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The Nitrous Oxide and Methane Emissions from *Miscanthus x giganteus* and *Salix viminalis x schwerinii* in Oakpark, Carlow, Ireland.

Sive Geoghegan BSc. (Hons.)

Department of Botany

School of Natural Sciences

University of Dublin

Trinity College

Ireland

Thesis submitted for the degree of Doctor of Philosophy

University of Dublin

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Declaration

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Summary

In investigating the reduction of the national greenhouse gas (GHG) footprint by replacing fossil fuels with bioenergy crops it is important to have a full GHG budget. We compared field emissions of nitrous oxide (N₂O) and methane (CH₄) for a *Miscanthus x giganteus* crop and a *Salix viminalis x schwerinii* (Tora) crop. We applied 150 kg N ha⁻¹ of an inorganic, 27% CAN, fertiliser and an organic Biofert fertiliser. The study was carried out on a site in Teagasc Oakpark, Carlow, Ireland on two separate crop sites. N₂O and CH₄ fluxes were measured weekly using static chambers from October 2008 to August 2010 for both crops. For the management year for the *Miscanthus* crop the N₂O fluxes were significantly smaller for the control plots (0kg N ha⁻¹) 0.2 kg N₂O-N ha⁻¹ a⁻¹, 1.5 kg N₂O-N ha⁻¹ a⁻¹ was observed for CAN fertiliser, and 1.7 kg N₂O-N ha⁻¹ a⁻¹ was observed for Biofert. Soil CH₄ fluxes observed were negligible for both crops. For the management period for Willow, N₂O fluxes of 0.38 kg N₂O-N ha⁻¹, 1.17 kg N₂O-N ha⁻¹ and 0.88 kg N₂O-N ha⁻¹ were observed for control, 27% CAN and Biofert treatments. Thus, bioenergy crops emit less GHGs when they receive no fertiliser and there is no significant difference between the type of fertiliser used. Comparisons of measured and modelled fluxes were carried out using the process-based model, DNDC, for *Miscanthus x giganteus*.

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Chapter 1 General Introduction

1.1 Background

Nitrous oxide (N_2O) and methane (CH_4) are natural trace gases in the atmosphere of the earth. In recent years, work on ice cores drilled in the Antarctic and Greenland ice caps have yielded ice dating back through several glacial-interglacial cycles to 650,000 yr BP. The air from these trapped samples has been analysed using high precision gas chromatography and has been used to determine the atmospheric concentration of N_2O and CH_4 over time. From these studies, N_2O concentrations were found to vary from highs of 270 ppbv in interglacial periods to lows of approximately 200ppbv in glacial periods (Sowers et al., 2003, Fluckiger et al., 2004). Over the last four thousand years, N_2O mixing ratios have been approximately 270 ppbv (Fluckiger et al., 2004). From 1850 AD there has been a 20% increase in this ratio, exceeding 280ppbv in 1905, at 300ppbv during the mid-1970s and measured at 319ppbv in 2005 (IPPC, 2007) and is currently over 320ppv. From the beginning of the industrial era, CH_4 atmospheric concentrations have more than doubled up to their current 1750ppb level (IPPC, 2007). There has been no precedent for these levels over the previous 650,000 years (MacFarling Meure et al., 2006, Wolff and Spahni, 2007).

Depending on how far back you go, fluctuations in atmospheric mixing ratios were kept to within a narrow range, thus the sources and sinks were broadly in line. A reasonable explanation for these significant increases has been the effect of anthropogenic activities on the sources and / or sinks of N_2O and CH_4 since the industrial era.

In an effort to mitigate the effects of these greenhouse gases by reducing their sources, the production of biofuel crops e.g. biodiesel from rapeseed;

bioethanol from corn (maize) has increased to reduce our reliance on fossil fuels. However, the extra N₂O produced through the production of these fuels can contribute significantly, if not more to global warming than any perceived global cooling effect by the resultant fossil fuel savings (Crutzen et al., 2008). Crops with lower nitrogen demand e.g. grasses, woody coppice species have more favourable climate impacts, but, full life cycle assessments need to be analysed.

The research for this thesis is concerned with measuring N₂O and CH₄ emissions from *Miscanthus x giganteus* and *Salix schwerinii x S. Viminalis* (commercially known as 'Tora') grown on separate sites in Oakpark Research Centre, Carlow, Ireland over a 20 month period (October 2008 – August 2010). The DNDC model was also used on an annual basis for modelling N₂O emissions from *Miscanthus*. In addition to these, the effect of fertiliser type used i.e. inorganic and organic, is being investigated to establish if it has any significant impact on N₂O or CH₄ emissions. This dissertation is organised into five chapters; Chapter 1 is a general introduction, Chapter 2 is concerned with the measurement of N₂O and CH₄ from *Miscanthus* plots treated with inorganic and organic fertiliser, Chapter 3 is concerned with the measurement of N₂O and CH₄ from Willow plots treated with inorganic and organic fertiliser, Chapter 4 discusses the results from DNDC modelled data as compared to measured data from *Miscanthus*, Chapter 5 discusses all of the major findings of this study.

1.2 N₂O and CH₄ production processes in Soil

Approximately 6% of the current greenhouse effect is related to the terrestrial production of atmospheric N₂O (IPPC, 2007). N₂O production in soil is a result of mainly biological, bacterial activity. The major pathways for production of N₂O in soils are nitrification (oxidation of ammonia and nitrifier denitrification), denitrification and nitrate ammonification (Baggs, 2008, Bremner, 1995, Davidson, 1991a, Wrage et al., 2001) (figure 1.2). These

processes are highly dependent on environmental factors, the soil microbial community structure and microsites within the soil matrix (Stevens et al., 1997). These processes also rarely occur on their own, there may be conditions where there is competition for resources and therefore the possibility of transferring N_2O or another intermediary product from one process to another. This can result in N_2O being produced via several processes which may form one pool before it is reduced to N_2 during denitrification (Baggs, 2008).

Denitrification is the reduction of NO_3^- or NO_2^- to N_2 under anaerobic conditions, N_2O and NO are intermediary gaseous products that are emitted during this process (Bremner, 1997, Robertson and Tiedje, 1987). Denitrifiers are mainly heterotrophic bacteria (over 50 genera) (Smith and Zimmerman, 1981, Knowles, 1982). Fungi e.g. *Fusarium* (Shoun et al., 1992) and archaea have shown denitrifying capabilities. All of these genera require organic compounds as their energy source (Robertson and Tiedje, 1987).

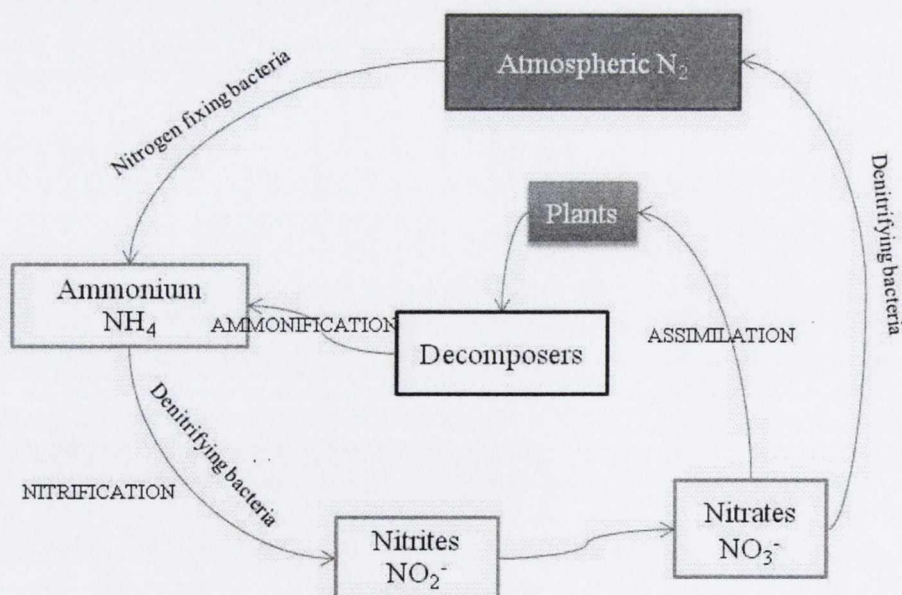


Figure 1.1 Basic outline of the Nitrogen Cycle, adapted (Smith et al., 2010).

The process is catalysed by the following enzymes: nitrate reductase, nitrite reductase, nitric oxide reductase and nitrous oxide reductase (see Figure 1.2). The synthesis of ATP (adenosine triphosphate) is coupled to the transport of electrons to N oxides or NO_3^- (Hochstein and Tomlinson, 1988).

The level of activity of denitrifying bacteria is controlled by the availability of carbon (C), N availability, temperature, concentration of O_2 (soil water content) and pH. Soils with water-filled pore space (WFPS) of $> 70\%$ have the largest contribution to production of N_2O flux through denitrification (provided carbon and soil nitrate are non-limiting) (Davidson, 1991a, Bateman and Baggs, 2005). The activity and synthesis of denitrification reductases is reduced with high O_2 concentrations (N_2O reductase is particularly sensitive resulting in higher ratio of $\text{N}_2\text{O}:\text{N}_2$ as O_2 availability increases (Otte et al., 1996, Weier et al., 1993)).

The addition of synthetic fertilisers to soil results in significant increase in soil available N i.e. N electron acceptors and significantly affects denitrification rates (Eichner, 1990). Soil NO_3^- concentrations also affect $\text{N}_2\text{O}/\text{N}_2$ ratio where concentrations exceeding 10ug g^{-1} soil lower the ratio as NO_3^- is preferred as an electron acceptor over N_2O (Blackmer and Bremner, 1976, Baggs et al., 2003a).

Many denitrifiers are heterotrophic, as such availability of organic carbon is a major factor affecting denitrification rates (Knowles, 1982, Bremner, 1997). The form of the carbon also can affect the denitrification rates i.e. easily oxidisable organic matter to soils e.g. soluble C-to-N ratio of applied residues (Millar and Baggs, 2005), total organic C (Baggs and Blum, 2004), available C (Stanford et al., 1975), water-soluble and mineralisable C (Burford and Bremner, 1975, Paul and Beauchamp, 1989).

Soil pH is another influencing factor on denitrification, as pH decreases denitrification rates are thought to decrease. However this is not always valid as denitrification has been observed at $\text{pH} < 4.9$ (Ellis et al., 1998). The

diversity of the denitrifier community and their potential adaptation to low pH may well reflect these observations (Enwall et al., 2005, Parkin et al., 1985).

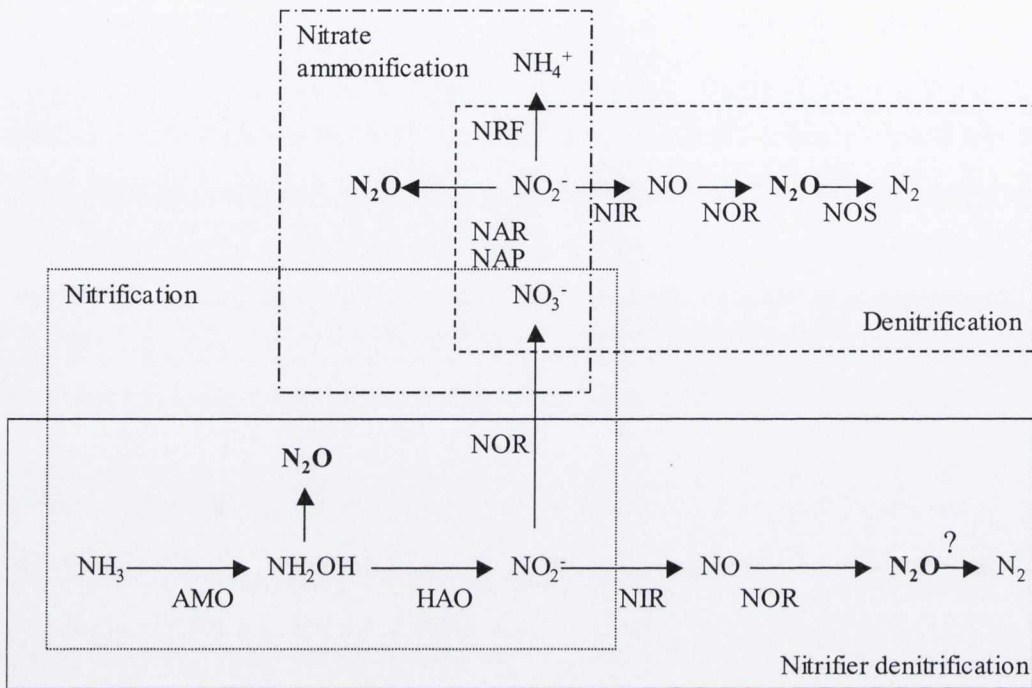


Figure 1.2 Microbial sources of N₂O in the soil (as adapted from (Baggs, 2008), enzymes are nitrate reductase (NAR), nitrite reductase (NIR), nitric oxide reductase (NOR), nitrous oxide reductase (NOR)).

Low pH conditions also affects N₂O:N₂ ratio, as pH declines the ratio increases (Šimek and Cooper, 2002, Nägele and Conrad, 1990, Firestone et al., 1980, Thomsen et al., 1994).

Nitrification occurs when ammonia is converted to nitrite by ammonia-oxidising bacteria as part of a two stage process where hydroxylamine acts as an intermediate (Figure 1.3). Ammonia is oxidised hydroxylamine by catalysis of the enzyme ammonia mono-oxygenase, hydroxylamine is further oxidised to nitrite by catalysis of the enzyme hydroxylamine oxidoreductase (Hooper et al., 1997). Two of the four electrons produced during this stage are available for energy production and reduction of O₂ to H₂O the last two are used to oxidise ammonia to hydroxylamine (Collicer and Stephenson, 2000). Ammonia availability is a major influence on oxidation of ammonia,

which is influenced by the conditions of low availability of NH_3 at low pH. Known bacterial autotrophic bacterial ammonia oxidisers all belong to the genus *Nitrosomonas* and *Nitrosospira* (Prosser and Nicol, 2008). However, the ability of ammonia oxidising bacteria to survive and compete for NH_3 under adverse conditions i.e. low pH, varies between the bacteria types after these ‘starvation’ conditions (Frijlink et al., 1992, Gerards et al., 1998, Bollmann et al., 2002).

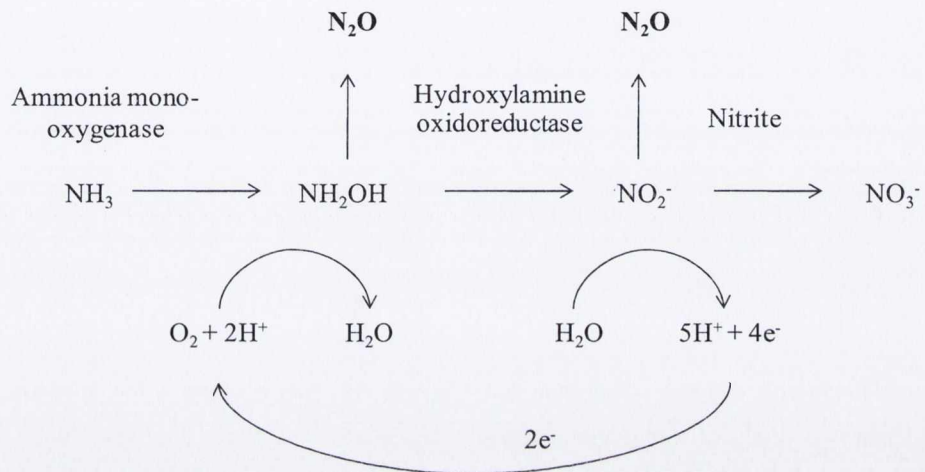


Figure 1.3 The Nitrification Pathway illustrating points of N_2O production (adapted from (Colliver and Stephenson, 2000, Wrage et al., 2001)).

There has been significant evidence to support the more important role that nitrifiers contribute to N_2O production i.e. that ammonia oxidation significantly contributes to net N_2O emissions from soils (Abbasi and Adams, 2000, Bateman and Baggs, 2005, Avrahami and Bohannan, 2009, Wan et al., 2009). The role of nitrification was generally considered to play a lesser role in soil N_2O emissions compared to denitrification. However, evidence from silt loam soil kept at 35-60% water filled pore space (WFPS) showed that soil N_2O emissions resulting from nitrification processes accounted for 81% of N_2O emitted at 60% WFPS (Bateman and Baggs, 2005). This is an important and significant finding due to the effects of this process on global warming.

A wide range of heterotrophic bacteria and fungi also carry out nitrification processes through organic substrates e.g. NH_3 , urea (Papen et al., 1989). Investigations into the direct effect of heterotrophic nitrification on arable soil

have been carried out using C_2H_2 to inhibit ammonia oxidation (Bateman and Baggs, 2005). High variability within the findings led to inconclusive results to directly measure the N_2O production. However, studies in culture have demonstrated N_2O production by heterotrophic nitrifiers (Papen et al., 1989).

The nitrate ammonification process (see Figure 1.2) provides a side-step in the nitrogen cycle by reducing NO_3^- to NO_2^- and NH_4^+ and thus bypassing N_2 fixation and denitrification (Mohan et al., 2004). This process is often coupled to ATP synthesis through a respiratory electron transport system. The nature of electron donors used by ammonifiers determines the level of energy conservatism, this process includes gram-negative and gram-positive bacteria, obligate anaerobes e.g. *Clostridium*, aerobes, e.g. *Bacillus* and facultative anaerobes e.g. *Enterobacter* which occur in a variety of environments (Fazzolari et al., 1990). The direct contribution of nitrate ammonification to N_2O soil emissions is as yet undetermined; however there is some evidence that the process may be significant in agricultural soils (Chen et al., 1995a, Chen et al., 1995b).

The process of nitrifier denitrification involves the oxidation of NH_3 to NO_2^- through ammonia-oxidising bacteria (Kuai and Verstraete, 1998). NO_2^- is then reduced to N_2O and possibly N_2 (Wrage et al., 2001). The enzymes involved in this process are ammonia monooxygenase, hydroxylamine oxidoreductase, nitrite reductase, nitric oxide reductase and possibly nitrous oxide reductase (Jiang and Bakken, 1999). The environmental regulation of nitrifier denitrification and its effect on N_2O production is not yet fully understood, however decreasing pH may influence nitrifier denitrification (Jiang and Bakken, 1999, Wrage et al., 2001). Also decreases in O_2 concentrations have been observed to result in higher N_2O production (Goreau et al., 1980, Lipschultz et al., 1981, Hynes and Knowles, 1984, Kester et al., 1996, Jiang and Bakken, 1999, Dundee and Hopkins, 2001).

Decomposition of organic matter to CH_4 and CO_2 through a complex microbial process involves cooperation of anaerobic bacteria and methanogenic archaea (Figure 1.4). Biopolymers are hydrolysed and

fermented to form compounds that are used by methanogens. Lipids convert to glycerol and long chain fatty acids, proteins are converted to amino acids and small peptides and polysaccharides yield sugars. Fermentive bacteria degrade sugars, amino acids, purines, pyrimidines and glycerol to fatty acids, CO_2 , formate and hydrogen. Acetogenic bacteria degrade fatty acid to acetate, CO_2 , H_2 and formate. These compounds are then used as substrates for methanogens (Schink and Stams, 2006, Stams and Plugge, 2010).

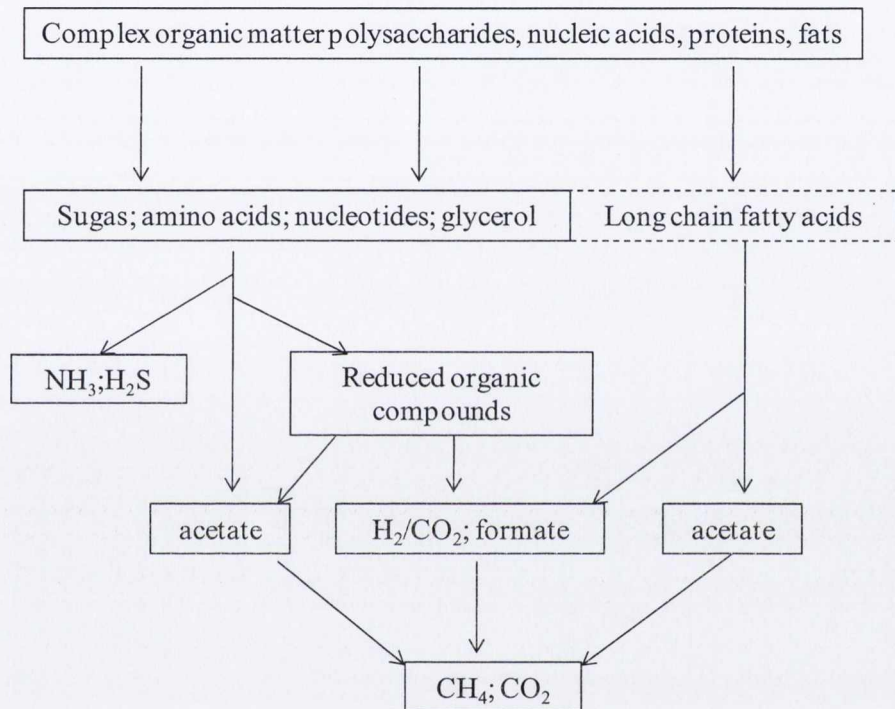


Figure 1.4 General scheme of the anaerobic digestion process. adapted (Stams and Plugge, 2010).

CH_4 is produced by methanogenic archaea in anaerobic soil (Philippot et al., 2009) they are a diverse group classified into established orders; *Methanobacteriales*, *Methanococcales*, *Methanomicrobiales*, *Methanosarcinales* and *Methanopyrales* and further divide into 10 families and 31 genera (Liu et al., 2008). The habitats of methanogens differ in temperature, pH and salinity and are physiologically very restricted. The three major substrates they grow on are divided into three types: (i) H_2 (hydrogen)/ CO_2 , formate and carbon monoxide (CO), (ii) methanol and methylated compounds, (iii) acetate.

The general pathway for methanogenesis is outlined in figure 1.5. Most methanogens reduce CO₂ to CH₄ with H₂ as the electron donor, however formate or CO can also be used. In the first stage CO₂ binds to methanofuran (MFR) and is reduced to formyl-MFR level with ferredoxin (Fd) which is reduced with H₂ is the electron donor. Formyl-MFR is then transferred to tetrahydromethanopterin (H₄MPT) to form formyl-H₄MPT. With reduced factor F₄₂₀(F₄₂₀H₂) is the electron donor, formyl-H₄MPT is then dehydrated to methenyl group which is further reduced to methylene-H₄MPT and then to methyl-H₄MPT.

The methyl group is then transferred to coenzyme M (HS-CoM), forming methyl-CoM. The methyl-CoM is further reduced to CH₄ by methyl coenzyme M reductase with coenzyme B (HS-CoB) acting as the electron donor after oxidation a heterodisulphide is formed with HS-CoM (CoM-S-S-CoB). CoM-S-S-CoB is then reduced to HS-CoB and HS-CoM. The reduction of CoM-S-S-CoB and methyl transfer from H₄MPT to HS-CoM are the energy conservation steps (Liu and Whitman, 2008, Thauer et al., 2008).

Methyl-containing compounds (e.g. methylated sulphides, methylated amines, methanol) are converted by methanogens (*Methanosarcinales*, *Methanospaera*) and transferred to a corrinoid protein and then to HS-CoM through methyltransferases. This methyl-CoM is then reduced to CH₄ in the methanogenesis pathway (Figure 1.5) via electrons obtained from oxidation of methyl-CoM to CO₂.

Acetate is converted by two genera, *Metanosarcina* and *Methanosaeta* (Jetten et al., 1992) in methanogenesis. Acetate is split into CO and methyl-CoM. CO is oxidized to CO₂ and methyl-CoM is reduced to CH₄ (Figure 1.5).

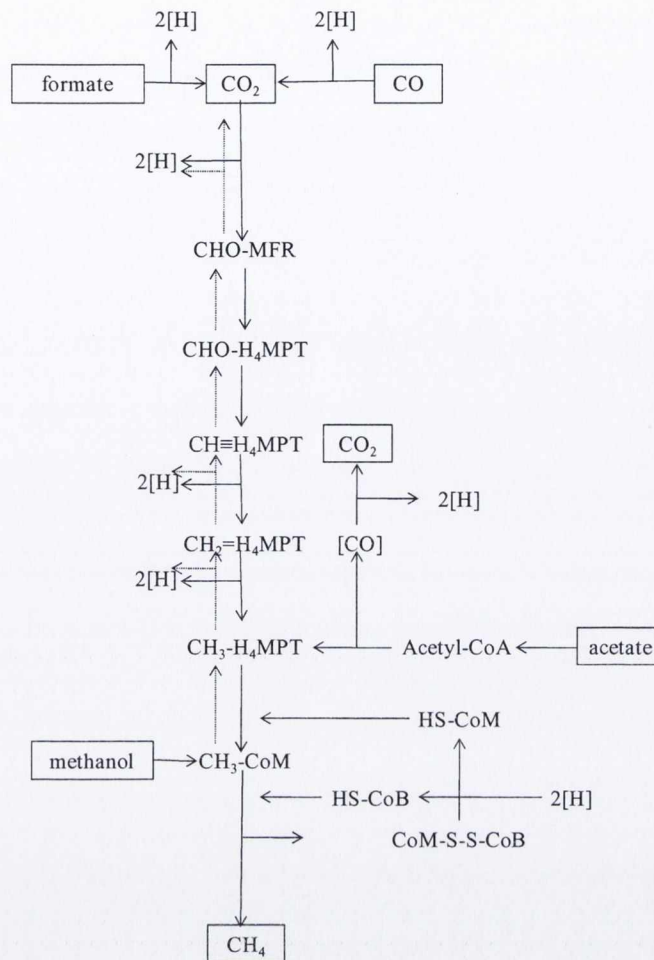


Figure 1.5 Methanogenesis pathways from acetate, methanol and H_2/CO_2 (CO, formate). MFR = methanofuran; H4MPT = tetrahydromethaopterin; HS-CoM = coenzyme M; HS-CoB = coenzyme B, as adapted (Stams and Plugge, 2010).

1.3 The Global N_2O and CH_4 Budget

A thorough knowledge of the overall N_2O and CH_4 budget requires balance of the sources and sinks of these gases and which principle influences affect their magnitude, the knowledge of the concentration of the gases on a global scale and the properties of those gases and how they change over time.

Also, it is important to understand the properties of these gases in relation to absorbing and re-emitting infrared radiation (heat). The Global Warming Potential (GWP) compares the direct climate forcing of greenhouse gases in terms of CO_2 . It combines the ability of a GHG to absorb infrared radiation, its atmospheric lifetime and the length of time over which its effects on

climate need to be quantified i.e. time horizon. It was a concept which was developed after countries committed to the Kyoto Protocol could use to compare the cost effectiveness of different mitigation measures (IPPC, 2007).

