in Soils

4.1 Abstract

Fresh hog manure was applied to soil microcosms in order to determine the total mineralization, mineralization rates, half-lives and sorption of glyphosate and trifluralin in three Manitoba soils with and without a history of manure application. The effect of a history of manure application on herbicide mineralization was not consistent over all three soil types. History of manure application generally increased glyphosate mineralization rates in Birtle and Neepawa soils, but had no effect on mineralization in Decker soil. Trifluralin mineralization was greater in the Birtle soil with a history, relative to Neepawa and Decker soils with a history of manure application. Total trifluralin mineralization was greater in Neepawa and Decker soils without a manure history compared to the same soils with a history. Glyphosate had higher sorption values in non-amended soils compared to soils with a history, but trifluralin sorption was similar in Neepawa and Decker soils regardless of a history of manure application. Fresh manure application had little effect on the mineralization and sorption of either herbicide, but increased trifluralin sorption in Birtle soils.

4.2 Objectives of the Study

The objective of this study was to quantify the effect of hog manure application history and fresh hog manure applications to Manitoba soils on the sorption and mineralization of glyphosate and trifluralin in soil. Because manure is generally applied in fall or early spring, and not at the same time as pesticides, it was of particular interest to determine the effects of allowing the manure to age (four weeks) in the soil prior to adding the pesticide.

4.3 Materials and Methods

4.3.1 Analytical Methods

Glyphosate stock solutions were prepared dissolving phosphonomethyl-labeled ^{14}C glyphosate (4.5 mCi $mmol^{-1}$ specific activity; Sigma Chemical Co., St. Louis, MO) and analytical grade glyphosate (99% purity; Chem Service, West Chester, PA) in deionized water. Trifluralin stock solutions were prepared by dissolving ring-UL-labeled ^{14}C-trifluralin (specific activity 16.8 mCi $mmol^{-1}$; Sigma-Aldrich Co., St. Louis, MO) in methanol. Radioactivity of solutions and NaOH samples was determined using Liquid Scintillation Counting (LSC) (LS 7500 Beckman Instruments, Fullerton, CA) using 10 mL of Scintisafe scintillation cocktail (Fisher Scientific, Fairlawn, NJ).

4.3.2 Soil and Manure Characteristics

Soil and manure chemical and nutrient analyses were carried out as described in sections 3.4 and 3.5, with results presented in Tables 3.1 and 4.1. Fresh hog manure was collected from a manure storage pit for a sow barn at the University of Manitoba Glenlea Research

Farm and stored at 4°C for one week until analyses could be performed. Manure was used in experiments at 28 days after manure collection.

The same soils and treatments were used in this procedure as in sections 3.4.1 and 3.4.2. Samples were collected from agricultural fields near Birtle, Neepawa and Decker, Manitoba (Figure 3.1). Each site was sampled from an area that had received a history of hog manure application, as well as an area with no previous hog manure amendment. Soil samples were kept at -20°C until use.

Samples from each field (H: history or NH: No History) were further split into two treatments: one treatment whereby soil was amended with 0.06 L fresh liquid hog manure kg^{-1} soil, and one treatment whereby no amendments were added to soil. The amount of fresh manure applied was equal to an application rate of 47 000 L ha^{-1} (or 112 kg N ha^{-1}) under the assumption that this manure would be incorporated into a top 7.5 cm soil layer with a field bulk density of 1.05 Mg m^{-3}.

Table 4.1. Selected chemical characteristics and nutrient contents of fresh hog manure used in mineralization study

EC ($dS\ m^{-1}$)	Total N	NH_4^+-N	Organic N	NO_3^--N	Phosphorus	Sulphate-S
				(kg 1000 L^{-1})		
19.1	3.0	2.4	0.6	<0.1	0.15	0.14

4.3.3 Herbicide Mineralization

Field moist soils were sieved (< 2 mm) and added (30 g oven-dry basis) to glass beakers in four replicates. Manure was then added to appropriate treatments and thoroughly mixed into soil. Soil water content was brought to 70% field capacity for all soil samples and samples were placed in microcosms consisting of sealed 0.5 L mason jars. Each microcosm also included one vial with 5 mL 0.5M NaOH to trap CO_2 and one vial with 5 mL acidified water (pH 3) to maintain a humid environment. Prior to herbicide applications, microcosms were incubated at 20°C for 28 days to stimulate microbial activity in soil.

Either glyphosate or trifluralin was thoroughly mixed with soil/manure at a rate of 0.68 mg kg^{-1} and 0.91 mg active ingredient kg^{-1} soil, respectively. These rates corresponded to recommended field application rates (Guide to Crop Protection 2000) when assuming a field bulk density of 1.3 Mg m^{-3} and a homogenous distribution of the herbicides into the top 7.5 cm soil layer. Microcosms were then incubated at 20°C to monitor $^{14}CO_2$ production using NaOH traps. NaOH traps in glyphosate microcosms were changed three times a week for the first 44 days, twice a week for the next 38 days, and once a week for the last 63 days for a total of 145 days after glyphosate application. NaOH traps in trifluralin microcosms were changed three times a week for the first 7 days, once a week for the next 180 days, once every two weeks in the next 28 days, once a month for the next 121 days, and twice in the last 3 months, for a total of 441 days after trifluralin application.

Herbicide mineralization rate constants and mineralization statistics were calculated as in Chapter 3, under the assumption that herbicide mineralization rates were first-order:

$$Mt = M_T (1 - e^{-kt}) \qquad \text{(Equation 4.1)}$$

where Mt = herbicide mineralization at time t, expressed as a percentage of the initially applied radioactivity (%); M_T = total herbicide mineralized at time infinity, expressed as a percentage of the initially applied radioactivity (%); k = first-order mineralization rate constant (day^{-1}); and t = time (day). The time that 50% of the mineralizable portion of the herbicide was mineralized (M½-lives) was calculated by dividing log e^2 by the calculated herbicide mineralization rate constants.

The experimental design was a factorial design: manure history x fresh manure applications. Statistical comparisons were done for each herbicide (i.e. glyphosate and trifluralin) and site (i.e. Birtle, Neepawa or Decker) combination separately. Statistical analyses were performed in SAS 8.2 (SAS Institute Inc. 2001) and included two-way analysis of variance and, if applicable, the Tukey comparison test with the significance level set at $\alpha = 0.05$.

4.3.4 Herbicide Sorption

Batch-equilibrium methods were used for each herbicide and each soil/manure treatment to determine the soil-water partitioning coefficient, Kd ($mL\ g^{-1}$):

$$Kd = C_s / C_e \qquad \text{(Equation 4.2)}$$

where C_s = the amount of herbicide sorbed to soil at equilibrium (μg g^{-1}), C_e = the amount of herbicide in solution at equilibrium (μg mL^{-1}). Larger Kd values indicate greater sorption of the herbicide compared to smaller Kd values.

Initial glyphosate and trifluralin concentrations were 1 μg mL^{-1} active ingredient of herbicide and containing 12.9 Bq mL^{-1} of phosphonomethyl-labeled ^{14}C-glyphosate and 15.2 Bq mL^{-1} of ring-UL-labeled ^{14}C-trifluralin. For each herbicide, 10 mL of solution in 0.01M $CaCl_2$ was added to 5 g of air-dried soil (duplicates) in Teflon centrifuge tubes. The solution and soil were rotated in the dark for 24 hours to reach equilibrium and then centrifuged for 10 minutes at 10 000 RPM. Two 1 mL subsamples (duplicates) of the supernatant were removed, added to 10 mL of Fisher Scinti-Safe 30% Advanced Safety LSC-Cocktail (Fairlawn, NJ) and analyzed for ^{14}C by Liquid Scintillation Counting (LSC) (LS 7500 Beckman Instruments, Fullerton, CA) to determine C_e. C_s was calculated as the difference between C_e and the initial amount of herbicide added to the soil solution.

4.4 Results and Discussion

Mineralization and sorption ANOVA tables are presented in Appendix IV.

4.4.1 Herbicide Mineralization

Overall, glyphosate mineralized more quickly and more completely than trifluralin. Glyphosate mineralization rate constants fit well to the herbicide mineralization model (Eq. 4.1), with r^2 values of 0.98 and greater (Table 4.2). Values for k ranged from 0.033 to 0.067 day^{-1} and half-lives ranged from 21 to 10 days, respectively (Table 4.2). Total glyphosate mineralization at 145 days ranged from 46.1 to 60.7% (Table 4.2). Trifluralin mineralization rate constants also fit well to the herbicide mineralization model (Eq. 4.1), with r^2 values of 0.98 to 0.99 (Table 4.3). The k values ranged from 0.003 to 0.005 day^{-1} and half-lives ranged from 257 to 141 days (Table 4.3), which were much lower values than in the glyphosate treatments. Total trifluralin mineralization ranged from 5.3 to 13.1% at 441 days (Table 4.3), substantially lower than the total mineralization values for glyphosate treatments.

For Birtle, the greatest glyphosate mineralization rate occurred in the non-amended (no fresh manure) H soil ($k = 0.39$ day^{-1}) (Fig. 4.1). The Neepawa soil had larger k values than Birtle for all corresponding treatments except amended (fresh manure) NH (Fig. 4.1). The greatest k value in Decker soil was measured in non-amended NH (Fig. 4.1). Within each soil location, however, the range in glyphosate mineralization half-lives was only 3 to 7 days, while the differences in glyphosate mineralization half-lives among soil sites were as much as 11 days (Table 4.2 and Fig. 4.3). This suggested that manure application had less of an effect on k and half-lives than soil location. This effect by sampling locations could be attributed to different microbial populations, different agronomic practices such as tillage regimes, or different climatic factors.

Birtle soils all had similar trifluralin mineralization rates, and trifluralin half-lives were also statistically similar across history and amendment treatments, with a range of 190 to 227 days (Table 4.3). The non-amended NH treatment had the highest trifluralin mineralization rates in Neepawa soil (Fig. 4.2). Both NH treatments in Decker soil had higher trifluralin mineralization rates than the H treatments (Fig. 4.2). Neepawa and

Table 4.2. First-order mineralization rate constants (k), half-lives (½-lives), total glyphosate mineralized at time infinity (M_T), and coefficients of determination of the mineralization model (r^2) as determined by fitting the evolved $^{14}C\text{-}CO_2$ in the soils to the equation: $Mt = M_T\,(1 - e^{-kt})$, where t = time (days). Experimental values for total glyphosate mineralization (Exp-M_T) are displayed for comparison with predicted values

	k (day^{-1})	½-lives (day)	M_T (%)	r^2	Exp-M_T (%)
			Birtle		
History - fresh manure	0.033 +/- 0.00*b**	21 +/- 1.5 * a**	49.6 +/- 3.97*b**	0.99 +/- 0.00*	50.1 +/- 3.00 * b**
History - control	0.039 +/- 0.00 a	18 +/- 0.7 b	53.6 +/- 0.80 a	0.99 +/- 0.00	54.3 +/- 0.78 a
No History - fresh manure	0.035 +/- 0.00 b	20 +/- 0.8 a	44.2 +/- 1.87 c	0.98 +/- 0.01	46.1 +/- 1.94 c
No History - control	0.034 +/- 0.00 b	21 +/- 2.2 a	47.3 +/- 1.91 bc	0.98 +/- 0.01	49.4 +/- 2.18 b
			Neepawa		
History - fresh manure	0.039 +/- 0.01*ab**	18 +/- 3.2 *ab**	59.1 +/- 2.22*a**	0.99 +/- 0.00 *	59.8 +/- 2.12 * a**
History - control	0.042 +/- 0.00 a	17 +/- 1.0 b	60.1 +/- 0.77 a	0.99 +/- 0.00	60.7 +/- 0.47 a
No History - fresh manure	0.033 +/- 0.01 b	21 +/- 3.6 a	51.3 +/- 5.12 b	0.99 +/- 0.02	52.6 +/- 4.39 b
No History - control	0.037 +/- 0.00 ab	19 +/- 2.0 ab	54.7 +/- 1.75 b	0.99 +/- 0.00	55.7+/- 1.16 b
			Decker		
History - fresh manure	0.040 +/- 0.00*c**	17 +/- 1.5 * a**	55.3 +/- 2.25*ab**	0.99 +/- 0.01 *	56.3 +/- 2.64 * ab**
History - control	0.050 +/- 0.00 b	14 +/- 0.4 b	55.9 +/- 2.29 ab	0.99 +/- 0.00	57.0 +/- 2.75 ab
No History - fresh manure	0.050 +/- 0.00 b	14 +/- 0.2 b	55.0 +/- 1.08 b	0.99 +/- 0.00	56.2 +/- 0.63 b
No History - control	0.067 +/- 0.01 a	10 +/- 0.1 c	57.9 +/- 0.86 a	0.99 +/- 0.00	59.3 +/- 0.96 a

*Mean of four replicates followed by standard deviation.

**Means followed by same letters are not significantly different at $P < 0.05$.

Table 4.3. First-order mineralization rate constants (k), half-lives (½-lives), total trifluralin mineralized at time infinity (M_T), and coefficients of determination of the mineralization model (r^2) as determined by fitting the evolved $^{14}C\text{-}CO_2$ in the soils to the equation: $Mt = M_T (1 - e^{-kt})$, where t = time (days). Experimental values for total trifluralin mineralization (Exp-M_T) are displayed for comparison with predicted values

	Birtle				
	k (day^{-1})	½-lives (day)	M_T (%)	r^2	Exp-M_T (%)
History - fresh manure	0.003+/- 0.00 * **a****	218 +/- 20.1 * **a****	10.1 +/- 0.82 * **a****	0.99 +/- 0.00*	7.3 +/- 0.52 * **a****
History - control	0.004 +/- 0.00 **a**	190 +/- 18.4 **a**	10.1 +/- 0.99 **a**	0.99 +/- 0.00	7.8 +/- 0.97 **a**
No History - fresh manure	0.003 +/- 0.00 **a**	227 +/- 43.3 **a**	7.8 +/- 2.36 **a**	0.99 +/- 0.01	5.9 +/- 1.26 **b**
No History - control	0.003 +/- 0.00 **a**	222 +/- 20.3 **a**	9.6 +/- 1.48 **a**	0.99 +/- 0.00	7.0 +/- 0.75 **ab**
	Neepawa				
	k (day^{-1})	½-lives (day)	M_T (%)	r^2	Exp-M_T (%)
History - fresh manure	0.003 +/- 0.00 * **b****	233+/- 45.9 * **a****	11.9 +/- 1.49 * **ab****	0.99 +/- 0.00*	8.8 +/- 0.78 * **b****
History - control	0.003 +/- 0.00 **b**	257 +/- 56.5 **a**	11.4 +/- 1.46 **b**	0.99 +/- 0.00	7.9 +/- 0.37 **b**
No History - fresh manure	0.003 +/- 0.00 **b**	200 +/- 5.4 **ab**	11.5 +/- 0.47 **b**	0.99 +/- 0.00	8.6 +/- 0.40 **b**
No History - control	0.004 +/- 0.00 **a**	159 +/- 18.2 **b**	13.5 +/- 0.24 **a**	0.98 +/- 0.00	10.8 +/- 0.56 **a**
	Decker				
	k (day^{-1})	½-lives (day)	M_T (%)	r^2	Exp-M_T (%)
History - fresh manure	0.003 +/ -0.00 * **b****	213 +/- 46.0 ***a****	6.9 +/- 1.92 * **c****	0.99 +/- 0.00*	5.3 +/- 1.20 * **c****
History - control	0.004 +/- 0.00 **a**	178 +/- 30.9 **a**	10.6 +/- 0.47 **b**	0.99 +/- 0.00	8.5 +/- 0.50 **b**
No History - fresh manure	0.005 +/- 0.00 **a**	141 +/- 11.6 **ab**	10.6 +/- 2.51 **b**	0.99 +/- 0.00	9.2 +/- 2.19 **ab**
No History - control	0.003 +/- 0.00 **b**	128 +/- 10.3 **b**	15.0 +/- 0.47 **a**	0.99 +/- 0.00	13.1 +/- 0.33 **a**

*Mean of four replicates followed by standard deviation.

**Means followed by same letters are not significantly different at $P < 0.05$.

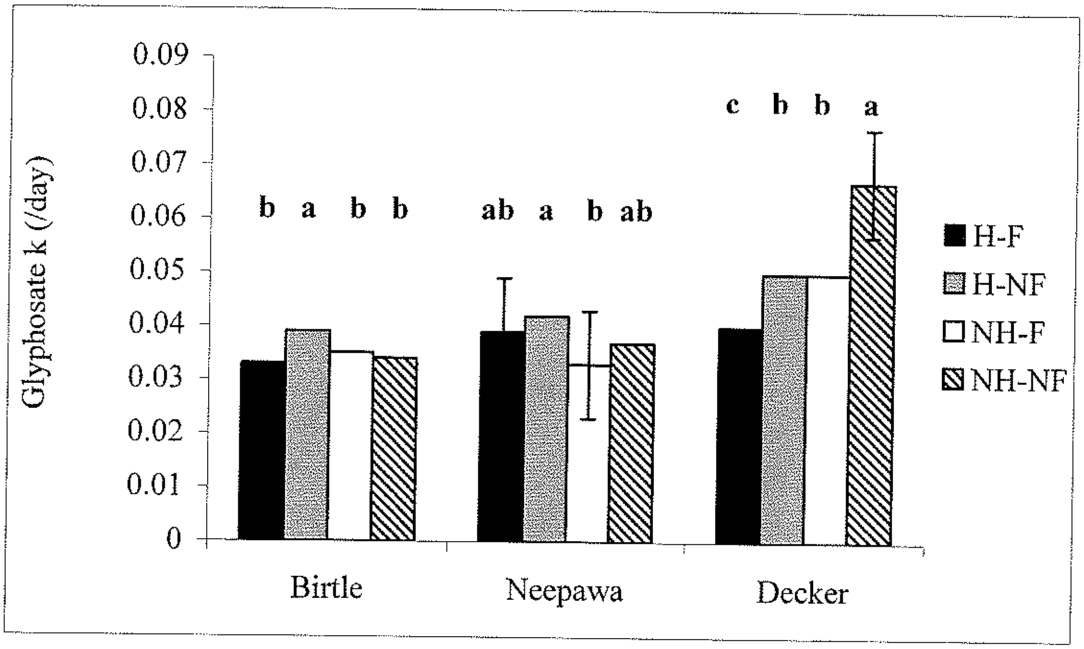

Figure 4.1. Glyphosate mineralization rate (k) (day^{-1}) in three amended soils.

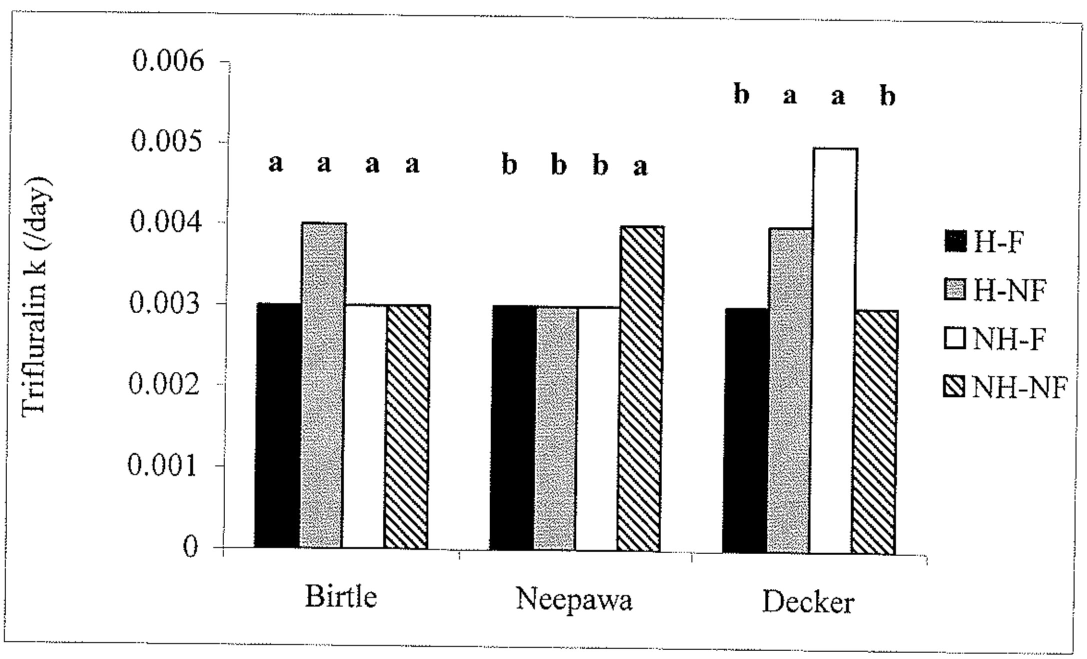

Figure 4.2. Trifluralin mineralization rate (k) (day^{-1}) in three amended soils.

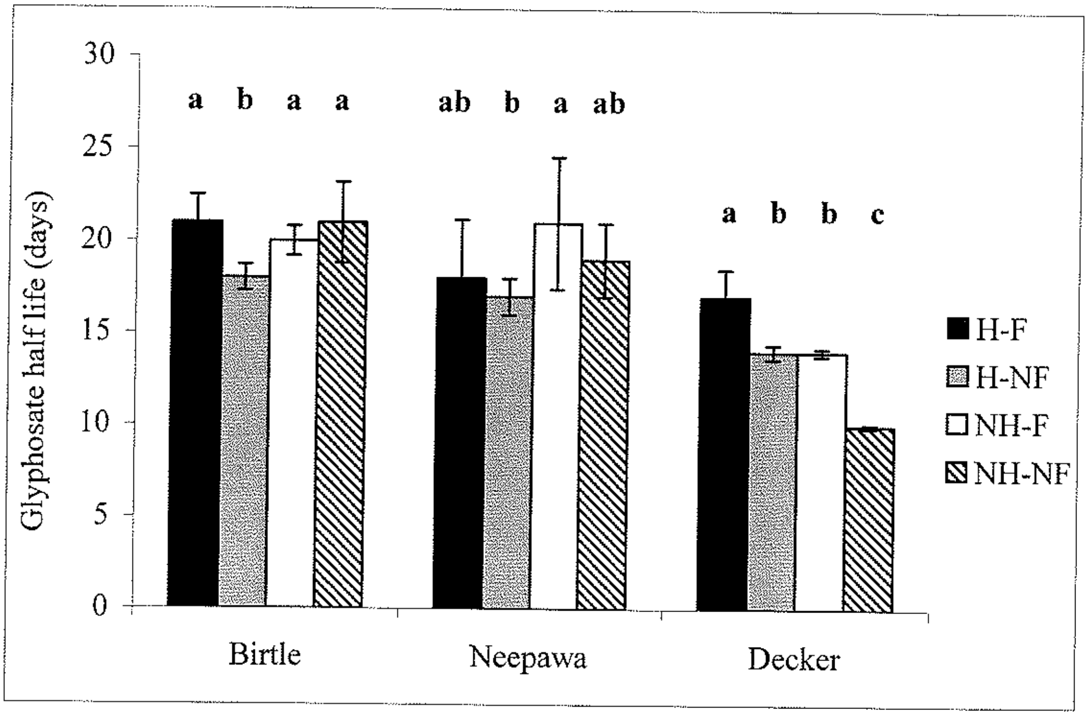

Figure 4.3. Glyphosate half life (days) in three amended soils.

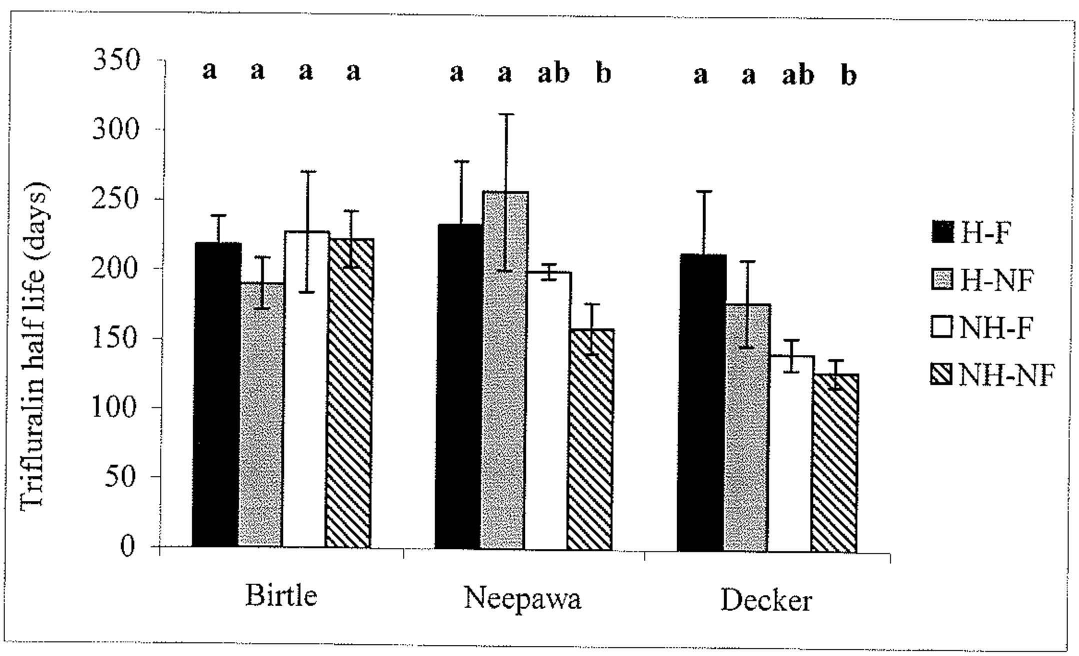

Figure 4.4. Trifluralin half life (days) in three amended soils.

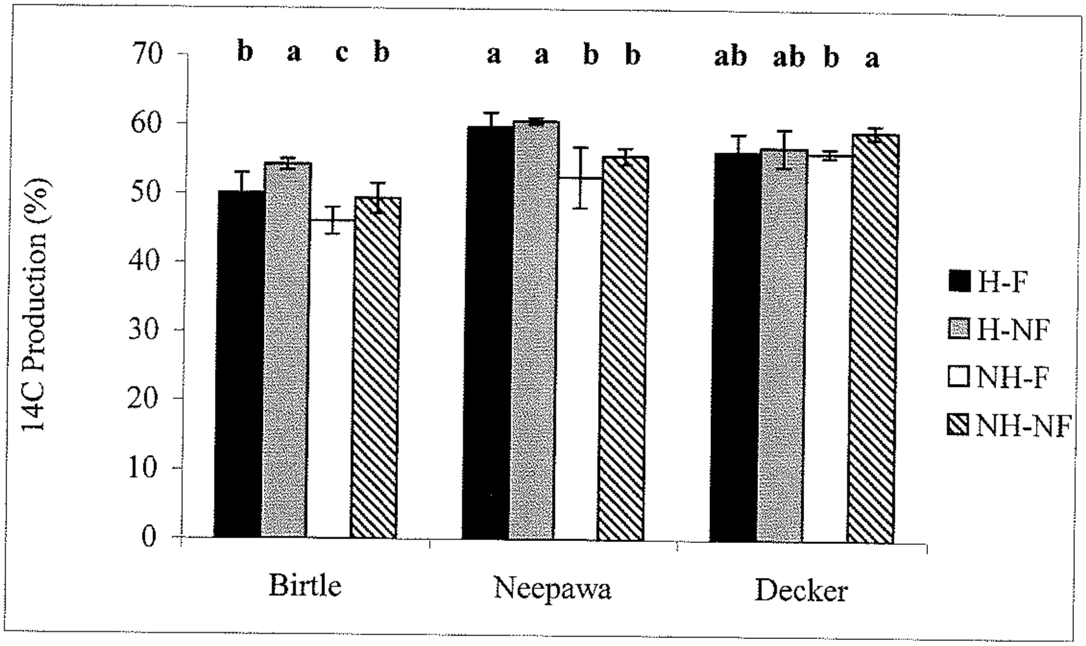

Figure 4.5. Total glyphosate mineralization (% ^{14}C production) in three amended soils.

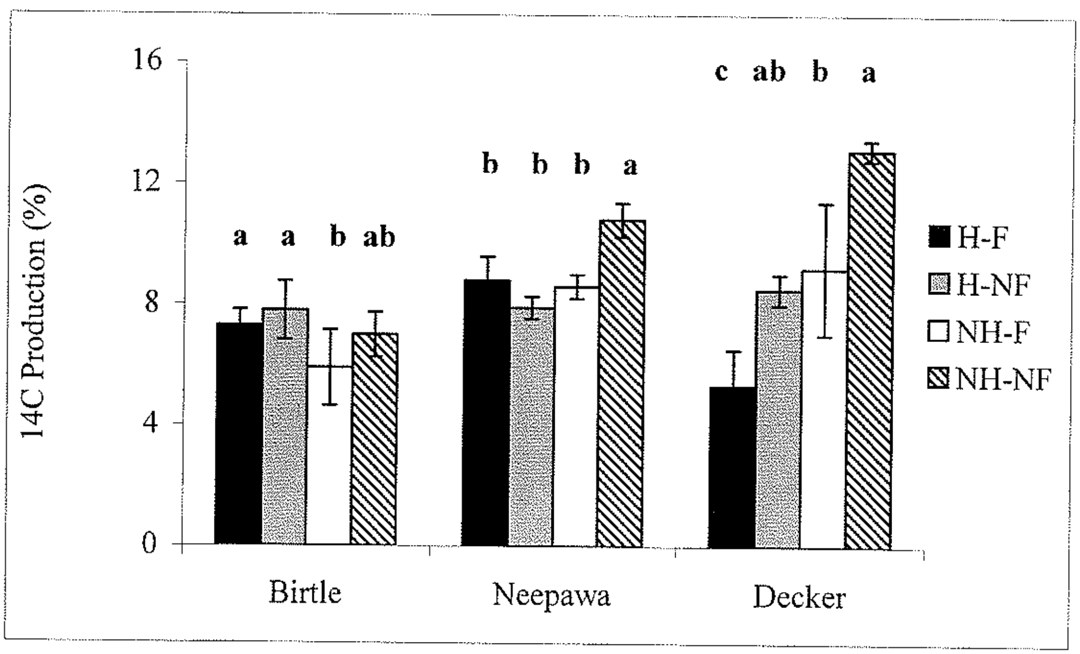

Figure 4.6. Total trifluralin mineralization (% ^{14}C production) in three amended soils.

Decker H soils had longer half-lives than NH soils (Fig. 4.4). The history of manure application in Neepawa and Decker soils contributed to an increase in trifluralin persistence, however, the longer history of manure application in Birtle soils did not result in greater trifluralin persistence.

Birtle soils had the greatest total glyphosate mineralization in the non-amended H treatment, while the lowest mineralization was measured in amended NH soil (Fig. 4.5). Total mineralization was generally greater in Neepawa soils with a manure history than without, but fresh manure application did not affect total mineralization (Fig. 4.5). Decker soils did not exhibit a strong difference in total mineralization between any of the treatments, with a range in total mineralization of only 3% (Fig. 4.5). Differences in total mineralization between treatments for Birtle and Neepawa soils were only slightly greater, 7 and 8%, respectively. This slight difference, while statistically significant, will not be noticeable under field conditions.

Birtle had greater total amounts of trifluralin mineralization in H soils than NH soils, regardless of fresh manure application (Fig. 4.6). Neepawa non-amended NH soils had the greatest total mineralization over all other treatments (Fig. 4.6). Decker NH soils had greater trifluralin mineralization compared to Decker H soils, regardless of fresh manure application (Fig. 4.6). Not only does a history of manure application in Neepawa and Decker soils increase trifluralin half life, it also decreases total mineralization, suggesting that a shorter or intermittent history of hog manure amendment increases trifluralin persistence.

Table 4.4. Factors influencing glyphosate and trifluralin mineralization in soil. The history factor compared herbicide mineralization in soils with and without a history of manure applications in the field. The fresh factor compared herbicide mineralization in soil with and without fresh manure additions in the laboratory. First-order mineralization rate constants (k) and half-lives (½-lives) were calculated assuming that mineralization was first-order. Exp-M_T refers to experimental values for total herbicide mineralization at 145 days for glyphosate and 441 days for trifluralin

	Glyphosate			Trifluralin		
	k (day^{-1})	½-lives (day)	Exp-M_T (%)	k (day^{-1})	½-lives (day)	Exp-M_T (%)
	Birtle – 40 year history of manure applications (applied annually)					
History	-*	-	P<0.01	-	-	P<0.05
Fresh	-	-	P<0.01	-	-	-
History x Fresh	P<0.05	P<0.05	-	-	-	-
	Neepawa - 35 year history of manure applications (applied every two years)					
History	P<0.05	-	P<0.001	P<0.01	P<0.01	P<0.001
Fresh	-	-	-	-	-	-
History x Fresh	-	-	-	P<0.05	-	P<0.001
	Decker – 10 year history of manure applications (applied annually)					
History	P<0.001	P<0.001	-	P<0.001	P<0.01	P<0.001
Fresh	P<0.001	P<0.001	-	-	-	P<0.01
History x Fresh	P<0.01	-	-	-	-	-

* not significant at *P*<0.05.

Effects of fresh manure and history of manure application on herbicide mineralization varied among different soil types and different herbicides applied (Table 4.4). For Birtle soils, total glyphosate mineralization was affected by history and fresh manure, but no significant interactions occurred, and for glyphosate k values and half-lives, only significant interactions were demonstrated. Trifluralin mineralization in Birtle soil was virtually unaffected by history or fresh manure except for total mineralization, which was significantly affected by the history factor.

The history effect in Neepawa soil stimulated glyphosate k values and total mineralization. Trifluralin was significantly affected by history for k values, half-lives and total mineralization, with interactions occurring for k values and total mineralization.

Glyphosate mineralization rates and half-lives in Decker soil were affected by both history and fresh manure factors, which also caused an interaction in the case of k values. Total glyphosate mineralization was not affected by either factor in this soil. Trifluralin mineralization was predominantly affected by history for k values, half-lives and total mineralization.

Comparison between Tables 3.5 and 4.4 indicates a substantial difference in the amount of significant effects. It is possible that delaying the application of the herbicide from 12 to 28 days after soil/manure incubation caused a dilution of previously significant history and fresh manure effects on herbicide mineralization rates, half-lives and total mineralization values.

Because glyphosate is readily degraded by soil microbes, it was expected that the addition of fresh manure, a source of microbes and a microbial stimulator, would increase the mineralization of glyphosate. However, fresh manure had no effect on total glyphosate mineralization in Decker and Neepawa soils, and decreased glyphosate mineralization in Birtle soils. It is possible that fresh manure was supplying a food source to microbes, but mostly increased populations of species incapable of degrading glyphosate. It is also possible that manure was not supplying a substantial food source (see 5.4.4) or that the manure was inhibiting microbial activity.

Understanding how trifluralin persistence in soil may be affected by manure application is important to reduce risks of crop injury due to trifluralin-residue in soil. The recommended application rate of 0.91 mg a.i. ha^{-1} (Guide to Crop Protection 2000) is less than the rate that caused damage in a study by Darwent et al. (1990) where fall-applied trifluralin rates above 1.1 to 1.4 kg a.i. ha^{-1} reduced barley yields. Trifluralin was found to be less damaging to corn at application rates of 0.125 to 0.4 kg a.i. ha^{-1} than at 0.8 to 1.25 kg a.i. ha^{-1} (Landi et al. 1999). The overall differences in trifluralin mineralization as a result of fresh manure application or a history of manure application were not large enough to suggest that there will be additional risk to subsequent crops.

4.4.2 Herbicide Sorption

Kd values for trifluralin were much greater than for glyphosate, indicating that more trifluralin sorbs to soil than glyphosate. Kd values for glyphosate were significantly affected by the history factor in Birtle, Decker and Neepawa soils. There were no significant effects of history or fresh manure applications on trifluralin Kd values.

Table 4.5. Soil-water portioning coefficients, Kd (mL g^{-1}), for glyphosate and trifluralin in each soil/manure treatment, determined by batch equilibrium fitting the Kd = C_s / C_e, where C_s = the amount of herbicide sorbed to soil at equilibrium (µg g^{-1}), C_e = the amount of herbicide in solution at equilibrium (µg mL^{-1})

	Birtle	Neepawa	Decker
		Glyphosate	
History - fresh manure	17.7 +/- 0.67 * **b****	19.0 +/- 0.75 * **b****	15.0 +/- 0.64 * **b****
History - control	15.9 +/- 0.98 **b**	18.3 +/- 0.28 **b**	15.1 +/- 0.99 **b**
No History - fresh manure	29.7 +/- 1.91 **a**	33.3 +/- 3.35 **a**	18.2 +/- 1.31 **a**
No History - control	29.7 +/- 1.73 **a**	22.6 +/- 9.43 **b**	19.5 +/- 2.01 **a**
		Trifluralin	
History - fresh manure	268.7 +/- 32.48 * **a**†**	216.4 +/- 47.36 * **a****	181.7 +/- 38.65 * **a****
History - control	201.1 +/- 6.56 **b**†	200.9 +/- 78.94 **a**	209.5 +/- 38.52 **a**
No History - fresh manure	237.1 +/- 19.16 **ab**	187.8 +/- 44.49 **a**	195.3 +/- 24.58 **a**
No History - control	198.2 +/- 46.98 **b**	205.4 +/- 50.91 **a**	215.4 +/- 79.53 **a**

*Mean of four subsamples from two replicates followed by standard deviation.

†Mean of three subsamples from two replicates followed by standard deviation.

**Means followed by same letters are not significantly different at $P < 0.05$.

Glyphosate Kd values ranged from 15 to 33 mL g^{-1} (Table 4.5). Glyphosate had higher Kd values for NH soils than H soils, while the addition of fresh manure had no effect on glyphosate sorption (Table 4.5). Compounds from the aged manure, particularly soil P, may be competing with glyphosate for sorption sites, resulting in lower Kd values in H soils. With lower sorption in soils with a history of manure amendment, more glyphosate is available for mineralization, as was the case with increased glyphosate mineralization in the Birtle and Neepawa soils. This decreases the bioavailability of the herbicide to plants and increases the risk of sorbed glyphosate being leached or transported by soil erosion to water sources.

Trifluralin Kd values ranged from 182 to 269 mL g^{-1} (Table 4.5). Fresh manure applications increased trifluralin sorption in both H and NH Birtle soils, but neither fresh manure nor a history of manure applications in the field significantly influenced trifluralin Kd values in Neepawa and Decker soils (Table 4.5). The decrease in trifluralin mineralization in Neepawa and Decker H soils is not caused by increased sorption to soil relative to NH soils.

4.5 Summary and Conclusions

The history of manure application increased total glyphosate mineralization and k values in Birtle and Neepawa soils, but had no effect on total mineralization and decreased k values in Decker soils. Trifluralin mineralization increased in Birtle soils with a history of manure application; however, a history of manure applications to Neepawa and Decker soils decreased trifluralin mineralization. Birtle soil had the longest history of manure application and was the only site to consistently stimulate herbicide mineralization as a result of a history of manure application. Conversely, herbicide mineralization in Decker soil, with the least history of manure application, was most negatively affected by history or fresh manure applications.

Although it was expected that glyphosate mineralization would increase as a result of increasing microbial activity in soil (Lalande et al. 2000), fresh manure applications generally had little effect on the total mineralization of either herbicide. It is possible that the manure failed to stimulate or inhibited the activity of microbes capable of degrading glyphosate.

Fresh manure addition to soil had no effect on the sorption of either herbicide, except for increasing trifluralin sorption in Birtle soils. However, more glyphosate sorbed to soils without a history of manure amendment, likely due to lower soil P present to compete for sorption sites compared to soils with a manure application history. Trifluralin Kd values were similar for Neepawa and Decker locations, regardless of manure application history, but were increased in Birtle soils treated with fresh manure.

One of the major differences between this mineralization experiment and the one described in Chapter 3 is the length of time the soil/manure was incubated for prior to herbicide application. Overall, the effects of manure application history and fresh manure applications on the half-lives and total mineralization of trifluralin were not large enough to suggest that there may be any increased risk of herbicide carryover damage to crops planted in these soils, which concurs with the results in Chapter 3. While glyphosate does not pose a carryover risk to crops, the risk of glyphosate entering the ground or surface water as a result of decreased sorption to soil is increased in soils with a history of manure application, but this may be offset somewhat by the increased total mineralization of glyphosate in soils with a history of manure application.

CHAPTER 5

2,4-D Mineralization in Amended Soils

5.1 Abstract

Hog manure and municipal biosolids were applied to Manitoba soils in order to determine the effect of these amendments on soil microbial activity, and on mineralization of 2,4-D in soils with: (1) different soil textures, (2) different rates of manure and biosolid applications and (3) different lengths of time between amendment and 2,4-D application. The addition of biosolids increased microbial activity in soil much more than the addition of hog manure. 2,4-D mineralization increased in the order of sandy clay loam < silty loam < sandy loam < clay loam soils. Increasing rates of amendment application and increasing the length of time between amendment and 2,4-D application decreased total 2,4-D mineralization. Producers should be aware of the potential for increased 2,4-D carryover in sandy clay loam soils, and with high rates of amendment additions.

5.2 Objectives of the Study

This study was designed to examine the effects of fresh hog manure and municipal biosolid applications on 2,4-D mineralization in a range of Manitoba soils. Four experiments were conducted: the effect of amendment applications on the mineralization of 2,4-D in different soil textures; the effect of different rates of amendment applications on 2,4-D mineralization; the effect of different lengths of time between amendment and herbicide applications on 2,4-D mineralization; and the effect of amendments on soil microbial activity.

5.3 Materials and Methods

5.3.1 Site and soil characteristics

Four different soils were collected from agricultural fields in Manitoba (Figure 5.1), a Newdale clay loam [CL] near Decker, MB and a Newdale sandy clay loam [SCL] near Birtle, MB (Ehrlich et al. 1956); a Wellwood silty loam [SiL] near Carberry, MB (Haluschuk and Podolsky 1999); and a Long Plain sandy loam [SL] near Macgregor, MB (Michalyna et al. 1982). All soils were sampled at 0-10 cm in the soil profile, sieved (< 2 mm) and stored at 4^{o}C until utilized in mineralization experiments. These soils did not have a history of manure or biosolids applications. Soil characteristics are listed in Table 5.1.

Fresh hog manure was obtained from a manure storage pit for a sow barn at the University of Manitoba Glenlea Research Farm in Glenlea, MB. Municipal biosolids were collected from the City of Winnipeg North End Water Pollution Control Centre in Winnipeg, MB. After collection, the amendments were stored at 4^{o}C until utilized in mineralization experiments. All soil and amendment analyses were carried out within one week of collection as described in sections 3.4.1 and 3.4.2. Manure and biosolids characteristics are described in Tables 5.2 and 5.3.

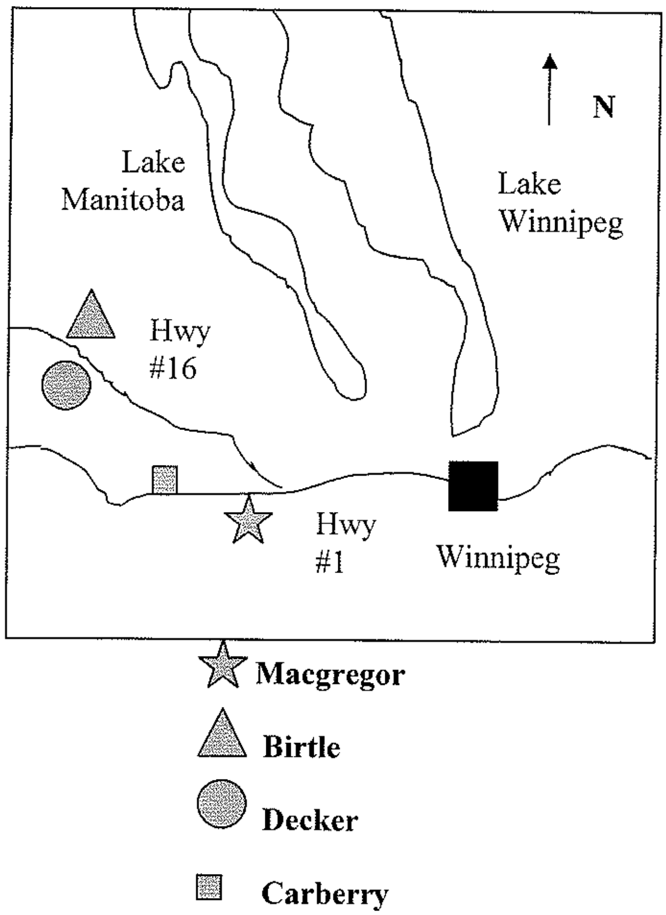

Figure 5.1. Soil sampling sites.

5.3.2 2,4-D mineralization

Soil microcosms were constructed using 0.5 L mason jars. 30 g (oven-dry basis) of each soil was placed in a small jar. Fresh hog manure [M] and municipal biosolids [B] treatments at rates equivalent to 56, 112 and 225 kg N ha^{-1} were prepared by thoroughly mixing the soil plus amendment. Amendment application rates were based on NH_4^+-N content because the manure had negligible amounts of NO_3^--N compared to the biosolids (Table 5.2). Rates were calculated based on the assumption that amendments are incorporated into the top 7.5 cm of a soil with a soil bulk density of 1.3 Mg m^{-3}. A non-amended [C] treatment was used as a control. Soil moisture contents were brought up to 70% field capacity with deionized water. The soil was incubated at 20°C prior to herbicide addition for various lengths of time as indicated in Table 5.4.

Table 5.1. Selected characteristics of soils used in mineralization and inorganic carbon studies (0-10 cm)

	Birtle - SCL	Decker - CL	Carberry - SiL	Macgregor - SL
Clay (%)	29*	33*	19**	13**
Sand (%)	54	36	62	79
Silt (%)	17	31	19	9
pH	6.9	7.9	5.9	7.7
Organic Carbon (%)	3.74	3.06	3.07	0.6
Total N (%)	0.36	0.33	na†	na
N-NO_3^- ($\mu g\ g^{-1}$)	55	19	na	25
P ($\mu g\ g^{-1}$)	56	24	na	57

* Pipette method (Gee and Bauder 1986).

** Hydrometer method (Gee and Bauder 1979).

† Not available

The experiments were factorial designs with treatments outlined in Table 5.4: 2,4-D mineralization in M-, B-, C-amended soils as affected by CL, SL, SiL, SCL textures; 2,4-D mineralization in M-, B-amended soils as affected by amendment application rates of 56, 112, 225 kg N ha^{-1}; and 2,4-D mineralization in M-, B-, C-amended soils as affected by soil/amendment pre-incubation lengths of 0, 7, 14, 28 days. Each treatment was replicated four times.

2,4-D stock solutions were prepared by dissolving 15 250 Bq mL^{-1} U-ring-labeled ^{14}C-2,4-D (5.17 mCi $mmol^{-1}$ specific activity; Sigma Chemical Co., St. Louis, MO) and 2.279

Table 5.2. Selected chemical characteristics and nutrient contents of municipal biosolids and fresh hog manure used in the mineralization study

	pH	EC ($dS\ m^{-1}$)	Organic C ($mg\ g^{-1}$)	Total N	NH_4^+-N	Organic N	NO_3^--N	Phosphorus	Sulphate-S
						($kg\ 1000\ L^{-1}$)			
Biosolids	7.8	1.03	5.11	8.6	2.5	6.1	<0.1	3.6	1.50*
Manure	na†	19.1	0.27	3.0	2.4	0.6	<0.1	0.15	0.14

† Not available

* Total S

Table 5.3. Selected chemical characteristics and nutrient contents of municipal biosolids and fresh hog manure used in the total CO_2 study

	pH	EC ($dS\ m^{-1}$)	Organic C ($mg\ g^{-1}$)	Total N	NH_4^+-N	Organic N	NO_3^--N	P	Sulphate-S	Moisture (%)
						($kg\ 1000\ L^{-1}$)				
Biosolids	7.1	793	na†	9.1	2.0	7.1	<0.1	3.55	1.31	72.6
Manure	7.4	12.3	na	1.9	1.7	0.2	<0.1	0.21	0.07	99.3

† Not available

Table 5.4. Experimental variables used in 2,4-D mineralization study

Experiment	Soil	Manure [M] Application Rate (kg N ha^{-1} soil)	Biosolids [B] Application Rate (kg N ha^{-1} soil)	Pre-incubation Length (days)	Treatments		
The effect of different soil textures on 2,4-D mineralization	CL SL SiL SCL	112[a]	112[b]	14	CL-M SL-M SiL-M SCL-M	CL-B SL-B SiL-B SCL-B	CL-C SL-C SiL-C SCL-C
The effect of different amendment application rates on 2,4-D mineralization	SL	56 112 225	56 112 225	14	56-M 112-M 225-M	56-B 112-B 225-B	
The effect of different lengths of soil/ amendment pre-incubation on 2,4-D mineralization	SL	112	112	0 7 14 28	0-M 7-M 14-M 28-M	0-B 7-B 14-B 28-B	0-C 7-C 14-C 8-C

[a] = equal to an application of 0.06 L fresh hog manure kg^{-1} soil or 43 710 L ha^{-1}
[b] = equal to an application of 57 kg municipal biosolids kg^{-1} soil or 44 870 kg ha^{-1}

mg mL^{-1} analytical grade 2,4-D (min. 95% purity; Sigma Chemical Co., St. Louis, MO) in methanol. 0.5 mL of the methanol-herbicide solution was applied to the surface of the soil and the jars were left open for several minutes to allow the methanol to evaporate. The soil was then thoroughly mixed. The 2,4-D application rate simulated a field application of 0.62 kg active ingredient ha^{-1}. The herbicide application rate was based on a recommended field application rate (Guide to Crop Protection 2000) and also assumed that this application was homogenously mixed in a 7.5 cm surface soil layer with a bulk density of 1.3 Mg m^{-3}.

Each microcosm contained a vial with 5 mL 0.5M NaOH to trap CO_2 evolved from the soil in addition to a vial with 5 mL acidified water (pH 3) to maintain air humidity. NaOH traps were changed three times a week for the first 46 days, twice a week for the next 20 days, and once a week for the last 34 days for a total of 100 days after herbicide application. Radioactivity in solutions and NaOH samples was determined using Liquid Scintillation Counting (LSC) (LS 7500 Beckman Instruments, Fullerton, CA) using 10 mL of Scinti-Safe scintillation cocktail (Fisher Scientific, Fairlawn, NJ).

Herbicide mineralization rate constants were calculated in SigmaPlot 2000 (SPSS Inc.) under the assumption that herbicide mineralization rates were first-order:

$$Mt = M_T\,(1 - e^{-kt}) \qquad \text{(Equation 5.1)}$$

where Mt = herbicide mineralization at time t, expressed as a percentage of the initially applied radioactivity (%); M_T = total herbicide mineralized at time infinity, expressed as a percentage of the initially applied radioactivity (%); k = first-order mineralization rate constant (day^{-1}); and t = time (day). The time that 50% of the mineralizable portion of the herbicide was mineralized (M½-lives) was calculated by dividing log e^2 by the calculated herbicide mineralization rate constants.