The simplified method most popularly used to integrate the global mean radiative forcing over time of a pulse emission of 1kg of a compound (*i*) relative to that of 1kg of CO₂ (IPCC, 1990). As such, GWP is defined as; *TH* is the time horizon; *RF_i* is the global mean RF (radiative forcing) of gas *i*; *a_i* is the RF per unit mass increase in atmospheric abundance of gas *i* (radiative efficiency), [*C_i(t)*] is the time-dependent abundance of *i*, and the corresponding quantities for the reference gas (*r*) in the denominator. The numerator and denominator are the absolute global warming potential (AGWP) of *i* and *r* respectively (IPPC, 2007):

$$GWP_i = \frac{\int_0^{TH} RF_i(t) dt}{\int_0^{TH} RF_r(t) dt} = \frac{\int_0^{TH} a_i \cdot [C_i(t)] dt}{\int_0^{TH} a_r \cdot [C_r(t)] dt}$$

Equation 1.1

The following table represents the GWPs of CO₂, CH₄ and N₂O over three timescales, 20, 100 and 500 years. The 100 year time horizon is most commonly referred to in climate change assessments and as you can see N₂O and CH₄ have 298 and 25, time greater potentials as global warming variables than CO₂ respectively (Table 1.1).

Table 1.1 Global warming potentials of greenhouse gases CO₂, CH₄ and N₂O over three time horizons.

Greenhouse Gas	GWP for each time horizon		
	20 years	100 years	500 years
CO ₂	1	1	1
CH ₄	72	25	7.6
N ₂ O	289	298	153

The present atmospheric N_2O concentration is about 319 ppb an increase of approximately 18% from pre-industrial values (Figure 1.6). This is a linear increase of approximately 0.8 ppb yr^{-1} over the past few decades and has led to a post-industrial era contribution to radiative forcing of $+0.16 \pm 0.02 \text{ Wm}^{-2}$. Anthropogenic factors, particularly agriculture and land-use change are currently estimated at causing 40% of N_2O emissions (IPPC, 2007).

It is quite concerning that levels of N_2O are increasing as this will contribute to (i) the enhanced greenhouse effect (Wang et al., 1976) which may lead to global warming and climate change, and (ii) to the destruction of stratospheric ozone (Crutzen, 1970), which may increase biologically harmful ultraviolet radiation or

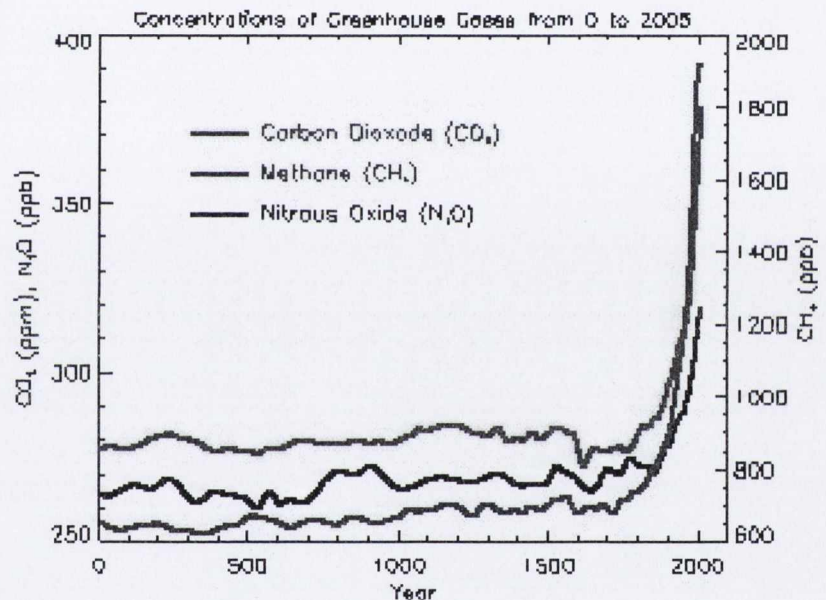


Figure 1.6 Atmospheric concentrations of important longlived greenhouse gases over the last 2,000 years. Increases since about 1750 are attributed to human activities during the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb) (IPPC, 2007).

Present CH_4 levels are at approximately 1774 ppb, pre-industrial levels increased from approximately 700 ppb (Fluckiger et al., 2004) to 1732 ppb recorded in the early 1990s (IPPC, 2007). However, over the 1990s, emission levels have evened out, suggesting that emissions are equal to removals. Current levels are due to continued anthropogenic emissions of CH_4 which are

greater than natural emissions i.e. where the balance between production by methanogenic bacteria and consumption by methanotrophic bacteria is positive, thus, leading to CH₄ emission. CH₄ emissions are mostly biogenic and include emissions from wetlands, ruminant animals, rice agriculture, biomass burning with smaller emission levels originating from industrial sources related to fossil-fuel usage.

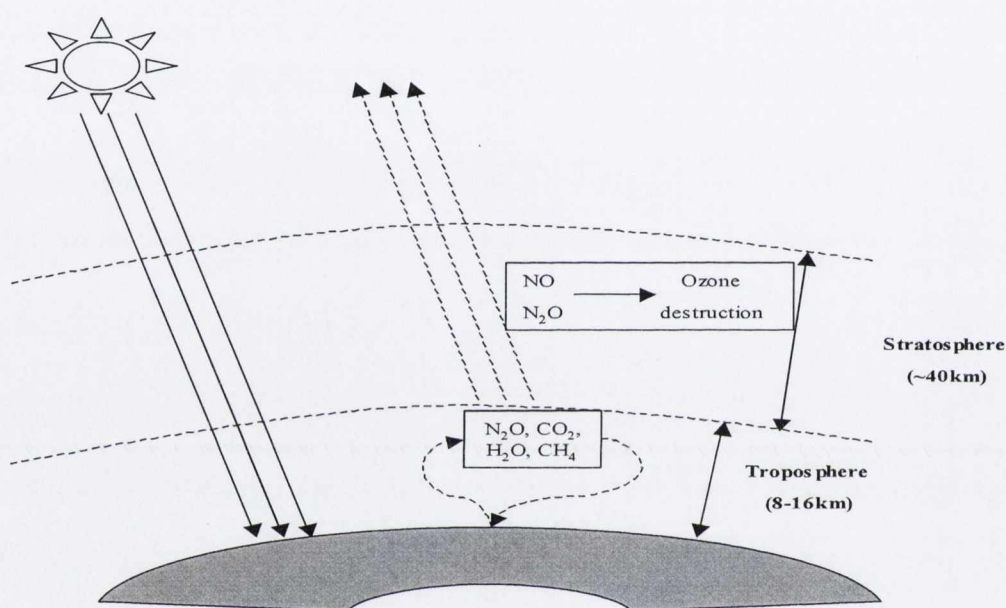


Figure 1.7 The impact of N₂O and CH₄ on the greenhouse effect. The sun's rays are absorbed by the surface of the earth, which in turn are emitted back at a longer wavelength to the upper troposphere. At this stage the rays are absorbed by greenhouse gases e.g. N₂O, CH₄, CO₂, H₂O and are re-emitted either back to earth or onto the stratosphere and beyond. In the upper stratosphere N₂O is oxidised to NO by UV light. NO destroys the ozone layer.

The global N₂O budget is a balance of the sink strength in the stratosphere and the atmospheric increase (Fowler et al., 2009). Soils act as a significant sink of atmospheric N₂O (Table 1.1) and also for CH₄ (accounting for approximately 6% of the global budget). Soil N₂O reduction has been

decreasing in recent decades (Chapuis-Lardy et al., 2007, Conen and Neftel, 2007).

As previously referred to, atmospheric N₂O has increasing over the last few decades at a linear rate of approximately 0.7 ppb year⁻¹. The third IPCC report concluded that this increase was caused by increases in microbial production of N₂O due to expanding and fertilised agricultural lands (IPCC, 2001). As in earlier IPCC reports, the agricultural factor was based on 'bottom-up' extrapolation to a global scale of data taken at a limited number of experimental sites (IPCC, 1990, IPCC, 1996, IPCC, 1992).

Table 1.2 Estimates of global N₂O and CH₄ budgets (Tg y⁻¹) (Fowler et al., 2009).

N ₂ O source ^a	Tg N ₂ O-N y ⁻¹	CH ₄ sources ^b	Tg CH ₄ y ⁻¹
<i>Natural sources</i>			
Oceans	3.8 (1.8 - 5.8)	Oceans	4 (0.2 - 20)
Atmosphere	0.6 (0.3 - 1.3)	Termites	20 (2 - 22)
Soils	6.6 (3.3 - 9)	Wetlands	100 (92 - 232)
		Others ^c	21 (10.4 - 48.2)
<i>Anthropogenic Sources</i>			
Agriculture	2.8 (1.7 - 4.8)	Rice cultivation	60 (25 - 90)
Biomass Burning	0.7 (0.2 - 1)	Biomass Burning	50 (27 - 80)
Energy and Industry	0.7 (0.2 - 1.8)	Energy ^d	106 (46 - 174)
Others ^c	2.5 (0.9 - 4.1)	Ruminants	81 (65 - 100)
		Waste Disposal	61 (40 - 100)
Total Sources	17.7 (8.5 - 27.7)		503 (410 - 660)
<i>Sinks</i>			
Stratosphere	12.5 (10 - 15) ^f	Stratosphere	40 (32-48)
Soils	1.5 - 3 ^g	Soils	30 (15-45)
		Tropospheric OH	445 (360-530)
Total Sinks	14 (11.5 - 18)		515 (430-600)

^a Sources are estimates for the 1990s as provided by (IPPC, 2007), ^b (Wuebbles and Hayhoe, 2002), ^c Others include marine sediments, geological sources and wild fires, ^d Energy includes natural gas, coal mining and other fuel related sources, ^e Atmospheric deposition, aquatic systems, sewage, ^f (Hirsch et al., 2006), ^g (Cicerone, 1989).

As illustrated in Table 1.3 the uncertainty of N₂O emissions in 1990 is quite large, covering two orders of magnitude (IPCC, 1990). However as increasing numbers of emission measurements were carried out on more agricultural sites from the 1990s onwards a narrower range of uncertainty was recorded in 1996 with a higher mean value (IPPC, 1996).

Table 1.3 Changing assessment since 1990 of agricultural contribution to global N₂O emissions (as adapted from (Smith et al., 2010)).

IPPC Assessment	Estimated global N ₂ O emission from agriculture (Tg N ₂ O-N yr ⁻¹)	Source
1990	0.01 – 2.2	Fertiliser, including emission from groundwater
1992	0.03 – 3.0	Cultivated soils
1996	3.5 (1.8 – 5.3)	Mineral N (fertiliser) + animal waste + N-fixation
2001 and Mosier et al., 1998 (Mosier et al., 1998).	4.2 (0.6 – 14.8) 2.1 (0.6 – 3.1) 0.5 (0.2 – 1.0) Total: 6.8 (1.0 – 18.9)	N added to soils + indirect emissions Manure management Biomass burning

Indirect Sources

Indirect pathways involves nitrogen that is removed from soil and animal waste management by volatilisation, leaching, runoff or harvest of crop biomass. The end product of these steps results in eventually providing substrate for nitrification and denitrification and ultimately N₂O emissions.

Direct Sources

An increase in soil available N increases nitrification and denitrification rates which then in turn increase the production of N₂O. Soil available N increases

can result from anthropogenic N inputs e.g. synthetic fertiliser (N), organic N e.g. manure, sewage sludge, or change of land-use and/or management practices that mineralise soil organic N. Agriculture is the main source of N₂O emissions (see figure 1.8).

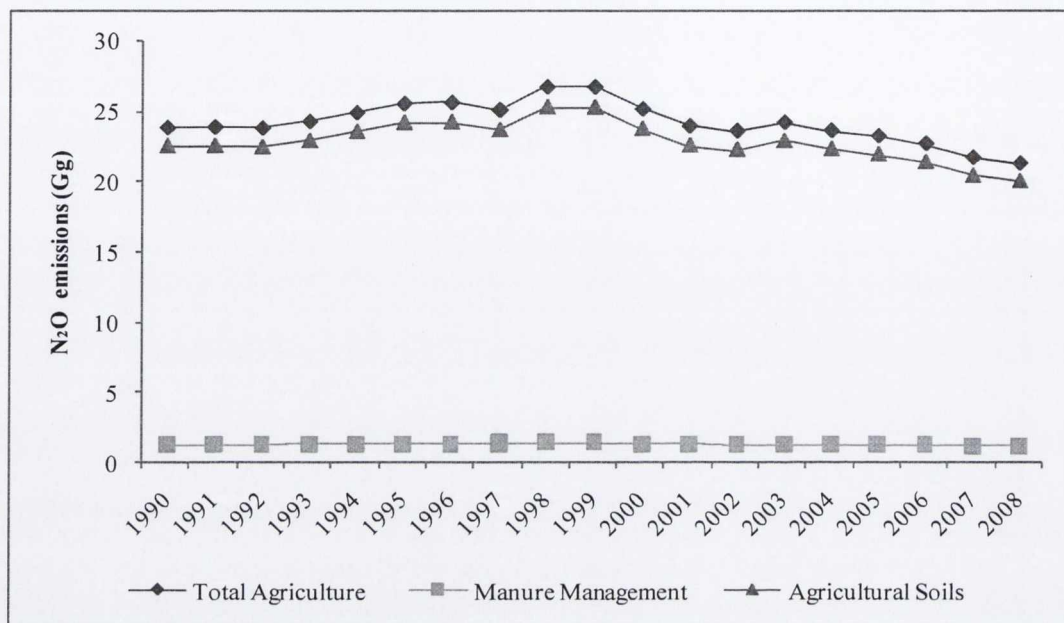


Figure 1.8 N₂O emissions (Gg) from total agriculture, manure management and agricultural soils(EUROSTAT, 2010).

With the development of the Haber-Bosch process, where ammonia could be synthesised by reacting atmospheric dinitrogen with hydrogen in the presence of iron at high pressures and temperatures, and its subsequent development on an industrial scale (for which it won a Nobel prize (Haber, 1920)) came the dawn of a new agricultural age. This process could be highly successful in meeting the growing demand for food with the increasing world population (see Figure 1.9).

The current worldwide usage of fertiliser nitrogen is approximately 100 Tg N yr⁻¹. Approximately 80% of manufactured nitrogen is produced for agricultural fertiliser (Galloway et al., 2008). Yet, nitrogen use-efficiency is quite low, in 2005 approximately 100 Tg N was used in global agriculture, whereas only 17 Tg was consumed in crop, dairy and meat products by humans (UNEP and WHRC, 2007).

It has been suggested that approximately 40% of fertiliser nitrogen is lost to the environment and is denitrified back to unreactive atmospheric dinitrogen (Galloway et al., 2004a). This represents a significant waste of energy (production of N via Haber-Bosch process) and also a loss of the excess nitrogen into environmental reservoirs, where it steps through atmospheric (NO and NH_3 emissions to the atmosphere have increased five-fold since preindustrial times (Galloway et al., 2004b)), terrestrial, aquatic and marine pools before being denitrified or stored as fossil reactive nitrogen. The mitigation of the effects of reactive nitrogen on the environment tend to focus on, but are not limited to, reducing the amount of reactive nitrogen created and increasing the efficiency with which it is used (Galloway et al., 2008).

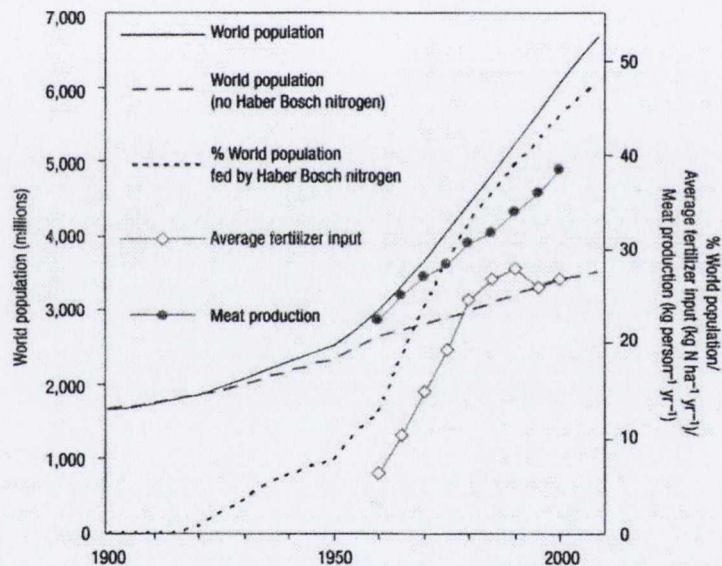


Figure 1.9 Trends in human population and nitrogen use throughout the twentieth century. The total world population (solid line) an estimate is made of the number of people that could be sustained without reactive nitrogen from the Haber-Bosch process (long dashed line), also expressed as a percentage of the global population (short dashed line). The recorded increase in acreage fertiliser use per hectare of agricultural land (non-filled diamond symbols) and the increase in per capita meat production (solid circular symbols) is also shown as adapted (Erisman et al., 2008).

A major factor with nitrogen is its link to many global environmental problems e.g. ozone layer depletion, global warming, surface and groundwater pollution, biodiversity loss, acidification of soils and surface waters, human health and vulnerability. As nitrogen is introduced to a

biogeochemical cycle pathway it can affect many processes. This sequence of effects is referred to as the ‘nitrogen cascade’ (Galloway and Cowling, 2002) (Figure 1.10).

The concept allows us to determine the links between the different variables of the nitrogen cycle and thus how a change to a part of the cycle may affect other parts of the cycle.

Reactive nitrogen released in gaseous forms (NH_3 , NO_x) can affect processes locally or can be transported to further environments and deposited into ecosystems. The nitrogen cycle is most altered in areas where there is a higher concentration of industrial and agricultural activity (Howarth et al., 1996, Howarth et al., 2002, Boyer and Howarth, 2002).

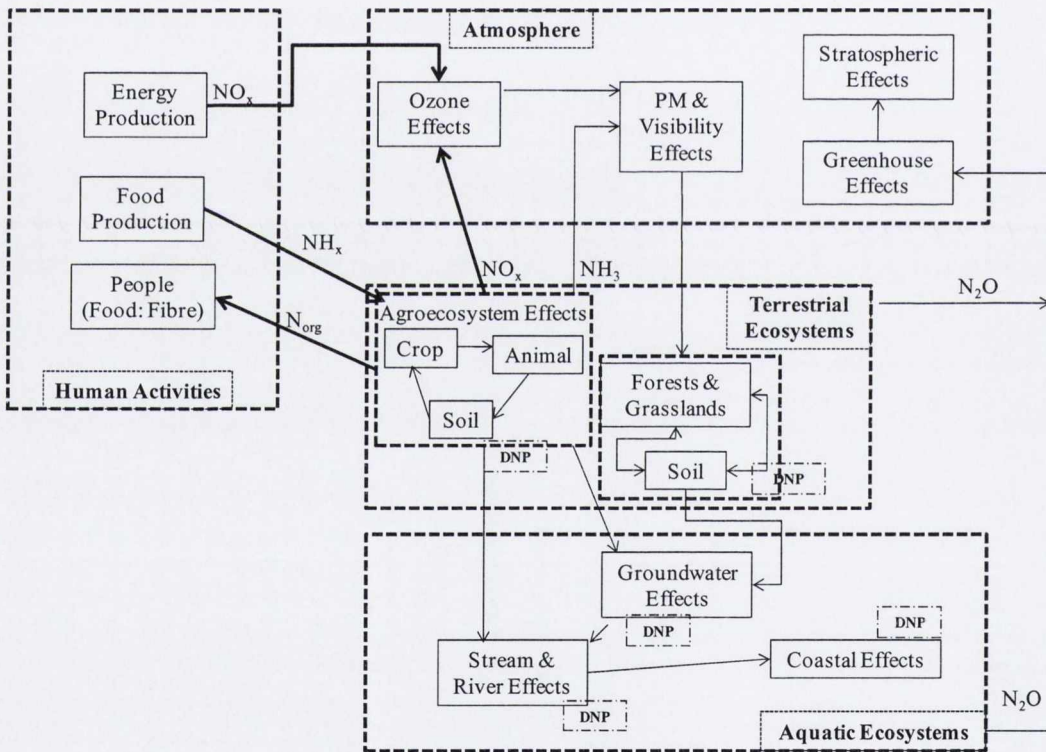


Figure 1.10 The nitrogen cascade, illustrates the movement of human-produced reactive nitrogen (Nr) as it cycles through the atmosphere, terrestrial ecosystems and aquatic ecosystems (Galloway and Cowling, 2002).

The largest proportion of N_2O emissions from nitrogen input in Ireland comes from the direct application of synthetic fertilisers (see Figure 1.11). One of

the most common types of synthetic fertilisers used are the Calcium-Ammonium-Nitrate (CAN) fertilisers.

Biofert is the commercial description of an organic by-product of urban wastewater treatment that is then treated to an approved standard for use on agricultural land as a soil conditioner / fertiliser. Some negative aspects of use of biofert would be the heavy metal content.

Also, with the use of currently > 6000 medicines for human use and >1000 for veterinary use licensed by the Irish Medicines Board (IMB), pharmaceuticals and personal care products (PPCPs) are also a significant concern e.g. increased microbial resistance to certain antibiotics (IMB, 2005, McMurry et al., 1998).

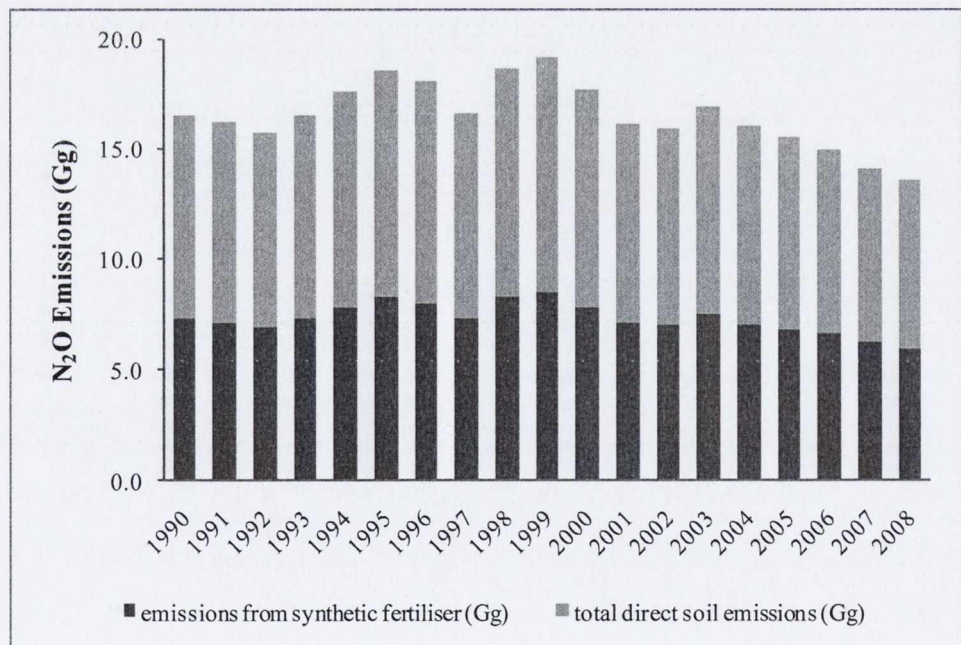


Figure 1.11 Trends in N₂O emissions (Gg) from total direct soil emissions and the proportion from emissions from synthetic fertilisers applied in Ireland from 1990 – 2008 (EUROSTAT, 2010).

PPCPs were still detectable in soil applied with sludge e.g. the antibacterial agent triclosan, 3-4 months after sludge spreading, this is despite the thermal drying process for the production of the pellicular biosolid fertiliser (Barron et al., 2010).

Major CH₄ sources are wetland ecosystems where methanogens and methanotrophs are present and active. CH₄ is consumed by methanotrophs active in the aerobic layers of most soils, the larger of the soil sinks are undisturbed soils (Table 1.2).

Atmospheric CH₄ originates from both biogenic and non-biogenic sources. Non-biogenic sources would include emissions from rice agriculture, livestock, waste landfill and treatment, geological sources (e.g. volcanic eruptions), fossil fuel mining and burning (natural gas, coal, petroleum). Agriculture is a major source of CH₄ emissions in Ireland (Figure 1.12). However, the vast porportion (≈70-80%) of atmospheric methane (CH₄) is biogenic.

There are a small number of CH₄ sinks to balance with a much greater number of CH₄ sources with any imbalance causing a change in atmospheric concentration. CH₄ sources are considered to be 70% due to anthropogenic activities, with the increase in animal husbandry being a significant contributor. Natural sources are also large and would have dominated global emissions until the 20th century.

Removal of atmospheric CH₄ through the oxidation reaction with hydroxyl (OH) radicals occuring mainly in the troposphere is the largest of three major sinks for CH₄ in the atmosphere:



In the stratosphere, CH₄ also reacts with Chlorine:



This reaction also produces peroxy radicals which can lead to ozone formation inducing an indirect climate-forcing effect of atmospheric CH₄. This reaction removes an estimated 360-530 Tg of CH₄ from the atmosphere each year (Table 1.2). The other sinks are much smaller, approximately 40 Tg CH₄ is removed by reaction with OH radicals in the stratosphere and approximately 30 Tg CH₄ is removed by methanotrophs (CH₄-oxidising bacteria) in soils using the CH₄ as a source of energy and carbon (Table 1.2).

CH₄ is also eliminated in soils by microbial oxidation, that occurs in the aerobic zone of methanogenic soils (methanotrophy) and in upland soils, which oxidise atmospheric methane. The soils with highest methanotrophy efficiency are usually submerged or water-saturated and where a significant methanogenic activity develops at intervals (Nesbit and Breitenbeck, 1992). Rice-fields soils, peat soils and soils from landfills usually have very high potential methanotrophic activity (Whalen et al., 1990). In these environments anaerobiosis usually predominates, thus the balance between CH₄ production and oxidation is usually positive.

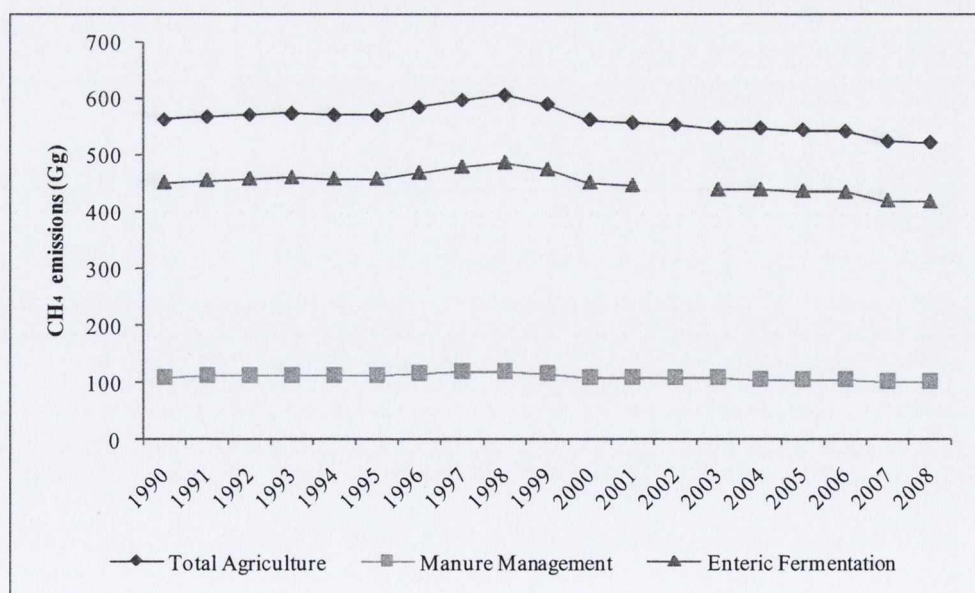


Figure 1.12 CH₄ emissions (Gg) for Ireland from total agriculture, manure management and enteric fermentation (EUROSTAT, 2010).

There have been marked decreases in atmospheric CH₄ levels during the 1990s and through to the earlier part of the 2000s where growth in global concentration of CH₄ had fallen to almost zero. However, increases in atmospheric CH₄ growth rose again during 2007 and 2008, this is attributed to increase in rainfall in the tropics in 2008 and increased temperatures in 2007 which led to increases in emissions of CH₄ in the Arctic (Dlugokencky et al., 2009).

The potential of this positive feedback loop for increased temperatures as projected may lead to increases in CH₄ emissions from wetlands, CH₄ hydrates and permafrosts.

Ireland

In Ireland, there was an decrease in N₂O emissions by 18.5% from their 1990 levels of 8,823.19Gg CO₂ equivalent to 7,194.86Gg CO₂ equivalent in 2008. N₂O emission levels peaked in 1999 due to an increase in the use of synthetic fertilisers and the production of higher levels of animal manure due to larger animal numbers. In 2002, Ireland's only nitric acid plant was closed down, this combined with reductions in synthetic fertiliser use and reduced organic nitrogen applications on land due to the effect of CAP reform on animal numbers led to a downward trend in N₂O emissions (EPA, 2010b, McGettigan et al., 2010).

CH₄ levels decreased 10.4% from 1990 levels of 13,574.62 Gg CO₂ equivalent to 12,165.04 Gg CO₂ equivalent in 2008. It is a significant contributor to greenhouse gas emissions in Ireland, due mainly to the large number of cattle in agriculture. There was an increase from 1990 to a 1998 peak of 14, 295.77 Gg CO₂ equivalent, due to an increase in cattle number. There is significant fluctuation in CH₄ emissions from 2001-2008. Landfill gas is also a significant contributor to CH₄ emissions, from 1990 – 2008 there has been a decrease of 20.2% due to the increased recovery of landfill gas (e.g. Ringsend WWTP; in conversation with Ciaran McCausland, PhD, Operations Engineer) and improved management of landfill facilities (EPA, 2010b, McGettigan et al., 2010).

1.4 The N and C cycle of Biomass Systems

Many different inputs to soil in agriculture affect emissions of greenhouse gases from soils and crops. Nitrogen input e.g. mineral fertiliser, green manures, organic manures represent major contributory factors to N₂O emissions. The complex interactions between soil properties, agricultural practices, climatic factors, microbial activity, soil pH, soil temperature, soil concentration of NH₄⁺ and NO₃⁻ soil aeration status and soil water content are very important in their affects on emissions. As these factors are complex, it is not always possible to directly correlate cause and affect of these variables.

1.5 Agricultural Emissions

The European Common Agricultural Policy (CAP) will be revised in the near future (2010-2013) and reform will effect many dimensions of sustainable development of agriculture, particuarly GHG emissions.

CH₄ and N₂O are for most EU countries, Ireland included, the main GHG sources from agriculture. The main sources of N₂O are manure management and soil emissions. Major sources of soil emissions can be identified (i) direct emissions from fertiliser and manure aplication, crop residues and mineralisation of peat soils, (ii) emissions from manure and urine during grazing, and (iii) direct emissions due to leaching and run-off of nitrogen. The major CH₄ sources are enteric fermentation by ruminants and emissions from manure management (Eurostat, 2010).

The total emission of GHG from agriculture is the sum of CO₂ + CH₄ + N₂O expressed in CO₂ equivalents, which are based on global warming potentials; CO₂ = 1, CH₄ = 25, N₂O = 298 (IPPC, 2007).

Ireland (Figure 1.14) has a relatively low level of GHG emission compared to other EU-15 states.

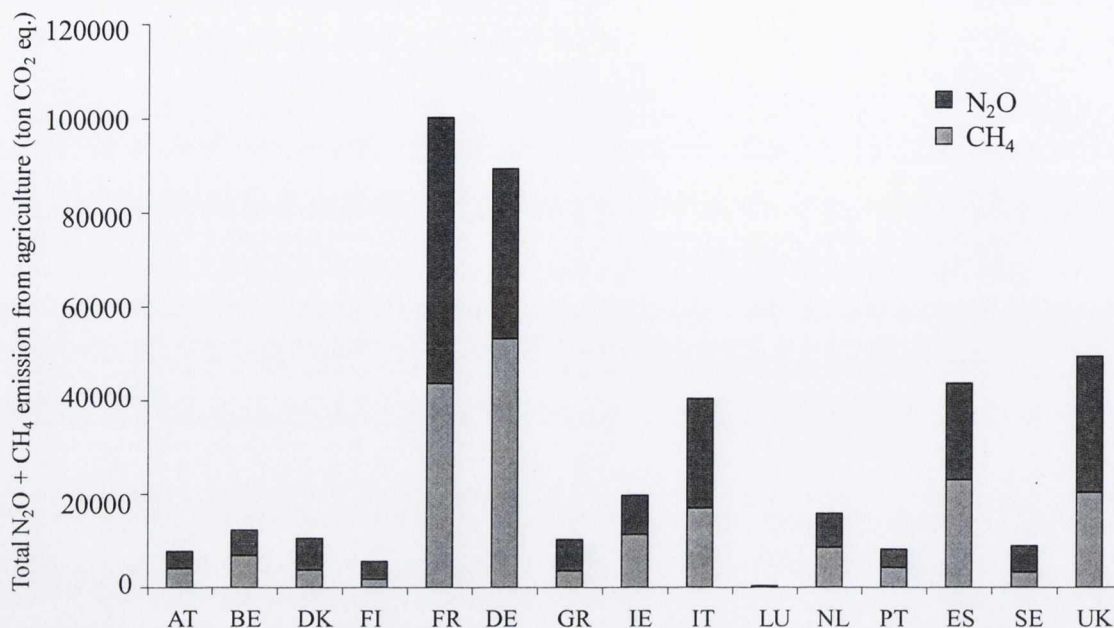


Figure 1.14 The total N₂O and CH₄ emissions from agriculture in ton CO₂ equivalents for EU-15 (AT-Austria, BE-Belgium, DK-Denmark, FI-Finland, FR-France, DE-Germany, GR-Greece, IE-Ireland, IT-Italy, LU-Luxembourg, NL-Netherlands, PT-Portugal, ES-Spain, SE-Slovenia, UK-United Kingdom) (EUROSTAT, 2010).

However, when GHG levels are compared in terms of agricultural land, Ireland has quite a high level (Figure 1.5) relative to its size. This is due mainly to the large livestock density in Ireland.

The Irish Environment Protection Agency (EPA) considers agriculture the largest source of N₂O emissions in Ireland and enteric fermentation is considered the largest source of CH₄ (McGettigan et al., 2010).

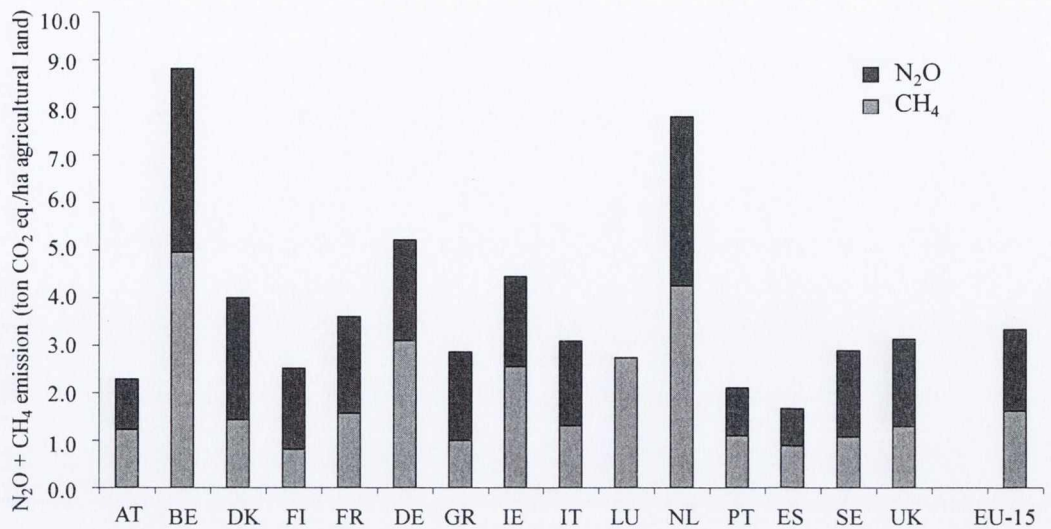


Figure 1.15 The total N₂O and CH₄ emissions from agriculture in ton CO₂ equivalents for EU-15 in terms of agricultural land (AT-Austria, BE-Belgium, DK-Denmark, FI-Finland, FR-France, DE-Germany, GR-Greece, IE-Ireland, IT-Italy, LU-Luxembourg, NL-Netherlands, PT-Portugal, ES-Spain, SE-Slovenia, UK-United Kingdom) (EUROSTAT, 2010).

1.6 Estimating GHG emissions

N₂O is produced mainly by microbial processes, the main processes are; denitrification (reduction of nitrate to dinitrogen); nitrification (oxidation of ammonium to nitrite). Agricultural systems lose a considerable portion of N additions through leaching and runoff, denitrification and ammonia volatilisation (IPPC, 2006). An estimated 60% of annual N input into food production was not converted into a useful end product (van der Hoek, 1998). A global estimate of a cereal crop N use efficiency stands at 40% (Cassman et al., 2002, Balasubramanian et al., 2004).

There are two main approaches in estimating GHG emissions:

(1) *Top-Down Approach*

Inverse modelling that relies on spatially distributed, temporally continuous observations of concentration, and in some cases isotopic composition in the

atmosphere (also includes aircraft and satellite observations (Xiao et al., 2004, Frankenberg et al., 2008). Approaches that are based on changes in atmospheric GHG concentrations and estimates of their sinks (Del Grosso et al., 2008).

Using data compiled for N₂O conversion, where new N input includes N produced by biological, chemical and atmospheric processes (i.e. biological N fixation, fossil fuel produced N oxides and fertiliser nitrogen produced industrially), a global scale estimate of 3-5% of all new reactive N input into terrestrial systems is converted to N₂O (Prather et al., 2001, Galloway et al., 2004a, Crutzen et al., 2008).

The atmospheric N₂O concentration at the beginning of the 21st century was approximately 315ppb with a stratospheric photochemical sink of N₂O of approximately 11.9 Tg N₂O-N yr⁻¹ is much greater compared to the pre-industrial era N₂O concentration of approximately 270 ppb with a sink of 10.2 Tg N₂O-N yr⁻¹ (including marine emissions) (Prather et al., 2001).

The total source of N₂O at the earlier part of the 21st century was equal to the atmospheric growth rate of 3.9 Tg N₂O-N yr⁻¹ plus the stratospheric photochemical sink of 11.9 Tg N₂O-N yr⁻¹ resulting in a total of 15.8 Tg N₂O-N yr⁻¹.

In order to calculate the anthropogenic source of N₂O we calculate the difference of the total source strength i.e. 11.9 Tg N₂O-N yr⁻¹ from the current natural source (which is equal to the pre-industrial source) 10.2 Tg N₂O-N yr⁻¹. This value is then subtracted by an uncertainty range of 0 - 0.9 Tg N₂O-N yr⁻¹, due to approximately 30% global deforestation causing a decrease in N₂O natural sources (Klein Goldewijk, 2001). This results in an anthropogenic source value of 5.6 – 6.5 Tg N₂O-N yr⁻¹. To further refine a

figure for the agricultural source of N_2O , the industrial source estimation of $1.3 \text{ Tg N}_2\text{O-N yr}^{-1}$ (Prather et al., 2001) is subtracted from the anthropogenic source to give a value range of $4.3 - 5.8 \text{ Tg N}_2\text{O-N yr}^{-1}$.

In the early 1990s, the anthropogenic reactive nitrogen input of 114 Tg N yr^{-1} was derived. This input value is based on 100 Tg of N which is fixed through the Haber-Bosch process, a 3.5 Tg N increase through Biological Nitrogen Fixation (BNF) plus $24 \text{ Tg of reactive N}$ released by fossil fuel combustion between pre-industrial and current times (Galloway et al., 2004b) this is then subtracted by 14 Tg of N not used as fertiliser but produced via the Haber-Bosch process (Smeets et al., 2007). The agricultural source of N_2O is estimated at $3.8 - 5.1 \%$ of the anthropogenic reactive nitrogen input of the early 114 Tg N yr^{-1} .

An estimated $6.2 - 7.2 \text{ Tg N}_2\text{O-N yr}^{-1}$ of the $10.2 \text{ Tg N}_2\text{O-N yr}^{-1}$ from the global source and sink of N_2O in natural i.e. pre-industrial times came from the land and coastal zones (Prather et al., 2001) and that was estimated from a fresh reactive N input of 141 Tg N yr^{-1} (Galloway et al., 2004b) giving a $\text{N}_2\text{O-N}$ yield of $4.4 - 5.1 \%$.

So, for natural terrestrial emissions before industrial fertiliser (i.e. Haber-Bosch process) production and agricultural emissions during industrial fertiliser production the N_2O output i.e. emission factor is $3 - 5 \%$ of the fresh reactive N input (Smith et al., 2010). However, this estimate is not dependent on an in-depth knowledge of the terrestrial N cycle, but it is based on atmospheric concentrations and known lifetime of N_2O and global budgets of reactive N input and N_2O . An important point about this estimation process is that when it used in fertiliser-N application to the production of biofuels, the global warming impact of the N_2O emissions resulting from fertiliser application was equal to or more than any positive 'cooling' effect which

would be achieved by replacing fossil fuels with biofuels (Crutzen et al., 2008).

(2) Bottom Up Approach

This approach involves the extrapolation from direct flux measurements and observations or models based on the application of N to soil. Some comparisons of global scale emission of industrial greenhouse gases can disagree with bottom-up emissions by factors of two or more (Levin et al., 2010, Stohl et al., 2009, Mühle et al., 2010). This approach is broadly covered by (a) field scale estimates which are based on experimental gas flux measurements from soils, (b) IPCC methodology from 2006, (c) Soil N₂O models e.g. DAYCENT and DNDC ecosystem models.

Calculation of Emission Factors

There has been a 20-fold increase in the worldwide consumption of synthetic N fertilisers worldwide since 1950 and approximately a 150% increase since 1970, resulting in approximately 82 Tg N y⁻¹ in 1996 (Mosier and Kroeze, 1999). This is widely recognised as the major factor causing increased atmospheric concentrations of atmospheric N₂O. Based on these figures, future projections of synthetic N fertiliser usage has pointed to a doubling of N fertiliser use in developing countries by 2025 (Vitousek and Matson, 1993, Bouwman, 1998).

There are three emission factors (EF) for estimating direct N₂O emissions from managed soils. The default values (see Table 1.2) can be used with Tier 1 equation of the Tier 2 equation in combination with country-specific emission factors: EF₁ refers to the amount of N₂O emitted from the different synthetic and organic N applications to soils (including crop residue and

mineralisation of soil organic carbon in mineral soils due to land-use change or management); EF_2 refers to the amount of N_2O emitted from an area of drained / managed organic soils; EF_3 estimates the amount of N_2O emitted from urine and dung N deposited by grazing animals on pasture, range and paddock (IPPC, 2006).

The IPCC have published default emission factors (Table 1.4) (from 1.25% of N applied as synthetic and organic fertilisers (from 1996 IPCC Guidelines) reduced down to 1% (result of new data and work (Bouwman et al., 2002b, Bouwman et al., 2002a, Stehfest and Bouwman, 2006), crop residues etc.; 2% of the N deposited by grazing animals (except sheep, 1%, as sheep have a more even urine distribution (smaller and more frequent urinations) and smaller effects on soil compaction during grazing (IPPC, 2006, de Klein, 2004).

A large body of research has been published in regard to these default values which strongly suggest that fluxes are significantly impacted by seasonal weather fluctuations, management variables and crop type (Bouwman et al., 2002a, Stehfest and Bouwman, 2006). A criticism of the bottom-up IPCC methodology is the sheer uncertainty ranges of its values, however the sum of the methodology is reasonably consistent with the total derived from the top-down methodology.

A methodology for bottom-up estimation based on the fact that the newly fixed N entering agricultural systems (N from BNF and synthetic N-fertiliser) is regarded as the source of all N_2O emissions related to agriculture (Crutzen et al., 2008).

These emissions involve longer cycling times and are considered in three categories:

- (i) direct emissions from N-fertilised soils

- (ii) secondary emissions which are a result of complex N compound transformations within agricultural systems: e.g.
- crop residues ploughed in as fertiliser for a successor crop
 - dung and urine from livestock (housed and grazing) fed on a varied diet of N-fertilised grain crops, feeds containing BNF-N (e.g. soya bean meal)
 - N mineralised from soil organic matter and root residues following cultivation or renewal of grassland.
- (iii) indirect emissions (as in IPCC methodology) arising from N leached from soils, volatilised N deposited onto natural ecosystems.

IPCC methodology is based on measurements of soil surface gas flux emissions from different global sites (IPCC, 2006). There is an assumed proportional relationship between soil nitrogen inputs and sources of emissions produced and also accounts for manure management systems.

The DAYCENT model (Del Grosso et al., 2006) accounts for the following factors which influence soil emission of N₂O; labile C availability, water, O₂, temperature and plant nitrogen demand as well as N inputs. Del Grosso et al., (Del Grosso et al., 2008) used DAYCENT to calculate N₂O emissions from US agricultural systems and emissions from the globe using bottom-up approaches and compared these with a range of N₂O emissions estimated using the top-down approach of Crutzen et al (Crutzen et al., 2008). They calculated a N₂O emission range of 3 – 5 % of the combined nitrogen inputs from symbiotic nitrogen fixation and synthetic fertiliser application (Del Grosso et al., 2008).

Table 1.4 Default emission factors to estimate direct N₂O emissions from managed soils (table amended from (IPPC, 2006)).

Emission factor	Default value	Uncertainty range
EF ₁ for N additions from mineral fertilisers, organic amendments and crop residues, and N mineralised from mineral soil as a result of loss of soil carbon [kg N ₂ O-N (kg N ⁻¹)]	0.01	0.003 - 0.03
EF _{1FR} for flooded rice fields [kg N ₂ O-N(kg N) ⁻¹]	0.003	0.000 - 0.006
EF _{2CG, Temp} for temperate organic crop and grassland soils (kg N ₂ O-N ha ⁻¹)	8	2.0 - 24.0
EF _{2CG, Trop} for tropical organic crop and grassland soils (kg N ₂ O-N ha ⁻¹)	16	5.0 - 48.0
EF _{2F, Temp, Org, R} for temperate and boreal organic nutrient rich forest soils (kg N ₂ O-N ha ⁻¹)	0.6	0.16 - 2.4
EF _{2F, Temp, Org, P} for temperate and boreal organic nutrient rich forest soils (kg N ₂ O-N ha ⁻¹)	0.1	0.02 - 0.3
EF _{2F, Trop} for tropical organic forest soils (kg N ₂ O-N ha ⁻¹)	8	0.00 - 24.00
EF _{3PRP, CPP} for cattle (dairy, non-dairy and buffalo), poultry and pigs [kg N ₂ O-N(kg N) ⁻¹]	0.02	0.007 - 0.06
EF _{3PRP, CPP} for sheep and other animals [kg N ₂ O-N(kg N) ⁻¹]	0.01	0.003 - 0.03
Sources:		
EF ₁ : (Bouwman et al., 2002b, Galloway, 1998, Bouwman et al., 2002a, Stehfest and Bouwman, 2006)		
EF _{1FR} : (Akiyama et al., 2005)		
EF _{2CG Temp} , EF _{2CG, Trop} , EF _{2F Trop} : (Klemedtsson et al., 1999, IPCC/OECD/IEA/IGES Penman J., 2000)		
EF _{2F Temp} : (Alm et al., 1999, Laine et al., 1996, Martikainen et al., 1995, Minkkinen et al., 2002, Regina et al., 1996, Klemedtsson et al., 2002)		
EF _{3 CPP} , EF _{3 SO} : (de Klein, 2004)		

At large scales, Del Grosso et al. concluded that bottom-up and top-down approaches in calculating N₂O emissions from agriculture produce similar

estimates. DNDC (DeNitrification-Decomposition) is a process-based model which was developed to model N₂O and CO₂ emissions from arable soils (Li et al., 1992).

The DNDC model is also used on forest soils (Reth et al., 2005). There has been generally better agreement between using DNDC for estimating N₂O emissions from croplands rather than grassland systems (Abdalla et al., 2009a, Beyhedt et al., 2007). DNDC has been recommended for use in systems where nitrogen input is medium to high, but less suitable to low level nitrogen input systems as accuracy of the model's predictions is highly dependent on the level of fertiliser applied (Abdalla et al., 2009b, Froelking et al., 1998).

It has been used to predict N₂O emissions on Irish soils with a good level of accuracy and agreement based on direct soil N₂O emissions (Abdalla et al., 2009b, Abdalla et al., 2010c, Abdalla et al., 2010b, Abdalla et al., 2010a).

Both of these models are evaluated based on soil based emission measurements. However, emissions of N₂O vary greatly in time and place and many methodologies do not always agree well particularly at small scales. However, it appears as the scale increases estimate agreement improves which is encouraging.

For CH₄, inventory stages are at a lesser level of development than for N₂O and as a result there are high levels of uncertainty. There is a high dependency of CH₄ emissions on the local climate, the level of management and current status of the soil as such extrapolation of emissions onto larger scales is quite difficult. Preliminary estimates of uncertainty for CH₄ stand at 30-35% for most sources. There has been a great increase in the number of CH₄ inventories reported over the last decade and this will lead to improvements in estimations.

There are inherent flaws in estimates of methane, for the bottom-up approach there are large temporal and spatial variations of fluxes and also a limited range of observational conditions. It is also considered that the actual emissions of industrial greenhouse gases tend to be greater than reported (Nisbet and Weiss, 2010).

A comparison of official CH₄ inventories and data from the EDGAR database found differences between the two data sets were a result of inappropriate use of emission factors and activity data used (Van Amstel, 2009).

Satellites e.g. SCIAMACHY have been used to identify real-time CH₄ concentration fields and troposphere profiles thus leading to increased accuracy of models and also aid in verification of measurements at ground level with data from space.

Accurate estimates of total N₂O losses from energy crops derived from flux chamber measurements are hampered by the large temporal and spatial variability of N₂O fluxes from these sites. These errors are particularly significant due to the time pattern of N₂O fluxes. They are characterised by short-lived high flux rates (peaks) which are a significant amount of the total annual loss (Flessa et al., 1995, Mogge et al., 1999). These variations are because the variables controlling the production of N₂O in soil during the microbiological denitrification and nitrification (Davidson, 1991c, Granli and Bockman, 1994) also vary in space and time (Bouwman, 1995). The variables include temperature and the contents of mineral nitrogen (N), mineralisable carbon (C), moisture and oxygen. The main source of error in flux rates relates to these large temporal and spatial variations.

The use of flux chamber techniques is very popular for measuring N₂O and CH₄ fluxes from the soil (Mosier, 1989, Matthias et al., 1980b, Hutchinson and Mosier, 1981a, Hutchinson and Livingston, 1993, Kaiser et al., 1996) and even within them there are variations that can be quite large (Ambus, 1994). Increasing the number of replicates would decrease the estimated variance, however it is not always feasible due to time and resource constraints.

Advantages of micrometeorological methods are that they integrate fluxes over a large area (Fowler and Duyzer, 1989). They do require a large area though which is uniform and they are less than ideal for comparing experimental treatments e.g. fertiliser applications. As such, flux chamber measurement techniques are a good compromise for field studies. Sample frequencies are typically either monthly (Ambus and Christensen, 1995b, Veldkamp and Keller, 1997) or weekly (Velthof et al., 1996, Flessa et al., 1998).

The use of ecosystem (patch) scale ($10^4 - 10^6 \text{ m}^2$) techniques i.e. the eddy-covariance (EC) technique are another technique used to directly measure the terrestrial carbon flux. The method is based on measurements of turbulent fluctuations of the vertical velocity and the concentration of passive tracer. When planning the site tower knowledge of the soil and vegetation of the area affecting the flux is very important to detection and also in interpreting the data (Finnigan, 2004). Assumptions used when the EC technique is adopted are that there are the following meteorological conditions i.e. horizontal homogeneity, zero advection, steady state are satisfied (Gökeke et al., 2004). The vegetation density is spatially diverse and it influences the lower atmospheric circulation and surface exchange of carbon, energy and water over a wide range of scales e.g. (Shen and Leclerc, 1995, Buermann et al., 2001, Cosh and Brutsaert, 2003).

The meteorological assumptions are often not valid at complicated terrain sites and as such EC data interpretation remains challenging (Sogachev et al., 2004) and the spatial variability also provides challenges regarding spatial representativeness of long-term accumulated data.

Ireland

Agricultural soils are a major N_2O source in Ireland. The IPCC methodologies for the source categories concerned are simplified and they are based on a consideration of separate direct and indirect contributions to national emissions. Ireland uses the IPCC good practice guidance

methodology completely to estimate N₂O emissions from agricultural soils. Values for emission factors for the calculation of direct and indirect soil emissions for the full time series 1990 – 2008 are 2.0 (EPA, 2010b). It has been recognised that a much more in-depth model approach is needed in order to take all determining factors on emissions into account. In Ireland a methodology which takes into account the influence of soil type fertiliser type and application rates, temperature and rainfall needs to be adopted. Recent research has suggested that N₂O rates from agricultural soils may be higher than the suggested 1.25% given by the current IPCC default emission factor.

1.7 Factors Affecting Soil N₂O

The major factors affecting soil N₂O emissions include soil moisture (soil water filled pore space (WFPS)), the soil concentration of NH₄⁺ and NO₃⁻ and the affects of agricultural management practices e.g. fertiliser application on these concentrations, soil temperature, soil pH, level of microbial activity and soil available organic material.

Soil Moisture

Water in soil is a vital link in the hydrological cycle that controls exchange with the atmosphere above and with the groundwater below. It controls and influences much of the physical, chemical and biological processes in soils. The high heat capacity of water causes a moderation of diurnal and seasonal temperature cycles at the soil surface. Water serves as the transport agent for dissolved inorganic chemicals and suspended biological components involved in the processes of soil development and degradation. Water in soil acts as a binding agent and lubricant among the soil particulate materials, influencing the strength of soil and geological materials and also its structural stability. Biological production from soil as agricultural crops is influenced primarily by water availability. This then depends on the water content and soil properties.

Soil moisture affects N_2O production by reducing the volume of gas in the soil, thus restricting oxygen supply and it dissolves the applied fertiliser. By reducing soil oxygen diffusion it in turn stimulates denitrification (Dobbie and Smith, 2001). It has been shown to be a significant factor in influencing N_2O emissions (Abdalla et al., 2010a). There is a significant relationship between water filled pore space and N_2O emissions; water filled pore space of 80% producing thirty times greater N_2O fluxes than at 60% water filled pore space (arable soil) (Dobbie and Smith, 2001). In a waterlogged soil, the rate of nitrification is restricted, which in turn limits denitrification (as it produces nitrate). In temperate climates, the water filled pore space for maximum N_2O production is between 80-85% (Dobbie et al., 1999) suggesting wetter conditions with higher levels of anaerobicity produce higher N_2O emissions.