Statistical analyses were performed in SAS 8.2 (SAS Institute Inc. 2001) and included two-way analysis of variance (ANOVA) and, if applicable, the Tukey comparison test with the significance level set at $\alpha = 0.05$.

5.3.3 Total CO_2 production

The capture of CO_2 by NaOH traps allows the relative determination of microbial activity in soil (Anderson 1982) and is a useful tool in observing the effects of amendment applications on soil respiration. Total CO_2 production was measured in the sandy loam soil amended with either 112 kg N ha^{-1} fresh hog manure or municipal biosolids and in non-amended soil. Soil microcosms were assembled using the method described in section 5.3.2, but no 2,4-D was applied. Microcosms were incubated at 20°C and CO_2 was trapped in 5 mL 0.5M NaOH traps for 128 days. Traps were changed three times a week for the first 18 days, two times a week for the next 28 days, and once a week for the last 82 days. Analysis by colorimeter determined the inorganic carbon content of the NaOH traps (Anderson 1982).

Carbon mineralization rate constants were calculated in SigmaPlot 2000 (SPSS Inc.) under the assumption that carbon mineralization rates were first-order:

$$Ct = C_T(1 - e^{-ct}) \qquad \text{(Equation 5.2)}$$

where Ct = carbon mineralization at time t, expressed as g C; C_T = total carbon mineralized at time infinity, expressed as g C; c = first-order mineralization rate constant (day^{-1}); and t = time (day).

Statistical analyses were performed in SAS 8.2 (SAS Institute Inc. 2001) and included one-way analysis of variance (ANOVA).

5.4 Results and Discussion

All mineralization ANOVA tables are presented in Appendix IV.

5.4.1 The effect of different soil textures on 2,4-D mineralization

There was an excellent fit of the 2,4-D mineralization data to the mineralization first-order reaction model (Eq. 5.1), with r^2 values of 0.96 to 0.99 (Table 5.5). Values for k ranged from 0.0086 day^{-1} for SCL-B to 0.0895 day^{-1} for CL-C, which correspond to 2,4-D half-lives of 96 and 8 days, respectively. 2,4-D mineralization rates were significantly greater (Fig. 5.2) and half-lives were significantly lower in CL soils relative to SL, SiL or SCL soils (Fig. 5.3). This suggests that clay loam textures may have a more efficient soil microbial population capable of mineralizing 2,4-D than more sandy soils, which agrees with results from van Veen et al. (1985).

Values for k were significantly greater in control soils than amended soils for the CL, SL and SCL treatments. The addition of an amendment, particularly manure, generally

Table 5.5. First-order mineralization rate constants (k), half-lives (½-lives), total 2,4-D mineralized at time infinity (M_T), and coefficients of determination of the mineralization model (r^2) as determined by fitting the evolved $^{14}C\text{-}CO_2$ in soils of different textures to the equation: $Mt = M_T\ (1 - e^{-kt})$, where t = time (days). Experimental values for total 2,4-D mineralization (Exp-M_T) are displayed for comparison with predicted values

	k (day^{-1})	½-lives (day)	M_T (%)	r^2	Exp-M_T (%)
			Clay loam		
Biosolids	0.0816+/- 0.01 * **a****	9 +/- 0.6 * **a****	37.1 +/- 1.03 * **a****	0.98 +/- 0.00*	38.0 +/- 0.94 * **a****
Manure	0.0777 +/- 0.00 **a**	9 +/- 0.4 **a**	31.4 +/- 0.52 **b**	0.98 +/- 0.00	33.1 +/- 0.62 **b**
Control	0.0895 +/- 0.00 **b**	8 +/- 0.2 **a**	30.2 +/- 0.58 **b**	0.96 +/- 0.00	32.8 +/- 0.63 **b**
			Sandy loam		
Biosolids	0.0517 +/- 0.00 **a**	13 +/- 0.7 **a**	29.1 +/- 1.49 **a**	0.97 +/- 0.00	29.1 +/- 1.40 **a**
Manure	0.0290 +/- 0.00 **b**	24 +/- 3.6 **a**	30.6 +/- 1.86 **a**	0.96 +/- 0.00	28.0 +/- 2.13 **a**
Control	0.0583 +/- 0.00 **c**	12 +/- 0.8 **a**	28.4 +/- 1.75 **a**	0.98 +/- 0.00	29.2 +/- 1.60 **a**
			Silty loam		
Biosolids	0.0533 +/- 0.00 **a**	13 +/- 1.1 **a**	28.7 +/- 0.98 **a**	0.99 +/- 0.00	29.2 +/- 1.15 **a**
Manure	0.0309 +/- 0.00 **b**	22 +/- 0.3 **a**	25.6 +/- 1.02 **a**	0.99 +/- 0.01	24.4 +/- 0.89 **b**
Control	0.0429 +/- 0.00 **c**	16 +/- 0.5 **a**	25.2 +/- 2.24 **a**	0.99 +/- 0.00	25.3 +/- 2.16 **b**
			Sandy clay loam		
Biosolids	0.0086 +/- 0.00 **a**	96 +/- 35.9 **a**	43.2 +/- 7.81 **a**	0.98 +/- 0.00	21.3 +/- 2.21 **a**
Manure	0.0145 +/- 0.00 **b**	49 +/- 2.9 **b**	29.3 +/- 0.89 **b**	0.98 +/- 0.00	21.3 +/- 1.41 **a**
Control	0.0353 +/- 0.01 **c**	20 +/- 2.9 **c**	26.8 +/- 0.69 **b**	0.99 +/- 0.00	25.9 +/- 0.98 **b**

*Mean of four replicates followed by standard deviation.

**Means within individual soil textures followed by same letters are not significantly different at $P < 0.05$.

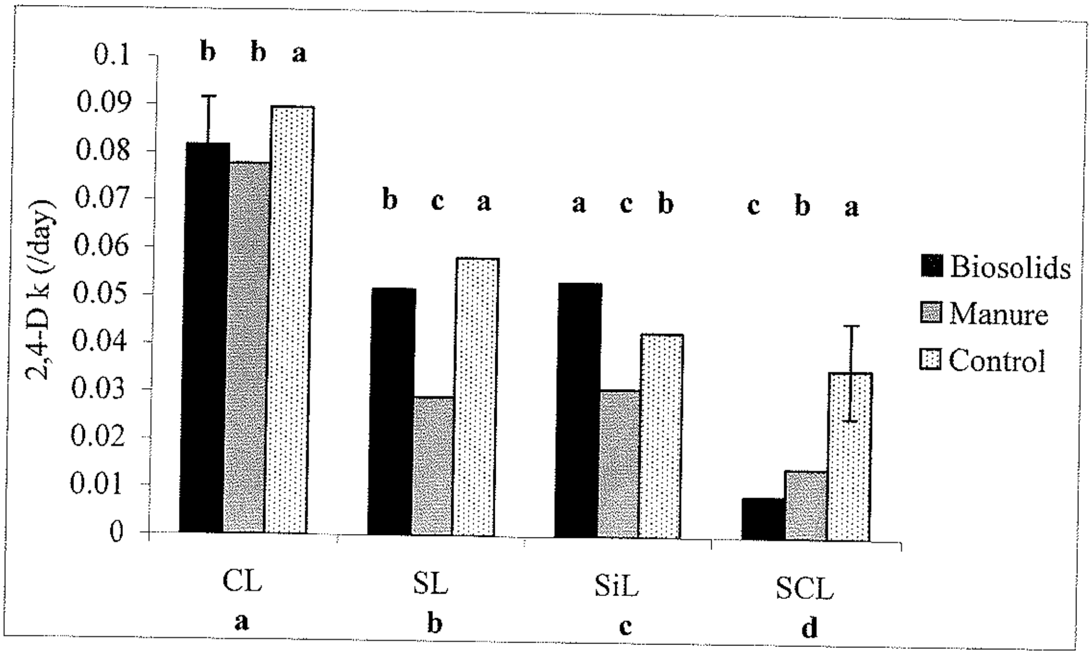

Figure 5.2. 2,4-D mineralization rates (k) (day^{-1}) in amended soils of different textures.

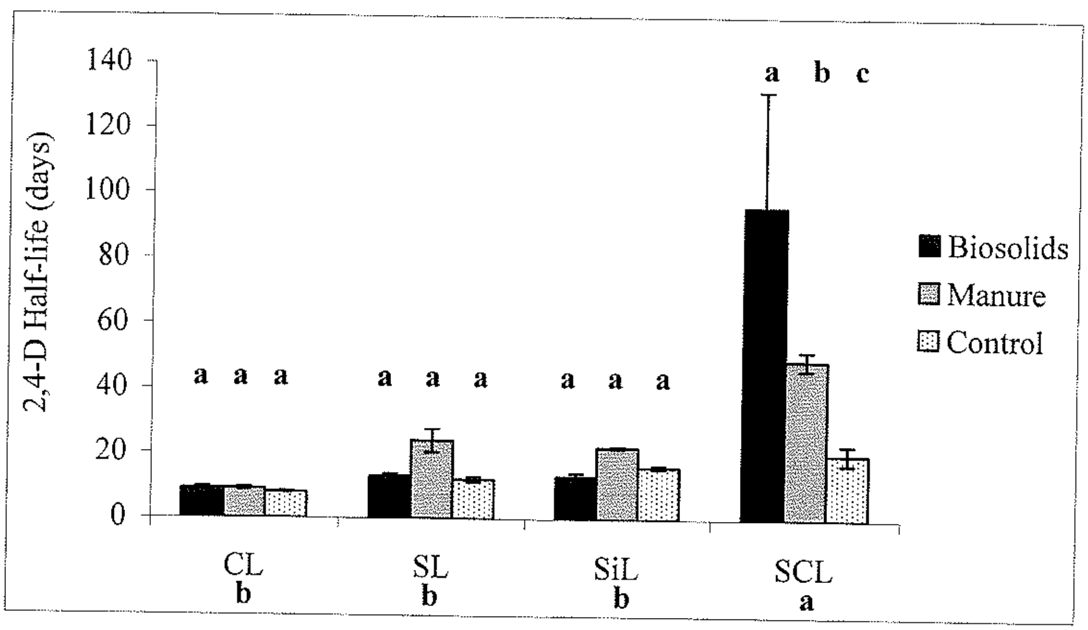

Figure 5.3. 2,4-D half life (days) in amended soils of different textures.

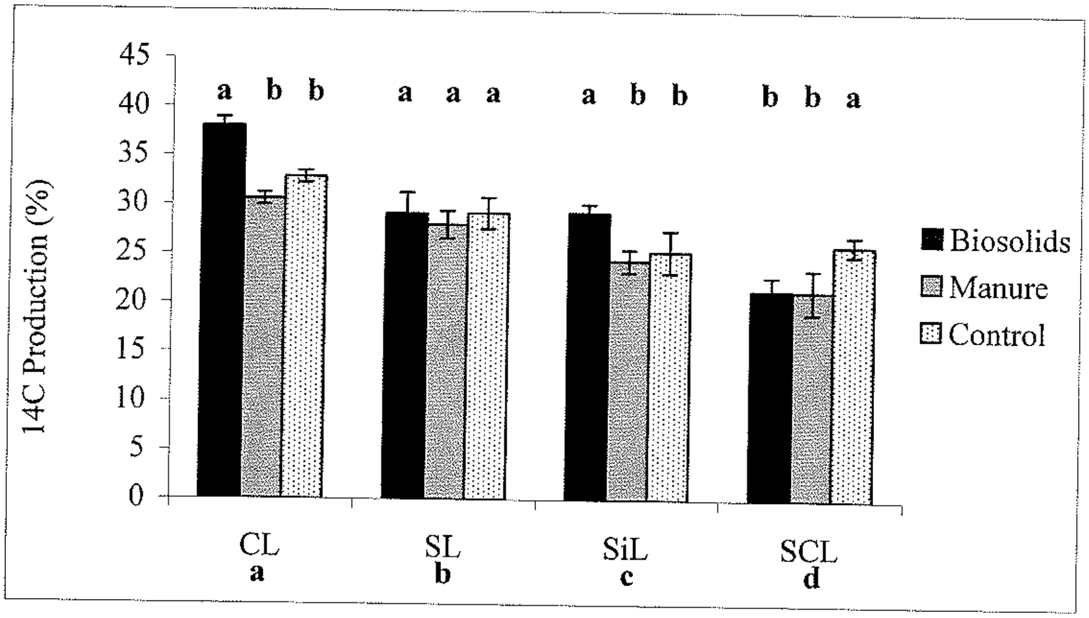

Figure 5.4. Total 2,4-D mineralization (% ^{14}C production) in amended soils of different textures.

decreased the rate at which 2,4-D was mineralized in soil. 2,4-D half-lives were not statistically different between amendment treatments in CL, SL or SiL soils, but half-lives increased in the SCL treatment as a result of both amendment additions (Table 5.5). The analyses of variance indicated a significant interaction between the soil texture and amendment factors for total 2,4-D mineralization, mineralization rates and half-life, suggesting that the effect of the amendment was dependent on the soil texture.

Total mineralization ranged from 21.3% for SCL-B and SCL-M to 38.0% for CL-B (Table 5.5). Overall, 2,4-D total mineralization increased in the order of SCL < SiL < SL < CL soils (Fig. 5.4), the same ranking as mineralization rates. Total mineralization was greater in biosolid-amended clay loam and sandy clay loam soils than manure-amended ones. However, soil textural differences had a greater effect on total 2,4-D mineralization than amendment application. CL soil experienced more mineralization than all other soils. This suggests that the variation in texture among Manitoba soils is important for determining risks of 2,4-D carryover and injury to subsequent crops that are sensitive to 2,4-D. The 5% increase in total mineralization as a result of the addition of biosolids to CL and SiL soils, and the 4% decrease in total mineralization as a result of the addition of manure and biosolids to SCL soils (Table 5.5), are not large enough to suggest that producers working with these soil textures need to be concerned about the effect of adding manure or biosolids on the mineralization of 2,4-D in-field. SL soils showed no significant change in total mineralization as a result of amendment additions (Table 5.5).

5.4.2 The effect of different amendment application rates on 2,4-D mineralization

Again, the mineralization data fit well to the 2,4-D mineralization model (Eq. 5.1), with r^2 values ranging from 0.95 to 0.98. Values for k ranged from 0.0087 day^{-1} for 225-M to 0.0840 day^{-1} for 56-B. Mineralization rates were always greater for lower rates than for higher rates of biosolid and manure applications (Table 5.6). Specifically, 2,4-D mineralized more quickly in soil amended with 56 kg N ha^{-1} of manure or biosolids than in soils amended at rates of 112 or 225 kg N ha^{-1} (Fig. 5.5). This experiment was done with SL soil, which was intermediate among the soil types in terms of rates and extents of 2,4-D mineralization, as well as impacts of manure and biosolids (Table 5.5).

2,4-D half-lives ranged from 8 days for 56-B to 80 days for 225-M (Table 5.6). Both the type of amendment and amendment application rates had strong effects on the persistence of 2,4-D in soil. Moreover, there were significant interactions between these two factors

Table 5.6. First-order mineralization rate constants (k), half-lives (½-lives), total 2,4-D mineralized at time infinity (M_T), and coefficients of determination of the mineralization model (r^2) as determined by fitting the evolved ^{14}C-CO_2 in soils with different amendment application rates to the equation: $Mt = M_T\ (1 - e^{-kt})$, where t = time (days). Experimental values for total 2,4-D mineralization (Exp-M_T) are displayed for comparison with predicted values

	k (day^{-1})	½-lives (day)	M_T (%)	r^2	Exp-M_T (%)
0 kg N ha^{-1}	0.0644 +/- 0.00 *	11 +/- 0.5 *	29.7 +/- 2.13 *	0.99 +/- 0.00 *	30.3 +/- 2.01 *
			Biosolids		
56 kg N ha^{-1}	0.0840 +/- 0.01 * **a****	8 +/- 1.3 * **a****	31.9 +/- 0.50 * **a****	0.96 +/- 0.01*	32.8 +/- 0.40 * **a****
112 kg N ha^{-1}	0.0594 +/- 0.01 **b**	12 +/- 1.6 **a**	28.5 +/- 1.58 **ab**	0.97 +/- 0.00	28.4 +/- 1.28 **b**
225 kg N ha^{-1}	0.0343 +/- 0.00 **c**	20 +/- 0.6 **b**	26.9 +/- 1.27 **b**	0.98 +/- 0.01	25.1 +/- 1.15 **c**
			Manure		
56 kg N ha^{-1}	0.0714 +/- 0.01 **a**	10 +/- 1.3 **a**	28.9 +/- 4.78 **a**	0.96 +/- 0.00	29.3 +/- 4.59 **a**
112 kg N ha^{-1}	0.0269 +/- 0.00 **b**	26 +/- 2.1 **b**	28.4 +/- 0.95 **a**	0.95 +/- 0.00	25.1 +/- 1.22 **b**
225 kg N ha^{-1}	0.0087 +/- 0.00 **c**	80 +/- 10.4 **c**	27.2 +/- 3.22 **a**	0.97 +/- 0.00	14.4 +/- 0.66 **c**

*Mean of four replicates followed by standard deviation.

**Means followed by same letters are not significantly different at $P < 0.05$.

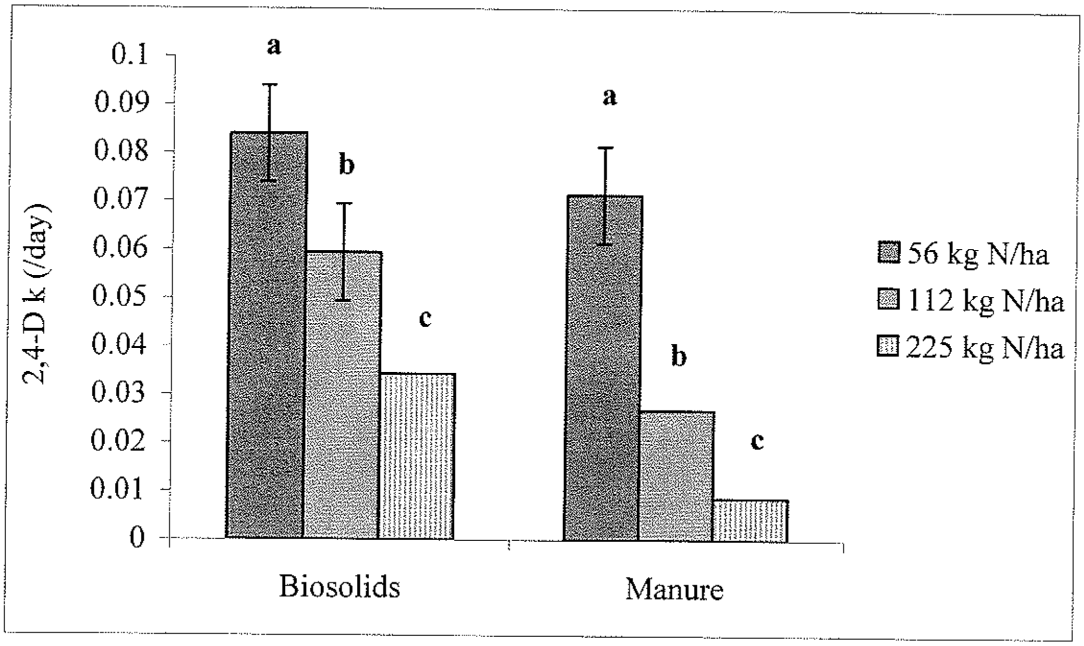

Figure 5.5. 2,4-D mineralization rates (k) (day^{-1}) in amended soils with different rates of amendment application.

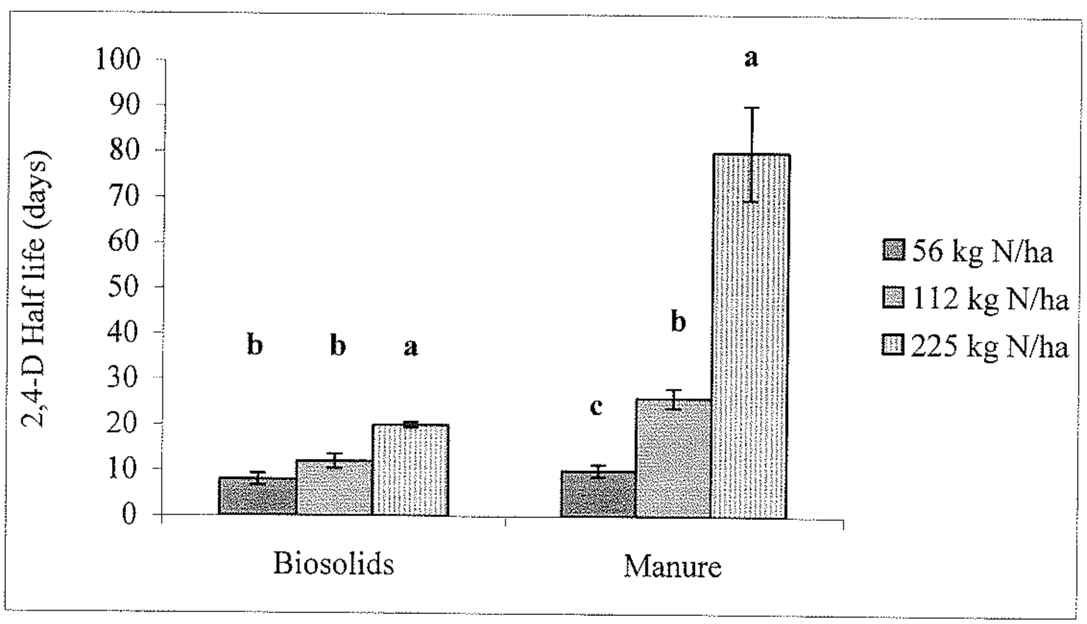

Figure 5.6. 2,4-D half life (days) in amended soils with different rates of amendment application.

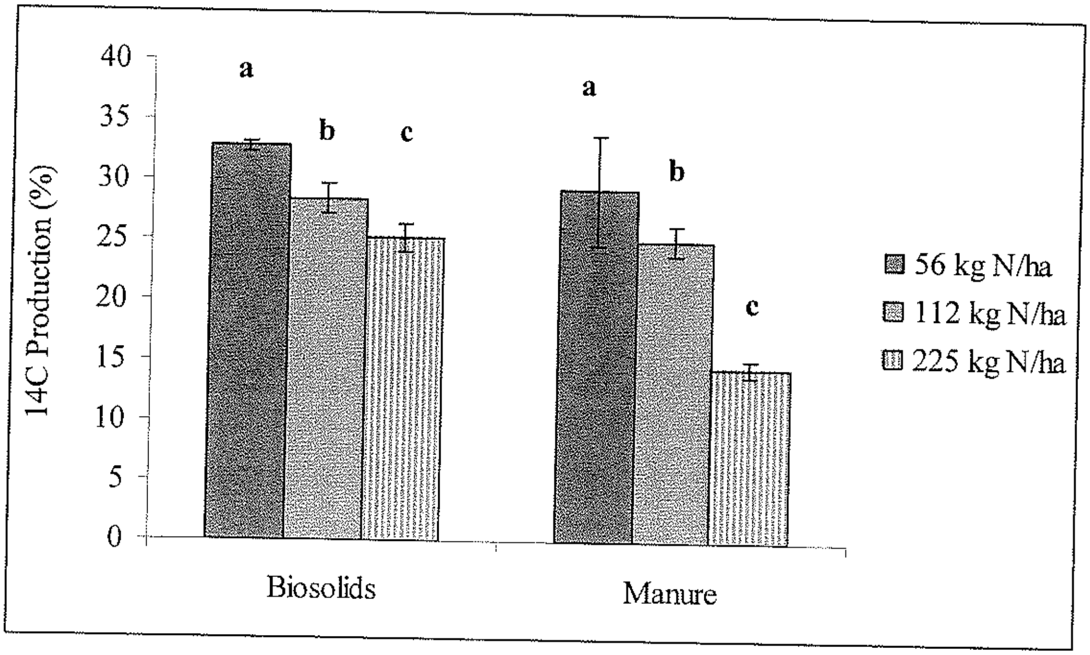

Figure 5.7. Total 2,4-D mineralization (% ^{14}C production) in amended soils with different rates of amendment application.

for 2,4-D mineralization rates, half-lives and total mineralization. Specifically, a significant increase in 2,4-D half life occurred when biosolids were applied at 225 kg N ha^{-1} compared to 56 or 112 kg N ha^{-1}, while manure applications of both 112 and 225 kg N ha^{-1} increased 2,4-D half-lives compared to 56 kg N ha^{-1} (Fig. 5.6).

Total 2,4-D mineralization increased in the order of 225 < 112 < 56 kg N ha^{-1} for both amendment applications, and was generally smaller in the manure-amended soil than the biosolid-amended soil (Fig. 5.7). Total mineralization ranged from 14.4% for 225-M to 32.8% for 56-B (Table 5.6). Total 2,4-D mineralization in biosolid-amended soil was 4% less in the 112 kg N ha^{-1} treatment and 8% less in the 225 kg N ha^{-1} treatment compared to the 56 kg N ha^{-1} treatment. Total 2,4-D mineralization in manure-amended soil was

4% less in the 112 kg N ha^{-1} treatment and 15% less in the 225 kg N ha^{-1} treatment compared to the 56 kg N ha^{-1} treatment.