The lowest emissions occur during times of low rainfall (low soil moisture content) e.g. during summer period. The high positive relationship between N_2O flux and soil moisture would suggest higher flux values during higher rainfall periods (i.e. winter, early spring) other soil properties e.g. soil drainage are important parameters to take into account during these periods to correctly assess fluxes (Choudhary et al., 2002).

Fertiliser

There have been vast increases in the use of fertiliser in order to meet the surging demands of a growing world population (see section 1.1). The addition of N fertiliser directly affects N_2O production as it provides N for denitrification and nitrification (Snyder et al., 2007).

Over the past 100 years the introduction of fertiliser production on an industrial scale has resulted in significantly increased use of synthetic N fertiliser use on agricultural soil, this in turn has significant effects on the global N budget (Galloway, 1998). In Ireland synthetic N fertilizer input has increased from 0.13 Mt in 1973 to 0.35 Mt in 2005 (see figure 1.16) (EUROSTAT, 2010).

In 1950 global synthetic N input into soils constituted 7% of a total N input of 56 Mt, whilst in 1996 synthetic N was approximately 43% of a total N input of 190 Mt (Mosier, 2001). Over this 46 year period the global input of synthetic N into soils has increased from 4 to 82Mt with a related increase in the amount of fertilizer-induced N₂O released to the atmosphere.

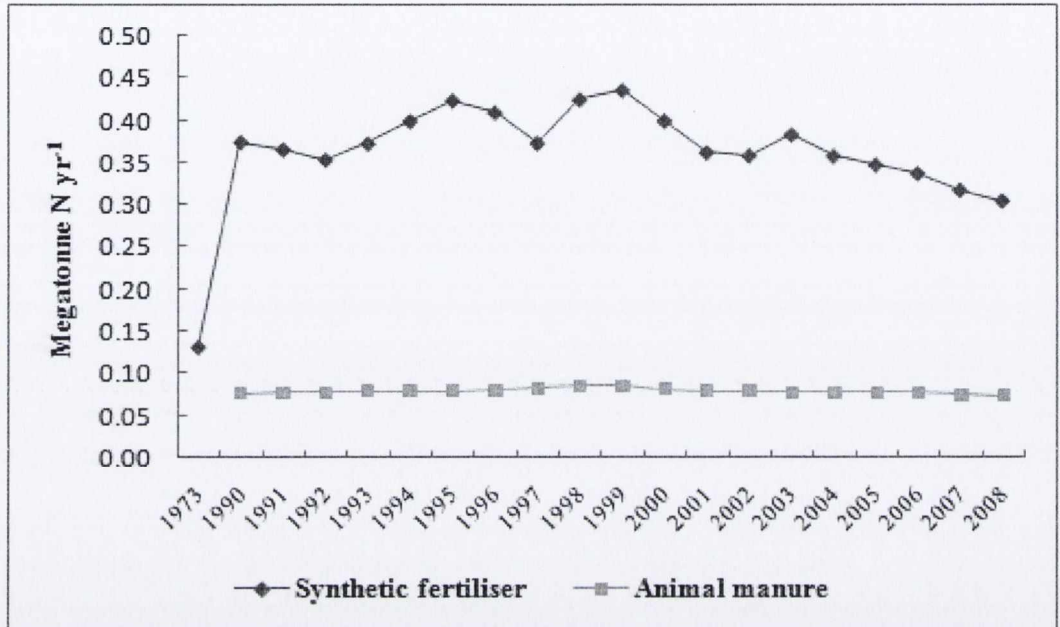


Figure 1.16 The amount (megatonne N yr⁻¹) of synthetic fertiliser (1973, 1990-2008) and animal manure (1990-2008) used on Irish soil (EUROSTAT, 2010).

This anthropogenic input is considered equivalent to biological N fixation (Galloway, 1998).

Soil Temperature

Microbial activity is related to temperature and as such denitrification and nitrification rates increase with an increase in temperature (Yamulki et al., 1995) (the parameter, Q₁₀, is a method of quantifying this increase). However, warmer soil temperatures alone are not enough to increase the N₂O emissions but they facilitate soil microbial populations to react to other factors e.g. rainfall, fertiliser but very often an increase in temperature leads to increased N₂O emissions (Smith, 1997, Smith et al., 2003).

Soil conditions for almost 1/3 of the year are exposed to soil temperatures of less than 0°C on the earth's terrestrial surface for 3-9 months. For the colder months there is generally a period of gradual decrease in temperature down towards 0°C, then a period of a completely frozen state and then a gradual melting of the ice with more frequent freeze-thaw cycles. The duration and extent of these cycles varies both spatially and yearly, as do the N-transformation rates.

In frozen sites the bacteria are covered by a thin film of water, this allows nutrients to reach the cells and the elimination of waste products by diffusion through small channels of liquid water. However these diffusion gradients eventually slow and stop (Figure 1.17).

High levels of N₂O emissions have been recorded during freeze-thaw cycles (Christensen and Tiedje, 1990, Flessa et al., 1995, Van Bochove et al., 2000, Singurindy et al., 2009). In unfrozen microsites, which are surrounded by ice, there is a limited gas exchange which leads to a development of O₂-deficiency thereby favouring denitification. Within these thin films, labile C availability is high due to microorganisms being killed by hygroscopic effects and/or freezing and also from organic matter from broken aggregates (Christensen and Tiedje, 1990).

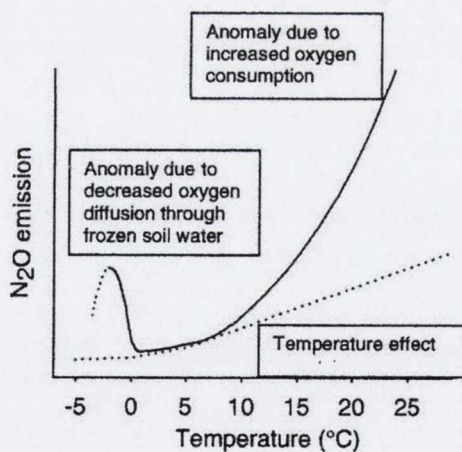


Figure 1.17 Conceptual illustration of the temperature effect on the production of N₂O in soils. The dotted line includes only the direct temperature effects, while the solid line combines both the direct temperature response and increased anoxic conditions from either reduced diffusion due to ice development or from increased oxygen consumption due to increased heterotrophic activity at increasing temperature, adapted (Öquist et al., 2004).

Another factor to consider is the nutrient concentrations in liquid water films which increases due to ion exclusion from the growing ice grid (Stähli and Stadler, 1997). These can contribute substantially to C- and N-enriched microsites covered with liquid water below 0°C.

Low soil temperature limits soil N-mineralisation, but earlier and deeper snow conditions with the associated warmer winter soil temperature dramatically increase over-winter N-mineralisation (Shmidt and Lipson, 2004). This along with nitrification occurred in soils at temperatures below 0°C. Denitrification, nitrification and N-mineralisation were measured in frozen soils down to -4°C simultaneously. The minimum temperature for mineralisation to occur was -9.3°C in Swedish cold adapted soils (Öquist et al., 2004).

Studies of methane oxidation in different ecosystems between the subarctic and the tropics have indicated only a weak correlation between the temperature optimum for methane oxidation and environmental in situ temperatures. The temperature optimum for methane oxidation increases ≤ 36 °C in subtropical paddy soil and from ca. 20 - 25°C in boreal bogs (Nesbit and Breitenbeck, 1992, Dunfield et al., 1993, Krumholz et al., 1995, Whalen and Reeburgh, 1996, Cai and Yan, 1999).

Soil pH

Within soil properties, soil pH is often referred to as a *master variable*, as it has such an effect on many processes and properties, chemical, biological and physical (Brady and Weil, 1999).

Three major processes that generate nitrous oxide and nitrogen are greatly affected by pH levels: i) nitrification, ii) denitrification and iii) dissimilatory NO_3^- reduction to NH_4 (DNRA) (Stevens et al., 1998).

The relationship between soil nitrification and pH is very complex, indeed the rate of the denitrification process itself is also complex. The ratio of gaseous products depends on pH values also. Generally, low pH values produce a low

overall denitrification activity and the fraction of N_2O produced is high. Extensive reviews of the effects of soil pH on denitrification have been done (Šimek and Cooper, 2002). They put forward the case where the phrase 'optimum pH for soil denitrification' which is frequently proposed, holds no real weight without reference to the specific attributes of the process.

In desert and dry ecosystems the conditions appear to be unsuitable for microbial denitrification, these soils would be described as hot, dry and nutrient-poor and receive high solar irradiation. In the summer, the soil surface temperatures can exceed $60^\circ C$ and in the winter temperatures drop below freezing. However, with this in mind, the rates of denitrification in mesic ecosystems are comparable to those of wet desert soil (Virginia et al., 1982). A large pool of desiccation-tolerant enzymes within the bacteria thriving there contribute to a significant fraction of the rates as found in other soils (Groffman and Tiedje, 1989). As moisture content in desert soils is quite sporadic, a rapid response by nitrifying and other bacteria is of particular significance. After soils are wet, there is often a quick increase in microbial activity and the availability of nutrients (Peterjohn, 1991).

1.8 Global Warming, The Kyoto Protocol and Ireland

The earth's atmosphere is unique in the solar system and is determined by biological processes in soils, oceans and vegetation interacting with physical and chemical processes within the atmosphere. Major and trace gas constituents of the atmosphere are significantly attributed to the interaction of the physical surface-atmosphere exchange and the biological production processes which are then transferred through the surface-atmosphere interface.

It is quite clear from much of the international assessment of changes in the composition of the atmosphere since the industrial revolution that the emission of these trace gases are affecting the earth's climate (IPPC, 2007), global biodiversity (MEA, 2005) and the biogeochemical cycling of major nutrients including nitrogen, carbon and sulfur.

The interactions between the earth's surface and atmosphere represents the zone where the control of fluxes occurs mainly between the sinks and sources. To understand these controlling processes is vital to quantify and model the impact of anthropogenic factors on the biogeochemical cycles. Examples of these anthropogenic impacts are changes in land usage, emissions of gases to the atmosphere as a result of industrial activities.

In regards to nitrogen, the combustion processes for oxidized nitrogen and the Haber Bosch process for reduced nitrogen is now dominant for the cycling of reactive nitrogen from the atmosphere back to the marine and terrestrial ecosystems. Indeed the total emissions of reactive nitrogen (104 T-g in 1993 of oxidized and reduce reactive nitrogen, N_r) from human activities at the end of the 20th century was four times greater than that attributed to natural sources (20.7 Tg) (Galloway et al., 2004b). This has a major effect on atmospheric composition, biodiversity and ecosystem function as nitrogen is a limiting nutrient in many ecosystems (Erisman et al., 2008).

Radiative Forcing (RF) is a concept used for the quantitative comparisons of the strength of different human and natural agents in causing climate change (IPPC, 2007). The global mean concentration of CH_4 in 2005 was 379ppm, leading to an RF of $+1.66 (\pm 0.17) W m^{-2}$. The global mean concentration of N_2O rose to a concentration of 319ppb in 2005, with an RF of $+0.16 (\pm 0.02) W m^{-2}$.

The Kyoto Protocol (UN, 1998) is an agreement that has been internationally negotiated and agreed by 37 industrialised countries and the European community, it is linked to the United Nations Framework Convention of Climate Change (UNFCCC). As required from the Kyoto Protocol, Annex 1, countries that have signed are committed to reducing their total greenhouse gas emission by binding targets, below that of the *base year*, 1990. The *Kyoto basket* of greenhouse gases includes: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and the so-called F-gases (hydrofluorocarbons, perfluorocarbons and sulphur hexafluoride (SF_6)). The reduction averages at 5% reduction from 1990 levels over the period 2008-2012. A national emission inventory is established for purposes of reporting annual emissions

using the same methodologies and templates for reporting and categorising the significant variables.

In general the base year is 1990 for the non-fluorinated gases and 1995 for the fluorinated gases. These gases are aggregated into a single unit using gas-specific global warming potential (GWP) factors. The aggregated greenhouse gas emissions are expressed in units of CO₂ equivalents. The indicator does not include emissions and removals related to land use, land-use change and forestry (LULUCF); nor does it include emissions from international aviation and international maritime transport. With the exception of Cyprus and Malta all Member States have individual targets under the Kyoto Protocol. The EU-15 agreed (Council Decision 2002/358/EC) to a collective 8 % reduction of its greenhouse gas emissions by 2008-12. This agreement sets the contribution of each individual EU-15 Member State towards reaching the common EU Kyoto target. Eastern European Member States have individual targets under the KP, with reduction requirements ranging from 6 % to 8 % (EUROSTAT, 2010).

Ireland

Ireland has had a steady increase in its total emissions (Figure 1.1) and is currently above the target for 2012. Emissions have increased to a peak in 2001. Fuel consumption in the energy sector has been the principal source of these emissions and a large increase in fuel use have further driven up emissions. There was the closure of nitric acid plant in 2002 and ammonia plant in 2001 which would account from N₂O reductions around this period.

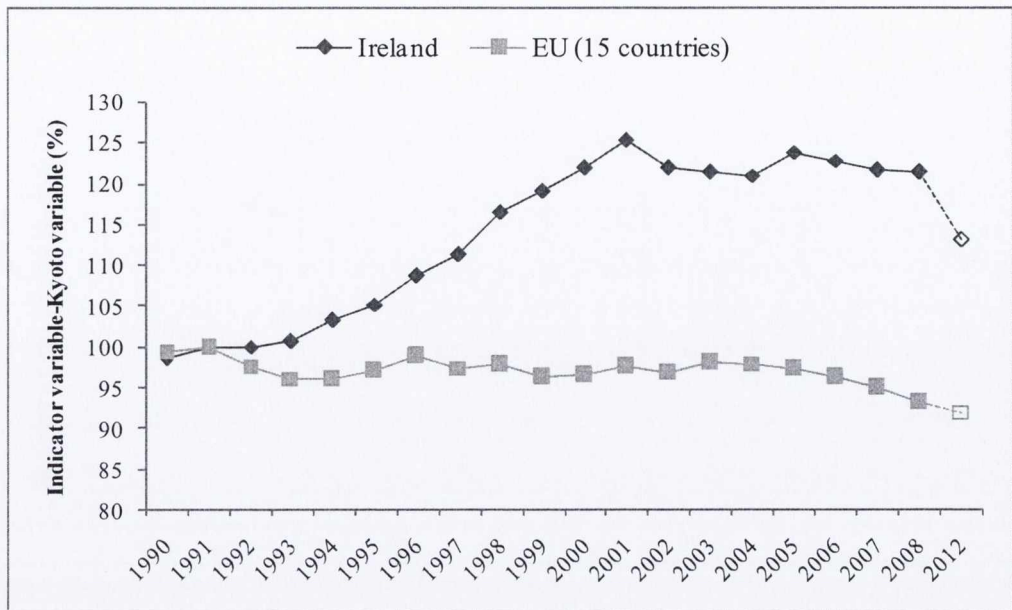


Figure 1.18 This indicator shows trends in total man-made emissions of the "Kyoto basket" of greenhouse gases of Ireland and the EU-15 countries, the dashed line represents the Kyoto "target" figures for 2012. It presents annual total emissions in relation to "Kyoto base year". (EUROSTAT, 2010).

In figure 1.19 the increase in emissions from 1990 to 2008 levels has been in all sectors but particularly in energy industries. Transport emissions increased by 176% from 1990 levels, electricity emissions increased 29% and industrial sectors emissions increased 19%.

The emissions from agriculture increased throughout the 1990s but decreased to 9% below 1990 levels in 2008. This is mainly due to a reduction in animal numbers and reduced amounts of synthetic fertiliser being spread on land due to reforms of Common Agricultural Policy (CAP). With the increase in emissions from energy, agriculture's contribution to the total emissions decreased from 35% in 1990 to 26% in 2008 (EPA, 2010b).

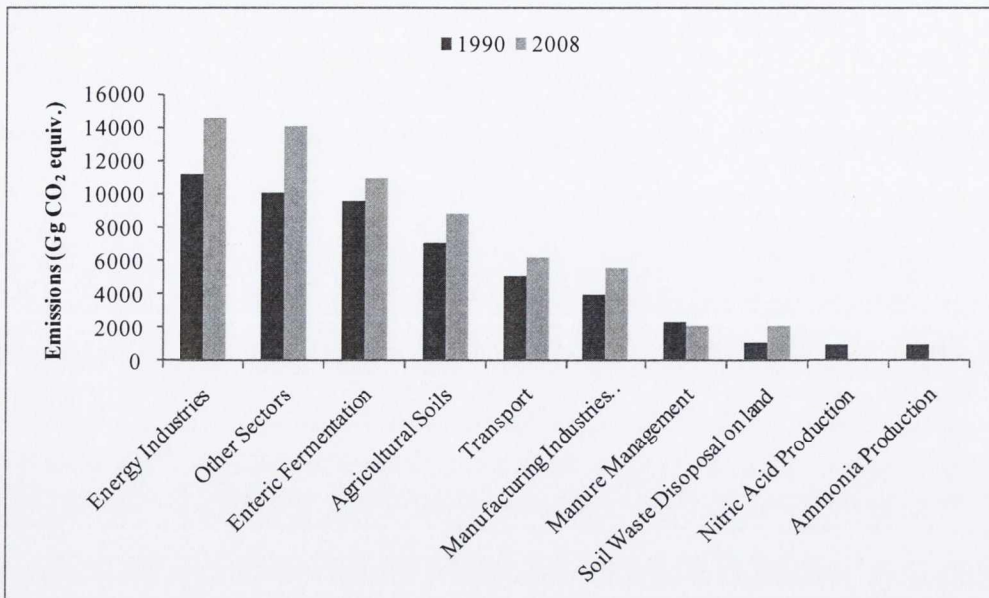


Figure 1.19 Emissions of GHG in Ireland for 1990 and 2008 in CO₂ equivalents. ((other sectors = Commercial, Residential and Agriculture). Nitric Acid and Ammonia Production plants closed down in 2002 and 2001 respectively.).

1.9 Mitigation Options

As the level of intense farming increased in the latter half of the last century environmental side-effects were noticed, although links were not yet clear. Intense agricultural production has since seen the result of increased detrimental emissions to the environment as a result of manure- and fertiliser-derived excess nitrogen and phosphorus (Steinfeld et al., 2006). With increases in the world population and a meat-rich diet, this type of intensive agricultural production looks set to continue (Oenema et al., 2005).

In Ireland, we are signatories of the Kyoto Protocol and as such have committed to reducing our greenhouse gas emissions by 2012. Currently the greenhouse gas emissions from Ireland are approximately 10% higher than the limit set by the Kyoto protocol (EPA, 2008). Future reduction targets made as part of the EU ‘Climate Action and Renewable Energy Package’ would see our emissions reduced by 20% in 2020 relative to 2005 levels (Adelle et al., 2009).

In Ireland, research into our options is ongoing. One example is the restoration of harvested peatlands to reinstate the carbon sink function. When peatlands are drained there is a large loss of carbon in the form of CO₂ when the organic material decomposes. There are points to note i.e. if the bogs are re-wetted this will lead to a decrease in CO₂ emissions and initiate growth of the peatland vegetation. However, in order for peatlands to be considered a sink of greenhouse gases, CH₄ and N₂O emissions also have to be taken into account in order to have a good idea of their emissions in CO₂ equivalence.

Another area considered for mitigation is the potential of grassland biomass for bioenergy production such as *Miscanthus x giganteus* and Willow. There are issues of land-use change and how these crops will affect the environment. It is important to consider the production of these crops in terms of their inputs e.g. fertiliser, their greenhouse gas emissions and also the management scenarios.

Biochar is a biomass-derived charcoal and is produced by pyrolysis and is considered a possible low-cost low-risk option to sequester carbon in soils (Lehmann, 2007, Tenenbaum, 2009). It has been found that soil fertility is stimulated by charcoal-amended soil and remains stable in the soil for significant time periods (Sombroek, 2003). If such an option is to be considered it would be very important to investigate the effect biochar would have on Irish native fauna and their parameters. The effect of biochar input on nutrient cycles and the knock-on effect on greenhouse gas emissions is also highly important. Suitable methods of biochar application techniques to Irish soils is also another important consideration.

CH₄ emissions in Ireland are largely attributed to animal numbers in agriculture, so reducing animal numbers would be one obvious solution. However, this would have significant financial consequences as farm revenues will fall in direct proportion to the fall in production output i.e. animal numbers.

Research in New Zealand has looked into improving the quality of the diet of ruminants. With higher quality feed intake, the productivity of the animals is increased and results may lead to an overall decrease in CH₄ emissions per unit product. Another possibility is to reduce CH₄ production from livestock by directly influencing the fermentation process through additives in feed. Ionophores are a group of commonly used compounds which have shown some results in reducing the amount of CH₄ produced per unit of feed consumed. Some evidence has suggested that they also decrease the levels of nitrogen excreted and thus may help reduce N₂O emissions from pasture.

1.10 *Miscanthus* and Willow Growth in Ireland

Miscanthus x giganteus is a C₄ perennial woody grass of east asian origin, it has been evaluated at Teagasc since 1993. It has received significant consideration as a potential energy crop in Ireland (Heaton et al., 2004, Clifton-Brown et al., 2007, Styles and Jones, 2007b). It has a high biomass production potential (Lewandowski et al., 2000, Hastings et al., 2009) with high water use efficiency and high nitrogen use efficiency. It has also been shown to accumulate soil organic C and indeed it has been shown to increase soil organic C to a level above that of native pasture on land previously under arable agriculture (Dondini et al., 2009).

In trials at Oakpark Research Centre, annual yields range from 10-15tDM ha⁻¹ (on medium textured soil of ca. 3% organic carbon). *Miscanthus* is at an advantage as a C₄ crop as it has a higher conversion of solar radiation into biomass, a higher water use efficiency and a higher nitrogen use efficiency. The ideal pH for the crop is within the range of 5.5 – 7.5. Crop establishment is done by planting rhizomes which are grown from nurseries at depths of 5-10cm. Optimal planting density as advised by Teagasc is 20,000 plants ha⁻¹. Planting is usually carried out in March or early April.

There are planting grants available through the BioEnergy Scheme which is administered by the Department of Agriculture, Fisheries and Food. There is also an Energy Aid Payment of €45 ha⁻¹ when it is grown on non-set aside

land. It is considered a low input crop once it has been established, however, weed control is required in the establishment phase (i.e. in spring an application of a broad-spectrum herbicide is used to control grass weeds) and should remain viable for at least 15 – 20 years (Lewandowski et al., 2000, Bullard, 2001).

It is harvested in winter once leaf senescence has occurred using a conventional conditioner mower. It is carried out then as moisture content is at its lowest, the lower the moisture content the higher the energy yield and bale value. During senescence a large amount of nutrients are relocated to the rhizomes and as the leaves fall a significant return of nutrients occurs through leaf litter decomposition. As such nutrient off-take is quite low as only stem nutrients are removed.

Miscanthus has a wide potential range use, it is very popular as animal-bedding as it is very absorbent. It is also used for heat and combined heat and power (CHP) e.g. home-heating, commercial sector (hotels etc.). Reduction of emissions from coal-powered stations is possible by substituting a proportion of the C-intensive fuels with co-fired biomass. A target of 30% biomass co-firing in the peat power stations was put forward in a White Paper on Energy (DCMNR, 2007). There has recently been secured commitments from ESB and Bord na Mona for the burning of *Miscanthus* for electricity generation, in May 2010 the Government announced a REFIT Price i.e. price to be paid for *Miscanthus* and other biomass in the peat power stations.

Miscanthus logs are currently available for stoves and solid fuel appliances and open fires. *Miscanthus* is also used in insulating and packaging materials, paper, plant and substrates.

Willow is another renewable energy crop which is used as a fuel to generate heat and electricity. It is grown in sites at a pH range of between 5 – 7. Medium to heavy clay-loams with good aeration and moisture retention are ideal for planting. Mechanical planting to depths of 20-25cm in areas with a good annual rainfall of 900 – 1100mm are ideal. Particularly boggy soils are not ideal as harvesting would be quite difficult. It is very important to fence

the area being planted as willow is eaten by rabbits, hares and deer, however, after establishment this is not a problem. The optimal planting density is 15,000 cuttings ha⁻¹. Cuttings are sown in a twin row arrangement with spacings of approximately 0.75m between rows and 1.5m between twin rows and 0.6m between cuttings. Planting is budgeted €2,900 ha⁻¹, as with *Miscanthus* there are planting grants available through the BioEnergy Scheme which is administered by the Department of Agriculture, Fisheries and Food. There is also an Energy Aid Payment of €45 ha⁻¹ when not grown on set aside land. It has a low N requirement and any additions of N should be based on the current N supply of the soil at planting. Crops are harvested from December to April, for the first crop harvest it will occur early in year 4 after planting. After that it will be harvested every two years and can either be stored and chipped later or both processes occur at harvest. Once again a low moisture content is desirable. Rust (*melampsora*) is the major disease of willow, it can reduce yields by up to 40% and can potentially cause crop failure. As such it has become essential to sow plantations with 5-6 different willow varieties to prevent a devastating attack. The blue and brassy willow beetle is also a potential pest but generally populations are low. After the first year of growth the plantations are cut back to encourage coppicing.

Both of these crops could be used in an overall greenhouse gas emissions reduction from utilising these as energy crops in the form of heating fuels in domestic and commercial dwellings (Styles and Jones, 2007b, SEI, 2004). Willow and *Miscanthus* fuel-chain emissions were calculated at 0.045 and 0.062 kg CO₂ eq.kWhth, compared with 0.248, 0.331 and 0.624 kg CO₂ eq.kWhth for gas, oil and electric heat, respectively (Styles et al., 2008). Their high yields and tolerance to wet soils makes these crops very promising for energy production (Jones and Walsh, 2001, Styles and Jones, 2007b, Londo et al., 2001). The economic competitiveness of willow and *Miscanthus* growth as a substitute for fossil-based fuels has been demonstrated (Styles and Jones, 2007a)(Styles and Jones, 2007b). Also identified were the hurdles which need to be overcome to utilise energy-crops in Ireland i.e. a reluctance to consider long-term economics; potential competition from cheaper sources of biomass; the requirement for a solid supply network (Styles and Jones, 2007b).

1.11 Modelling N₂O Emissions

Total annual N₂O emissions from soils can be quantified by field measurements, but as large temporal and spatial variability exists, intensive sampling is required (Ambus and Christensen, 1995a). There are different models used to predict N₂O estimate emissions, which have different levels of complexity.

The simpler models are the empirical or regression models or a combination of both and provide reasonable estimates of fluxes and total emissions of N₂O but these models are site specific by definition (Clayton et al., 1994). At the more complex end, there are mechanistic models that simulate the basic processes that are involved in N₂O emissions (Grant et al., 1993b, Grant et al., 1993a). These are not easily applicable to a field scale (Rolston, 1990).

It is generally applicable that the variations of N₂O fluxes within a particular site are attributed to variations of mainly moisture contents and the amounts of nitrate (NO₃⁻) and ammonium (NH₄⁺) in the soil (Clayton et al., 1994), to a lesser extent temperature and mineralisable carbon (C) also have an affect. These variables can be obtained readily from sites and studies and have been used also in regression models. With the availability of this type of data, models of medium complexity have been developed which have the objective of simulating the terrestrial ecosystem carbon and nitrogen biogeochemistry e.g. DeNitrification-DeComposition (DNDC), century, ExpertN and NASA-Ames model. These models include soil physics, decomposition, plant growth and N transformations, but depending on the case may use different algorithms for these processes.

The DNDC model is a widely-used ecosystem biogeochemistry model and is used to estimate N₂O, NO, N₂ and CO₂ emissions from agricultural lands (Li et al., 1992, Li, 2000). The rainfall driven process-based model for DNDC was originally developed for conditions in the USA (Li et al., 1992) and has been simulated on a regional scale there (Li et al., 1996). The model has data requirements that are not too difficult to obtain and it is suitable for simulation

at spatial and temporal scales appropriate to its application. It has also been quite extensively tested between measured and modelled results with reasonable agreement for different ecosystem types; cropland (Tang et al., 2006, Yeluripati et al., 2006), forest (Kesik et al., 2006) grassland (Saggar et al., 2007).

The field based DNDC model contains four main sub-models (Li et al., 1992, Li, 2000):

- i) The soil climate sub-model calculates hourly and daily soil temperature and moisture fluxes in one dimension
- ii) The crop growth sub-model simulates crop biomass accumulation and partitioning
- iii) The decomposition sub-model calculates decomposition, nitrification, NH_3 volatilisation and CO_2 production
- iv) The denitrification sub-model tracks the sequential biochemical reduction from nitrate (NO_3^-) to NO_2^- , NO , N_2O and N_2 based on soil redox potential and dissolved organic carbon.

1.12 Aims and Objectives

In this study we selected a stand of *Miscanthus x giganteus* and a stand of *Salix viminalis x schwerinii* 'Tora' in the Teagasc Oakpark Research Centre in Carlow, Ireland and followed typical management practices. The chamber technique was used to measure the N₂O and CH₄ fluxes over eighteen months. The overall aim of the work was to collect the N₂O and CH₄ flux data set, to investigate the influencing factors controlling N₂O and CH₄ emissions and perform process based modelling (i.e. DNDC) validation. The project was divided into 3 projects, each with specific aims:

1. **Measurement of N₂O and CH₄ emissions from *Miscanthus x giganteus* plots treated with inorganic and organic fertiliser (Chapter 2)**
 - a. an increase in N₂O fluxes after fertiliser application is dependent on fertiliser type,
 - b. fluxes of CH₄ are insignificant,
 - c. there is a greater increase in yield on application of fertiliser than increase in N₂O flux.

2. **Measurement of N₂O and CH₄ emissions from Willow plots treated with inorganic and organic fertiliser (Chapter 3)**
 - a. an increase in N₂O fluxes after fertiliser application is dependent on fertiliser type,
 - b. fluxes of CH₄ are insignificant,
 - c. there is a greater increase in yield on application of fertiliser than increase in N₂O flux.

3. **Validation of field measurements of N₂O with DNDC-model N₂O emissions (Chapter 4)**
 - a. that DNDC would be a predictive N₂O model for soil under a *Miscanthus* crop using conventional management practice. We aimed to validate DNDC for annual data set of emissions from a *Miscanthus* plot.

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Chapter 2 Measurement of N₂O and CH₄ emissions from *Miscanthus* plots treated with inorganic and organic fertiliser.

2.1 Introduction

This chapter is concerned with measuring N₂O and CH₄ emissions from plots of *Miscanthus* that have been treated with inorganic (27% CAN) and organic (Biofert) fertiliser over a 20 month period, from October 2008 – August 2010. The experiment was to determine the potential benefits of using a readily available, cheap alternative organic fertiliser, Biofert, on a *Miscanthus* crop. This could then be compared to the inorganic CAN fertiliser and the difference between the N₂O and CH₄ emissions from both treatments as compared to the control i.e. no fertiliser application plots. As such, the hypotheses of this study were, a) an increase in N₂O fluxes after fertiliser application is dependent on fertiliser type, b) fluxes of CH₄ are insignificant and c) there is a greater increase in yield on application of fertiliser than increase in N₂O flux.

Agriculture is one of Ireland's most important industries and with a land area of approximately 6.9 million hectares, ca. 4.3 million hectares is dedicated to agricultural production. However, agriculture is attributed with producing 26.4% of our national total greenhouse gases (GHG). Approximately 80% of agricultural land is used as pasture, hay and silage production with approximately 11% used as rough grazing and then the last 9% used for crop production. Beef and milk account for some 55% of agricultural output. Cattle account for approximately 90% of agricultural CH₄ emissions with agriculture contributing 86% of our national CH₄ total. N₂O emissions from agriculture account for approximately 83% of national N₂O emissions (EPA, 2010b).

Nitrous oxide (N₂O) is produced by soils as a part of the soil by processes of microbial activity through nitrification (aerobic microbial oxidation of ammonium to nitrate) and denitrification (anaerobic microbial reduction of

nitrate to dinitrogen gas). N_2O is the gaseous intermediate in the reaction sequences of both processes that leaks from microbial cells in the soil atmosphere. N_2O production is highly regulated by soil moisture content, temperature, pH, N-fertiliser application, type of fertiliser used, target crop, soil drainage, organic content, soil structure (Bouwman et al., 2002b). Increasing the amount of available N to the soils increases the N availability for nitrification and denitrification and therefore the amount of N_2O produced (Bouwman, 1990). N_2O is produced both directly (directly from the soils: synthetic fertilisers; nitrogen from animal waste; sewage sludge application; biological nitrogen fixation; reutilised nitrogen from crop residues) accounting for approximately 14% of agricultural emissions and indirectly (leaching and runoff, also volatilisation in the fields as NH_3 and NO_x and following redeposition) which accounts for approximately 7% of agricultural emissions.

Methane (CH_4) emissions from soils are largely attributed to rice farming, the Intergovernmental Panel on Climate Change (IPCC) estimated a global emission rate range from paddy fields at 20-100 Tg yr⁻¹ and a global emission rate of 60 Tg yr⁻¹ (IPCC, 2006). This accounts for 5-20 % of total emissions from anthropogenic sources. In Ireland, GHG emissions are dominated by N_2O and CH_4 (Mc Gettigan et al., 2010). This dominance relates to the large output from farming which is based on cattle and sheep livestock production. Livestock enteric fermentation is the primary source of CH_4 and accounts for almost 50% of total GHG emissions (Schulte et al., 2011). There are large temporal variations with CH_4 fluxes, these are influenced by climate, agricultural practice, soil type and texture, application of mineral fertiliser and organic matter (Neue and Sass, 1994). CH_4 is produced by the reduction of CO_2 with H_2 where fatty acids or alcohols act as hydrogen donors or via the transmethylation of acetic acid or methanol by methane-producing bacteria (Takai, 1970, Conrad, 1989). Carbon substrate and nutrient availability are also important variables for CH_4 production. Soil temperature is also very important as this effects the rate of conversion of substrate to CH_4 .

It has been raised that energy crops may contribute as much or more to global warming by N₂O emissions than cooling by fossil fuel savings (Crutzen et al., 2007) and as such a full life cycle assessment of these crops is required. Very few direct measurements on Irish energy crops are available. To ensure an accurate reflection and assessment of GHG emissions from energy crops such as *Miscanthus*, direct measurement studies are vital. The IPCC provides a list of emission factor default values to the Environmental Protection Agency (EPA) to use in calculating national emissions. These factors are based on studies where 20 data sets were taken and an emission factor was calculated (Bouwman, 1996). An emission factor of 1% is used for N₂O, so for the total amount of fertiliser that is spread, 1% will be converted to N₂O. It has been recommended that emission factors based on national figures be recalculated to reflect the influence of different variables on N₂O emissions (IPCC, 2006). N₂O emissions of 1.8-4.92% of applied fertiliser were reported at the Teagasc Research Centre at Johnstown Castle, Wexford for a grazed pasture where total N applied was 303 and 493 kg N kg N ha⁻¹ respectively (Hyde et al., 2005).

Miscanthus x giganteus is a C4 perennial woody grass of east asian origin, it has been evaluated at Teagasc since 1993. It has received significant consideration as a potential energy crop in Ireland (Heaton et al., 2004, Clifton-Brown et al., 2007, Styles and Jones, 2007b). It has a high biomass production potential (Lewandowski et al., 2000, Hastings et al., 2009) with high water use efficiency and high nitrogen use efficiency. It has also been shown to accumulate soil organic C and indeed it has been shown to increase soil organic C to a level above that of native pasture on land previously under arable agriculture (Dondini et al., 2009).

Biofert is a commercial derivative fertiliser which is produced in Ringsend waste water treatment plant in Dublin. It is a by-product of the treatment of Dublin's wastewater after processing at the plant. Approximately 12,000 tonnes of Biofert is produced at the plant per annum, it is considered a Class A sludge in Ireland by the Department of Environment, Heritage and the Environment. It is considered an effective soil conditioner (e.g.

improvements in surface drainage, earthworm populations (in conversation with John Byrne, John Byrne Consultancy & Quinns of Baltinglass)) and reasonable alternative to commercial fertiliser due to its stable nutrient levels. It is used for treating land under a Department Code of Good Practice for the Use of Biosolids in Agriculture (Fehily, 2008), which follows on from European best practice.

2.2 Materials and Methods

2.2.1 Experimental Site

Using measuring tape and twine, the full length and breadth of the area was measured in the *Miscanthus* stand. A 5-block randomised set up was deemed most appropriate (in conversation with Mike Williams, TCD; Per Ambus, Institute of Population Biology, Copenhagen University, Denmark; Eamonn Mullins, Dept. of Statistics, TCD; Jan Willem van Groeningen & Gerard Velthof, Wageningen University, The Netherlands.) to reduce or eliminate the contribution to experimental error contributed by *nuisance* factors. The treatment plots of 4m x 4m were decided to be best and were replicated 5 times (Williams, M., TCD; van Groeningen, J.W., University of Wageningen, The Netherlands; van Groeningen, K.J., TCD). We then calculated the maximum spaces between the 4 x 4 m plots within the total area to maximise distance between treatment plots. This was done to reduce the possibility of an affect of fertilisers on neighbouring plots by lateral flow of fertilisers through the soil (Williams, M., TCD; van Groeningen, K.J., TCD; Johnston, P., Dept. of Civil, Structural and Environmental Engineering, TCD). Approximately 20 months of measurements of N₂O and CH₄ emissions were collected from a *Miscanthus* stand at the Oak Park Research Centre, Carlow, Ireland. Measurements were taken from October 2008 to August 2010, in 2008 the *Miscanthus* was not fertilized, in 2009, 150kgN ha⁻¹ of Biofert and 150kgN ha⁻¹ of 27% Calcium Ammonium Nitrate (CAN) were spread on June 6th in five block replicates. In June of 2010 150kgN ha⁻¹ of Biofert and 150kgN ha⁻¹ of 27% Calcium Ammonium Nitrate (CAN) were spread in five

block replicates (see figure 2.1). Harvesting took place on 12th February 2009 and 27th March 2010.

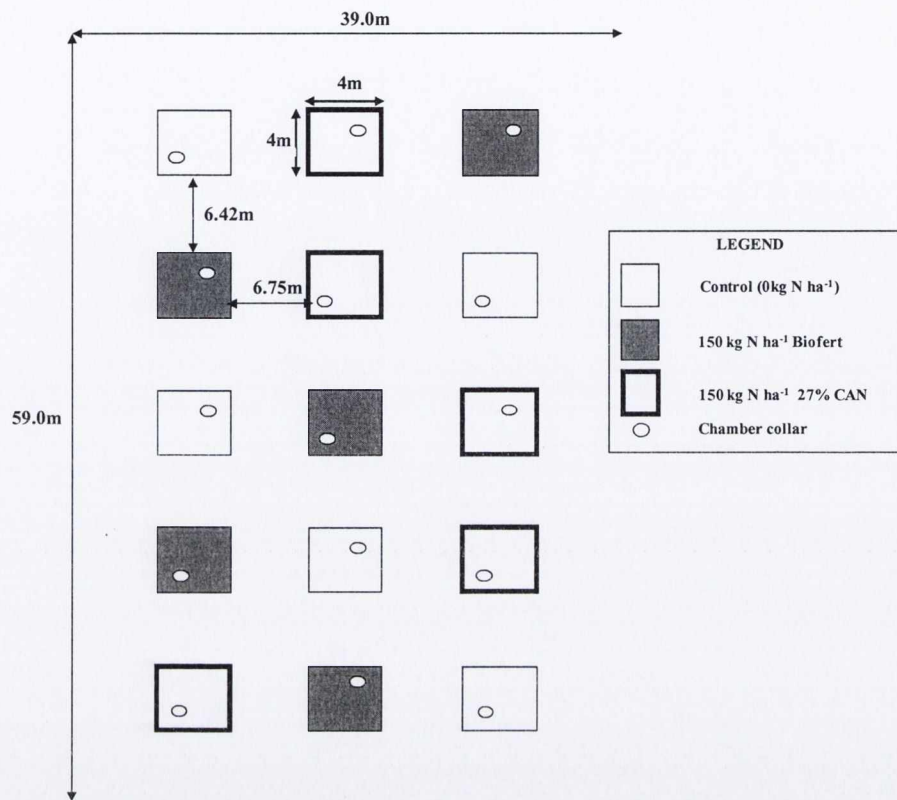


Figure 2.1 Experiment design of fertiliser application on *Miscanthus* site.

The site had an elevation of 58m, an annual rainfall in 2008 of 945 mm, in 2009 of 1085 mm and from January to June 2010 of 338 mm and a mean annual maximum air temperature in 2008 of 13.2°C, in 2009 13.1°C and from January to June 2010 of 16.8°C and a mean annual minimum air temperature of 5.6°C in 2008, of 5.4°C in 2009 and 7.6°C in 2010. The soil is classified as sandy loam with a pH of 6.4. The *Miscanthus* site has been permanent for the past eight years.

2.2.2 Measurement of N₂O flux

Fluxes were measured using vented closed flux chambers (Mosier, 1989).

The flux chambers were constructed of polypropylene (PP) cylinders with one end closed (CJK Packing Ltd., U.K.) with an internal diameter of 20cm and a height of 19cm (Figure 2.2(i)). They were placed on permanently positioned PVC collars of height 8cm, which were placed 2cm into the soil. An air tight

seal was made by lining the top of the chambers with neoprene sealant (Figure 2.2 (ii)). All chambers were vented with a tube with an internal diameter of 0.3cm and length of 20cm and covered approximately 0.02m² of the soil surface. The closed flux chamber method involves placing the chamber over the soil surface, after which the flux is calculated according to the change in N₂O concentration in the headspace of the chamber.

Due to the funding and deployment nature of our project, we built our own chamber. We used polypropylene plastic which is non-permeable, nonreactive, and is not a source or sink of our target gases (<http://www.cjk.co.uk/chemical-resistance-data-sheet.shtml>) and CH₄ (http://www.chemindustrial.com/theory/pp_resist.htm#m) i.e. at temperatures less than 50°C it will not react with or absorb either of these gases.). We chose a cylindrical shape so as to promote consistent mixing within the enclosed air volume.

The basal area of our chamber measures 0.03m², this lies within the ranges of 0.02 to 1m² for chambers (Hutchinson and Mosier, 1981a), where 0.05 to 0.07m² are most common. This size was chosen due to the nature of the areas of our study i.e. site of Willow and *Miscanthus* (see Figure 2.5) where there are small areas between individual shoots (Hutchinson and Livingston, 1993).

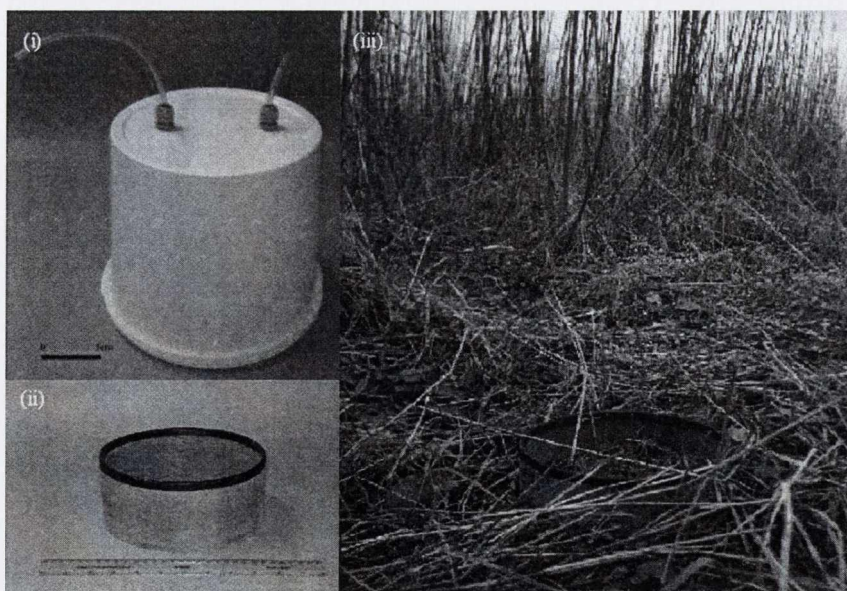


Figure 2.2 (i) Flux chamber used for N₂O and CH₄ sampling (including scale bar 5cm), (ii) Collar with neoprene sealing tape (scale bar = 30cm), (iii) and collar *in situ*.

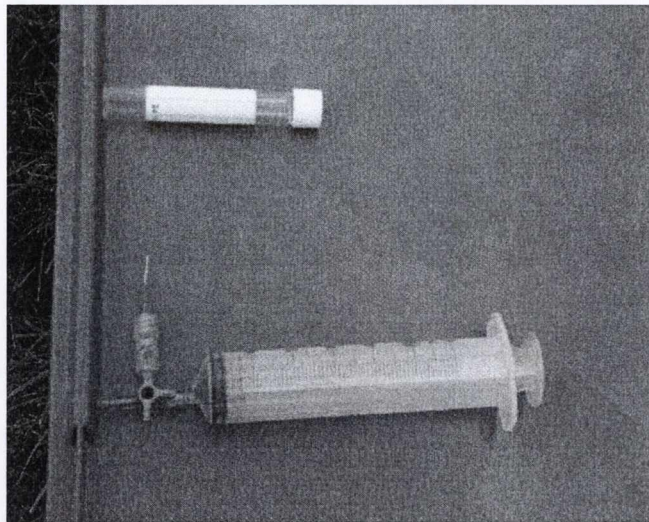


Figure 2.3 The 60 ml syringe, septum and vials used to measure N_2O and CH_4 flux.

The use of this particular design was preferred in order to detect the smaller fluxes of CH_4 and N_2O that were expected (Hutchinson and Mosier, 1981a, Crill, 1991, Christiansen et al., 2011), as such we concluded our design was most suitable for our study. The tightness of the static chamber was tested by checking the linearity of N_2O gas flux within the chamber, this would reduce the possibility of introducing any systematic error due to non-linearity of the flux measurements (Kroon et al., 2008).

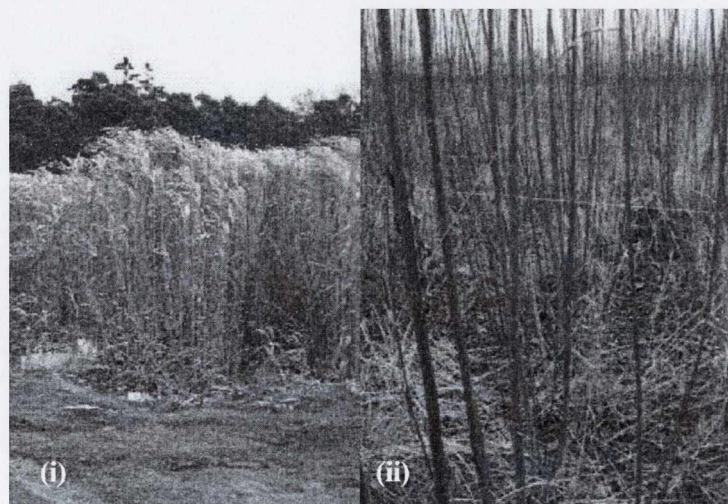


Figure 2.4 Site of (i) *Miscanthus* and (ii) Willow stands in November 2008 at Oakpark Research Centre, Carlow.

The volume to area ratio of our chambers was chosen as it was small enough to detect a change in the target gas concentration over a period as short as possible, but also so that it was large enough to minimise disturbance of the covered soil vegetation. We used deployment periods of 30 mins with deployment periods ranging from 20 to 60 mins being common in non-steady-state chambers.

We used multiple-component chambers as the open base (pvc collar) can be sealed to the soil i.e. installed prior to making observations. This way it will completely enclose the volume of air and can be done without creating further disturbance in the soil. As our studies uses repeated observations at fixed locations, this will reduce the risk of chamber-induced measurement error. Using a multiple-component chamber we required a good seal between components (i.e. chamber and collar), we employed a compressible, nonreactive neoprene seal with air-tight overlapping.

In order to preserve mean ambient temperature and pressure (and fluctuations about their means) we made deployment times short and fabricated the chamber from white PP material in order to minimise temperature disturbance (Matthias et al., 1980a). We also used reflective material on the collars (Hutchinson and Mosier, 1981b). After consultation with colleagues, a provision for measuring the temperature of enclosed air has been added in order to verify that the difference from ambient air temperature is small (in conversation with Jukka Pumpanen and Mari Pihlatie, Department of Physics, Division of Atmospheric Sciences and Geophysics, University of Helsinki).

We used a pressure vent as it is strongly recommended for non-steady-state chambers to:

- (i) facilitate compensating for volume changes that occur during chamber deployment, air sample withdrawal, or as a consequence of changes in the temperature of the enclosed air.
- (ii) Transmit barometric pressure changes to the enclosed air volume

- (iii) Preserve the pumping action that is associated with rapid turbulence-induced air pressure fluctuations (Hutchinson and Mosier, 1981b).

We used the appropriate guidelines for vent tube diameter and length as a function of wind speed and chamber volume (Hutchinson and Mosier, 1981b). We placed the tube's internal opening as widely apart from the chamber's sampling port so as to avoid any unwanted interactions. The vent tube end was also located near the ground pointing downwind, this was to minimise its potential for depressurising the chamber in conformance with the Bernoulli equation as wind blows over its external open end (Conen and Smith, 2000, Hutchinson and Livingston, 2001).

It has been argued that thermal buoyancy and or external turbulence-induced pressure fluctuations generally will support the uniform mixing of the chamber head space, and also, that forced head space mixing sometimes artificially enhanced gas exchange rates, in particular when pre-deployment mixing is poor (e.g. within a dense vegetation canopy on a calm cloudy day) (Hutchinson et al., 2000).

A disadvantage associated with the use of closed chambers is that the conditions within the chamber may be disturbed due to closing of the chamber, which may affect the flux (Mosier, 1989, Christiansen et al., 2011). There are also problems with measurements using flux chambers on fertilised grassland soil as they are strongly hampered by the large spatial variability of N₂O flux (Velthof et al., 1996, Ball et al., 1993). Therefore a large number of chambers is generally required to improve the accuracy of the estimate of the field flux (Folorunso and Rolston, 1984).

In order to increase the accuracy and precision of flux measurements an automated evacuation system was constructed ((Scott et al., 1999): in collaboration with Eduard W.J. Hummelink and Jan Willem van Groenigen (Wageningen University and Research Centre, The Netherlands)). Our sample containers are 20ml glass vials, with a rubber butyl septum crimped

onto the vial using a cap. An evacuation system was designed in order to (i) reduce any artefact sources or sinks of the target gas attributable to chemical, biological or photochemical reactions in the air before vials being sealed e.g. in laboratory, (ii) produce a consistent vial vacuum in order to reduce any inherent error in sampling.

A pump was used to create a vacuum within the system. It was then necessary to test for consistency of vacuum within this system for the 20ml glass vials. Each glass vial was sealed using a cap which was crimped on over the rubber butyl septum.

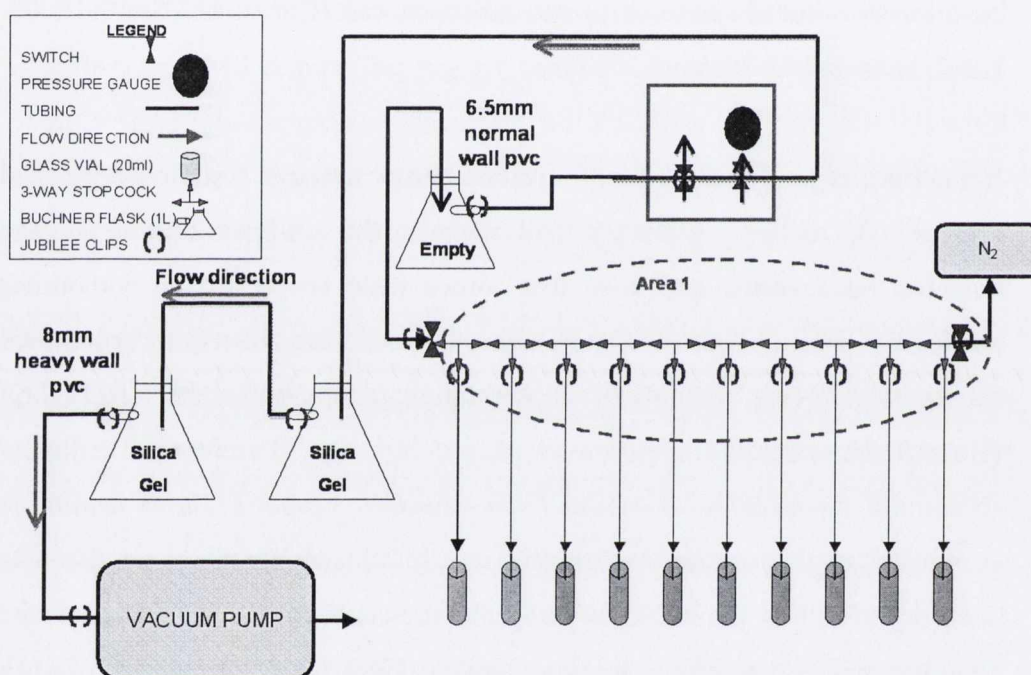


Figure 2.5 Schematic set-up of glass vial evacuation system (system adapted from Eduard Hummelink and Jan Willem van Groenigen, Wageningen University, The Netherlands). Area 1 refers to area being tested / altered.

A series of tests were carried out based around Area 1 (see Figure 2.5) investigating different needle / stopcock numbers, shortening of pvc piping of system, vacuum times required and potential storage times.

As such it was concluded that 45 seconds vacuum time for the vials carried out immediately preceding field measurements would be the most effective and efficient preparation and that sample vials should be analysed as soon as

possible after sampling. This would reduce the possibility of contamination and also of leakage through the stoppers (Brooks et al., 1993).

2.2.3 Evacuation Vs Flush Technique

The vial evacuation system was tested against vials which used the flush technique, where 60ml of air sample is flushed through the 20ml glass vial (see figure 2.6). No significant difference was detected between the two techniques, however, using pre-evacuated vials proved quicker in field applications than using the flush technique. The pre-evacuated vials were also preferable due to the smaller volume of sample required from the chamber headspace, thus reducing any potential effect of sampling on the flux.