Increasing the application rate of amendments will significantly increase the length of time it takes for 2,4-D to be mineralized in soil and higher rates of manure application will have a greater inhibitory effect on 2,4-D mineralization compared to soils with lower rates of manure application. This may be due to toxic effects of the excessive addition of nitrogen, salts or metals in the amendments (Eck and Stewart 1995; Mathers and Stewart 1971), or to the addition of microbes that prey on degrading microbes. A practical implication for producers is that increasing the rate of hog manure application prior to 2,4-D application may decrease the amount of 2,4-D mineralization in soil, therefore resulting in an accumulation of 2,4-D, which may cause damage to subsequently-planted susceptible crops.

5.4.3 The effect of different lengths of soil/amendment incubation on 2,4-D mineralization

2,4-D mineralization data fit well to the 2,4-D mineralization model (Eq. 5.1), with r^2 values ranging from 0.91 to 0.99 (Table 5.7). Values for k ranged from 0.0245 day^{-1} for 7-M to 0.0760 day^{-1} for 0-C and half-lives ranged from 9 days for 0-C to 54 days for 28-C (Table 5.7). When 2,4-D was applied immediately after amendment application (0-day treatment), there was no difference in 2,4-D mineralization rates across soils amended with manure or biosolids, or soil free of amendments (Table 5.7). However, when the application of 2,4-D was delayed 7, 14 or 28 days after amendment application, soils

Table 5.7. First-order mineralization rate constants (k), half-lives (½-lives), total 2,4-D mineralized at time infinity (M_T), and coefficients of determination of the mineralization model (r^2) as determined by fitting the evolved ^{14}C-CO_2 in soils with different pre-incubation lengths to the equation: $Mt = M_T (1 - e^{-kt})$, where t = time (days). Experimental values for total 2,4-D mineralization (Exp-M_T) are displayed for comparison with predicted values

	k (day^{-1})	½-lives (day)	M_T (%)	r^2	Exp-M_T (%)
			0-days		
Biosolids	0.0725 +/- 0.00*a**	10 +/- 0.6 * a**	47.1 +/- 1.16 * a**	0.93 +/- 0.01*	46.7 +/- 0.99 * a **
Manure	0.0701 +/- 0.01 a	10 +/- 1.1 a	47.7 +/- 2.32 a	0.91 +/- 0.02	47.1 +/- 1.93 a
Control	0.0760 +/- 0.01 a	9 +/- 1.7 a	29.6 +/- 3.88 b	0.97 +/- 0.02	30.2 +/- 3.40 b
			7-days		
Biosolids	0.0629 +/- 0.01 a	11 +/- 1.4 a	32.2 +/- 3.65 a	0.98 +/- 0.01	32.5 +/- 3.77 a
Manure	0.0245 +/- 0.00 b	29 +/- 3.0 a	28.9 +/- 3.94 a	0.95 +/- 0.01	24.9 +/- 3.79 b
Control	0.0705 +/- 0.00 a	10 +/- 0.6 a	29.1 +/- 1.52 a	0.98 +/- 0.00	30.0 +/- 1.56 ab
			14-days		
Biosolids	0.0531 +/- 0.01 ab	13 +/- 2.7 a	25.7 +/- 4.41 a	0.95 +/- 0.01	25.5 +/- 4.57 ab
Manure	0.0357 +/- 0.01 b	20 +/- 5.0 a	25.1 +/- 0.98 a	0.98 +/- 0.01	23.4 +/- 1.71 b
Control	0.0644 +/- 0.00 a	11 +/- 0.5 a	29.7 +/- 2.13 b	0.99 +/- 0.00	30.3 +/- 2.01 a
			28-days		
Biosolids	0.0402 +/- 0.01 a	18 +/- 5.6 a	21.5 +/- 1.76 a	0.98 +/- 0.00	21.1 +/- 2.41 a
Manure	0.0338 +/- 0.01 a	21 +/- 3.2 a	22.1 +/- 3.21 a	0.97 +/- 0.01	21.0 +/- 3.31 a
Control	0.0694 +/- 0.00 † b	10 +/- 0.5 † a	24.3 +/- 0.36 † a	0.98 +/- 0.00†	24.8 +/- 0.48 † a

*Mean of four replicates followed by standard deviation.
**Means within individual pre-incubation lengths followed by same letters are not significantly different at $P < 0.05$.
†Mean of three replicates followed by standard deviation.

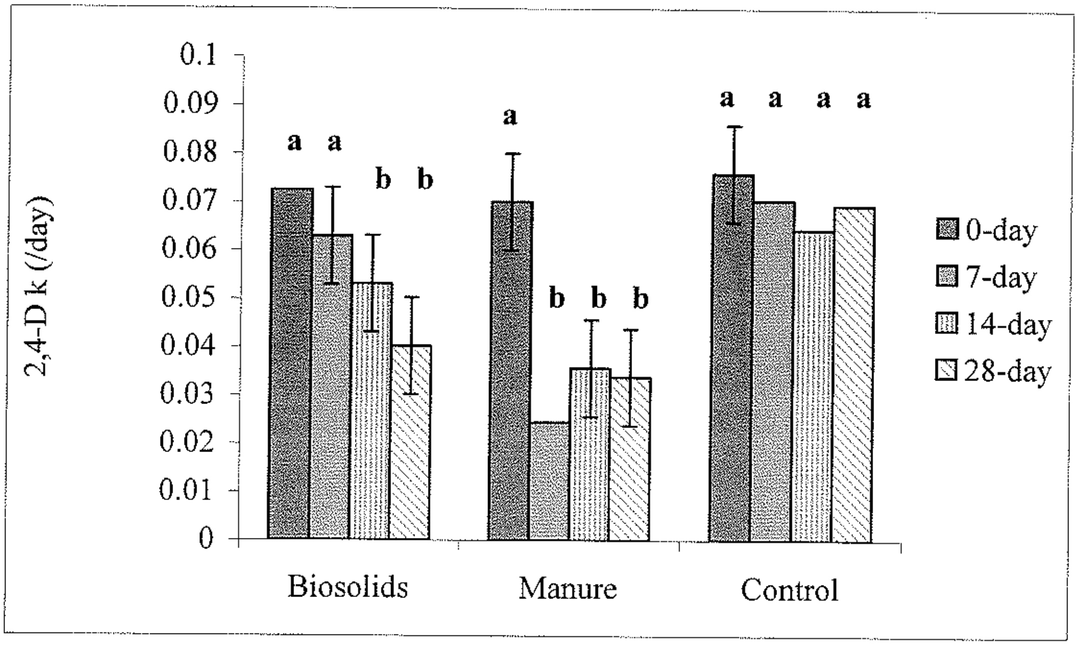

Figure 5.8. 2,4-D mineralization rates (k) (day^{-1}) in amended soils with different lengths of soil/manure incubation prior to 2,4-D addition.

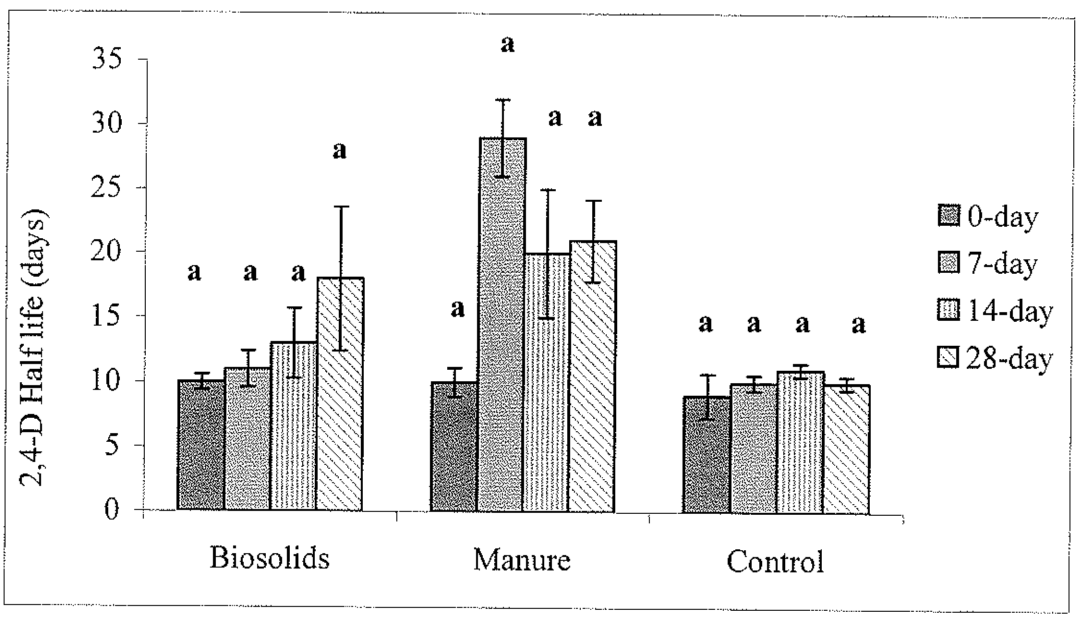

Figure 5.9. 2,4-D half life (days) in amended soils with different lengths of soil/manure incubation prior to 2,4-D addition.

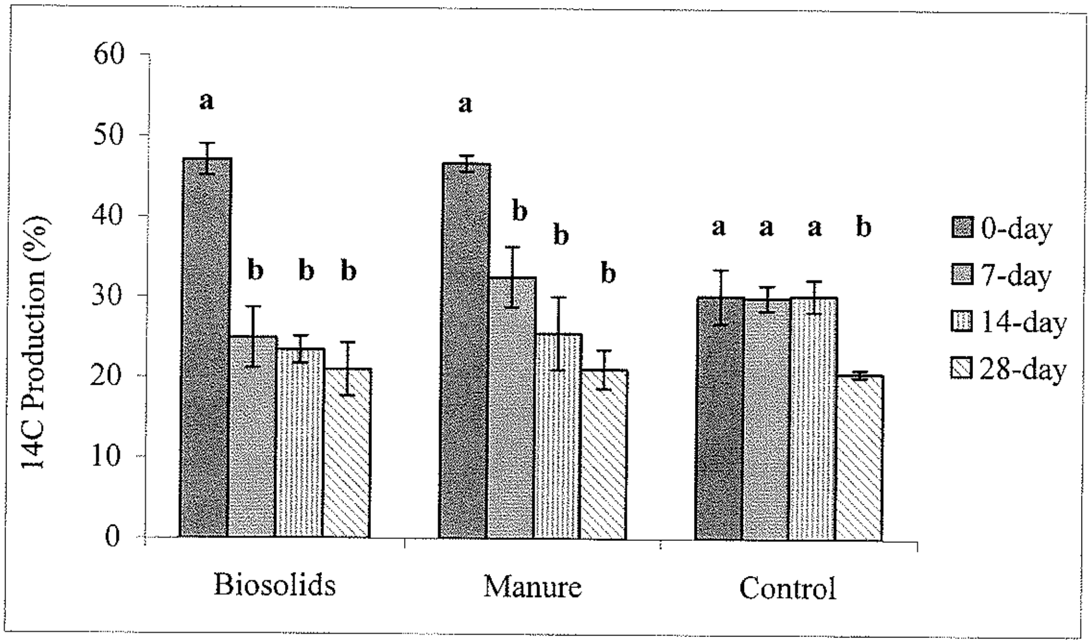

Figure 5.10. Total 2,4-D mineralization (% ^{14}C production) in amended soils with different lengths of soil/manure incubation prior to 2,4-D addition.

which received manure showed lower 2,4-D mineralization rates than soils amended with biosolids and soil free of amendments. The rates were low regardless of whether the manure was incubated for 7, 14 or 28 days. In contrast, k decreased with greater pre-incubation times for biosolids, while the controls did not change over time (Fig. 5.8).

2,4-D half-lives were not statistically different regardless of pre-incubation length or amendment addition (Table 5.7 and Fig. 5.9). However, as the pre-incubation length increases, k values and total 2,4-D mineralization are affected because over time the amendments are affecting the microbial community and/or 2,4-D binding. While the effect of the control treatment on 2,4-D k and total mineralization changes little over time, there is a significant change in the effects of biosolids and manure on 2,4-D k and total mineralization, resulting in suppression of 2,4-D mineralization as time passes between amendment and 2,4-D applications.

Total 2,4-D mineralization increased from 28 < 7 = 14 < 0 days of pre-incubation of the amendment. Total mineralization ranged from 20.6% for 28-C to 47.1% for 0-M (Table 5.7). Total 2,4-D mineralization of biosolid-amended treatments were generally similar to manure-amended treatments, but biosolid-amended soil had greater 2,4-D mineralization in the 7-day treatment. The longer the organic amendment was in the soil prior to 2,4-D application, the less 2,4-D was mineralized (Fig. 5.10). 15 to 25% more total 2,4-D mineralization occurred when the 2,4-D was applied at the same time as the amendment than when 7 to 28 days passed between amendment and 2,4-D applications (Table 5.7). By waiting longer to apply 2,4-D after an amendment application, producers increase the risk of crop injury because 2,4-D is more persistent.

5.4.4 The effect of amendment applications to soil on total CO_2 production

CO_2 evolution rates (c) increased from control < manure < biosolids, with biosolids mineralizing over two times the total amount of carbon at 128 days compared to the control soil (Table 5.8). Total CO_2 production was greatest in soils amended with municipal biosolids, with a total of 56.4 mg C produced over 128 days, while soils with fresh hog manure and soils with no amendment produced 30.1 and 29.1 mg C, respectively (Table 5.8). This is indicative of the significant amount of carbon that is added when applying biosolids to soil. Biosolids contain more solids than liquid hog manure, containing almost 70% less moisture per gram (Table 5.3). Organic carbon contents in the biosolids and manure used in the mineralization study were 5.11 and 0.27

Table 5.8. First-order mineralization rate constants (c), total inorganic carbon (CO_2) mineralized at time infinity (C_T), and coefficients of determination of the mineralization model (r^2) as determined by fitting the evolved CO_2 from soil treated with municipal biosolids and fresh hog manure after 128 days with the equation: $Ct = C_T(1-e^{-ct})$, where t = time (days). Experimental values for total CO_2 mineralization (Exp-M_T), less background CO_2, are displayed for comparison with predicted values

	c (day^{-1})	C_T (mg)	r^2	Exp-C_T (mg)
Municipal Biosolids	0.024 +/- 0.001 * **a****	55.8 +/- 01.39 * **a****	0.99 +/- 0.00 *	56.4 +/- 1.47 * **a****
Fresh Hog Manure	0.017 +/- 0.001 **b**	31.5 +/- 1.83 **b**	0.96 +/- 0.00	30.1 +/- 1.15 **b**
Control	0.010 +/- 0.000 **c**	39.8 +/- 0.76 **c**	0.99 +/- 0.00	29.1 +/- 0.42 **b**

*Mean of four replicates followed by standard deviation.

**Means followed by same letters are not significantly different at $P < 0.05$ using Tukey's Test.

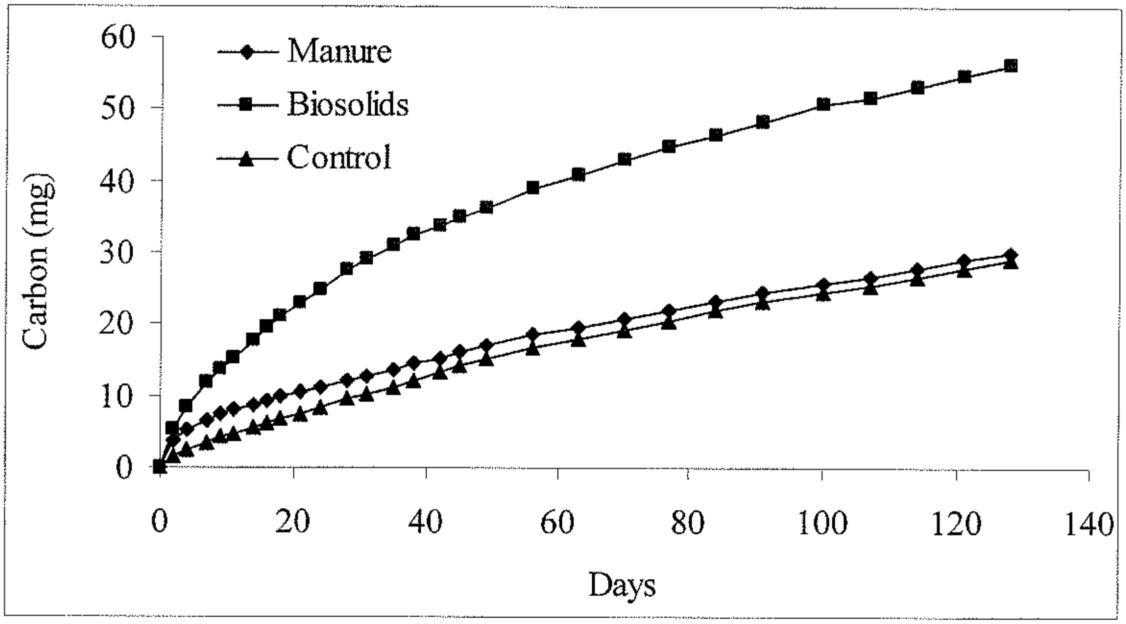

Figure 5.11. Total carbon production (mg) in an amended sandy loam soil.

mg g^{-1}, respectively. Carbon is rapidly mineralized by soil microorganisms in the first few weeks following amendment application. Mineralization rates were greatest in the first 7 days of incubation for all treatments (Fig. 5.11) and slowed thereafter, suggesting that the microbial growth was more stimulated immediately after amendment and water addition.

Total CO_2 production was greatest in soils amended with municipal biosolids, with a total of 56.4 mg C produced during 128 days, while soils with fresh hog manure and the control produced 30.1 and 29.1 mg C, respectively (Table 5.8). Increased carbon addition in biosolid-amended soils versus manure-amended soils or control soils resulted in increased total respiration of the microbial population by supplying a readily available food source. Lalande et al. (2000) found that the addition of liquid hog manure increased soil microbial biomass. Another study found that sewage sludge additions increased total CO_2 production in soil, with an enhanced effect up to 50 days after addition (O'Connor et al. 1981). Soil microbial activity is dependent on available C, which is greatest in the first two weeks after addition of manure to soil (Hadas et al. 1996). This agrees well with the current study as total CO_2 production was greatest in the first 14 days of incubation for all treatments (Fig. 5.11) and rate of production decreased thereafter, indicating that the readily available C had been mineralized and, subsequently, the more stable fractions were being mineralized more slowly.

5.4.5 General Discussion

Biosolids and manure either had similar effects on total 2,4-D mineralization or manure suppressed 2,4-D mineralization to a greater extent than manure (Table 5.9). In another study, total 2,4-D mineralization and k values decreased in soil with added composted biosolids compared to soil alone (Barriuso et al. 1997). However, Entry and Emmingham (1995) found that dairy manure increased total 2,4-D mineralization compared to non-amended soil. Doyle et al. (1978) found that sewage sludge increased 2,4-D mineralization, while dairy manure had no effect on 2,4-D mineralization.

Because 2,4-D is degraded by co-metabolism, the process by which a pesticide is not utilized for microbial nutritional benefit or energy (Topp et al. 1997), the increase in microbial activity following biosolids application was expected to cause an increase in total 2,4-D mineralization. However, amendment applications generally decreased 2,4-D mineralization, perhaps because of increased 2,4-D sorption and a decreasing availability of 2,4-D molecules to soil microorganisms. The exception was when 2,4-D was added at the same time as manure or biosolids, and increased microbial activity (as measured by CO_2 production) stimulated 2,4-D mineralization compared to the control.

Table 5.9. Trends in 2,4-D mineralization rates (k) and total mineralization (Exp-M_T) as a result of amendment addition

Experiment	k	Exp-M_T
The effect of different soil textures on 2,4-D mineralization	CL: M = B < C * SL: M < B < C SiL: M < C < B SCL: M < C < B	CL: M = C < B SL: M = B = C SiL: M = C < B SCL: M = B < C
The effect of different amendment application rates (kg N ha^{-1}) on 2,4-D mineralization	56: M < B 112: M < B 225: M < B	56: M < B 112: M < B 225: M < B
The effect of different lengths of soil/amendment pre-incubation (days) on 2,4-D mineralization	0: M = B = C 7: M < B = C 14: (M = B) < (B = C) 28: M = B < C	0: C < M = B 7: (M = C) < (B = C) 14: (M = B) < (B = C) 28: M = B = C

* Differences significant at P < 0.05.

5.5 Summary and Conclusions

Soil texture had a large impact on 2,4-D mineralization. More 2,4-D was mineralized in a clay loam soil compared to sandy loam, silty loam or sandy clay loam soils. The effect of texture on 2,4-D mineralization has practical implications for producers across Manitoba. Different textures play a significant role in determining the mineralization of 2,4-D, and the subsequent risk of damage to susceptible crops. By realizing the increased risk of

2,4-D carryover in soils of sandier texture, producers can make cropping choices that will minimize risk of 2,4-D carryover damage.

Increasing the application rate of amendments decreased the amount of 2,4-D mineralized. Producers utilizing biosolids or manure as an organic amendment may see small differences in the amount of 2,4-D remaining in soil as a result of the type of amendment applied, with the greatest effects in soils with high rates of amendment application. Less 2,4-D mineralization occurs at higher rates of amendment application, possibly resulting in greater residual effects of 2,4-D, unless 2,4-D is not bioavailable to plants due to greater sorption of 2,4-D by soil.

Increasing the length of time between amendment application and 2,4-D application decreased the amount of 2,4-D mineralized. Producers who allow several weeks to pass between amendment and herbicide applications need to consider the possibility of increased herbicide residues in soil.

Soil respiration was greater in soils amended with biosolids than with manure or no amendments. Biosolids stimulated microbial activity in soil to a greater extent than hog manure, but this did not increase herbicide mineralization.

CHAPTER 6

2,4-D Sorption to Amended Soils

6.1 Abstract

2,4-D sorption was measured over a range of ten 2,4-D concentrations in a sandy loam soil amended with fresh hog manure at rates of 0, 56, 112 or 225 kg N ha^{-1}. The soil-water partitioning coefficient (Kd) and the Freundlich distribution coefficient (Kf) were calculated. Greater Kd and Kf values were measured in soils with lower manure application rates and lower 2,4-D concentrations.

6.2 Objectives of the Study

The objective of this study was to determine the effect of fresh hog manure on the sorption of 2,4-D, as influenced by increasing rates of manure and 2,4-D application. This knowledge is useful to producers who utilize hog manure as a soil amendment, in terms of understanding the magnitude of 2,4-D residues that may be in the field available for degradation or plant uptake.

6.3 Materials and Methods

Batch-equilibrium methods were used to determine the soil-water partitioning coefficient (Kd) and the Freundlich distribution coefficient (Kf) of 2,4-D in a manure-amended Long Plain sandy loam soil (see section 5.3.1). The soil was obtained from an agricultural field near Macgregor, MB. This soil had not previously received manure applications. Fresh liquid hog manure was added to sieved (< 2 mm) soil at 0, 0.03, 0.06 or 0.12 L fresh liquid hog manure kg^{-1} soil, equivalent to rates of 0, 21 855, 43 710 or 87 420 L ha^{-1} manure. These application rates were equal to a calculated application rate of 0, 56, 112 and 225 kg N ha^{-1}, assuming the amendment would be incorporated into the top 7.5 cm of soil. Manure application was based on NH_4^+ content because NO_3^- concentration in liquid hog manure is negligible and NH_4^+ makes up the majority of the total N present. Deionized water was added to achieve soil moisture contents of 70% field capacity. After 14 days of incubation at 20°C, the soil was removed and frozen until use.

The top 10 cm of surface soil had a clay content of 13%, pH of 7.7, organic carbon content of 0.6%, and NO_3^--N and P content of 25 and 57 μg g^{-1}, respectively. The fresh hog manure had a pH of 7.4, electrical conductivity of 12.3 dS m^{-1}, total N content of 1.9 kg 1000 L^{-1}, NH_4^+-N content of 1.7 kg 1000 L^{-1}, organic N content of 0.2 kg 1000 L^{-1}, NO_3^--N content of < 0.1 kg 1000 L^{-1}, P content of 0.21 kg 1000 L^{-1} and SO_4^{2-}-S content of 0.07 kg 1000 L^{-1}.

2,4-D stock solutions were prepared by dissolving U-ring-labeled ^{14}C-2,4-D (5.17 mCi $mmol^{-1}$ specific activity; Sigma Chemical Co., St. Louis, MO) and analytical grade 2,4-D (min. 95% purity; Sigma Chemical Co., St. Louis, MO) in 0.01M $CaCl_2$. 2,4-D concentrations used were: 0.0625, 0.125, 0.25, 0.5, 1, 2, 4, 8, 16 and 32 μg mL^{-1} of 2,4-D, containing 10, 20, 40, 80, 160, 320, 640, 1280, 2560, 5120 Bq U-ring-labeled ^{14}C-2,4-D mL^{-1}, respectively. 10 mL of 2,4-D solution was added to 5 g of air-dried soil in Teflon centrifuge tubes. Three replicates of each 2,4-D concentration were carried out for each manure treatment. The solution and soil were rotated in the dark for 24 hours to reach equilibrium and then centrifuged for 10 minutes at 10 000 RPM. Two 1 mL subsamples of the supernatant were removed and each was added to 10 mL of Scinti-Safe scintillation cocktail (Fisher Scientific, Fairlawn, NJ) in plastic scintillation vials (Fisher Scientific, Fairlawn, NJ). Samples were analyzed for ^{14}C activity by LSC (Packard TriCarb 2100TR, Meridian, CT).

Sorption of 2,4-D to soil was determined as the difference between the initial concentration of 2,4-D (C_s) (μg g^{-1}) and the equilibrium concentration of 2,4-D (C_e) (μg mL^{-1}). The soil-water partitioning coefficient, Kd (mL g^{-1}), was determined for each concentration of 2,4-D:

$$Kd = C_s / C_e \qquad \text{(Equation 6.1)}$$

where C_s = the amount of herbicide sorbed to soil at equilibrium (μg g^{-1}), C_e = the amount of herbicide in solution at equilibrium (μg mL^{-1}). Larger Kd values indicate greater sorption of the herbicide compared to smaller Kd values.

The Freundlich distribution coefficient, Kf ($\mu g^{1-1/n}$ g^{-1} $mL^{1/n}$), was calculated using Sigma-Plot 2000 (SPSS Inc.) after log transformation of C_s and C_e:

$$\log C_s = \log Kf + {}^{1/n}\log C_e \qquad \text{(Equation 6.2)}$$

where $1/n$ = slope of the sorption isotherm. The Kf calculation was carried out using the five lowest concentrations of 2,4-D and also the five highest concentrations of 2,4-D and for all ten concentrations at once. This was done to see whether increasing the rate of 2,4-D application had an effect on the Kf value, thereby providing insight as to whether the sorption sites would become saturated. For both the lowest and highest calculations, the isotherms included the point $C_e = 1$, an important consideration as described in Bowman (1982).

Statistical analyses were performed in SAS 8.2 (SAS Institute Inc. 2001) and two-way analysis of variance (ANOVA) for Kd and Kf data and, if applicable, the Tukey comparison test with the significance level set at $\alpha = 0.05$.

6.4 Results and Discussion

All sorption ANOVA tables and Kd values are presented in Appendix IV. The Kd values were significantly affected by the concentration of 2,4-D in solution and the level of manure applied to soil, with values ranging from 0.63 to 4.04 mL g^{-1} (Fig. 6.1). Kd values were greatest for the lowest concentrations of 2,4-D and decreased as 2,4-D concentrations increased. Increasing the rate of 2,4-D application will result in increased bioavailability of 2,4-D to plants, which will increase the risk of damage to sensitive crops.

Greater Kd values occurred in soils with 0, 56 or 112 kg N ha^{-1} than in soil that had received 225 kg N ha^{-1}, with Kd values increasing in the order of $225 < 0 < 112 < 56$ kg N ha^{-1}. Manure adds organic carbon to the soil and it is possible the manure is adding

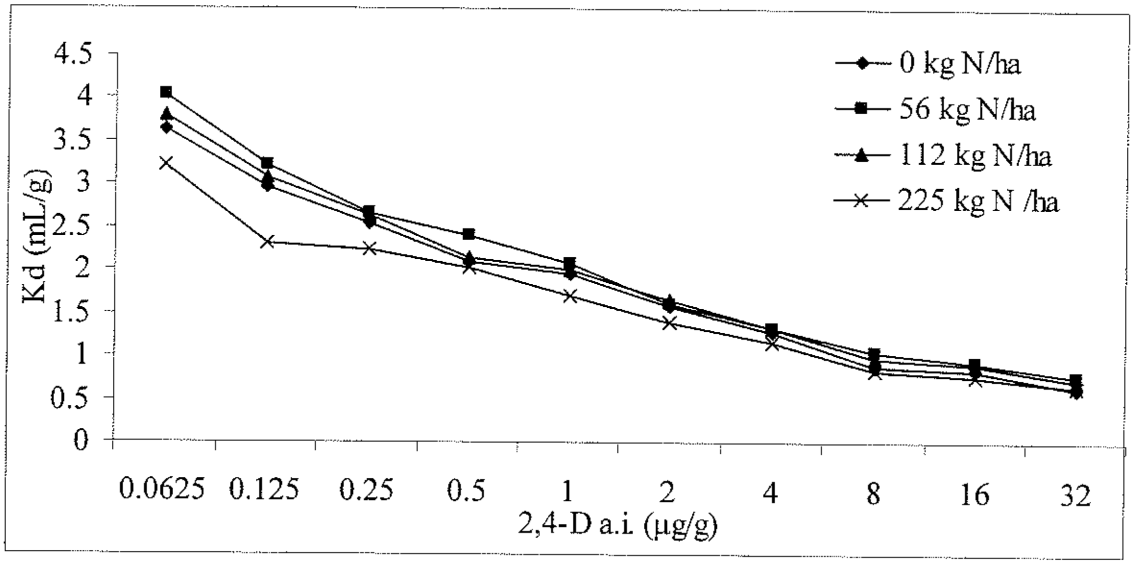

Figure 6.1. Kd values (mL g^{-1}) over a range of 2,4-D concentrations in manure-amended soil.

compounds, such as dissolved organic carbon, that are competing with the 2,4-D for sorption sites on soil (Barriuso et al. 1992).

Both 2,4-D concentration and amendment application rate strongly affected the Kd values for 2,4-D, as well as created a significant interaction, indicating that the change in amendment rates stimulated a change in the effect of increasing the 2,4-D concentration on 2,4-D sorption.

The data provided an excellent fit to the Freundlich distribution model (Eq. 6.2), with r^2 values of 0.98 to 0.99 (Table 6.1). A significant difference was found between the Kf values for the 0.0625 to 1 µg 2,4-D mL^{-1} range and the 2 to 32 µg 2,4-D mL^{-1} range (Table 6.1), which agrees with the results for Kd; lower 2,4-D concentrations have

Table 6.1. Freundlich distribution coefficients (Kf) and isotherm slopes (1/*n*) of 2,4-D over two sets of five concentrations in soil with different application rates of manure, fitted to the equation: Log C_s = log Kf + $^{1/n}$ log C_e, where C_s = concentration of 2,4-D sorbed to soil at equilibrium, C_e = concentration of 2,4-D in solution at equilibrium, *n* = empirical constant

Initial 2,4-D Concentration ($\mu g\ mL^{-1}$)	Manure Application Rate ($kg\ N\ ha^{-1}$)	Kf ($\mu g^{1-1/n}\ g^{-1}\ mL^{1/n}$)	1/*n*	r^2
0.0625 to 1.0	0	1.63 +/- 0.05 ***a****	0.80 +/- 0.02 ***a****	0.99 +/- 0.00 *
	56	1.77 +/- 0.11 **a**	0.80 +/- 0.03 **a**	0.98 +/- 0.03
	112	1.68 +/- 0.05 **a**	0.79 +/- 0.00 **a**	0.99 +/- 0.00
	225	1.51 +/- 0.06 **b**	0.81 +/- 0.01 **a**	0.99 +/- 0.00
2.0 to 32.0	0	1.62 +/- 0.06 **a**	0.70 +/- 0.01 **a**	0.99 +/- 0.00
	56	1.62 +/- 0.06 **a**	0.76 +/- 0.01 **a**	0.99 +/- 0.00
	112	1.66 +/- 0.04 **a**	0.74 +/- 0.03 **a**	0.99 +/- 0.00
	225	1.43 +/- 0.08 **b**	0.74 +/- 0.01 **a**	0.99 +/- 0.00
0.0625 to 32.0	0	1.49 +/- 0.01 **ab**	0.75 +/- 0.01 **a**	0.99 +/- 0.00
	56	1.66 +/- 0.01 **a**	0.76 +/- 0.00 **a**	0.99 +/- 0.01
	112	1.41 +/- 0.16 **b**	0.77 +/- 0.01 **a**	0.99 +/- 0.00
	225	1.38 +/- 0.03 **b**	0.77 +/- 0.00 **a**	0.99 +/- 0.00

*Mean of three replicates followed by standard deviation.

**Means followed by same letters are not significantly different at $P < 0.05$.

significantly higher Kd and Kf values than higher 2,4-D concentrations. Comparing Kf values for the manure treatments shows that the only significant difference was a lower value of Kf for the 225 kg N ha^{-1} treatment in both 2,4-D concentration ranges.

Values for the Freundlich slope of the isotherm ($1/n$ value) for the two 2,4-D concentration ranges were less than unity, ranging from 0.74 to 0.80 (Table 6.1), indicating that sorption of 2,4-D decreased as the concentration of 2,4-D present in solution increased. There were no significant differences in $1/n$ for manure treatments, but $1/n$ was lower for the 2 to 32 μg mL^{-1} range than the 0.0625 to 1 μg mL^{-1} range. This is an indication that a greater portion of the chemical could be held at lower concentrations than at greater concentrations.

Because 2,4-D is a weakly acidic herbicide (pKa = 2.8), it is predominantly found in its anionic form at the slightly alkaline pH of the soil used in this experiment (Table 5.1). Little bonding of anionic 2,4-D molecules in soil is expected due to the repulsion between 2,4-D and the negatively charged soil constituents (Barriuso et al. 1997; Wu et al. 2000). The addition of manure to soil in the current study only shows an effect on Kf values at a high application rate, while Kd values were greater in soils with lower manure application rates. In other studies, the addition of organic amendments to soil has been found to increase 2,4-D sorption compared to soil alone (Barriuso et al. 1997; O'Connor et al. 1981). 2,4-D Kd values in composted municipal waste of 5.63 L kg^{-1} were over ten times greater than in soil alone (0.40 kg L^{-1}) (Barriuso et al. 1997). O'Connor et al. (1981) found no effect of fresh sludge additions to soil on 2,4-D sorption, but adding preconditioned sludge to soil increased 2,4-D sorption. The preconditioned sludge was believed to contain more humus-like components that increased 2,4-D sorption (O'Connor et al. 1981). Wu et al. (2000) found that 2,4-D had a Kf constant of 7.3 (no unit given) in surface soils treated with sewage sludge. This high Kf value can likely be attributed to the high soil/sewage sludge organic carbon content of 9.2% (Wu et al. 2000).

6.5 Summary and Conclusions

Greater 2,4-D Kd and Kf values occurred in soils with lower 2,4-D concentrations and with 0, 56 or 112 kg N ha^{-1} of manure than in soil that had received 225 kg N ha^{-1}. The slope of the isotherms indicated decreasing herbicide sorption with increasing 2,4-D concentrations. There is more plant-available 2,4-D in soils with high manure application rates as a result of decreased 2,4-D sorption, which may lead to damage of sensitive crops.

Kd and Kf values are used as parameters in modelling pesticide fate and leaching; however, there is no standard protocol in the use of these values or the herbicide concentrations at which they are determined. The problem with this lack of protocol is seen clearly in this study where large differences in Kd values are seen among different concentrations of pesticide. This presents a challenge when creating models without a standardized procedure, resulting in an over or underestimation of pesticide persistence and movement in the environment.

CHAPTER 7

General Discussion

The information available on the effects of hog manure on the mineralization of pesticides was limited; therefore, this work provides information to Manitoba producers who utilize manure as a soil amendment and use glyphosate, trifluralin and 2,4-D in their crop protection plans.

The effect of a history of hog manure application on glyphosate and trifluralin mineralization was not consistent among soils and fresh manure generally had little effect on the mineralization of glyphosate and trifluralin. It was expected that this study would show an increase in microbial activity that would relate to an increase in herbicide mineralization. Fauci and Dick (1994) and Hadas et al. (1996) found that a history of manure application to soil increased microbial biomass and activity, as well as the pool of available organic C in soil.

There was a general increase in total glyphosate and trifluralin mineralization as a result of a history of manure application in the Birtle soil relative to soil without a history, which had a 40-year history of manure application. These increases were not generally seen in the Neepawa soils with intermittent manure application over 35 years, or in Decker soils with 10 years of manure history.

Fresh manure effects on the mineralization of glyphosate and trifluralin in this study were dependent on the history of manure application. While the addition of fresh manure has been shown to stimulate microbial activity in soil (Lalande et al. 2000), it does not necessarily stimulate microbial mineralization of glyphosate and trifluralin. Doyle et al. (1978) found that manure-amended soil rapidly degraded trifluralin compared to non-amended soil, while Moorman et al. (2001) found that compost and manure amendments had no effect on trifluralin degradation.

The addition of municipal biosolids to soil had less of an inhibitory effect on 2,4-D mineralization compared to fresh hog manure additions. Municipal biosolids have generally been shown to have stimulatory effects on microbial activity (Barriuso et al. 1997; Quemada and Menacho 2001). O'Connor et al. (1981) have shown increased 2,4-D mineralization as a result of the addition of biosolids to soil, and others found that dairy manure also increased 2,4-D mineralization compared to non-amended soil (Entry and Emmingham 1995). However, Barriuso et al. (1997) found that 2,4-D mineralization decreased in biosolid-amended soil compared to non-amended soil. As indicated by the increased soil respiration measured in biosolid-amended soil compared to manure- or non-amended soils in Chapter 5, it was anticipated that 2,4-D mineralization in this study would be greater in biosolid-amended soil compared to non-amended soil, but this was not the case.

Glyphosate and trifluralin sorption were not affected by fresh manure application. In contrast, Kd and Kf values for 2,4-D were greater in soils with lower amounts of manure amendment added. Sorption of pesticides has been shown to be affected by amendment additions. A study by Barriuso et al. (1997) measured increased sorption of 2,4-D in biosolids compared to soil, while O'Connor et al. (1981) found that the addition of pre-conditioned biosolids increased 2,4-D sorption compared to fresh biosolids in soil. The results of this study indicate that fresh manure applications increase 2,4-D sorption by soil, but this effect was dependent on herbicide application rates and high manure application rates.

Laboratory microcosms and field mineralization experiments have the potential to produce different results in studies due to inherent in-field variation, as well as lack of control over environmental factors that would play a significant role in microbial activity and populations. Because of the controlled laboratory situation of these studies, translating these results into suggestions for producers is difficult. However, most of the statistical differences between laboratory treatments in this study suggest that manure has little effect on the fate of glyphosate and trifluralin in field soils. In contrast, 2,4-D fate was more strongly and consistently influenced by manure application, which is seen specifically over a range of manure application rates.

While the emphasis in this study has focused on the total mineralization of pesticides, it is important to look at these results from another angle: what is remaining in the soil? A significant implication for producers facing the issues of manure amendment and pesticide application is to realize that while some treatments may increase total pesticide mineralization, a large amount of pesticides remain in the soil. For instance, total trifluralin mineralization averaged 10% in these experiments, leaving up to 90% of the chemical in the soil or being volatilized. This poses a serious concern, not only for herbicide persistence and subsequent damage to susceptible crops, but also to the environment and water sources. The chemical present in soil may be transported through leaching or erosion to sensitive areas. Pesticide volatilization contaminates the atmosphere and deposition of pesticides by rainfall may injure crops (Hill et al. 2002). While glyphosate and 2,4-D typically have greater total mineralization and shorter half-lives than trifluralin, which is not due to removal of trifluralin from soil solution due to sorption, these compounds are still potential environmental contaminants.

CHAPTER 8

Summary and Conclusions

Laboratory studies were conducted using soil microcosms to determine the effect of soils with a history of hog manure application and fresh manure applications on the mineralization of glyphosate and trifluralin in soils. Soil microcosms were also used to determine the effect of fresh hog manure and municipal biosolids on the mineralization of 2,4-D in soil. Batch equilibrium techniques were used to measure the sorption of herbicides in soil by calculating the soil-water partitioning coefficient (Kd) for glyphosate, trifluralin and 2,4-D, and also by calculating the Freundlich distribution coefficient (Kf) for 2,4-D.

The mineralization rates of glyphosate, trifluralin and 2,4-D fit closely to the mineralization model, indicating that mineralization of these herbicides followed a first-order reaction.

The effect of a history of hog manure application on herbicide persistence in soil was not definitive because this study observed stimulatory, inhibitory and no effects on the mineralization of glyphosate and trifluralin. Increased herbicide mineralization due to a history of manure applications was generally seen in the Birtle soil with a 40-year history of manure application, but not in Neepawa or Decker soils which had received manure applications less frequently or over fewer years.

Fresh manure had little effect on the mineralization of glyphosate and trifluralin. In the experiment studying total CO_2 production, an application of fresh hog manure did not stimulate microbial respiration beyond the first two weeks. These results may explain why fresh manure applications had no major and consistent effects on glyphosate and trifluralin mineralization rates in soil.

The addition of municipal biosolids to soil had less inhibitory effects on 2,4-D mineralization compared to fresh hog manure additions. Also, more 2,4-D was mineralized in a clay loam soil than in sandy loam, silty loam or sandy clay loam soils. Increasing the application rate of manure and biosolids decreased 2,4-D mineralization. Applying 2,4-D up to 28 days after the manure or biosolids application decreased 2,4-D mineralization compared to simultaneous applications of 2,4-D and amendment.

Both Kd and Kf values are a measure of sorption. Kd values were determined for glyphosate and trifluralin to establish the amount of initially applied herbicide that had sorbed to the soil. Sorption of glyphosate and trifluralin was not affected by fresh manure application, but more glyphosate sorbed to soils without a manure application history than to soils with a history. Increased sorption of glyphosate to soils with a manure application history may increase the risk of glyphosate movement with eroded soil particles and cause environmental contamination. Kd and Kf values for 2,4-D were greater in soils with lower concentrations of 2,4-D and at lower amounts of fresh manure application.

It was of importance to conclude whether histories of manure application or fresh manure applications increased the risk of trifluralin persistence in soil. This study suggests that the effects of manure applications, as shown in the laboratory, will not increase the risk of herbicide carryover and damage to subsequent crops due to increased herbicide persistence.

Because of the increased area cropped with glyphosate-tolerant canola, more 2,4-D is being applied to control glyphosate-tolerant volunteers. 2,4-D residue in soil can harm sensitive crops, like peas, if they are planted too soon after 2,4-D application. This study demonstrates that this risk is greater in sandy clay loam soils than in clay soils due to decreased total mineralization of 2,4-D in these soils. Producers who utilize manure or biosolids as soil amendments also risk increasing 2,4-D carryover damage if amendments are applied at high rates, or if the 2,4-D is applied several weeks after amendment application.

Further study needs to take place concerning the effects of manure and biosolids on herbicide mineralization and sorption. Field work is needed to determine whether the laboratory results are directly transferable to processes occurring in the field, or whether in-field variations in soil and environmental factors erase or enhance the effects of hog manure and biosolids amendments. More complete study of herbicide sorption to biosolid-amended soils and to different soil textures, including the effects of aged biosolids and manure versus fresh, or dried amendments versus moist, is needed to provide Manitoba producers with a more comprehensive understanding of herbicide fate in amended soils.

Another area of further study is to investigate the presence and persistence of pesticide metabolites. This study only measured total pesticide mineralization, and it would be valuable to identify initial degradation of the pesticide molecule and subsequent metabolite mineralization in order to create a timetable of degradation events and determine whether the fractions left are harmful or benign to agronomic and environmental concerns.

CHAPTER 9

Contribution to Knowledge

Hog manure applications had no strong effect on glyphosate and trifluralin mineralization, indicating that producers can continue to apply manure without risking an increase in glyphosate and trifluralin persistence. However, 2,4-D mineralization decreased as manure and biosolid application rate increased and sorption of 2,4-D also decreased as manure application rate increased. This suggests that producers need to manage manure applications wisely when considering 2,4-D application in order to reduce the risk of damage to sensitive crops. The high rate of manure application resulted in the presence of more 2,4-D residue in soil that is likely plant-available as the 2,4-D is not being mineralized or sorbed to soil.

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APPENDICES

I. Calculations for Amendment Application Rates

1. Volume amendment needed (ha^{-1})= (Target N application rate) / (NH_4^+ concentration of amendment)

2. Volume of soil (ha furrow $slice^{-1}$) = (7.5 cm) * (10 000 m^2)

3. Mass of soil (ha furrow $slice^{-1}$) = (Volume soil) * (Bulk density of soil)

4. Volume amendment applied to soil = (Volume amendment needed) / (Mass soil)

5. Sample calculation for fresh liquid hog manure application:

   (1) (112 kg NH_4^+ ha^{-1}) / (2.4 kg NH_4^+ 1000 L^{-1}) = 46 667 L ha^{-1} fresh hog manure needed

   (2) (7.5 cm) * (10 000 m^2) = 750 m^3 of soil in ha furrow slice

   (3) (750 m^3) * (1.05 Mg m^{-3}) * (1000 kg Mg^{-1}) = 787 500 kg ha^{-1} soil in ha furrow slice

   (4) (46 667 L ha^{-1}) / (787 500 kg ha^{-1}) = 0.059 L manure kg^{-1} soil in microcosm

II. Calculations for Herbicide Application Rates

1. Amount herbicide needed (ha^{-1})= (Herbicide application rate) * (Concentration of active ingredient)

2. Volume of soil (ha furrow $slice^{-1}$) = (0.1 m) * (10 000 m^2)
   (Assume herbicide will be applied and incorporated into top 10 cm of soil)

3. Mass of soil (ha furrow $slice^{-1}$) = (Volume soil) * (Bulk density of soil)

4. Amount herbicide applied to soil = (Amount herbicide needed) / (Mass soil)

5. Sample calculation for glyphosate application rate:

   (1) (2.47 L ha^{-1}) * (0.356 kg L^{-1}) = 0.88 kg ha^{-1} active ingredient (a.i.) to be applied

   (2) (0.1 m) * (10 000 m^2) = 1 000 m^3 soil in ha furrow slice

   (3) (1 000 m^3) * (1.3 Mg m^{-3}) * (1000 kg Mg^{-1}) = 1 300 000 kg soil in ha furrow slice

   (4) (0.88 kg ha^{-1}) / (1 300 000 kg) = 6.77×10^{-7} kg a.i. kg^{-1} soil in microcosm (or g a.i. g^{-1} soil)

6. Total a.i. needed per microcosm = (Amount herbicide needed per microcosm) * (Amount of soil per microcosm)

7. Total a.i. needed if met only by radioactive a.i. = (Total a.i. needed) * (a.i. radioactivity)

8. Apply 8 333 Bq per microcosm: Total radioactivity needed = (8 333 Bq) / (Total a.i. from radioactive a.i.)

9. Amount of a.i. supplied by radioactivity = (Total a.i. needed per microcosm) / (Total radioactivity needed)

10. Amount of a.i. needed from analytical grade a.i. = (Total a.i. needed per microcosm) – (Amount of a.i. supplied by radioactivity)

11. Sample calculation for radioactive glyphosate solution:

    (1) (6.77×10^{-7} g a.i. g^{-1} soil) * (30 g soil in each microcosm) = 2.03×10^{-5} g a.i. needed for study (or 20.3 μg a.i. glyphosate)

    (2) (20.3 μg a.i.) * (0.027 μCi μg^{-1} glyphosate) = 0.55 μCi per microcosm

(3) (8 333 Bq) * (1 µCi / 37 000 Bq) / (0.55 µCi per microcosm) = 0.41 (or 41%) of a.i. met by radioactive a.i.

(4) (20.3 µg a.i.) * (41%) = 8.32 µg a.i. needed from radioactive a.i.

(5) (20.3 µg a.i.) – (20.3 µg a.i. * 41%) = 11.98 µg a.i. needed from analytical grade a.i.

III. Mineralization Charts

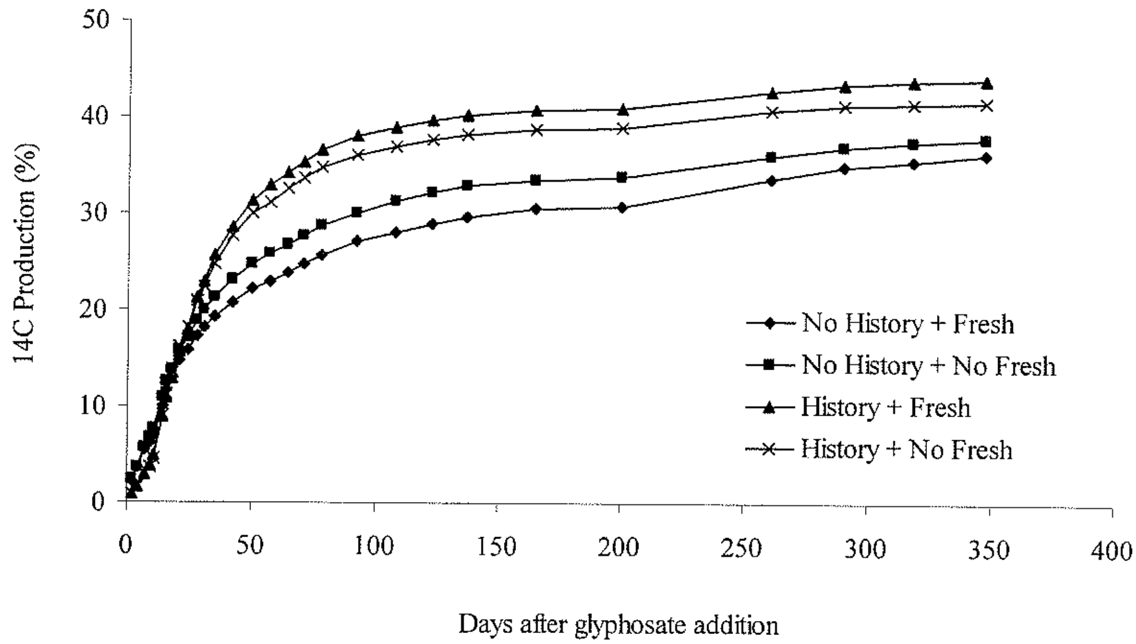

Figure 1. Glyphosate mineralization (measured as % ^{14}C production) in Birtle soil in Chapter 3.