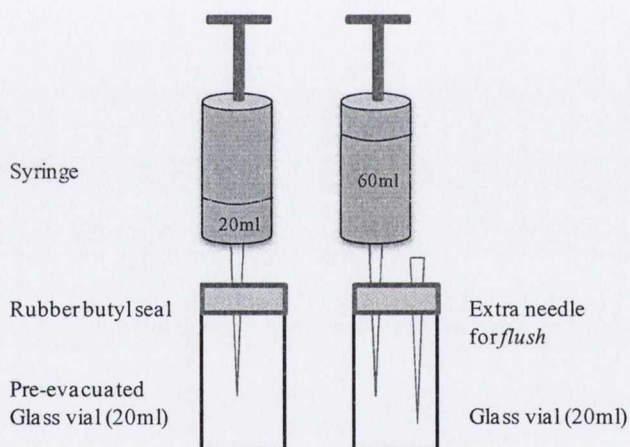


Figure 2.6 Set up for pre-evacuated 20ml vial and for non-evacuated vial with extra needle for flushing through air.

As such, pre-evacuated vials were used. If upon occasion a pre-evacuated vial lacked sufficient vacuum, the flush technique would be used as a substitute.

N₂O and CH₄ emissions from 5 replicated chambers were measured on a weekly basis. Samples were taken at four times; (t = 0) 0 mins, (t = 1) 10 mins, (t = 2) 20 mins and (t = 3) 30 mins, after the chamber was placed over the collar. Samples were taken using a 60 ml gas-tight syringe after pre-

evacuating the 20 ml vials. 20 ml of the sample was then injected into the 20ml gas-tight vial and stored until analysis (Figure 3.2). Samples were taken as far as possible at the same time of day to minimize the effects of diurnal variation.

Gas samples were measured at Trinity College Dublin using a gas chromatograph (PerkinElmer Clarus 500 Gas Chromatograph) with Electron Capture Detection (ECD) and Flame Ionization Detector (FID). The ECD consists of radioactive (^3H / ^{63}Ni) source with two electrodes (cathode and anode) at a fixed potential that can be carried from 20 to 200V. β -radiation from the radioactive source ionizes the carrier gas (N_2 or 95:5 AR / CH_4 mixture) and the applied potential causes a current to flow. Any electrophilic molecule (e.g. N_2O) is exiting the column reacts with an electron to form either a negative ion or a neutral radical and a negative ion, which is then swept out of the detector by the carrier gas flow. The net result is a removal of electrons from the system and a decrease in the standing current.

The equation for closed flux chambers was used for calculating the daily flux of N_2O and CH_4 from each chamber (Smith et al., 1995, Baggs et al., 2003b):

$$\text{Equation 2.1} \quad \text{g N}_2\text{O-Nha}^{-1}\text{d}^{-1} = \frac{\text{Vol. (ml)} \times \text{ppm change (X-X}_0) \times 28 \text{ (g N)} \times 60 \text{ (mins.)} \times 24 \text{ (h)} \times 10^8}{\text{Area (cm}^2) \times \text{time closed (mins.)} \times 24000 \text{ (1 mole as ml)} \times 10^6}$$

as adjusted for CH_4 :

$$\text{Equation 2.2} \quad \text{g CH}_4\text{ha}^{-1}\text{d}^{-1} = \frac{\text{Vol. (ml)} \times \text{ppm change (X-X}_0) \times 16 \text{ (g CH}_4) \times 60 \text{ (mins.)} \times 24 \text{ (h)} \times 10^8}{\text{Area (cm}^2) \times \text{time closed (mins.)} \times 24000 \text{ (1 mole as ml)} \times 10^6}$$

N_2O emission factors are defined as the amount of N emitted as N_2O per year as a percentage of the total N fertiliser applied. Emission factors (EFs) for N fertilizer were calculated by expressing the cumulative emissions from fertilized plots minus that of the control plots as a percentage of the total N applied after being adjusted for ammonia volatilisation:

Equation 2.3 $EF = [(Cumulative\ flux\ (fertilizer\ treatment) - Cumulative\ flux\ (control)) / (fertilizer\ applied \times (1 - Frac_{GASF}))] \times 100$ (IPCC, 2000)

with cumulative annual N₂O-N loss=cumulative annual N₂O-N loss (with fertiliser or manure input)-cumulative annual N₂O-N loss (zero-N control). *Frac_{GASF}* is the fraction of nitrogen that volatilises as NH₃ and NO_x from applied synthetic fertiliser (*Frac_{GASF}* = 10%).

Nitrous oxide emissions in term of global warming potential (GWP) were calculated using the equation of Watson et al. (Watson et al., 1996) where;

Equation 2.4 $GWP = CO_2 + CH_4 * 21 + N_2O * 310.$

The Biofert fertiliser was applied in its final dried pellet form as produced by the wastewater treatment plant in Ringsend, Dublin. The chemical analysis for the final dried product is outlined in Table 2.1 below.

Table 2.1 Analytical test results for Biofert product produced by Ringsend WWTP, Dublin.

Description	Result	Unit
Cadmium	0.8	mg/kg DM
Chromium	27	mg/kg DM
Copper	301	mg/kg DM
Mercury	0.5	mg/kg DM
Potassium	1602	mg/kg DM
Total Nitrogen	5.2	% DM
Nickel	16	mg/kg DM
Organic Matter	59.3	%
Phosphorous	1.18	% DM
Lead	58	mg/kg DM
Zinc	319	mg/kg DM

2.2.4 Soil Temperatures, Soil Moisture, Water Filled Pore Space (WFPS) and Bulk Density

At each sampling a digital handheld thermometer was used to measure the soil temperature at a depth of 10cm. The Teagasc Oak Park Research Centre weather station also measured the soil temperature at a depth of 10cm every half hour.

Daily rainfall (mm) was recorded at the Teagasc Oak Park Research Centre weather station. At each sampling 4 soil samples were taken at a depth of 20cm. These samples were weighed (fresh weight) then placed in an oven set at 105°C and dried until they were a constant mass and were then reweighed (dry weight). Their gravimetric Soil Water Content (SWC) was calculated as the difference between the dry weight and the fresh weight (Choudhary et al., 2002);

$$\text{Equation 2.5} \quad \text{SWC (\%)} = (D_w / S_w) \times 100$$

SWC = Soil Water Content (%)

D_w = (Fresh weight of soil (g)) – (Dry weight of soil)

S_w = Stable soil dry weight (g)

Total Soil Porosity was calculated using the following equation:

$$\text{Porosity} = (1 - (\text{bulk density} / \text{particle size}^a)) \times 100$$

^a fixed particle size of 2.65cm³

WFPS was calculated by determining volumetric soil water and then dividing volumetric soil water by total porosity.

Soil Bulk Density

At the beginning of our experiment October 2008, we used the core method to measure the bulk density in the sample plots where core samples of a known

volume are taken using a metal sampling tool. The samples are then dried in an oven, weighed and the dry bulk density is calculated.

We used thin-walled aluminium cans as corers, with one end open and the other end pierced with several small holes. We then carefully removed the container and its contents from the soil, trimming soil extending from each end of the container with a straight edged knife. The sample volume is thus equal to the sample of the container. We then dried the containers in an oven at 105°C until constant mass was reached, they were then cooled and weighed (m_t). The dry bulk density (${}^b\rho_s$; g cm^{-3}) was calculated using the following equation 2.6:

$$\text{Eqn. 2.6} \quad {}^b\rho_s = m_d / V \quad \text{where; } (m_d = m_t - m_s)$$

where, m_d is the mass in grams of the core sample dried at 105°C minus the mass of the core sample holder, V is the volume (cm^3) of the container, m_s , is the mass (g) of the empty container, m_t is the mass (g) of the container with the soil sample dried at 105°C.

2.2.5 Nitrate and ammonium content of the soil

Once a month during sampling 4 soil samples at a depth of 20cm were taken from the site, during the period of fertiliser application samples were taken weekly.

Nitrate and ammonium concentrations were measured colorimetrically, based on the Armstrong et al., (1976) using a Bran and Luebbe Auto Analyser (Bran and Luebbe, Norderstedt, Germany). Soil samples were homogenised by being sieved through a 2 mm mesh. For each replicate, 20g of soil was taken and added to 100ml of 2 M KCl and was mixed using an automatic shaker for 1 hour. This solution was then filtered through Whatman No.2 filter paper for nitrate analysis. For ammonium analysis the sample was then filtered again through a cellulose acetate membrane with a pore size of 45 μm .

2.2.6 Biomass Yield

Above ground biomass was measured at harvest time for Miscanthus, February 2009 by cutting a 4 x 4 m plot using clippers. The cut biomass was removed from the plot and weighed. A sub-sample was then dried to constant weight in order to quantify dry matter content.

2.2.7 Statistics

Emission data was checked for normal distribution and log transformed if necessary. Multiple regression was carried out for flux vs soil temperature, soil moisture, soil nitrate and soil ammonium. 1-way and 2-way ANOVAs were carried out for flux and soil nitrate concentrations. All statistical analysis was carried out using DataDesk (Data Description Inc. New York, USA) and MiniTab (Minitab 15.1.30.0, Minitab Inc.).

2.3 Results

Table 2.2 Management detail for *Miscanthus* crop for experimental period.

Date of 150 kg N ha ⁻¹ application	Harvest	Harvest Yield (t DM ha ⁻¹)
06/06/09	27/3/10	10.1
06/06/10	12/2/11	10.1

When analysed using 1-way ANOVA, treatment was not found to have a significant effect on above ground biomass yield (see Table 2.2).

2.3.1 Rainfall and Soil Parameters

Figure 2.7 illustrates the monthly rainfall experienced at the Teagasc Research Centre weather station in Oak Park for 2008, 2009, 2010 and the 30 year mean (1967-1997). This was situated approximately a half a kilometre from the *Miscanthus* field. A plot of the 30 year mean monthly rainfall is also included. What is apparent is that the 2008 and 2009 data sets differ significantly from the 30 year mean values if late winters, mid-summer and spring months are considered.

Table 2.3 General description of the soil parameters of the *Miscanthus* site.

Soil Parameter	<i>Miscanthus</i>
Soil Type	Sandy Loam
% Sand	83
% Silt	16
% Clay	1.8
Bulk Density	0.95 g cm ⁻³
Porosity	0.66
Field capacity	0.32
Wilting point	0.15
Initial soil organic carbon (SOC) content at surface soil (0-5cm) (kg C kg ⁻¹)	0.054
pH	6.4

In January of 2010 rainfall increased by 85mm (215%) from 2009 levels, in April and May of 2010 rainfall levels decreased by 61 mm (57%) and 40 mm (26%) from 2009 levels. Rainfall levels in June of 2009 were more than

double the 30 year mean at 125mm and rainfall decreased significantly the following year in June by 108mm (86%).

There was heavy rainfall in August and September of 2009, 161 mm in August (nearly two and a half times the 30 year mean) and 219 mm in September (nearly three times the 30 year mean).

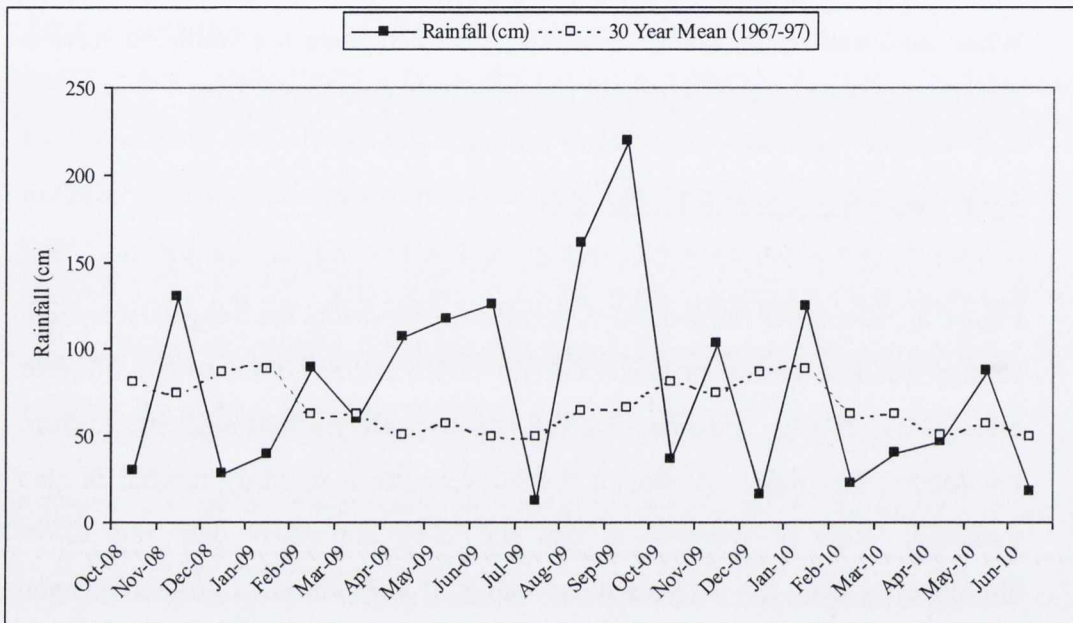


Figure 2.7 Monthly rainfalls for 2008 – 2010 at the Teagasc Oak Park Research Centre, Carlow and the 30 year mean. Symbols indicate rainfall in 2008, 2009, 2010 and the 30 year mean. Data provided by Met Eireann and John Hogan, Teagasc.

2.3.2 Soil Moisture, Water Filled Pore Space (WFPS) and Temperature

Figure 2.8 illustrates the weekly rainfall data measured at the weather station at Oakpark Research Centre, Carlow and the weekly soil moisture measurements taken when flux sampling was carried out on the *Miscanthus* site. There is a clear relationship between the two variables.

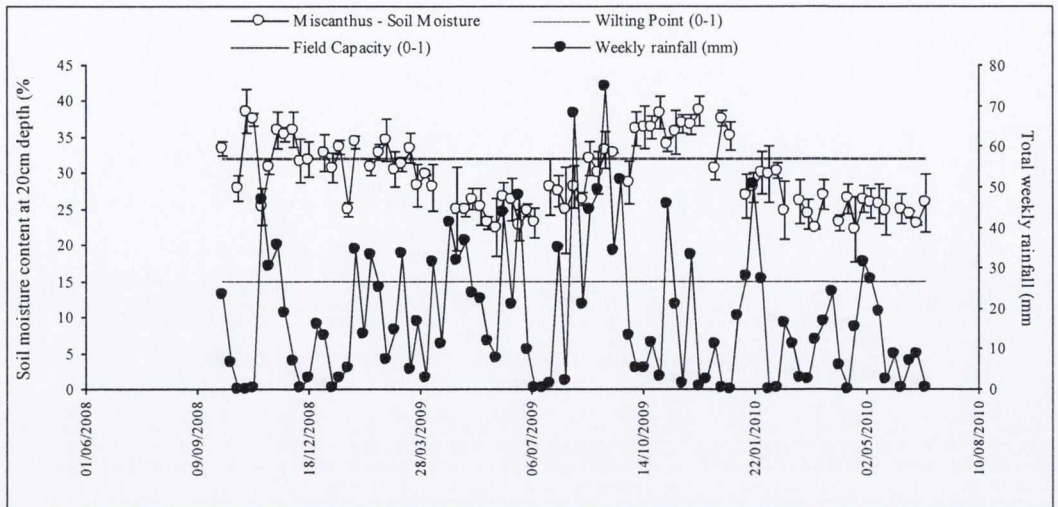


Figure 2.8 Weekly rainfall for October 2008 – July 2010 at the Teagasc Oak Park Research centre, Carlow and the moisture content at the *Miscanthus* site. Symbols indicate weekly rainfall, wilting point, field capacity and daily soil moisture content.

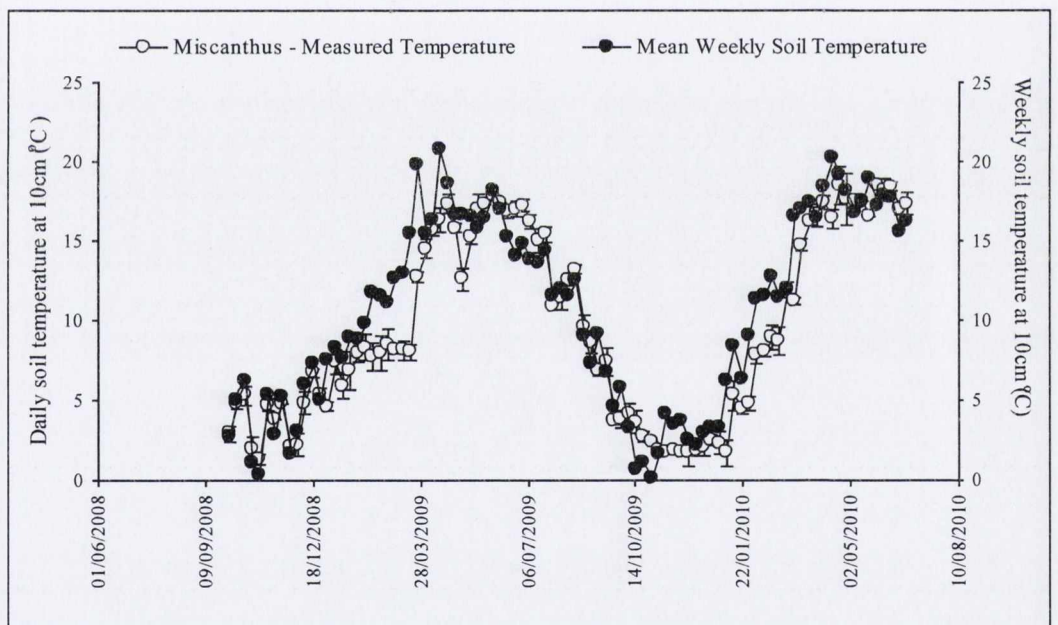


Figure 2.9 Weekly average soil temperature for October 2008 – July 2010 at the Teagasc Oak Park Research Centre, Carlow and the daily average soil temperature measured at the *Miscanthus* site. Symbols indicate average weekly temperature and average daily temperature.

Low rainfall in the spring of 2010 resulted in a low soil moisture content, 22%, which itself related to a WFPS value of 34.6% also due to low rainfall, soil moisture in late spring of 2010 resulted in soil moisture levels of 22.5%, relating to a WFPS of 35%. In comparison, very high rainfall in September

2009 led to very high soil moisture content of 38.4% resulting in a WFPS value of 60%.

Figure 2.9 illustrates mean weekly soil temperature and measured daily temperature at the *Miscanthus* site on the days where gas sampling took place. The weekly soil temperatures were measured at the Oak Park Research Centre weather station.

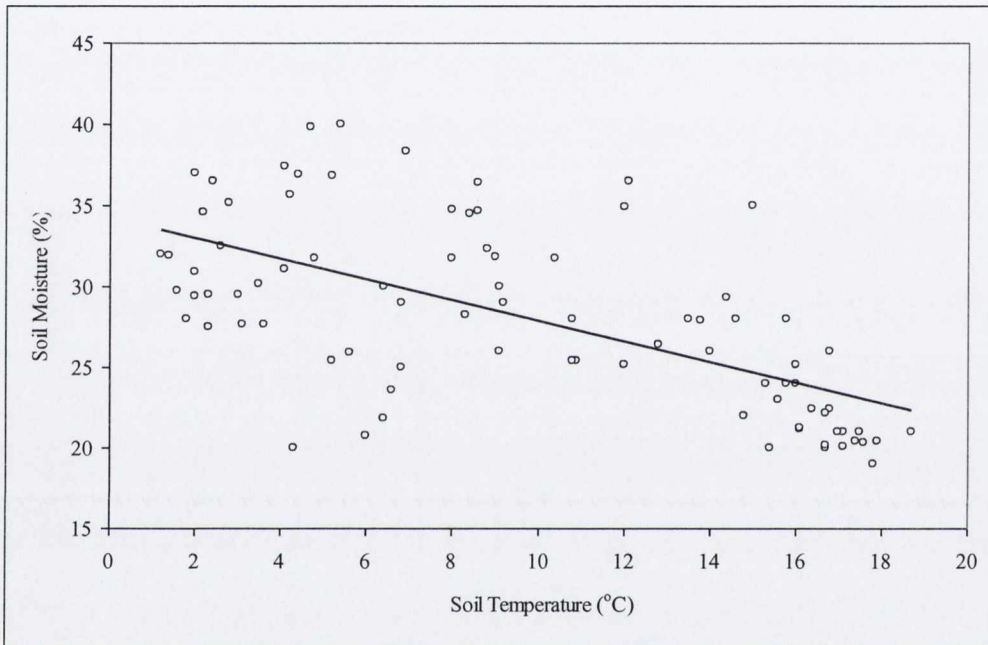


Figure 2.10 Relationship between daily average temperature at 10cm depth and daily average soil moisture content at 20cm depth at the *Miscanthus* site ($y = -0.6746x + 36.089$; $r^2 = 0.68$).

There is close correlation between the two data sets and as such data from the weather station may be used as a replacement for data for the *Miscanthus* site for the purposes of multiple regression analysis for flux measurements with soil variables. Figure 2.10 is a comparison of soil moisture content of soil samples taken on days where gas samples were collected with soil temperatures taken at a depth of 10cm on the same day. There is a negative linear relationship between the two variables.

A negative relationship between the two variables is observed with the equation accounting for 68% of the observed variation. This correlation may

be used to estimate soil moisture content from the data set of soil temperature if necessary.

Figure 2.11 illustrates the monthly mean soil temperatures measured for the end of 2008, then 2009 and until July 2010. These temperatures were measured at a depth of 10cm at the Teagasc Research Centre weather station. In December of 2008 the soil temperature was 2°C warmer than the same month in 2010.

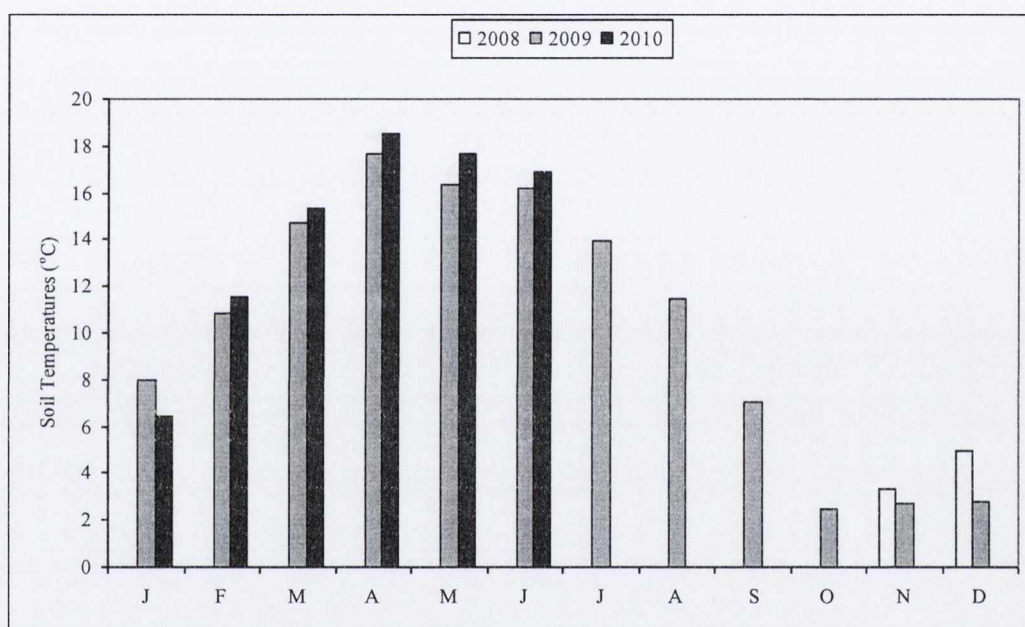


Figure 2.11 Monthly average soil temperatures for November 2008 – July 2010 at the Teagasc Oak Park Research Centre, Carlow. Data provided by Met Eireann.

Soil Nitrate and Ammonium content

Figures 2.12 and 2.13 illustrate the changes in the levels of nitrate and ammonium concentration in the soils, respectively.

Table 2.4 illustrates the results for ANOVA for log soil nitrate with the treatment effect, time and interaction of time and treatment. The results are significant for treatment effect (ANOVA, $p < 0.000$), for the time (ANOVA, $p < 0.000$) and for interaction of treatment and time (ANOVA, $p < 0.000$).

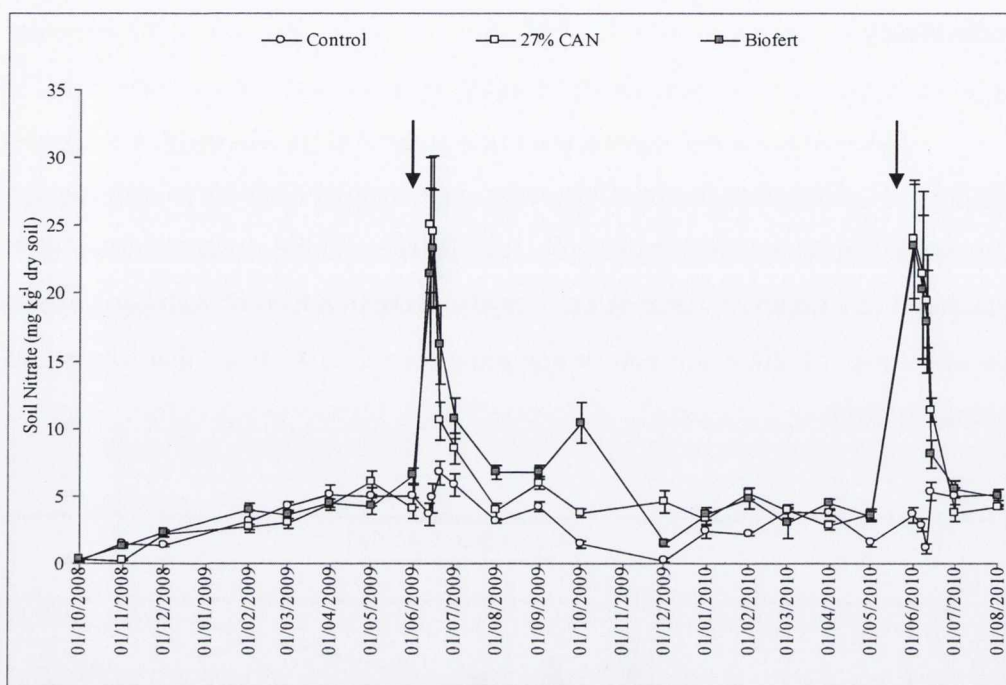


Figure 2.12 Measured soil nitrate in the fertilised and control plots for 2008-2010 throughout the experimental periods. Arrows indicate first measurement following fertiliser application ($n = 5$). Symbols indicate control plots, CAN fertilised plots and Biofert fertilised plots.

Table 2.4 Results for ANOVA for log soil nitrate concentration for *Miscanthus* ($r^2 = 0.84$).

Source	df	Seq Sums of Squares	Adj Mean Square	F-ratio	Probability
Treatment	2	7.02	3.51	59.70	0.000
Time	27	53.31	1.97	33.57	0.000
Interaction Time*Treatment	54	20.24	0.37	6.37	0.000
Error	252	14.82	0.06		
Total	335	95.40			

The control, CAN fertilised plots and Biofert fertilised plots are illustrated and the arrows represent the application of fertilisers for 2009 and 2010. The control plots were not spread with any fertiliser. Peak concentrations of soil nitrate corresponded to the application of fertilisers with significant differences between the control and fertilised plots. This is further illustrated in Figure 2.14 where each point represents the difference between the control

and the CAN fertilised plot and the control and the Biofert fertilised plot. It can be observed from the figure that the applied fertiliser was found in the soil for approximately 6 months after application.