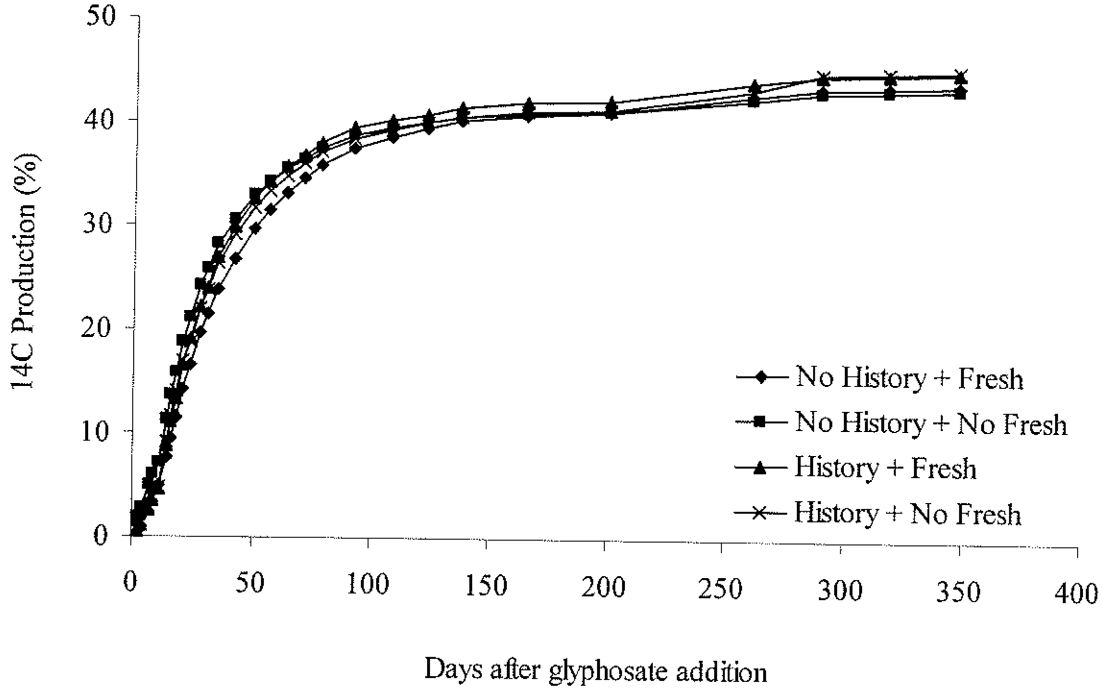

Figure 2. Glyphosate mineralization (measured as % ^{14}C production) in Neepawa soil in Chapter 3.

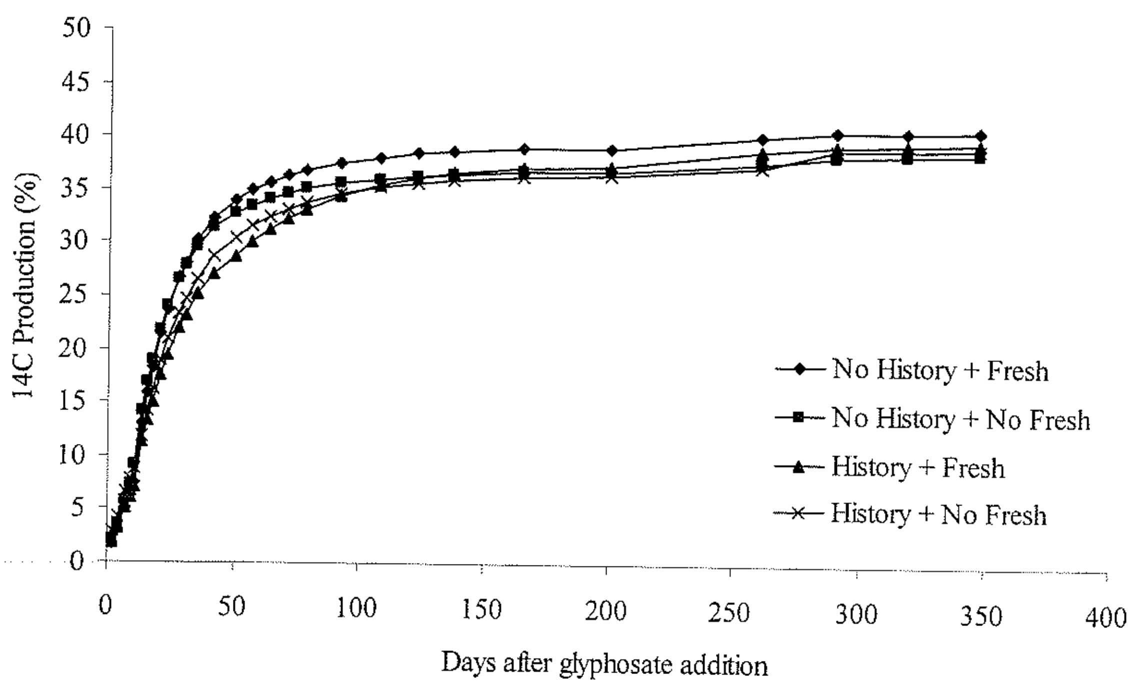

Figure 3. Glyphosate mineralization (measured as % ^{14}C production) in Decker soil in Chapter 3.

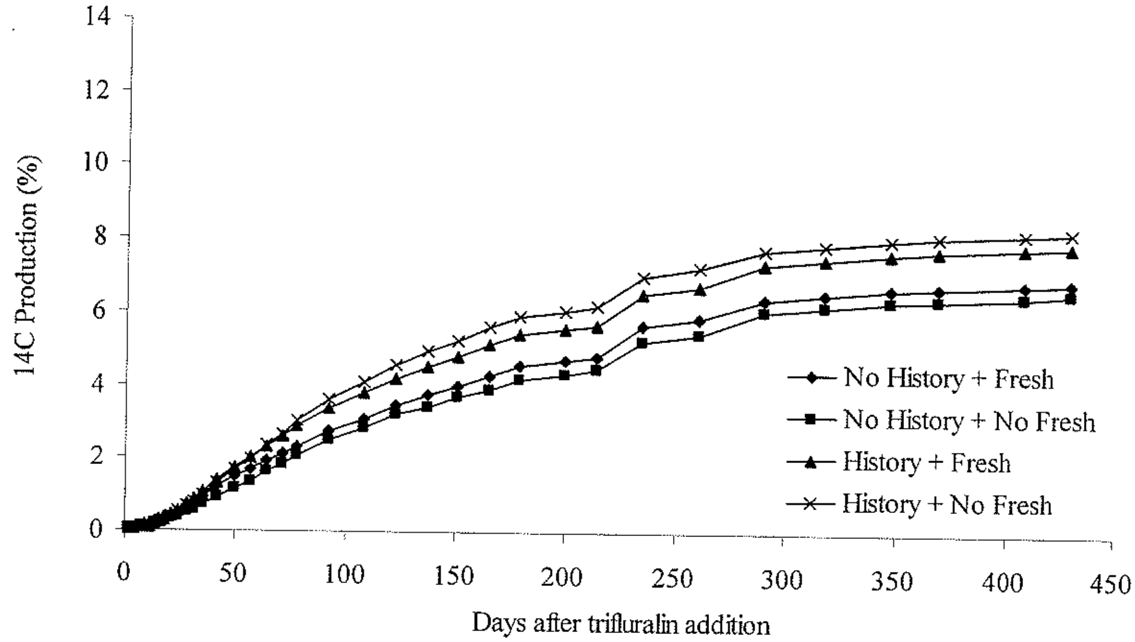

Figure 4. Trifluralin mineralization (measured as % ^{14}C production) in Birtle soil in Chapter 3.

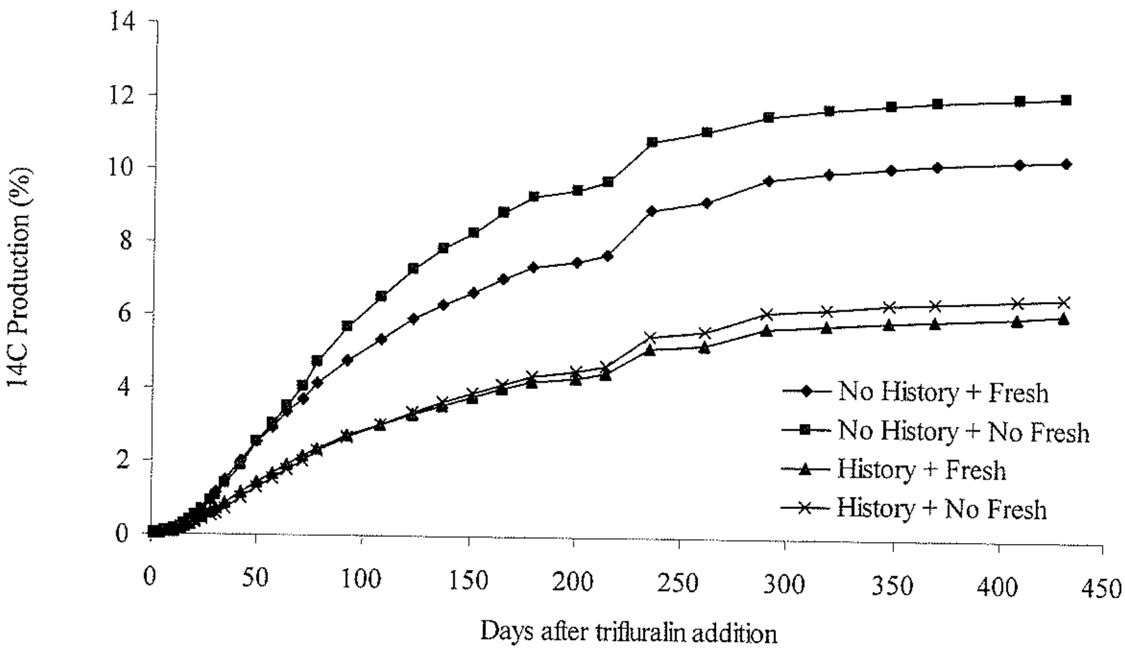

Figure 5. Trifluralin mineralization (measured as % ^{14}C production) in Neepawa soil in Chapter 3.

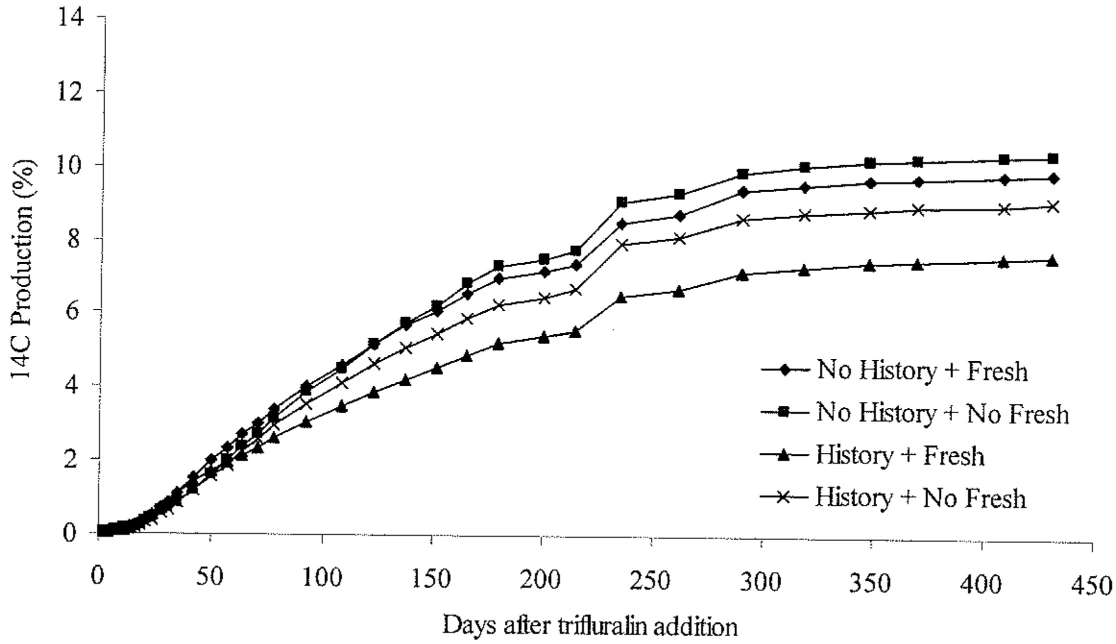

Figure 6. Trifluralin mineralization (measured as % ^{14}C production) in Decker soil in Chapter 3.

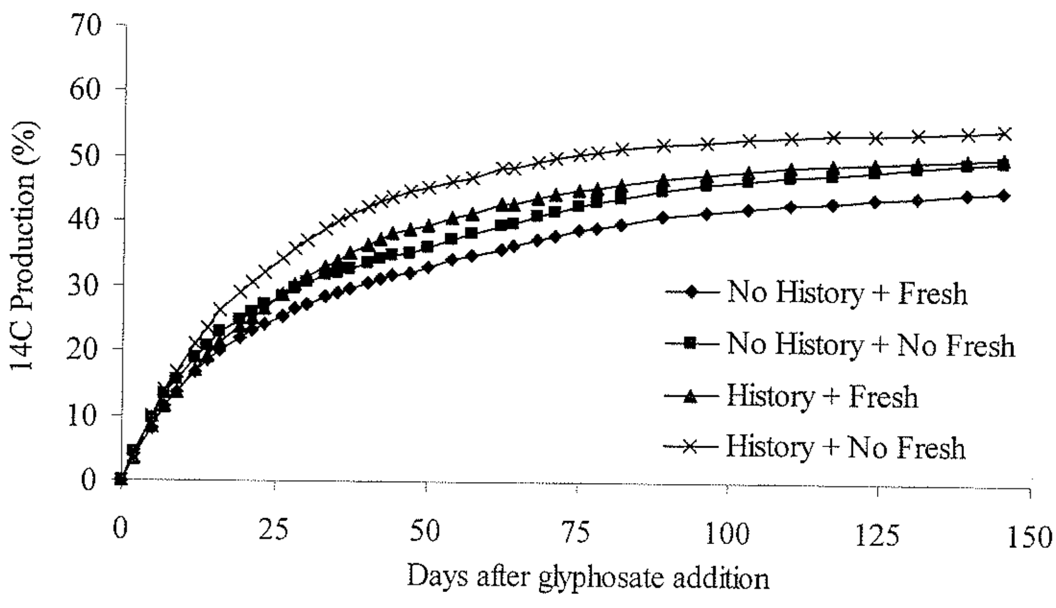

Figure 7. Glyphosate mineralization (measured as % ^{14}C production) in Birtle soil in Chapter 4.

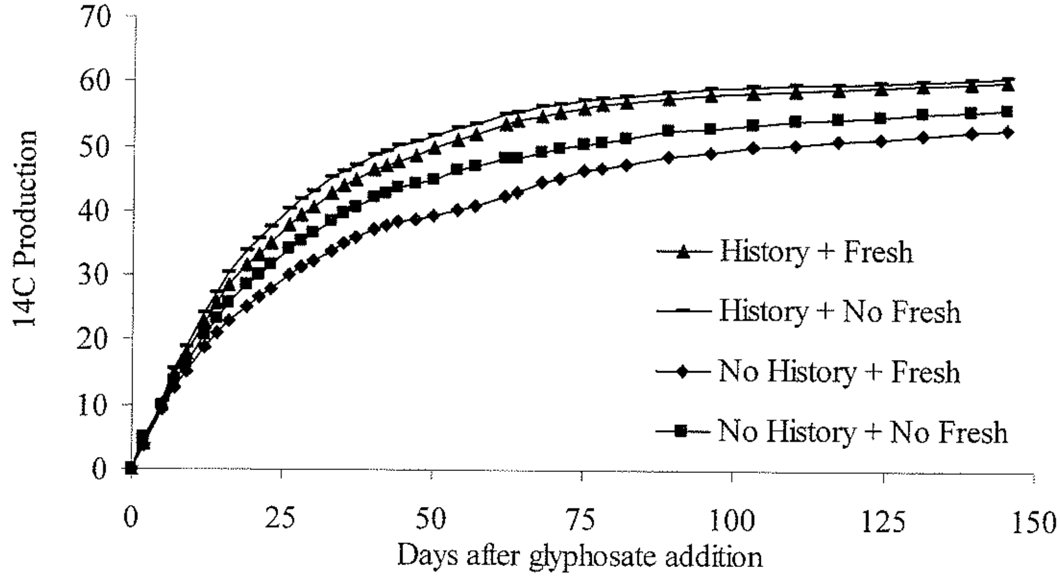

Figure 8. Glyphosate mineralization (measured as % ^{14}C production) in Neepawa soil in Chapter 4.

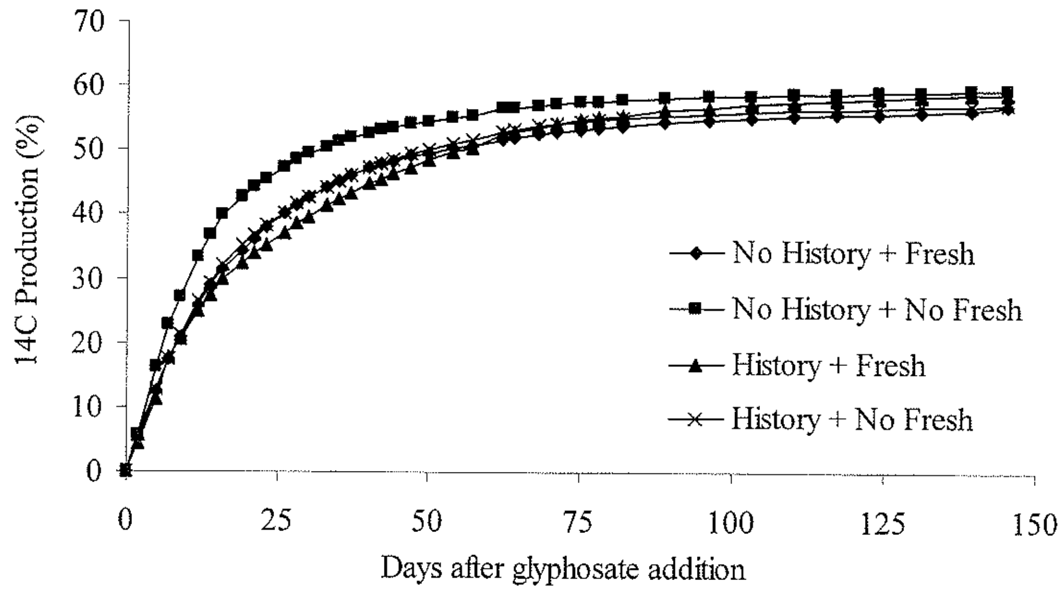

Figure 9. Glyphosate mineralization (measured as % ^{14}C production) in Decker soil in Chapter 4.

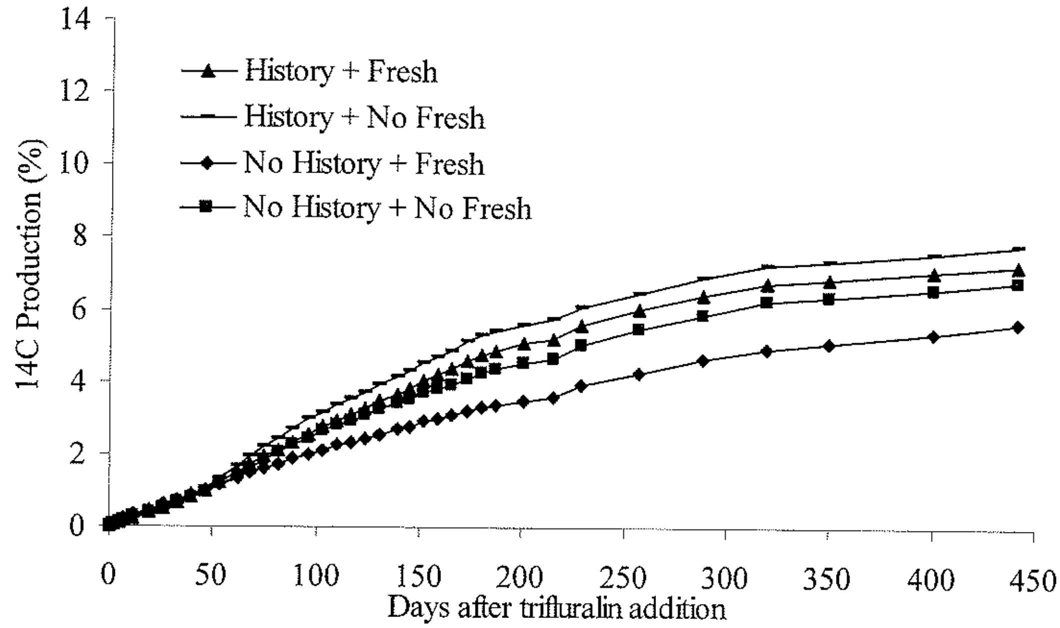

Figure 10. Trifluralin mineralization (measured as % ^{14}C production) in Birtle soil in Chapter 4.

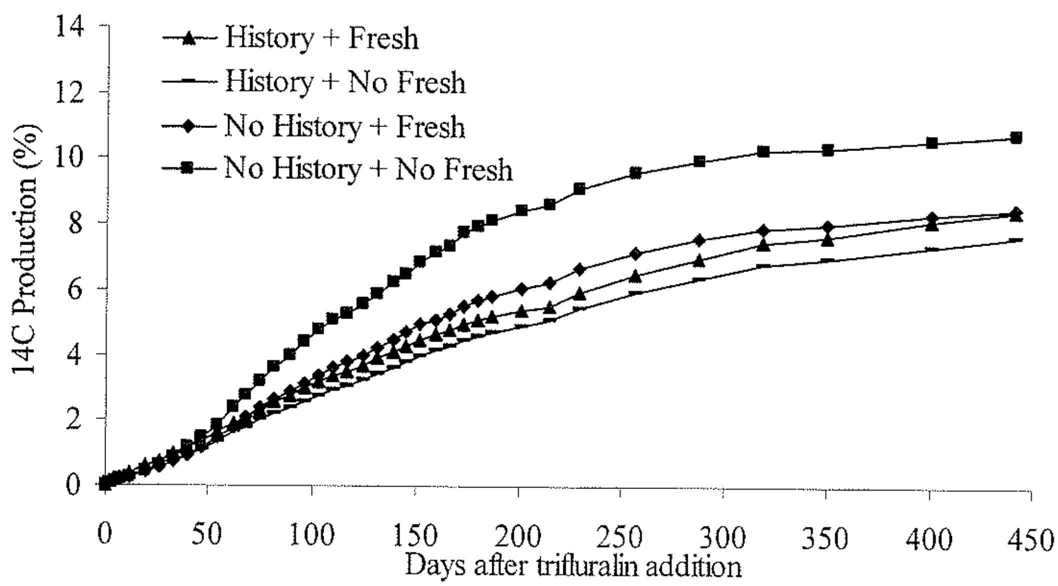

Figure 11. Trifluralin mineralization (measured as % ^{14}C production) in Neepawa soil in Chapter 4.

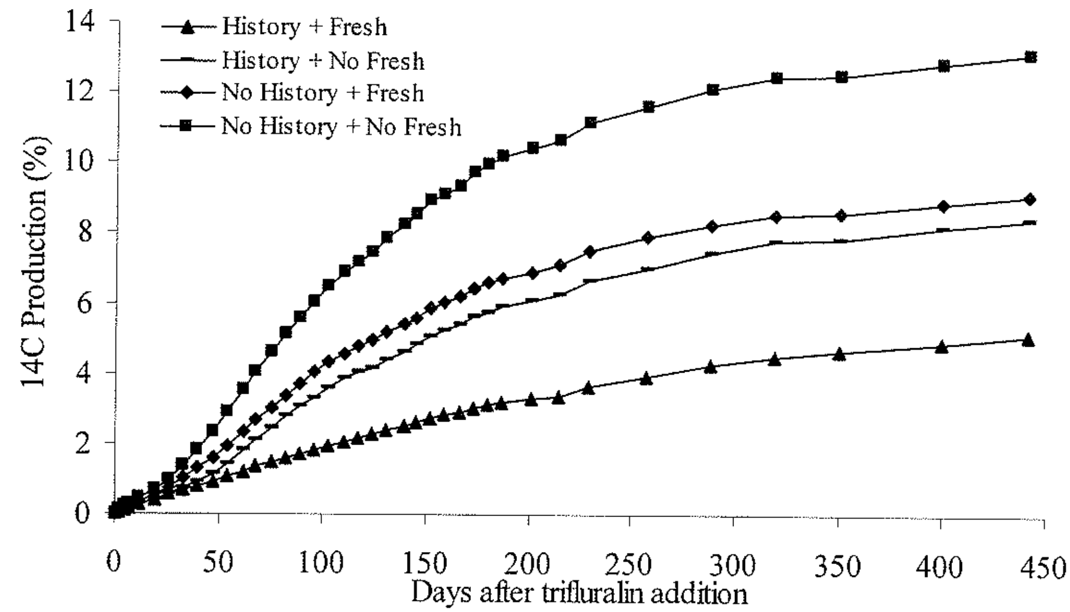

Figure 12. Trifluralin mineralization (measured as % ^{14}C production) in Decker soil in Chapter 4.