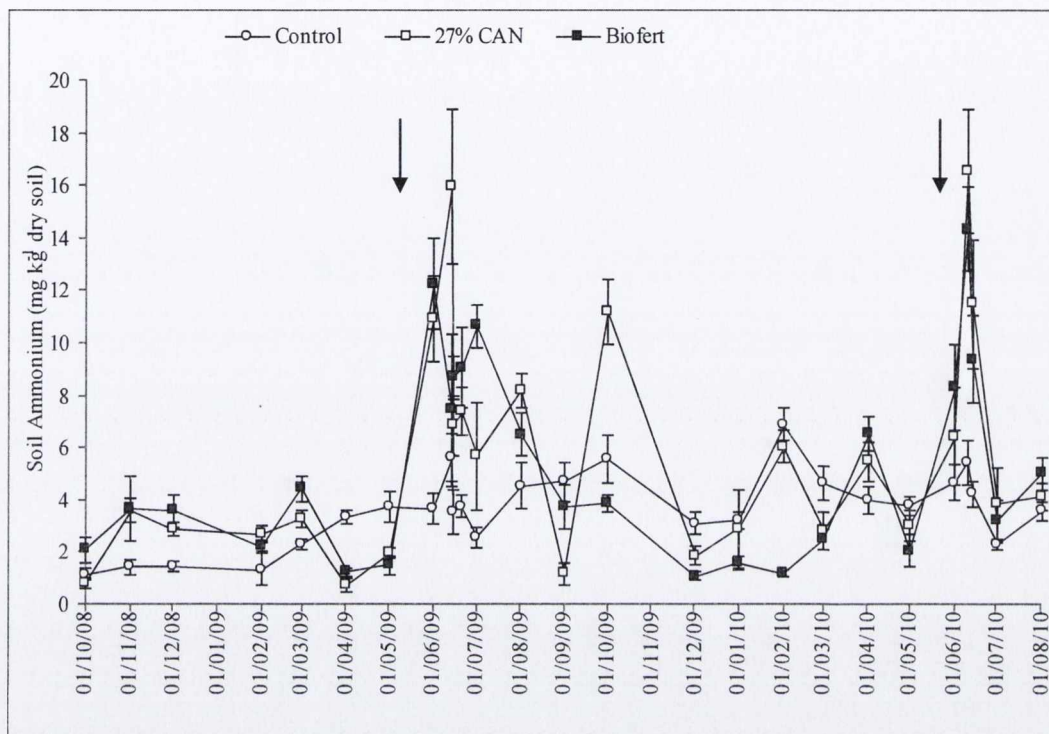


Figure 2.13 Changes in soil ammonium in the fertilised and control plots for 2008-2010 throughout the experimental periods. Arrows indicate first measurement following fertiliser application (n =5). Symbols indicate control plots, CAN fertilised plots and Biofert fertilised plots.

Table 2.5 illustrates the results for general linear model ANOVA for log soil nitrate with the treatment effect, time and interaction of time and treatment.

Table 2.5 Results for a general linear model ANOVA for soil ammonium concentration for *Miscanthus* ($r^2=0.69$).

Source	df	Seq Sums of Squares	Adj Mean Square	F-ratio	Probability
Treatment	2	0.39	0.18	3.17	0.044
Time	25	18.11	0.73	12.63	0.000
Interaction Treatment*Time	50	12.20	0.24	4.22	0.000
Error	232	13.43	0.06		
Total	309	44.13			

The results are significant for treatment effect (ANOVA, $p < 0.05$), for the time (ANOVA, $p < 0.000$) and for interaction of treatment and time (ANOVA, $p < 0.000$).

Figure 2.14 illustrates the soil nitrate concentrations due to fertiliser application on the soil. The arrows indicate the fertiliser application.

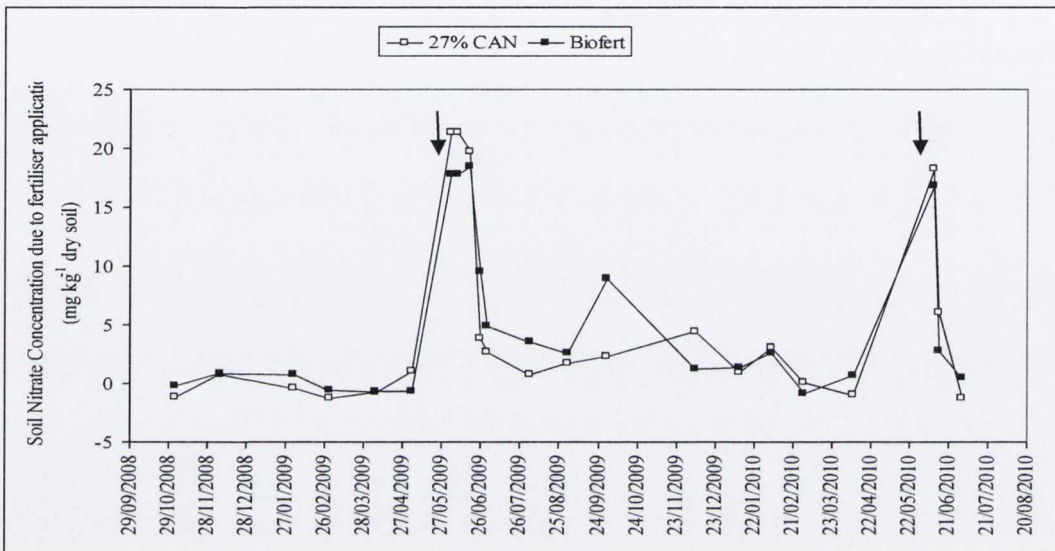


Figure 2.14 Changes in soil nitrate concentration in the *Miscanthus* site due to fertiliser application in 2009 and 2010. Arrow indicates the first measurement following fertiliser application.

2.3.3 Nitrous oxide emissions

The experiments on the *Miscanthus* field were carried out over approximately 20 months. Using this data it is possible to calculate an annual flux of N₂O from a *Miscanthus* field. Also by recording the environmental variables i.e. soil temperature, soil moisture, rainfall and soil nitrate and ammonium we can use this data to develop models for N₂O flux. A typical management approach was adopted to represent a typical agricultural regime.

Figure 2.15 represents the daily average N₂O emission rates for 2008 – 2010. During this period two applications of 150kg N ha⁻¹ CAN-nitrogen fertiliser and 150kg ha⁻¹ Biofert was applied on 12th June 2009, the same fertiliser treatments were applied on the 6th June 2010.

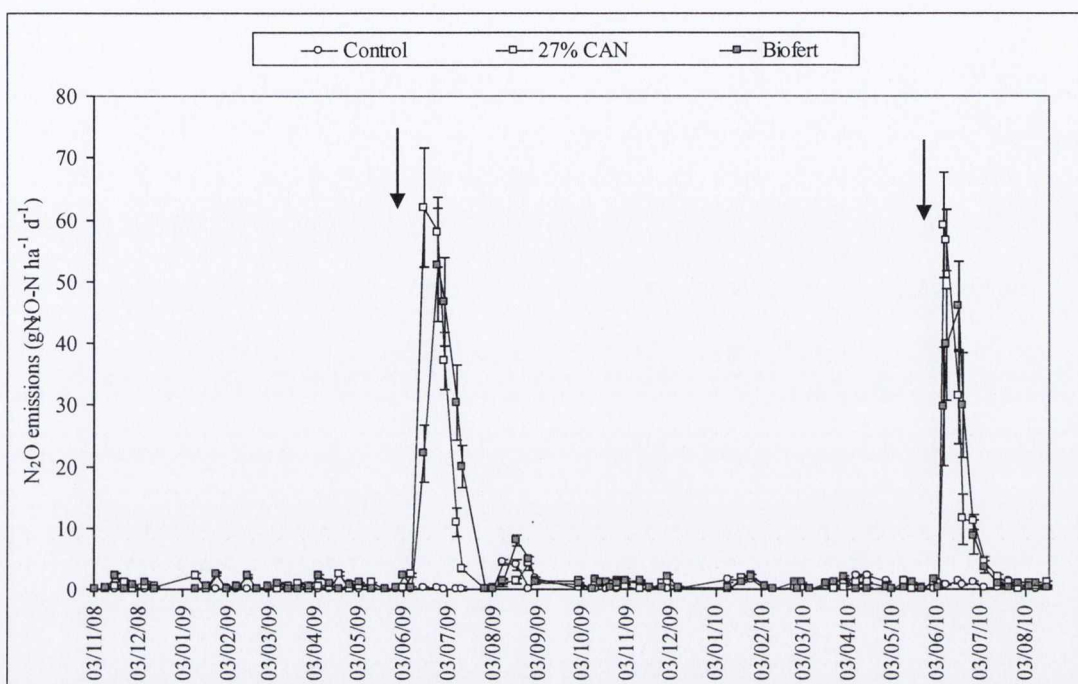


Figure 2.15 Daily N_2O emissions measured on a weekly basis from the *Miscanthus* site 2008-2010. Arrows indicate fertiliser application time (150kg N ha^{-1}). Symbols indicate treatment at which N_2O flux was measured: Control plots, CAN plots and Biofert plots (each point represents a sample number, $n = 5 (\pm\text{s.e.})$).

From late 2008 to 2009, the emissions from the control plots were low ranging from $-0.0989 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ to $5.481 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, there were some peaks around particularly wet periods. In 2009, N_2O fluxes from CAN and Biofert plots showed maximum peaks shortly after application of fertiliser. N_2O fluxes from CAN plots reached a maximum of $69.01 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, these levels returned to background low levels approximately 5 weeks after fertiliser application. N_2O fluxes from Biofert plots reached a maximum of $50.10 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, these levels returned to low background levels after approximately 6 weeks.

In 2010, the emissions from the control plots were low ranging from $-0.057 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ to $2.392 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$. N_2O fluxes from CAN and Biofert plots showed maximum peaks shortly after application of fertiliser. N_2O fluxes from CAN plots reached a maximum of $65.20 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, these

levels returned to background low levels approximately 4 weeks after fertiliser application. N₂O fluxes from Biofert plots reached a maximum of 48.99 gN₂O-N ha⁻¹ d⁻¹, these levels returned to low background levels after approximately 5 weeks.

Table 2.6 illustrates the results for a GLMANOVA for log soil N₂O flux for *Miscanthus*, Treatment (GLM, p < 0.000), time (GLM, p < 0.000) and the interaction of treatment and time (GLM, p < 0.000) are all significant factors and account for 89% of the data analysed.

Table 2.6 Results for a GLM ANOVA for soil log N₂O flux for *Miscanthus* (r²=0.89).

Source	df	Sums of Squares	Mean Square	F-ratio	Probability
Replicate	4	293.2	73.3	4.45	0.001
Date	84	78435.9	933.8	56.74	0.000
Treatment (Date)	170	54836.3	322.6	19.60	0.000
Error	1016	16719	16.5		
Total	1274	150285.2			

Using post-hoc Bonferroni analysis we were unable to illustrate a significant difference between the two fertiliser types of 27% CAN and Biofert outside of the peak N₂O periods immediately following fertiliser application, however they were both significantly different from control treatments (Table 2.6). We then used grouping information using the Bonferroni method and a 95% confidence interval to determine which dates were significantly different. Using this grouping method, twelve statistically significant groups were illustrated in the data, one group representing the background data outside of fertiliser application period (Table 2.7).

The major peaks occurred directly following fertilisation where CAN had the significantly highest peak in June of 2009 and June of 2010. Biofert treatment plots also showed high peaks post fertiliser application but were significantly lower than CAN at these two dates, approximately 2 weeks post fertiliser application peaks of CAN and Biofert are similar.

Table 2.7 Bonferroni method of grouping of N₂O data for entire experimental period (October 2008 – August 2010) illustrating statistically significant groups and their treatments (150 kg N ha⁻¹ 27% CAN and 150 kg N ha⁻¹ Biofert and a control).

Date	Treatment	N	Mean	Grouping
08/06/2009	CAN	5	61.9	I
08/06/2010	CAN	5	59.1	II
17/06/2009	CAN	5	58	
09/06/2010	CAN	5	56.7	
17/06/2009	BF	5	52.7	III
26/06/2009	BF	5	46.7	IV
18/06/2010	BF	5	46	V
09/06/2010	BF	5	39.7	
26/06/2009	CAN	5	37.1	VI
18/06/2010	CAN	5	31.3	
01/07/2009	BF	5	30.4	
21/06/2010	BF	5	29.9	
08/06/2010	BF	5	29.7	VII
08/06/2009	BF	5	22.2	VIII
09/07/2009	BF	5	20	IX
21/06/2010	CAN	5	11.4	
28/06/2010	CAN	5	11	
01/07/2009	CAN	5	10.9	
13/07/2009	BF	5	10.5	X
28/06/2010	BF	5	8.6	
19/08/2009	BF	5	8	XI

However, in the peaks illustrated in 2009 there is a delayed return to background levels in Biofert application treatment plots.

The mean cumulative N₂O flux in 2009 from the control plots was 0.629 ± 0.42 kg N₂O-N ha⁻¹ (0.06 g N m⁻²) over the period from May to August, compared to 11.483 ± 5.51 kg N₂O-N ha⁻¹ (1.15 g N m⁻²) and 12.873 ± 4.39 kg N₂O-N ha⁻¹ (1.29 g N m⁻²) for the 27% CAN and Biofert fertilised plots, respectively. The mean cumulative N₂O flux in 2010 from the control plots was 0.483 ± 0.13 kg N₂O-N ha⁻¹ (0.04 g N m⁻²) over the period from May to August, compared to 10.238 ± 4.42 kg N₂O-N ha⁻¹ (1.02 g N m⁻²) and 9.957 ± 3.96 kg N₂O-N ha⁻¹ (1.00 g N m⁻²) for the 27% CAN and Biofert fertilised plots, respectively.

Using the management year as the time period and the fertilizer treatment of 150 kg ha⁻¹ CAN-nitrogen and 150 kg ha⁻¹ Biofert, an emission factor value of 0.47 and 0.55 were calculated, respectively for the management year.

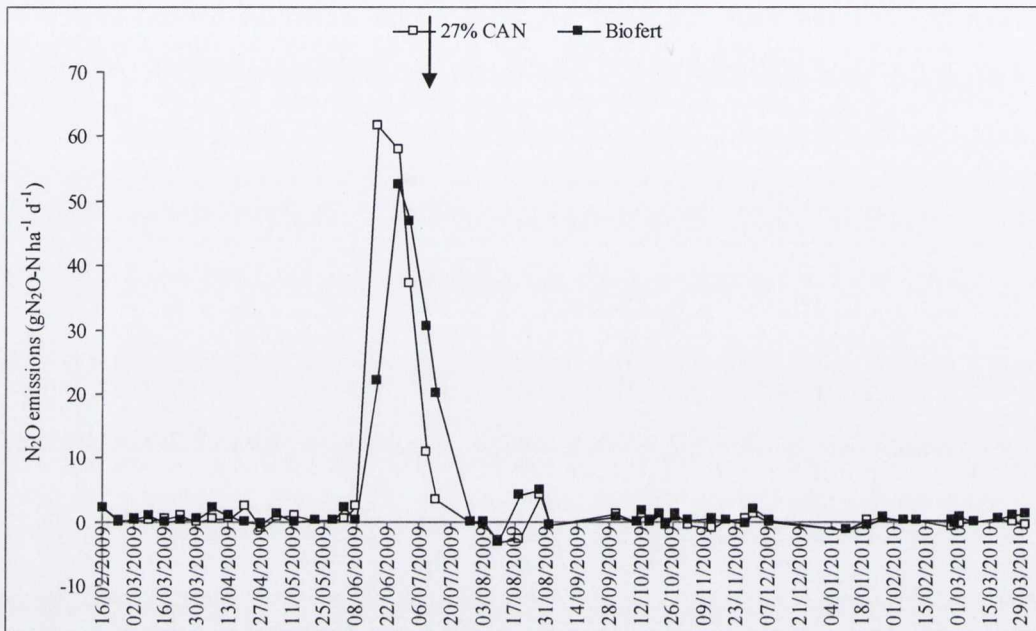


Figure 2.16 N₂O emissions due to addition of fertiliser for 150 kg N ha⁻¹ for 27% CAN and 150 kg N ha⁻¹ Biofert for the management year.

Figure 2.16 illustrates the N₂O emissions due to addition of fertiliser from the Miscanthus crop over the management year, the peaks occur following addition of Biofert and 27% CAN fertiliser.

Figure 2.17 represents daily N₂O emissions relative to WFPS (%) with different bands representing different 10% bins. We can see from the figure that the majority of N₂O pulses occurred in the 30-40% and 40-50% bands.

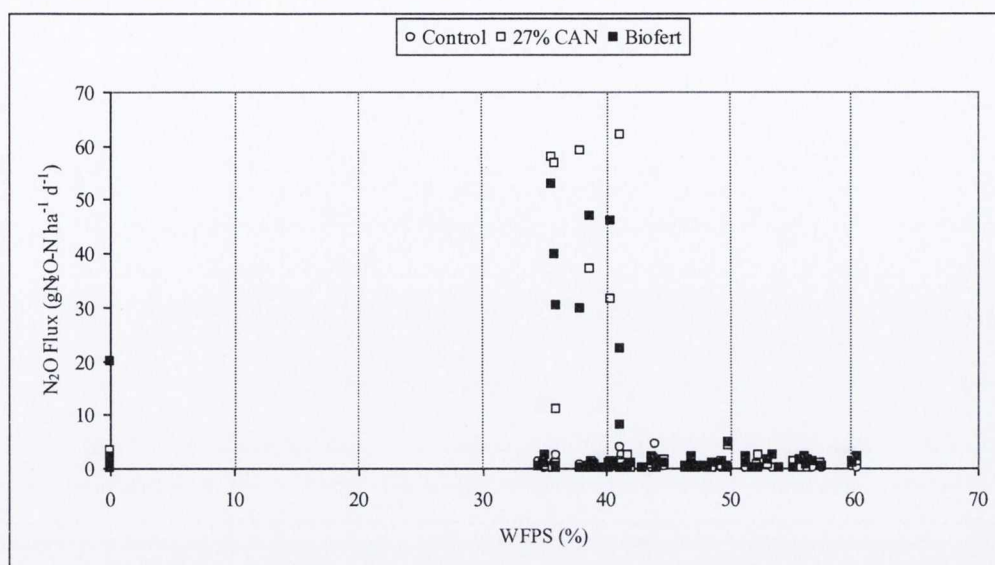


Figure 2.17 Daily N₂O emissions measured on a weekly basis from the *Miscanthus* site 2008-2010 versus Water Filled Pore Space (WFPS)(%). The different symbols indicate treatment at which N₂O flux was measured: Control plots, CAN plots and Biofert plots (each point represents a sample number, n = 5 (±s.e.)). The different lines represent bands of 0-10: 10-20 : 20-30: 30-40: 40-50: 50-60: 60-70 (%).

2.3.4 Cumulative N₂O Emissions

Figure 2.18 illustrates cumulative N₂O emissions for the control, 150 kg N 27% CAN and 150 kg N Biofert fertiliser treated plots for *Miscanthus* for each replicate taken during the management year 2009-2010. As is illustrated fertiliser application resulted in increased cumulative N₂O emissions compared to our control plots.

An analysis of variation for the cumulative data illustrated in Table 2.8 reveal that fertiliser application as “Treatment” resulted in variation in isolation of N₂O accumulation. No significant difference was detected between fertiliser types.

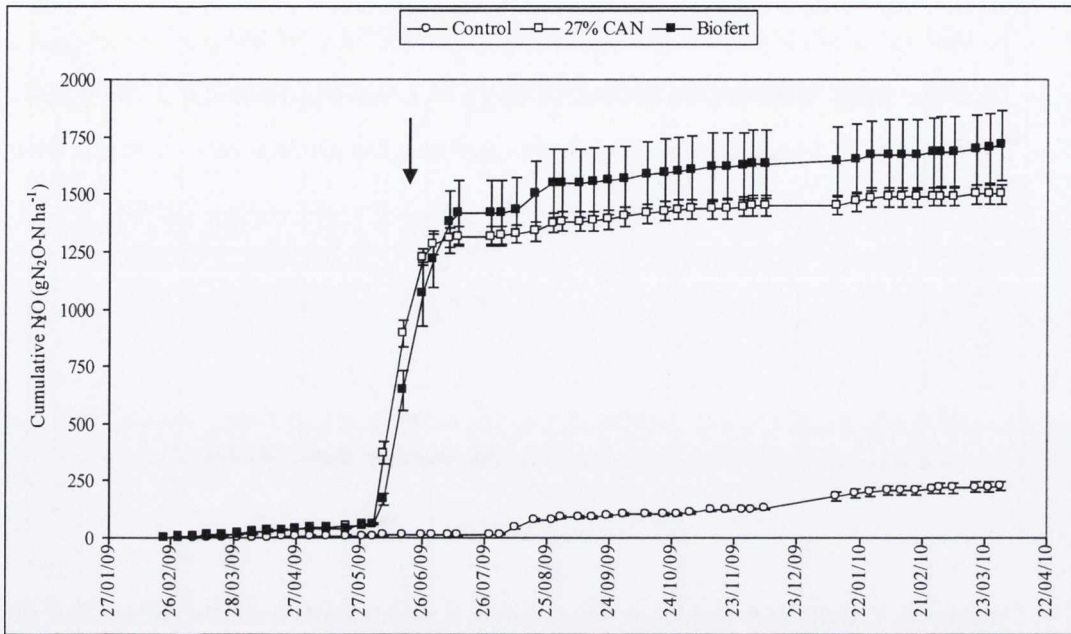


Figure 2.18 The cumulative N₂O emissions for control, 27% CAN fertiliser and Biofert fertiliser treated plots for the management year. Each point represents the mean \pm s.e. of five measurements.

Table 2.8 Results for a 1-way ANOVA for log cumulative N₂O flux for *Miscanthus* ($r^2=0.23$).

Source	df	Sums of Squares	Mean Square	F-ratio	Probability
Treatment	2	198.04	99.02	110.79	0.000
Error	752	672.12	0.89		
Total	754	870.17			

Total cumulative flux for the management year for the control was 0.2 kg N₂O-N ha⁻¹ y⁻¹, for the CAN fertiliser application value of 1.5 kg N₂O-N ha⁻¹ y⁻¹ and 1.7 kg N₂O-N ha⁻¹ y⁻¹ for Biofert fertiliser.

2.3.6 Methane Emissions

Figure 2.19 illustrates the daily average CH₄ emissions from 2008 – 2010 incorporating the same treatment regime, control plots, 150kg N CAN

fertiliser and 150kg N Biofert fertiliser applied in June of 2009 and June 2010.

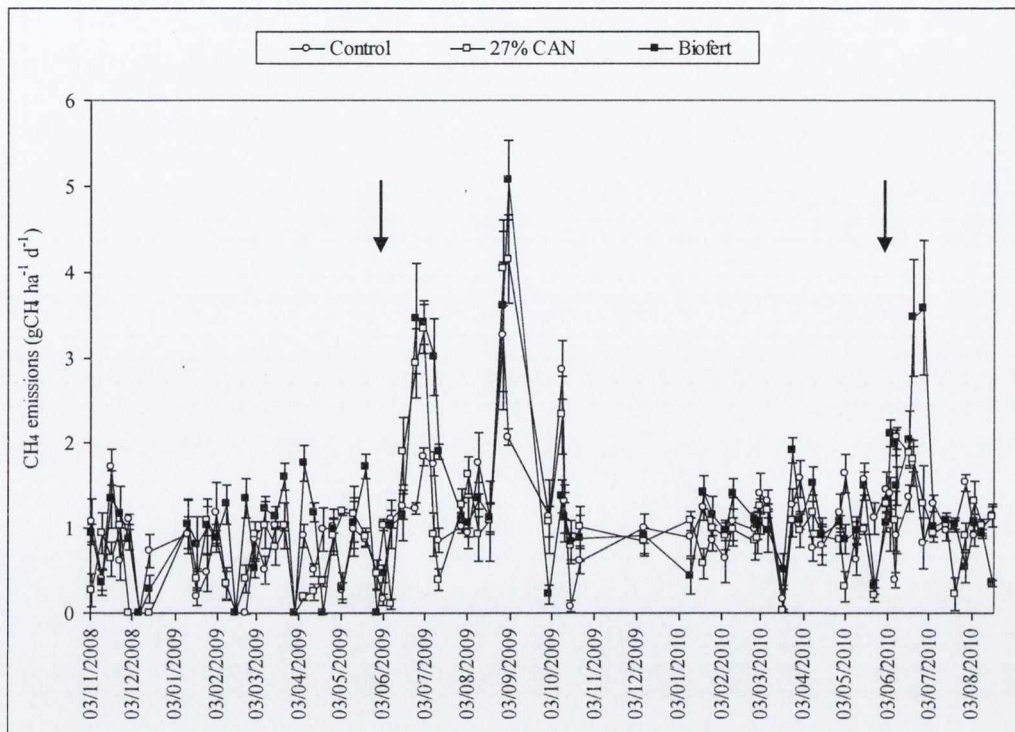


Figure 2.19 Daily CH₄ emissions measured on a weekly basis from the *Miscanthus* site 2008-2010. Arrows indicate fertiliser application time (150kg N ha⁻¹). Symbols indicate treatment at which CH₄ flux was measured: Control plots, CAN plots and Biofert plots (n = 5).

The CH₄ emissions were quite low over the experimental period. From late 2008 to 2009, the emissions from the control plots were low ranging from $-0.003 \text{ gCH}_4 \text{ ha}^{-1} \text{ d}^{-1}$ to $4.201 \text{ gCH}_4 \text{ ha}^{-1} \text{ d}^{-1}$, there were some peaks around particularly wet periods. In 2009, CH₄ fluxes from CAN and Biofert plots showed maximum peaks shortly after application of fertiliser. CH₄ fluxes from CAN plots reached a maximum of $4.20 \text{ gCH}_4 \text{ ha}^{-1} \text{ d}^{-1}$, these levels returned to background low levels approximately 3 weeks after fertiliser application. CH₄ fluxes from Biofert plots reached a maximum of $5.204 \text{ gCH}_4 \text{ ha}^{-1} \text{ d}^{-1}$.

CH₄ ha⁻¹ d⁻¹, these levels returned to low background levels after approximately 4 weeks.

In 2010, the emissions from the control plots were low ranging from 0.0979 gCH₄ ha⁻¹ d⁻¹ to 1.929 gCH₄ ha⁻¹ d⁻¹. CH₄ fluxes from CAN and Biofert plots showed maximum peaks shortly after application of fertiliser. CH₄ fluxes from CAN plots reached a maximum of 2.008g CH₄ ha⁻¹ d⁻¹, these levels returned to background low levels approximately 3 weeks after fertiliser application. CH₄ fluxes from Biofert plots reached a maximum of 3.445 gCH₄ ha⁻¹ d⁻¹, these levels returned to low background levels after approximately 2 weeks.

Some negative fluxes were observed from control plots and treatment plots on occasion.

2.3.7 Cumulative CH₄ emissions

Figure 2.20 represents the cumulative CH₄ emissions for the Miscanthus crop over the management year for both fertiliser treatments i.e. Biofert and 27% CAN fertilisers and includes control plots.