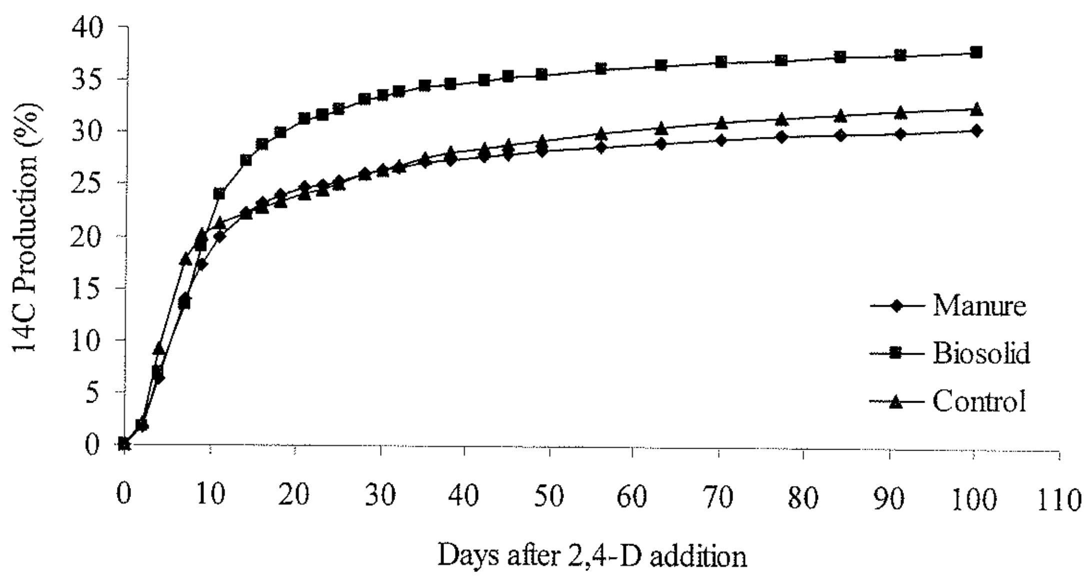

Figure 13. 2,4-D mineralization (measured as % ^{14}C production) in clay loam soil.

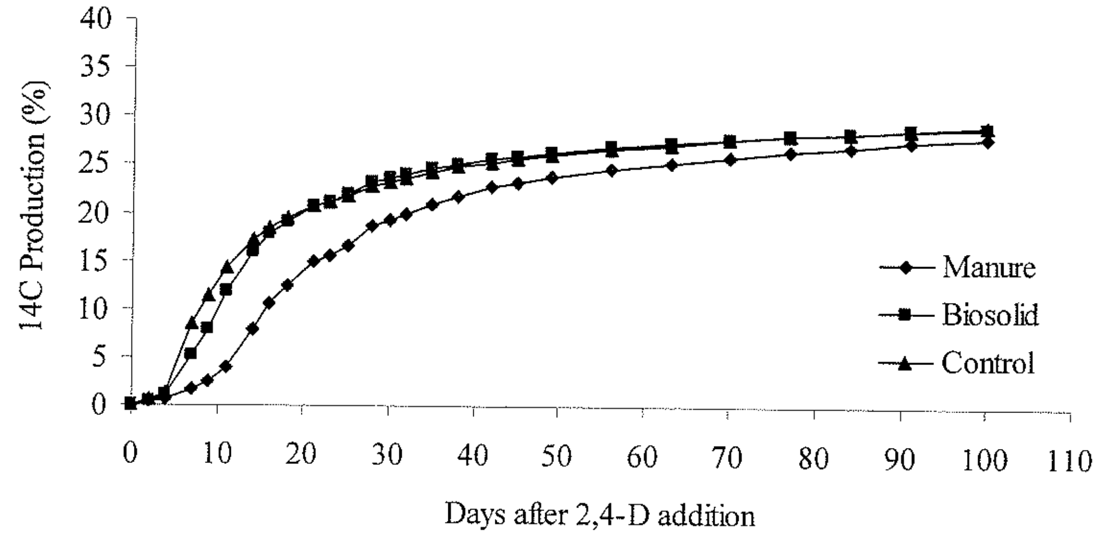

Figure 14. 2,4-D mineralization (measured as % ^{14}C production) in sandy loam soil.

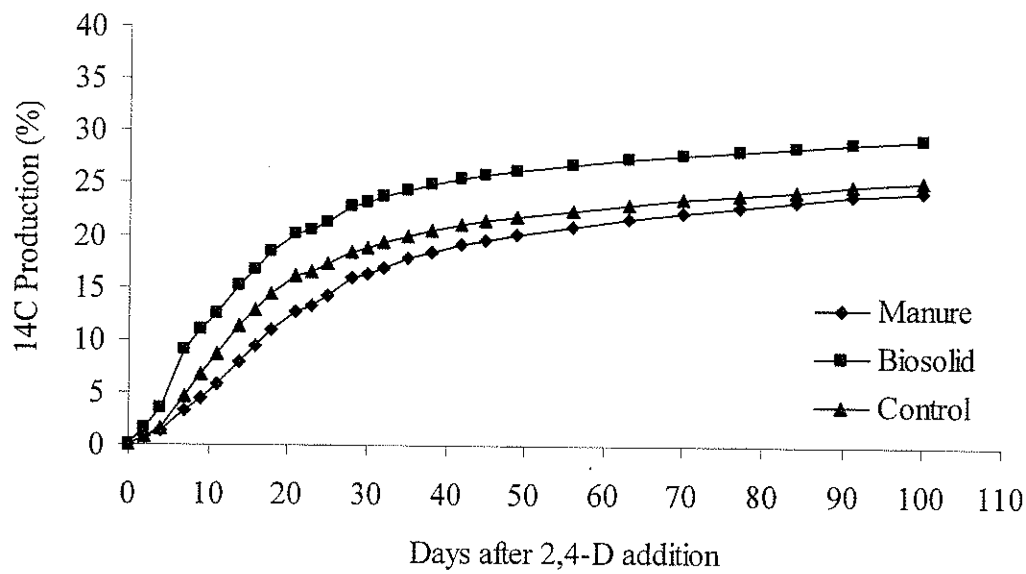

Figure 15. 2,4-D mineralization (measured as % ^{14}C production) in silty loam soil.

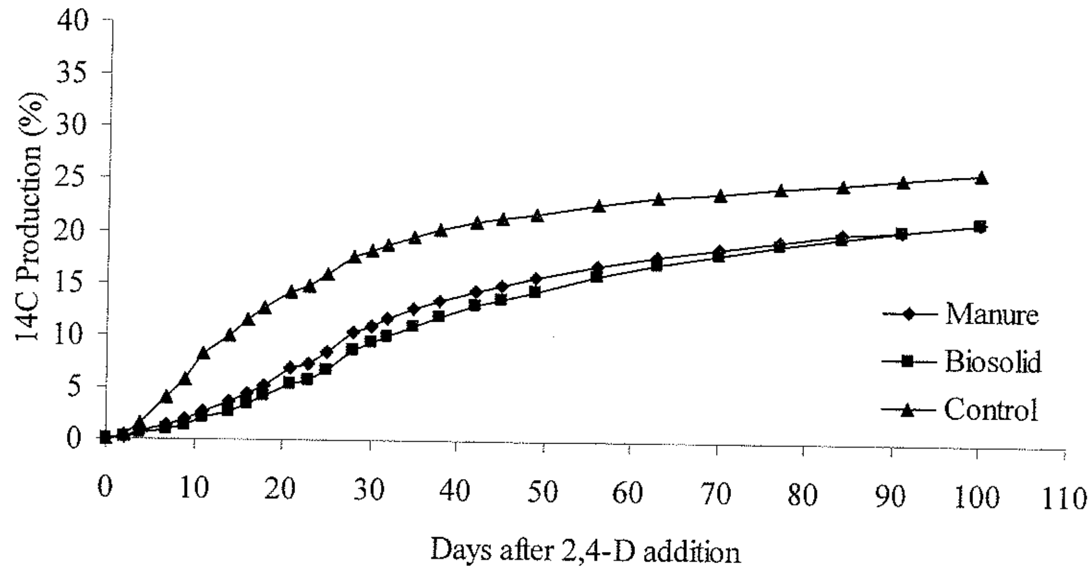

Figure 16. 2,4-D mineralization (measured as % ^{14}C production) in sandy clay loam soil.

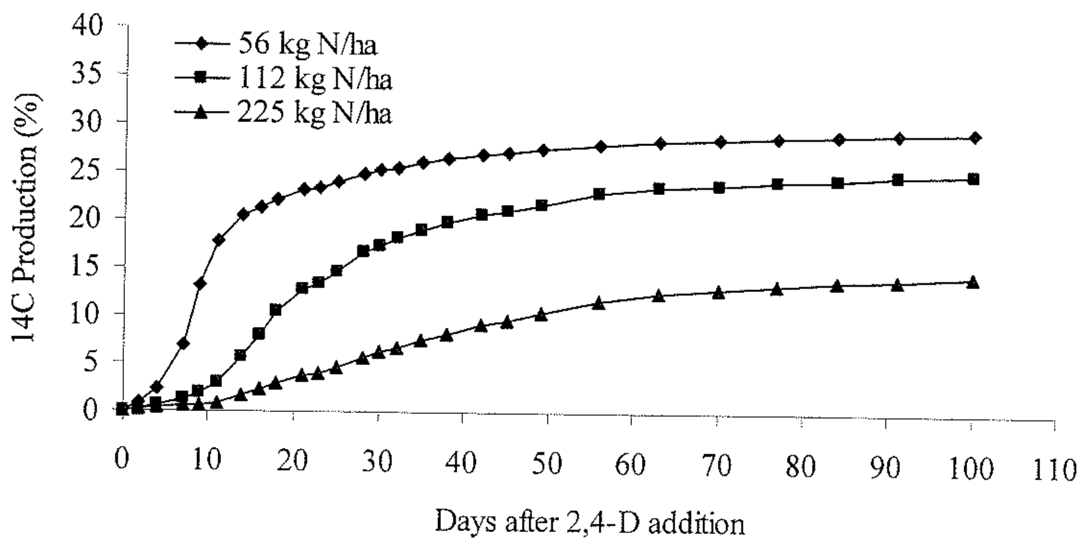

Figure 17. 2,4-D mineralization (measured as % ^{14}C production) in sandy loam soil amended with different rates of manure.

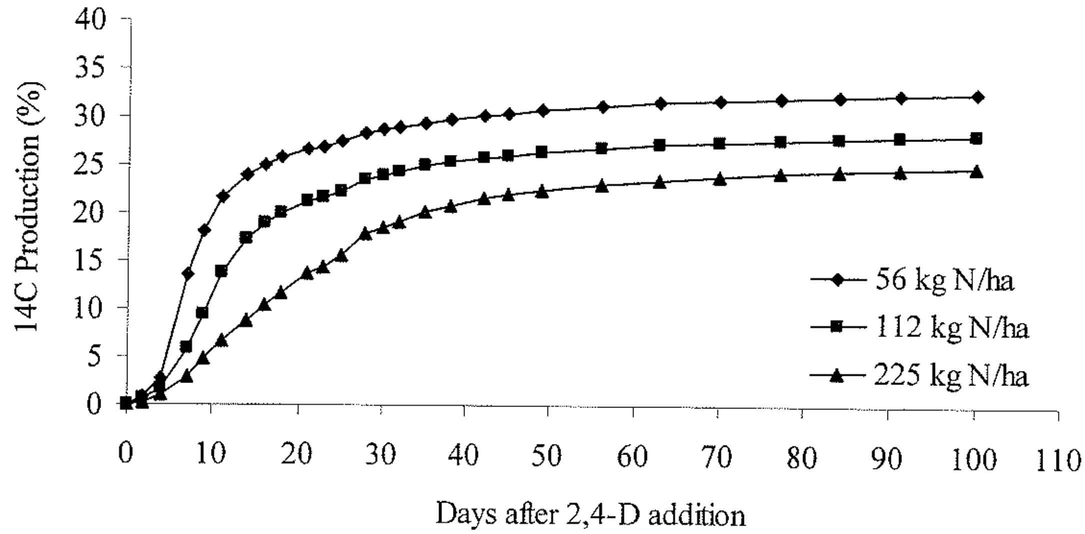

Figure 18. 2,4-D mineralization (measured as % ^{14}C production) in sandy loam soil amended with different rates of municipal biosolids.

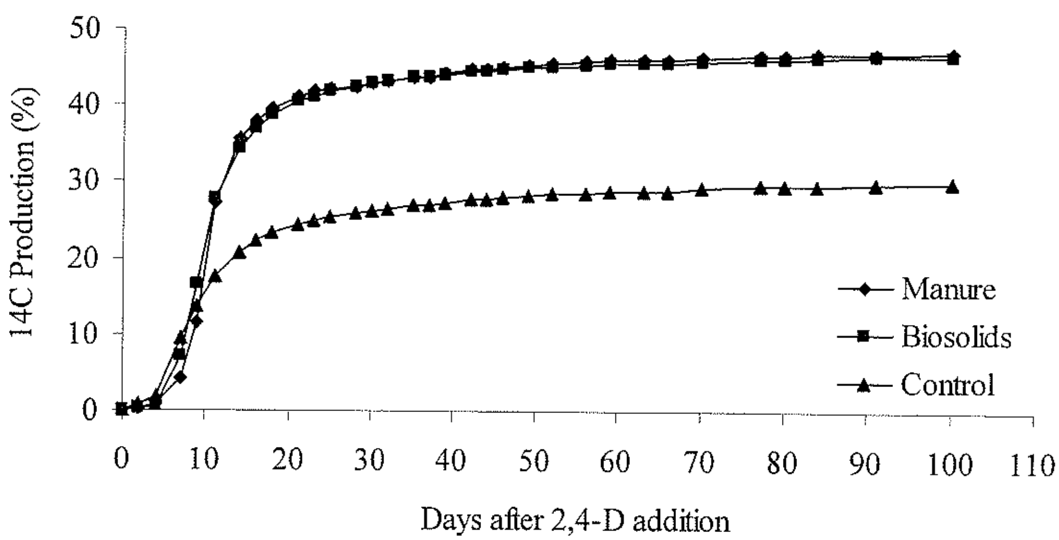

Figure 19. 2,4-D mineralization (measured as % ^{14}C production) in sandy loam soil incubated for 0 days prior to 2,4-D application.

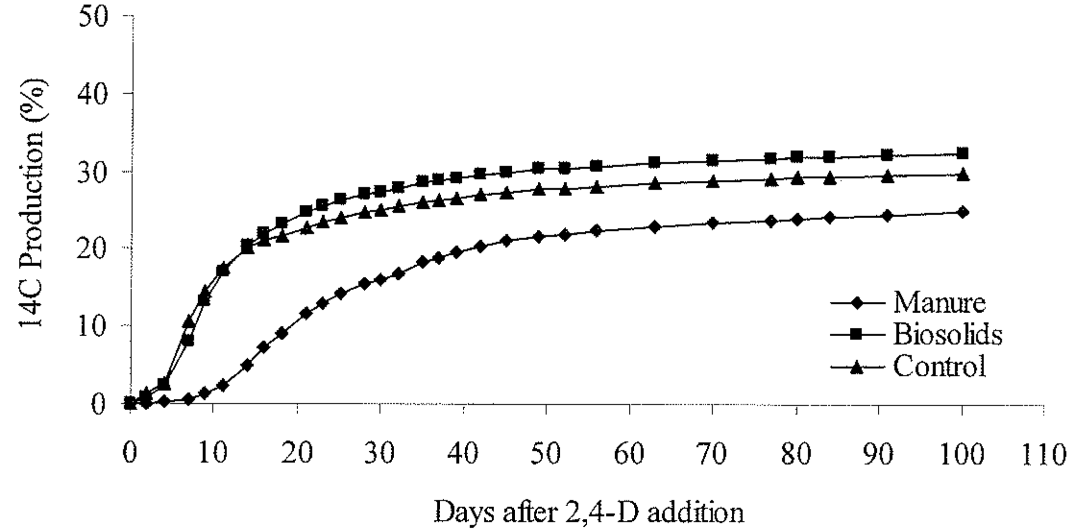

Figure 20. 2,4-D mineralization (measured as % ^{14}C production) in sandy loam soil incubated for 7 days prior to 2,4-D application.

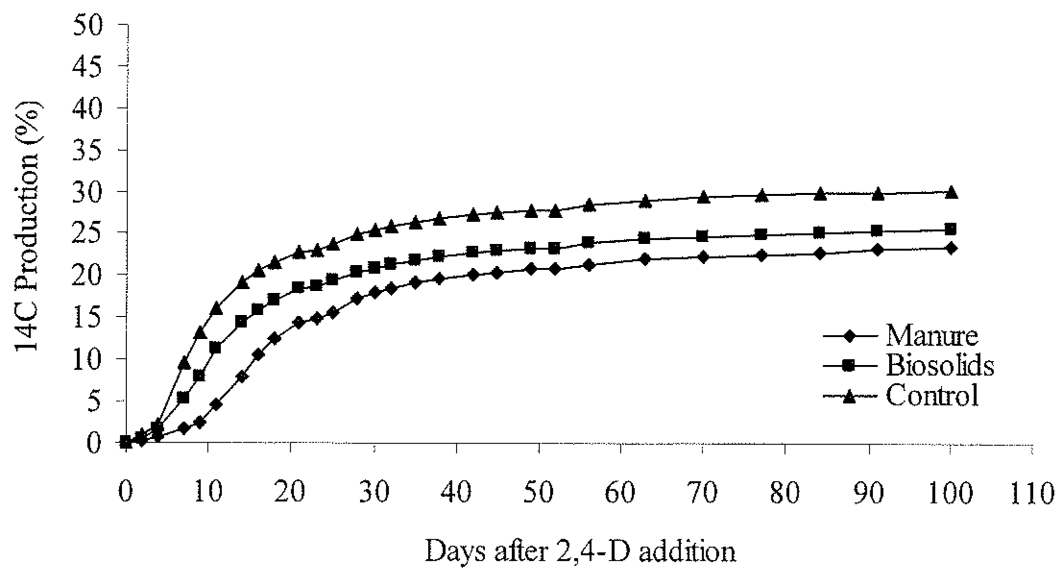

Figure 21. 2,4-D mineralization (measured as % ^{14}C production) in sandy loam soil incubated for 14 days prior to 2,4-D application.

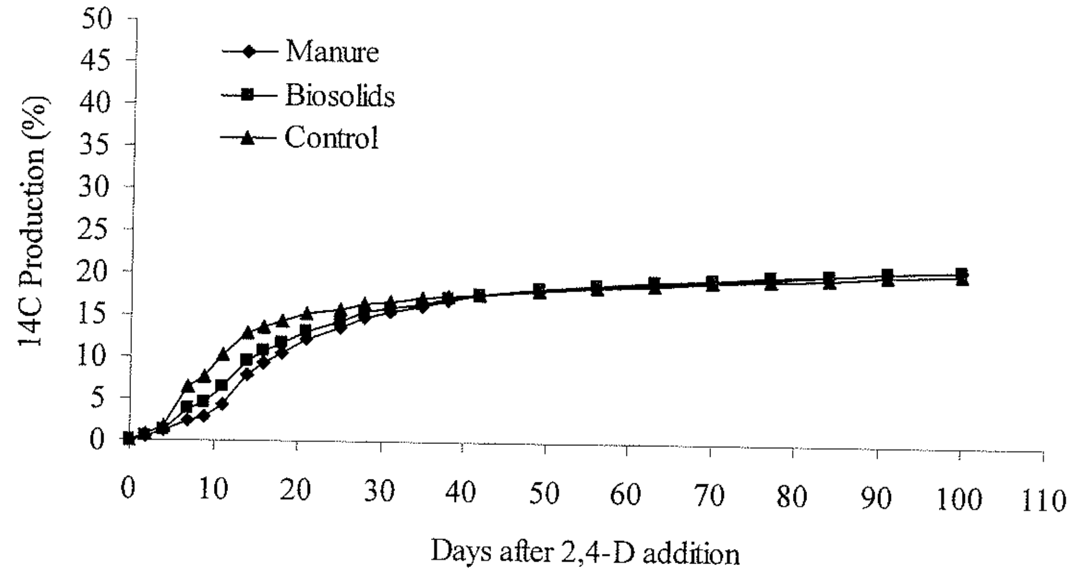

Figure 22. 2,4-D mineralization (measured as % ^{14}C production) in sandy loam soil incubated for 28 days prior to 2,4-D application.

IV. ANOVA Tables

Table 1. DF, SS, F values and P levels of the two-way analysis of variance of total glyphosate mineralization in Birtle soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	199.008	78.96	<0.0001
History	1	175.797	209.24	<0.0001
Fresh Manure	1	0.33	0.39	0.5483
History*Fresh	1	22.88	27.23	0.0008
Error	8	6.7212		

*Significant at P < 0.05.

Table 2. DF, SS, F values and P levels of the two-way analysis of variance of total glyphosate mineralization in Neepawa soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	2.7186	0.66	0.5982
History	1	1.4352	1.05	0.3358
Fresh Manure	1	0.161	0.12	0.7404
History*Fresh	1	1.1224	0.82	0.3916
Error	8	10.94827		

*Significant at P < 0.05.

Table 3. DF, SS, F values and P levels of the two-way analysis of variance of total glyphosate mineralization in Decker soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	11.9183	6.09	0.0184
History	1	4.1184	6.31	0.0362
Fresh Manure	1	0.03968	0.06	0.8114
History*Fresh	1	7.7602	11.9	0.0087
Error	8	5.218		

*Significant at $P < 0.05$.

Table 4. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate mineralization rates (k) in Birtle soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	1.53×10^{-5}	11.07	0.0032
History	1	1.344×10^{-5}	29.17	0.0006
Fresh Manure	1	1.84×10^{-6}	3.99	0.0807
History*Fresh	1	2.0×10^{-8}	0.05	0.8369
Error	8	3.69×10^{-6}		

*Significant at $P < 0.05$.

Table 5. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate mineralization rates (k) in Neepawa soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	6.886×10^{-5}	10.85	0.0034
History	1	3.52×10^{-6}	1.66	0.233
Fresh Manure	1	3.234×10^{-5}	15.29	0.0045
History*Fresh	1	3.3×10^{-5}	15.6	0.0042
Error	8	1.692×10^{-5}		

*Significant at $P < 0.05$.

Table 6. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate mineralization rates (k) in Decker soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	1.8384×10^{-4}	123.8	<0.0001
History	1	1.015×10^{-4}	205.05	<0.0001
Fresh Manure	1	8.164×10^{-5}	164.93	<0.0001
History*Fresh	1	7.0×10^{-7}	1.42	0.2682
Error	8	3.96×10^{-6}		

*Significant at $P < 0.05$.

Table 7. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate half-lives in Birtle soils used in Chapter 3

Source	DF	SS	F Value	Pr > F *
Model	3	21.57	11.47	0.0029
History	1	18.852	30.08	0.0006
Fresh Manure	1	2.714	4.33	0.071
History*Fresh	1	0.00394	0.01	0.9387
Error	8	5.014		

*Significant at $P < 0.05$.

Table 8. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate half-lives in Neepawa soils used in Chapter 3

Source	DF	SS	F Value	Pr > F *
Model	3	108.317	6.62	0.0147
History	1	1.098	0.2	0.6655
Fresh Manure	1	52.91	9.7	0.0143
History*Fresh	1	54.309	9.96	0.135
Error	8	43.634		

*Significant at $P < 0.05$.

Table 9. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate half-lives in Neepawa soils used in Chapter 3

Source	DF	SS	F Value	Pr > F *
Model	3	78.99	170.95	<0.0001
History	1	42.205	274.03	<0.0001
Fresh Manure	1	34.376	223.2	<0.0001
History*Fresh	1	2.408	15.63	0.0042
Error	8	1.232		

*Significant at $P < 0.05$.

Table 10. DF, SS, F values and P levels of the two-way analysis of variance of modeled glyphosate mineralization (M_T) in Birtle soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	229.775	82.74	<0.0001
History	1	206.906	223.52	<0.0001
Fresh Manure	1	0.00105	0	0.974
History*Fresh	1	22.8677	24.7	0.0011
Error	8	7.4053		

*Significant at $P < 0.05$.

Table 11. DF, SS, F values and P levels of the two-way analysis of variance of modeled glyphosate mineralization (M_T) in Neepawa soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	6.324	1.04	0.4255
History	1	3.9775	1.96	0.198
Fresh Manure	1	2.2275	1.1	0.325
History*Fresh	1	0.1191	0.06	0.8145
Error	8	16.2083		

*Significant at $P < 0.05$.

Table 12. DF, SS, F values and P levels of the two-way analysis of variance of modeled glyphosate mineralization (M_T) in Decker soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	11.5268	4.9	0.0322
History	1	2.88365	3.67	0.0915
Fresh Manure	1	0.46819	0.6	0.4621
History*Fresh	1	8.1749	10.42	0.0121
Error	8	6.277		

*Significant at P < 0.05.

Table 13. DF, SS, F values and P levels of the two-way analysis of variance of total trifluralin mineralization in Birtle soils used in Chapter 3

	DF	SS	F Value	Pr > F*
Model	3	5.817	64.63	<0.0001
History	1	5.333	177.78	<0.0001
Fresh Manure	1	0.00333	0.11	0.7475
History*Fresh	1	0.48	16	0.0039
Error	8	0.24		

*Significant at P < 0.05.

Table 14. DF, SS, F values and P levels of the two-way analysis of variance of total trifluralin mineralization in Neepawa soils used in Chapter 3

Source	DF	SS	F Value	Pr > F *
Model	3	78.7133	669.9	<0.0001
History	1	74.0033	1889.45	<0.0001
Fresh Manure	1	3.63	92.68	<0.0001
History*Fresh	1	1.08	27.57	0.0008
Error	8	0.3133		

*Significant at P < 0.05.

Table 15. DF, SS, F values and P levels of the two-way analysis of variance of total trifluralin mineralization in Decker soils used in Chapter 3

Source	DF	SS	F Value	Pr > F *
Model	3	13.7158	13.92	0.0015
History	1	8.8408	26.93	0.0008
Fresh Manure	1	3.9675	12.08	0.0084
History*Fresh	1	0.9075	2.76	0.135
Error	8	2.627		

*Significant at $P < 0.05$.

Table 16. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin mineralization rates (k) in Birtle soils used in Chapter 3

Source	DF	SS	F Value	Pr > F *
Model	3	2.60917×10^{-6}	40.14	<0.0001
History	1	2.1675×10^{-6}	100.04	<0.0001
Fresh Manure	1	1.40833×10^{-7}	6.5	0.342
History*Fresh	1	3.00833×10^{-7}	13.88	0.0058
Error	8	1.733×10^{-7}		

*Significant at $P < 0.05$.

Table 17. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin mineralization rates (k) in Neepawa soils used in Chapter 3

Source	DF	SS	F Value	Pr > F *
Model	3	2.336×10^{-6}	7.72	0.0095
History	1	1.2675×10^{-6}	12.57	0.0076
Fresh Manure	1	3.675×10^{-7}	3.64	0.0927
History*Fresh	1	7.0083×10^{-7}	6.95	0.0299
Error	8	8.067×10^{-7}		

*Significant at $P < 0.05$.

Table 18. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin mineralization rates (k) in Decker soils used in Chapter 3

Source	DF	SS	F Value	Pr > F *
Model	3	1.0492×10^{-6}	2.8	0.1088
History	1	7.5×10^{-9}	0.06	0.8127
Fresh Manure	1	1.02083×10^{-6}	8.17	0.0212
History*Fresh	1	2.0833×10^{-8}	0.17	0.6938
Error	8	1×10^{-6}		

*Significant at P < 0.05.

Table 19. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin half-lives in Birtle soils used in Chapter 3

Source	DF	SS	F Value	Pr > F *
Model	3	6885.9	43.81	<0.0001
History	1	5310.1	101.36	<0.0001
Fresh Manure	1	593.47	11.33	0.0098
History*Fresh	1	982.28	18.75	0.0025
Error	8	419.12		

*Significant at P < 0.05.

Table 20. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin half-lives in Neepawa soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	3697.7	7.32	0.0111
History	1	1871.9	11.12	0.0103
Fresh Manure	1	691.75	4.11	0.0772
History*Fresh	1	1134.07	6.74	0.0318
Error	8	1346.8		

*Significant at P < 0.05.

Table 21. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin half-lives in Decker soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	3564.6	2.07	0.1825
History	1	103.88	0.18	0.6817
Fresh Manure	1	3308.2	5.77	0.0431
History*Fresh	1	152.56	0.27	0.62
Error	8	4589.2		

*Significant at $P < 0.05$.

Table 22. DF, SS, F values and P levels of the two-way analysis of variance of modeled trifluralin mineralization (M_T) in Birtle soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	2.519	10.87	0.0034
History	1	2.0458	26.48	0.0009
Fresh Manure	1	0.4139	5.36	0.0493
History*Fresh	1	0.0594	0.77	0.4062
Error	8	0.618		

*Significant at $P < 0.05$.

Table 23. DF, SS, F values and P levels of the two-way analysis of variance of modeled trifluralin mineralization (M_T) in Neepawa soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	106.848	262.7	<0.0001
History	1	96.858	714.42	<0.0001
Fresh Manure	1	9.535	70.33	<0.0001
History*Fresh	1	0.4544	3.35	0.1045
Error	8	1.0846		

*Significant at $P < 0.05$.

Table 24. DF, SS, F values and P levels of the two-way analysis of variance of modeled trifluralin mineralization (M_T) in Decker soils used in Chapter 3

Source	DF	SS	F Value	Pr > F*
Model	3	41.7823	40.83	<0.0001
History	1	20.5827	60.34	<0.0001
Fresh Manure	1	20.5995	60.39	<0.0001
History*Fresh	1	0.6	1.76	0.2213
Error	8	2.7288		

*Significant at P < 0.05.

Table 25. DF, SS, F values and P levels of the two-way analysis of variance of total glyphosate mineralization in Birtle soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	138.3467	10.18	0.0013
History	1	80.955	17.88	0.0012
Fresh Manure	1	56.5128	12.48	0.0041
History*Fresh	1	0.8789	0.19	0.6673
Error	12	54.3336		

*Significant at P < 0.05.

Table 26. DF, SS, F values and P levels of the two-way analysis of variance of total glyphosate mineralization in Neepawa soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	169.286	8.9	0.0022
History	1	148.474	23.43	0.0004
Fresh Manure	1	15.6816	2.47	0.1417
History*Fresh	1	5.13023	0.81	0.3859
Error	12	76.0424		

*Significant at P < 0.05.

Table 27. DF, SS, F values and P levels of the two-way analysis of variance of total glyphosate mineralization in Decker soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	25.6782	2.16	0.1453
History	1	5.1529	1.3	0.2759
Fresh Manure	1	14.6689	3.71	0.0781
History*Fresh	1	5.8564	1.48	0.247
Error	12	47.4497		

*Significant at P < 0.05.

Table 28. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate mineralization rates (k) in Birtle soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	8.982×10^{-5}	5.3	0.0147
History	1	1.502×10^{-5}	2.66	0.1289
Fresh Manure	1	2.475×10^{-5}	4.38	0.0582
History*Fresh	1	5.006×10^{-5}	8.86	0.0115
Error	12	6.777×10^{-5}		

*Significant at P < 0.05.

Table 29. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate mineralization rates (k) in Neepawa soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	1.6281×10^{-4}	2.44	0.1147
History	1	1.1556×10^{-5}	5.2	0.0417
Fresh Manure	1	1.69×10^{-6}	0.08	0.7875
History*Fresh	1	4.556×10^{-5}	2.05	0.1778
Error	12	2.6684×10^{-4}		

*Significant at P < 0.05.

Table 30. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate mineralization rates (k) in Decker soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	1.5037×10^{-3}	111.58	<0.0001
History	1	7.6729×10^{-4}	170.81	<0.0001
Fresh Manure	1	6.8382×10^{-4}	152.23	<0.0001
History*Fresh	1	5.256×10^{-5}	11.7	0.0051
Error	12	5.39×10^{-5}		

*Significant at $P < 0.05$.

Table 31. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate half-lives in Birtle soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	25.869	4.27	0.0288
History	1	3.89	1.92	0.1905
Fresh Manure	1	6.087	3.01	0.1082
History*Fresh	1	15.892	7.86	0.0159
Error	12	24.250		

*Significant at $P < 0.05$.

Table 32. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate half-lives in Neepawa soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	46.5074	2.24	0.1356
History	1	29.6686	4.29	0.0604
Fresh Manure	1	15.7669	2.28	0.1568
History*Fresh	1	1.07189	0.16	0.7006
Error	12	82.9092		

*Significant at $P < 0.05$.

Table 33. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate half-lives in Decker soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	99.499	53.06	<0.0001
History	1	52.864	84.57	<0.0001
Fresh Manure	1	46.633	74.61	<0.0001
History*Fresh	1	0.0015	0	0.9624
Error	12	7.5007		

*Significant at $P < 0.05$.

Table 34. DF, SS, F values and P levels of the two-way analysis of variance of modeled glyphosate mineralization (M_T) in Birtle soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	190.472	10.79	0.001
History	1	138.942	23.62	0.0004
Fresh Manure	1	50.837	8.64	0.0124
History*Fresh	1	0.694	0.12	0.7372
Error	12	70.5916		

*Significant at $P < 0.05$.

Table 35. DF, SS, F values and P levels of the two-way analysis of variance of modeled glyphosate mineralization (M_T) in Neepawa soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	197.526	7.57	0.0042
History	1	173.317	19.94	0.0008
Fresh Manure	1	18.591	2.14	0.1696
History*Fresh	1	5.619	0.65	0.4371
Error	12	104.3195		

*Significant at $P < 0.05$.

Table 36. DF, SS, F values and P levels of the two-way analysis of variance of modeled glyphosate mineralization (M_T) in Decker soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	20.126	2.2	0.1415
History	1	2.7142	0.89	0.3646
Fresh Manure	1	11.971	3.92	0.0712
History*Fresh	1	5.441	1.78	0.2069
Error	12	36.675		

*Significant at P < 0.05.

Table 37. DF, SS, F values and P levels of the two-way analysis of variance of total trifluralin mineralization in Birtle soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	8.28709	3.29	0.0583
History	1	5.3843	6.4	0.0264
Fresh Manure	1	2.557	3.04	0.1067
History*Fresh	1	0.34568	0.41	0.5334
Error	12	10.0889		

*Significant at P < 0.05.

Table 38. DF, SS, F values and P levels of the two-way analysis of variance of total trifluralin mineralization in Neepawa soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	15.5025	16.81	0.0002
History	1	7.32168	23.82	0.0005
Fresh Manure	1	1.60985	5.24	0.429
History*Fresh	1	8.5515	27.82	0.0003
Error	11	3.3816		

*Significant at P < 0.05.

Table 39. DF, SS, F values and P levels of the two-way analysis of variance of total trifluralin mineralization in Decker soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	124.331	25.11	<0.0001
History	1	72.5304	43.94	<0.0001
Fresh Manure	1	51.2369	31.04	0.0001
History*Fresh	1	0.56355	0.34	0.5698
Error	12	19.8059		

*Significant at $P < 0.05$.

Table 40. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin mineralization rates (k) in Birtle soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	7.81875×10^{-7}	1.3	0.3198
History	1	3.30625×10^{-7}	1.65	0.2235
Fresh Manure	1	2.25625×10^{-7}	1.12	0.3098
History*Fresh	1	2.25625×10^{-7}	1.12	0.3098
Error	12	2.4075×10^{-6}		

*Significant at $P < 0.05$.

Table 41. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin mineralization rates (k) in Neepawa soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	4.9358×10^{-6}	7.42	0.0054
History	1	3.78519×10^{-6}	17.08	0.0017
Fresh Manure	1	4.20577×10^{-7}	1.9	0.1957
History*Fresh	1	1.27442×10^{-6}	5.75	0.0353
Error	11	2.4375×10^{-6}		

*Significant at $P < 0.05$.

Table 42. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin mineralization rates (k) in Decker soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	1.032×10^{-5}	10.94	0.0009
History	1	9.150625×10^{-6}	29.11	0.0002
Fresh Manure	1	1.155625×10^{-6}	3.68	0.0793
History*Fresh	1	1.5625×10^{-6}	0.05	0.8273
Error	12	3.77×10^{-6}		

*Significant at P < 0.05.

Table 43. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin half-lives in Birtle soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	3340.12	1.47	0.2722
History	1	1688.16	2.23	0.1613
Fresh Manure	1	1154.18	1.52	0.2407
History*Fresh	1	497.782	0.66	0.4333
Error	12	9089.33		

*Significant at P < 0.05.

Table 44. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin half-lives in Neepawa soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	18639.79	4.1	0.0351
History	1	15890.96	10.5	0.0079
Fresh Manure	1	264.347	0.17	0.6841
History*Fresh	1	3830.82	2.53	0.14
Error	12	16651.14		

*Significant at P < 0.05.

Table 45. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin half-lives in Decker soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	17565.4	7.08	0.0054
History	1	14797.3	17.89	0.0012
Fresh Manure	1	2252.83	2.72	0.1248
History*Fresh	1	515.322	0.62	0.4452
Error	12	9925.17		

*Significant at $P < 0.05$.

Table 46. DF, SS, F values and P levels of the two-way analysis of variance of modeled trifluralin mineralization (M_T) in Birtle soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	14.5711	2.06	0.1593
History	1	8.5138	3.61	0.0817
Fresh Manure	1	3.0321	1.29	0.279
History*Fresh	1	3.025	1.28	0.2795
Error	12	28.303		

*Significant at $P < 0.05$.

Table 47. DF, SS, F values and P levels of the two-way analysis of variance of modeled trifluralin mineralization (M_T) in Neepawa soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	8.9509	2.36	0.1271
History	1	2.295	1.82	0.2047
Fresh Manure	1	2.12625	1.68	0.221
History*Fresh	1	5.7667	4.57	0.0559
Error	11	13.8916		

*Significant at $P < 0.05$.

Table 48. DF, SS, F values and P levels of the two-way analysis of variance of modeled trifluralin mineralization (M_T) in Decker soils used in Chapter 4

Source	DF	SS	F Value	Pr > F*
Model	3	131.919	16.82	0.0001
History	1	66.0392	25.26	0.0003
Fresh Manure	1	65.5427	25.07	0.0003
History*Fresh	1	0.337	0.13	0.7258
Error	12	31.374		

*Significant at P < 0.05.

Table 49. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate Kd values in Birtle soil

Source	DF	SS	F Value	Pr > F
Model	3	667.922	110.36	<0.0001
History	1	660.99	327.66	<0.0001
Fresh Manure	1	3.579	1.77	0.2076
History*Fresh	1	3.352	1.66	0.2217
Error	12	24.2079		

*Significant at P < 0.05.

Table 50. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate Kd values in Neepawa soil

Source	DF	SS	F Value	Pr > F
Model	3	574.7	7.6	0.0041
History	1	346.853	13.76	0.003
Fresh Manure	1	129.698	5.15	0.0425
History*Fresh	1	98.149	3.89	0.0719
Error	12	302.4141		

*Significant at P < 0.05.

Table 51. DF, SS, F values and P levels of the two-way analysis of variance of glyphosate Kd values in Decker soil

Source	DF	SS	F Value	Pr > F
Model	3	61.7207	11.49	0.0008
History	1	57.8969	32.33	0.0001
Fresh Manure	1	2.34396	1.31	0.2749
History*Fresh	1	1.4799	0.83	0.3812
Error	12	21.4885		

*Significant at P < 0.05.

Table 52. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin Kd values in Birtle soil

Source	DF	SS	F Value	Pr > F
Model	3	72776.02	0.92	0.4613
History	1	66927.24	2.53	0.1374
Fresh Manure	1	5846.82	0.22	0.6464
History*Fresh	1	1.9572	0	0.9933
Error	12	316968.4		

*Significant at P < 0.05.

Table 53. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin Kd values in Neepawa soil

Source	DF	SS	F Value	Pr > F
Model	3	1686.45	0.17	0.913
History	1	585.5795	0.18	0.6792
Fresh Manure	1	4.61498	0	0.9706
History*Fresh	1	1096.2555	0.34	0.5728
Error	12	39133.806		

*Significant at P < 0.05.

Table 54. DF, SS, F values and P levels of the two-way analysis of variance of trifluralin Kd values in Decker soil

Source	DF	SS	F Value	Pr > F
Model	3	2741.722	0.37	0.7768
History	1	379.7627	0.15	0.7022
Fresh Manure	1	2302.8	0.93	0.3539
History*Fresh	1	59.159	0.02	0.8797
Error	12	29720.43		

*Significant at P < 0.05.

Table 55. DF, SS, F values and P levels of the two-way analysis of variance on the effect of amended soils and different soil textures on total 2,4-D mineralization

Source	DF	SS	F Value	Pr > F*
Model	11	1046.1	44	<0.0001
Texture	3	835.4	128.84	<0.0001
Amendment	2	58.67	13.57	<0.0001
Texture*Amendment	6	122.1	9.42	<0.0001
Error	36	75.65		

*Significant at P < 0.05.

Table 56. DF, SS, F values and P levels of the two-way analysis of variance on the effect of amended soils and different soil textures on 2,4-D mineralization rates (k)

Source	DF	SS	F Value	Pr > F*
Model	11	0.0287	177.74	<0.0001
Texture	3	0.0233	529.74	<0.0001
Amendment	2	0.0026	89.84	<0.0001
Texture*Amendment	6	0.002	22.52	<0.0001
Error	36	0.0292		

*Significant at P < 0.05.

Table 57. DF, SS, F values and P levels of the two-way analysis of variance on the effect of amended soils and different soil textures on 2,4-D half-lives

Source	DF	SS	F Value	Pr > F*
Model	11	27713.2	20.79	<0.0001
Texture	3	15397.4	42.36	<0.0001
Amendment	2	2901.1	11.97	0.0001
Texture*Amendment	6	9337.8	12.84	<0.0001
Error	36	31954.2		

*Significant at $P < 0.05$.

Table 58. DF, SS, F values and P levels of the two-way analysis of variance on the effect of amended soils and different soil textures on modeled 2,4-D mineralization (M_T)

Source	DF	SS	F Value	Pr > F*
Model	11	1127.98	15.02	<0.0001
Texture	3	348.72	17.03	<0.0001
Amendment	2	413.97	30.32	<0.0001
Texture*Amendment	6	356.99	8.72	<0.0001
Error	36	1366.9		

*Significant at $P < 0.05$.

Table 59. DF, SS, F values and P levels of the two-way analysis of variance on the effect of amended soils and different amendment application rates on total 2,4-D mineralization

Source	DF	SS	F Value	Pr > F*
Model	5	791.34	36.32	<0.0001
Amendment	1	203.76	46.76	<0.0001
Application Rate	2	517.07	59.33	<0.0001
Amendment*Rate	2	70.51	8.09	0.0031
Error	18	78.43		

*Significant at $P < 0.05$.

Table 60. DF, SS, F values and P levels of the two-way analysis of variance on the effect of amended soils and different amendment application rates on 2,4-D mineralization rates (k)

Source	DF	SS	F Value	Pr > F*
Model	5	0.0166	57.82	<0.0001
Amendment	1	0.0033	57.95	<0.0001
Application Rate	2	0.129	112	<0.0001
Amendment*Rate	2	0.00041	3.57	0.0494
Error	18	0.001		

*Significant at P < 0.05.

Table 61. DF, SS, F values and P levels of the two-way analysis of variance on the effect of amended soils and different amendment application rates on 2,4-D half-lives

Source	DF	SS	F Value	Pr > F*
Model	5	15065.5	152.44	<0.0001
Amendment	1	3816.8	193.1	<0.0001
Application Rate	2	7423.96	187.8	<0.0001
Amendment*Rate	2	3824.77	96.75	<0.0001
Error	18	355.78		

*Significant at P < 0.05.

Table 62. DF, SS, F values and P levels of the two-way analysis of variance on the effect of amended soils and different amendment application rates on modeled 2,4-D mineralization (M_T)

Source	DF	SS	F Value	Pr > F*
Model	5	65.68	2.05	0.1199
Amendment	1	5.2095	0.81	0.3793
Application Rate	2	47.01	3.67	0.0462
Amendment*Rate	2	13.46	1.05	0.3705
Error	18	115.405		

*Significant at P < 0.05.

Table 63. DF, SS, F values and P levels of the two-way analysis of variance on the effect of soil/amendment pre-incubation length and different amendments on total 2,4-D mineralization

Source	DF	SS	F Value	Pr > F*
Model	11	3397.1	39.15	<0.0001
Preinc Length	3	2348.86	99.26	<0.0001
Amendment	2	65.63	4.16	0.0239
Preinc*Amendment	6	922.97	19.50	<0.0001
Error	35	276.1		

*Significant at P < 0.05.

Table 64. DF, SS, F values and P levels of the two-way analysis of variance on the effect of soil/amendment pre-incubation length and different amendments on 2,4-D mineralization rates (k)

Source	DF	SS	F Value	Pr > F*
Model	11	0.01396	18.68	<0.0001
Preinc Length	3	0.0046	22.46	<0.0001
Amendment	2	0.0065	48.00	<0.0001
Preinc*Amendment	6	0.0026	6.48	0.0001
Error	35	0.0024		

*Significant at P < 0.05.

Table 65. DF, SS, F values and P levels of the two-way analysis of variance on the effect of soil/amendment pre-incubation length and different amendments on 2,4-D half-lives

Source	DF	SS	F Value	Pr > F*
Model	11	1668.07	19.89	<0.0001
Preinc Length	3	367.64	16.07	<0.0001
Amendment	2	793.88	52.06	<0.0001
Preinc*Amendment	6	491.99	10.75	<0.0001
Error	35	266.89		

*Significant at P < 0.05.

Table 66. DF, SS, F values and P levels of the two-way analysis of variance on the effect of soil/amendment pre-incubation length and different amendments on modeled 2,4-D mineralization (M_T)

Source	DF	SS	F Value	Pr > F*
Model	11	3248.56	37.68	<0.0001
Preinc Length	3	2271.97	96.62	<0.0001
Amendment	2	100.80	6.43	0.0042
Preinc*Amendment	6	819.64	17.43	<0.0001
Error	35	274.34		

*Significant at P < 0.05.

Table 67. DF, SS, F values and P levels of the one-way analysis of variance on the effect of amendment application on total CO_2 production after 7 days

Source	DF	SS	F Value	Pr > F*
Model	2	141.98	434.4	<0.0001
Error	9	1.47		
Total	11	143.45		

*Significant at P < 0.05.

Table 68. DF, SS, F values and P levels of the one-way analysis of variance on the effect of amendment application on total CO_2 production after 14 days

Source	DF	SS	F Value	Pr > F*
Model	2	310.18	1224.96	<0.0001
Error	9	1.14		
Total	11	311.32		

*Significant at P < 0.05.

Table 69. DF, SS, F values and P levels of the one-way analysis of variance on the effect of amendment application on total CO_2 production after 28 days

Source	DF	SS	F Value	Pr > F*
Model	2	752.59	1959.14	<0.0001
Error	9	1.73		
Total	11	754.32		

*Significant at P < 0.05.

Table 70. DF, SS, F values and P levels of the one-way analysis of variance on the effect of amendment application on total CO_2 production after 56 days

Source	DF	SS	F Value	Pr > F*
Model	2	1218.60	1777.13	<0.0001
Error	9	3.09		
Total	11	1221.68		

*Significant at P < 0.05.

Table 71. DF, SS, F values and P levels of the one-way analysis of variance on the effect of amendment application on total CO_2 production after 128 days

Source	DF	SS	F Value	Pr > F*
Model	2	1921.21	784.96	<0.0001
Error	9	11.01		
Total	11	1932.22		

*Significant at P < 0.05.

Table 72. DF, SS, F values and P levels of the two-way analysis of variance on the effect of 2,4-D concentration and amendment application rate on 2,4-D Kd

Source	DF	SS	F Value	Pr > F*
Model	39	106.62	294.17	<0.0001
Concentration	9	103.64	1239.1	<0.0001
Amendment Rate	3	2.08	74.67	<0.0001
Conc*Amend Rate	27	0.902	3.59	<0.0001
Error	80	0.036		

*Significant at P < 0.05.

Table 73. DF, SS, F values and P levels of the two-way analysis of variance on the effect of two ranges of 2,4-D concentration and amendment application rate on 2,4-D Kf

Source	DF	SS	F Value	Pr > F*
Model	7	0.2305	7.32	0.0005
Concentration	1	0.0246	5.47	0.0326
Amendment Rate	3	0.1901	14.08	<0.0001
Conc*Amend Rate	3	0.0157	1.17	0.3536
Error	16	0.0720		

*Significant at P < 0.05.

Table 74. DF, SS, F values and P levels of the two-way analysis of variance on the effect of two ranges of 2,4-D concentration and amendment application rate on 2,4-D Kf 1/*n*

Source	DF	SS	F Value	Pr > F*
Model	7	0.0286	411.45	<0.0001
Concentration	1	0.0236	66.35	<0.0001
Amendment Rate	3	0.0026	2.40	0.1063
Conc*Amend Rate	3	0.0024	2.21	0.1265
Error	16	0.0057		

*Significant at $P < 0.05$.

Table 75. DF, SS, F values and P levels of the one-way analysis of variance on the effect of a range of ten 2,4-D concentrations and amendment application rate on 2,4-D Kf

Source	DF	SS	F Value	Pr > F*
Model	3	0.1388	6.17	0.0178
Error	8	0.0600		
Total	11	0.1988		

*Significant at $P < 0.05$.

Table 76. DF, SS, F values and P levels of the one-way analysis of variance on the effect of a range of ten 2,4-D concentrations and amendment application rate on 2,4-D Kf 1/*n*

Source	DF	SS	F Value	Pr > F*
Model	3	0.0003	2.04	0.1874
Error	8	0.0004		
Total	11	0.0007		

*Significant at $P < 0.05$.

V. 2,4-D Kd Table

Table 6.1. Soil-water partitioning coefficients, Kd (mL g^{-1}), of 2,4-D determined over manure application rates of 0 to 225 kg N ha^{-1} and fitted to the equation: Kd = C_s / C_e, where C_s = the amount of 2,4-D sorbed to soil at equilibrium (μg g^{-1}), C_e = the amount of 2,4-D in solution at equilibrium (μg mL^{-1})

2,4-D active ingredient (μg mL^{-1})	0	56	112	225
	(kg N ha^{-1})			
0.0625	3.63 +/- 0.22 *	4.04 +/- 0.24 *	3.81 +/- 0.17 *	3.22 +/- 0.13 *
0.125	2.96 +/- 0.11	3.22 +/- 0.08	3.07 +/- 0.08	2.53 +/- 0.11
0.25	2.53 +/- 0.18	2.65 +/- 0.08	2.64 +/- 0.14	2.24 +/- 0.05
0.5	2.11 +/- 0.08	2.41 +/- 0.02	2.15 +/- 0.14	2.03 +/- 0.12
1	1.95 +/- 0.07	2.07 +/- 0.11	2.00 +/- 0.07	1.71 +/- 0.04
2	1.58 +/- 0.08	1.61 +/- 0.01	1.65 +/- 0.01	1.41 +/- 0.03
4	1.29 +/- 0.02	1.33 +/- 0.12	1.34 +/- 0.06	1.16 +/- 0.14
8	0.89 +/- 0.01	1.04 +/- 0.02	0.99 +/- 0.07	0.83 +/- 0.02
16	0.85 +/- 0.03	0.94 +/- 0.04	0.92 +/- 0.04	0.78 +/- 0.02
32	0.63 +/- 0.03	0.77 +/- 0.05	0.73 +/- 0.06	0.65 +/- 0.02

*Mean of three replicates followed by standard deviation.