Table 2.9 illustrates a 1-way ANOVA for a significant treatment effect (ANOVA, $p < 0.05$) on cumulative CH₄ emissions over the management year for *Miscanthus*.

Table 2.9 Results for a 1-way ANOVA for log cumulative CH₄ flux for *Miscanthus* ($r^2=0.01$).

Source	df	Sums of Squares	Mean Square	F-ratio	Probability
Treatment	2	1.73	0.86	3.51	0.030
Error	672	165.24	0.25		
Total	674	166.97			

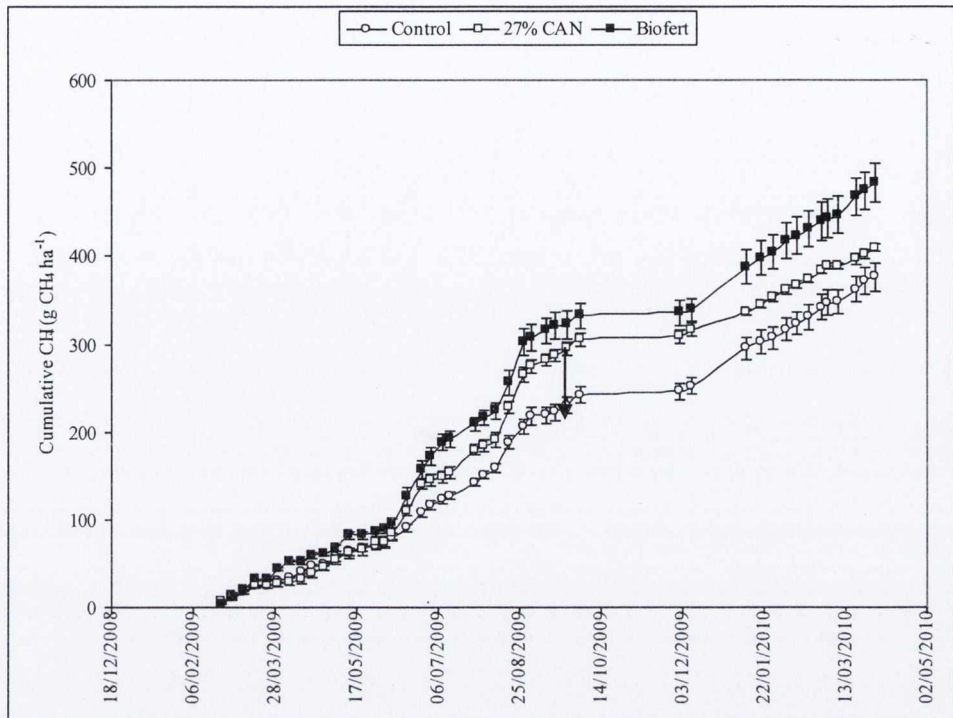


Figure 2.20 The cumulative CH₄ emissions for control, 27% CAN fertiliser and Biofert fertiliser treated plots for the management year. Each point represents the mean \pm s.e. of five measurements.

Figure 2.21 illustrates the changes in CH₄ emissions due to fertiliser application over the management year. There is high variability within the data due to the low levels detected.

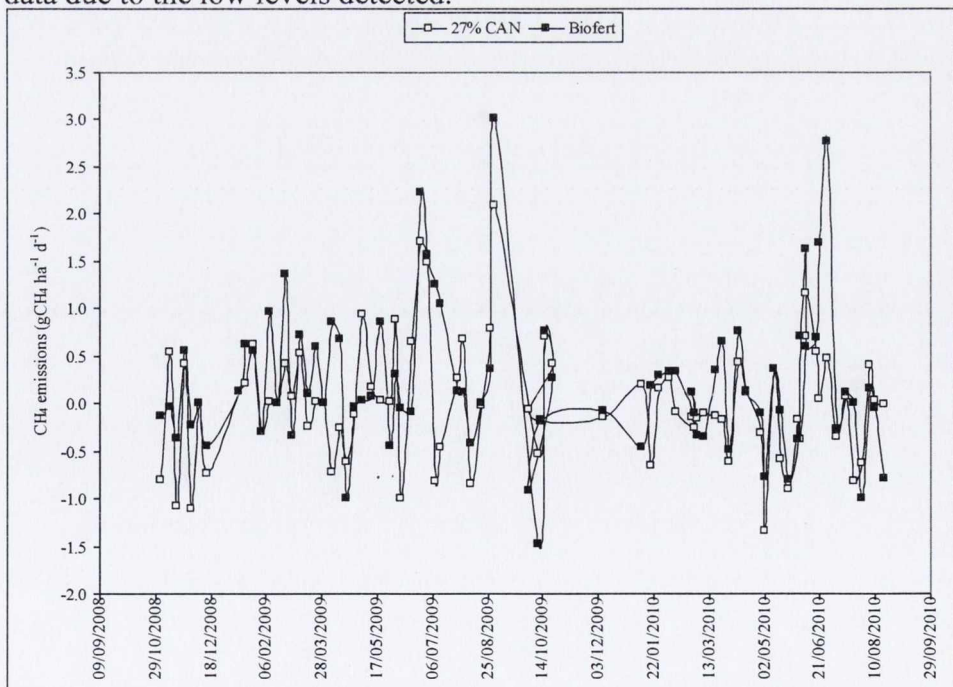


Figure 2.21 Changes in CH₄ emissions in the *Miscanthus* site due to fertiliser application in 2009 and 2010. Arrow indicates the first measurement following fertiliser application.

Table 2.10 illustrates the N₂O and CH₄ emissions in terms of CO₂ equivalents for *Miscanthus* over the management year for Biofert and 27% CAN fertiliser application and for control plots where no fertiliser was applied. For the control plots, total CO₂ equivalents were 79.28 kg CO₂, for 150 kg N 27% CAN 473.61 kg CO₂, for 150 kg N Biofert 530.58 kg CO₂.

Table 2.10 illustrates the EFs for both fertiliser treatments at application rates of 150 kg N ha⁻¹ for: the overall study period (October 2008 – August 2010), two growing seasons and for the management year. EFs for both fertiliser treatments were greater during growing season 2009 with Biofert being the greater of the two treatments. For the management year, Biofert had a higher EF value than CAN. Over the entire measurement period Biofert had a higher EF value than CAN.

Table 2.10 Total amount of N applied and emission factor for the growing seasons (June-August) for 2009, 2010 and the management year (February 2009-March 2010).

Treatment	Emission Factor (%)			
	Growing Season 2009	Growing Season 2010	Management Year	Entire Measurement Period
150 kg N ha ⁻¹ 27% CAN	0.46	0.26	0.47	0.77
150 kg N ha ⁻¹ Biofert	0.52	0.31	0.55	0.84

2.3.8 Multiple Regression Analysis

A multiple regression of the data set with log N₂O flux as the Y variable was carried out, results of which are given in Table 2.11. Log soil ammonium and log of soil nitrate showed correlation with emissions of N₂O with a r² value of 63% and 68% respectively, accepting a threshold probability of 95%. However, a best fit linear regression that accounted for 72% of the variations was calculated by including log soil nitrate and log soil ammonium in the

analysis and excluding the less correlated factors, the results of which is illustrated in Table 2.12. This regression revealed that the interaction between soil nitrate concentration and soil ammonium concentration is significantly correlated with N₂O flux ($p < 0.05$).

Table 2.11 Regression analysis results for log N₂O versus log soil moisture, log soil nitrate, log ammonium and log temperature for *Miscanthus*.

Predictor	Coef	SE Coef	T-ratio	Probability
Constant	-0.014	3.622	-0.00	0.997
Log Soil Moisture	-1.161	2.304	-0.50	0.617
Log Soil Nitrate	1.7547	0.2922	6.01	0.000
Log Soil Ammonium	1.1058	0.3411	3.24	0.002
Log Soil Temperature	-0.1723	0.5032	-0.34	0.734
Source	DF	Sum of Squares	Mean of Squares	F-ratio
Regression	4	31.5255	7.8814	28.14
Residual Error	44	12.3241	0.2801	
Total	48			

Table 2.12 Regression analysis results for log N₂O versus log soil nitrate, log soil ammonium for *Miscanthus* ($r^2=0.72$: $\log N_2O = -1.84 + 1.10 \log \text{soil ammonium} + 1.76 \log \text{soil nitrate}$).

Predictor	Coef	SE Coef	T value	Probability
Constant	-1.8405	0.1957	-9.41	0.000
Log Soil Ammonium	1.0952	0.3281	3.34	0.002
Log Soil Nitrate	1.7564	0.2755	6.38	0.000

2.3.9 Correlation of N₂O flux with Soil Nitrate and Soil Ammonium

A positive linear relationship is illustrated in figure 2.22 between log soil N₂O and log soil nitrate as soil nitrate increases, soil N₂O flux increases ($y =$

$0.2917x + 0.6525$; $r^2 = 0.54$). A Pearson correlation of log N₂O and log soil nitrate concentration resulted in a value of 0.734, $p < 0.05$.

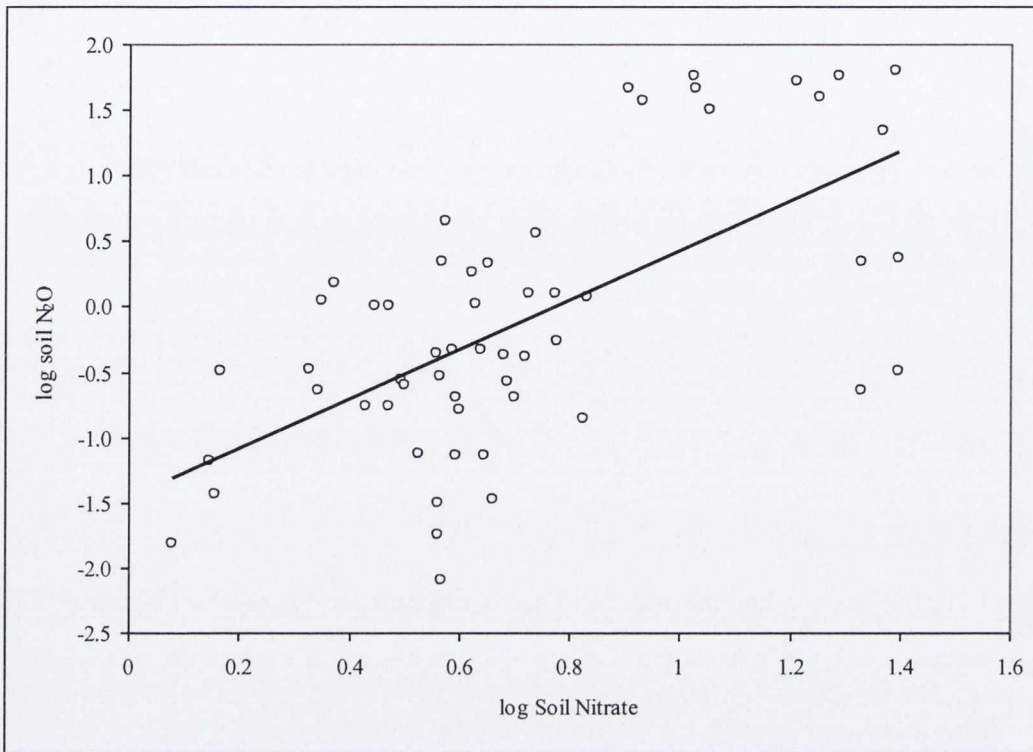


Figure 2.22 Scatterplot of log soil N₂O flux versus log soil nitrate concentration illustrating a positive linear relationship ($y = 0.2917 x + 0.6525$; $r^2 = 0.54$).

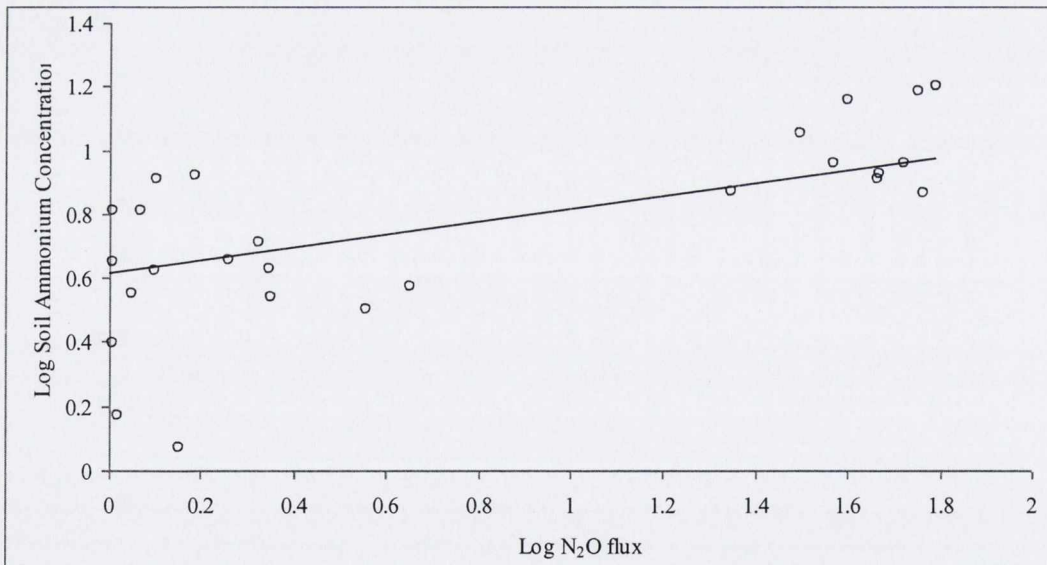


Figure 2.23 Scatterplot of log soil N₂O flux versus log soil ammonium concentration illustrating a positive linear relationship ($y = 0.2015 x + 0.6164$; $r^2 = 0.47$).

Figure 2.23 illustrates a positive correlation between soil N₂O flux and soil ammonium concentration ($r^2 = 0.47$; $y = 0.2015 x + 0.6164$) a Pearson

correlation of log N₂O and log soil ammonium concentration resulted in a value of 0.684, $p < 0.05$).

2.4 Discussion

Results from this study support the concept that cumulative emissions of N₂O from agricultural soils are directly related to the application of N-fertiliser and the post-application concentration of nitrate in the soil (Bouwman et al., 2002a, Tilsner et al., 2003). This observation was found over the total measurement period (Figure 2.15) and the management year (Figure 2.16).

WFPS was measured throughout the experimental period, Figure 2.17 outlines the 10% bands for N₂O flux measurements recorded. Peak N₂O fluxes occurred between 35-45% WFPS. Above this range for WFPS, N₂O measurements made were very low. The ideal WFPS values for N₂O emission are a result of several physical and biological process within the soil and vary from soil to soil (Bouwman, 1998). Nitrification has been observed to occur up to a value of 60% WFPS (Davidson and Verchot, 2000), above this value, denitrification becomes dominant (Lemke et al., 1998). At very high values i.e. greater than 80% WFPS, there is restricted doxygen diffusion and N₂ is the primary product of denitrification (Veldkamp et al., 1998).

The key factors influencing the rate of nitrification are the concentrations of free oxygen (O₂) and concentration of NH₄-N by being substrates for nitrification (Firestone and Davidson, 1989). WFPS has a direct relationship to the concentration of free oxygen (O₂) in the soil. According to (Tiedje, 1988), nitrate produced in nitrification may be subject to: low level of oxygen; the presence of bacteria having the metabolic pathway; the availability of suitable reductants e.g. carbon; the supply of NO₃ or other nitrogen oxides. The presence of O₂ is often a limiting factor for denitrification followed by NO₃-N availability. An association of soil NH₄-N content with N₂O emissions can be seen by comparing N₂O emission levels with soil NH₃-N contents (Figure 2.23). There is a stronger association between N₂O emission levels and soil NO₃ ($r^2 = 0.54$). Throughout the experimental period, short

term peaks in N_2O emissions coincided with short term peaks in soil NO_3 and soil NH_4-N concentrations which occurred after application of fertiliser, following application peaks, soil NO_3 and soil NH_4-N returned to background level. Compared to NO_3 , NH_4-N contents generally remained low during the experimental period. Regression analysis show that soil NO_3 and soil NH_4-N have positive correlations with soil N_2O emissions. A multiple regression analysis of log N_2O flux against the single factors log soil nitrate concentration, log soil ammonium concentration, log soil moisture and log soil temperature revealed soil nitrate and soil ammonium to be significant factors (Table 2.9). Best-fit regression analysis revealed soil nitrate concentration and soil ammonium concentration to be correlated positively with soil N_2O flux. Soil nitrate concentration correlated with soil N_2O flux positively and resulted in an equation accounting for 54% of the variation (Figure 2.21). N_2O flux correlated to soil ammonium concentration resulting in a positive linear relationship accounting for 47% of the data variation (Figure 2.22). This would suggest more of the N_2O flux is derived from denitrification than from nitrification. A stronger correlation between soil N_2O flux and soil nitrate concentration has been observed in agricultural soils where there is also a weaker correlation with soil N_2O flux and soil ammonium concentration relating to soil denitrification (Bouwman, 1996). Significant N_2O flux peaks were observed during periods of N-fertiliser application.

Results of multiple regression analysis did not find soil temperature or soil moisture to be significant determinants of N_2O flux alone which may well be caused by the limitation of N_2O flux by available soil nitrate. Soil moisture stimulates denitrification by temporarily reducing the oxygen diffusion into the soil (Dobbie and Smith, 2001) and increasing organic carbon and nitrate solubility (Abdalla et al., 2009a). It is clear from Figure 2.7 that the management year was a wet year particularly when compared to the 30 year mean, over 2008 and 2009 the late winters, mid summers and spring months were wetter than the 30 year mean. In early 2010 rainfall increased to twice the levels of 2009, the levels in April and May were significantly down in 2010 from 2009 levels. Rainfall in June 2009 was greater than twice the 30

year mean and the following year the June rainfall levels were greatly decreased. There were also heavy rainfall in August and September of 2009, far above the levels of the 30 year mean. It has been long advised to avoid application of fertiliser during periods of high rainfall (Choudhary et al., 2002, DEHLG and DAFF, 2010).

A continuous data set over the entire experimental period i.e. October 2008 – August 2010 was available for calculating emission factors (Table 2.10). From this data we calculated EFs for growing seasons 2009, 2010, a typical management year and for the entire period. From this data it is illustrated that the vast proportion of N₂O flux is produced during the growth period i.e. post-fertiliser application.

In Table 2.13 results of total cumulative N₂O and CH₄ equivalents have been calculated in CO₂ equivalents. CH₄ results are low as expected and make up a small proportion of the total CO₂ equivalents for control, CAN and Biofert treatments. There is a significant increase in total CO₂ equivalents for CAN and Biofert, with Biofert results being slightly higher.

Table 2.13 Cumulative N₂O, CH₄ and CO₂ equivalent values for the management year for *Miscanthus*.

Treatment	N ₂ O (kg N ₂ O-N ha ⁻¹)	N ₂ O (kg CO ₂ equivalents)	CH ₄ (kg CH ₄ ha ⁻¹)	CH ₄ (kg CO ₂ equivalents)	Total CO ₂ equivalents (kg CO ₂)
Control	0.23 (± 0.02)	71.3	0.38 (± 0.02)	7.98	79.28
150 kg N ha ⁻¹ 27% CAN	1.50 (± 0.04)	465.0	0.41 (± 0.004)	8.61	473.61
150 kg N ha ⁻¹ Biofert	1.71 (± 0.15)	530.1	0.48 (± 0.02)	10.01	530.58

In order to relate N-fertiliser application to N₂O emissions an emission factor is calculated in order to determine the percentage of applied N lost to the atmosphere as N₂O. We calculated emission factors for the entire experiment period (Table 2.8). From Table 2.8 an emission factor of 0.47 was calculated

during the management year which includes the growing season 2009, which alone has an emission factor of 0.46, which illustrates further that the majority of N₂O flux occurs during this period. This related to a total cumulative flux of 0.2 kg N₂O-N ha⁻¹ y⁻¹ for control plots, 1.5 kg N₂O-N ha⁻¹ y⁻¹ for CAN fertiliser applications and 1.7 kg N₂O-N ha⁻¹ y⁻¹ for Biofert fertiliser application. An emission factor of 0.83 was observed on grassland sites in Carlow (Abdalla et al., 2010a). Annual emissions for (Abdalla et al., 2010a) calculated 2.4 kg N₂O-N ha⁻¹ y⁻¹ for grassland sites. Studies carried out in Wexford in 2002 and 2003 recorded annual flux values of 6.5 and 18.5 kg N₂O-N ha⁻¹ y⁻¹ (Hyde et al., 2006). Data from an eddy covariance study from a fertilised grazed grassland in Cork resulted in annual emissions of 2.4 kg N₂O-N ha⁻¹ y⁻¹ (Hsieh et al., 2005). The soils from these two sites are classified as clay loams, our soil for the experiments are classified as a sandy clay loam. This may well account for the lower emissions from our site. The Wexford and Cork sites received 225 kg N ha⁻¹ y⁻¹ of inorganic N and 207 kg N ha⁻¹ y⁻¹ of synthetic N (Hyde et al., 2006) and 130 kg N ha⁻¹ y⁻¹ of organic N (Hsieh et al., 2005) respectively. N₂O flux values for summer fluxes (June, July, August) for grassland site at the Grassland Research and Innovation Centre, Moorepark (Teagasc) in Fermoy, Co. Cork were measured at 1.81±0.7 kg N₂O-N ha⁻¹ and during the spring (March, April, May) were recorded fluxes of 1.51±0.6 kg N₂O-N ha⁻¹ (Rafique et al., 2012). Annual N₂O flux values ranged from 2 ± 3-51 – 12.55 ±2.83 kg N₂O-N ha⁻¹y⁻¹ (Rafique et al., 2011a).

The application of 27% CAN and Biofert fertiliser during our experiment increased soil nitrate and soil ammonium (Figure 2.12, 2.13, 2.14). This in turn effected soil nitrification and denitrification processes thus increasing soil N₂O flux from the soil (Kaiser and Ruser, 2000, McSwiney and Robertson, 2005, Dobbie and Smith, 2003). The emission factor calculated for our entire experimental period of 0.84 for Biofert and 0.77 for CAN fertiliser are similar to emissions from an extensive study carried out by which included 10 grassland sites in 8 European countries which resulted in an overall emission factor of 0.75 (Flechard et al., 2007) which are similar again to work carried out in Carlow on grasslands (Abdalla et al., 2010a). However, our

management year emission factor values of 0.47 and 0.55 for CAN and Biofert treatment regimes, respectively are still substantially lower than those mentioned from Irish studies.

There was no significant increase in crop yield in relation to addition of N-fertiliser (Table 2.2). In field trials, fertiliser application at a low level has been used successfully to support initial development of the rhizome system of a newly planted crop, at levels of approximately 60 kg N ha⁻¹ (Greef, 1995). In establishing the new crop N levels of 50 – 70 kg N ha⁻¹ year⁻¹ of N would meet requirements (Lewandowski et al., 2000). Fertiliser application did not have significant effect on yields in Danish trials at levels of 70-100 kg N (Jorgensen et al., 1996) and at levels of 0-150 kg N (Jorgensen et al., 1997). In Austrian trials, there was no yield response to fertiliser application over 90 kg N ha⁻¹ (Schwarz et al., 1994). There was a significant increase in N₂O fluxes using addition of Biofert and 27% CAN over the growing year with no significant increase in yield. It has been determined that the largest proportion of N contained within a *Miscanthus* plant comes from mineralisation and deposition and not from fertiliser (Lewandowski et al., 2000). In work carried out in NE England on *Miscanthus* and Willow, the addition of fertiliser produced significant increases in N₂O emissions (Drewer et al., 2012a). They concluded that the bioenergy crops e.g. *Miscanthus* and Willow only produce less GHGs than annual crops when they receive no or very low rates of N fertilisation (Drewer et al., 2012a). As such Biofert fertiliser would be useful as an addition to establishing crops and for crops with low N contents as its costs are minimal compared to those for purchasing 27% CAN fertiliser (this will be discussed further in Chapter 5).

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Chapter 3 Measurement of N₂O and CH₄ emissions from *Salix viminalis x schwerinii* plots treated with inorganic and organic fertiliser.

3.1 Introduction

Data sources from 2009 for total energy consumption in Ireland consists of 52% petroleum products, 29% gases, 15% solid fuel and 4% renewable. Of this energy produced in Ireland is generated through solid fuels (38%), renewable (39%), gases (21%), petroleum products (1%) and other products (1%) (Data Sources: EC (ESTAT, ECFIN) EEA, June 2011). Increases in the last few years of oil and gas prices have made fossil fuel based electricity and production more expensive. Increases in oil supply to emerging economies such as China and India have put further limitations on the supply of oil and have led to a new era of energy sources emerging (Styles and Jones, 2007a). Concerns relating to increasing levels of global warming caused by use of fossil fuels have led to increased interest in the use of renewable energy sources.

The Irish government's White Paper on Sustainable Energy Development published in 2007 was produced to promote the use of renewable energy sources alongside the EU Directive for Renewable Energy (DCMNR, 2007, European Commission, 2008b). The White Paper targets 10% of transport fuel and 12% of heat energy to be produced by renewable energy sources. It also aims for 800 MWe of electricity from Combined Heat and Power (CHP) with an *emphasis* placed on biomass usage. It also aims for the three power stations which are currently solely burning peat to be using 30% biomass for co-firing. The EU Directive set a target of 16% for Ireland's total energy production to come from renewable resources and committed Ireland to develop a National Action plan to achieve these targets (National Energy Efficiency Action Plan Maximising Ireland's Energy Efficiency - The National Energy Efficiency Action Plan 2009 – 2020).

The traditional source of fuel for heating and power generation would be forest resources, however, renewable energies are important sources of this wood-for-energy and could potentially become more competitive in the future (Mola-Yudego and Pelkonen, 2008). In order to meet targets for biomass heat and electricity estimates of 3.3 million m³ of whole softwood per annum would have to be provided by 2020 (Wickham et al., 2010). However, current estimates of production for 2015 for forest production are approximately 5 million m³ per annum (Gallagher and O'Carroll, 2001). As such, a long-term plan of increasing biomass production is required, but 2020 targets would be difficult to meet at current conventional forested area production levels.

Over the last number of years, as the popularity of biomass production as a potentially abundant energy source has increased (Hall and Scrase, 1998, Righelato and Spracklen, 2007), willow is considered a potentially promising source of this biomass (Rowe et al., 2009c). Willow biomass can be burnt or gasified to generate electricity and or heat in combustion or gasification plants (Hughes et al., 2003). It can be grown on abandoned or contaminated soil and has comparatively less intensive management requirements than food crops (Tillman et al., 2006, Schmer et al., 2008).

In trials carried out in Loughall, Co. Armagh, a short rotation coppice Willow variety 'Tora' was the highest yielding variety originating from the Svalöf-Weibull breeding programme with an average yield of 12.8 ODT ha⁻¹ yr⁻¹ from 23 harvests (Lindegaard and Barker, 1996). This particular breed is a cross between a Swedish variety Orm and a Siberian basket willow, it is considered almost free from leaf rust and attacks from insects and gall midges are less common. Perennial energy crops provide significant biomass yields and offers considerable potential to fulfil environmental and energy targets (Mola-Yudego and Pelkonen, 2008).

Measurements carried out in NE England of N₂O and CH₄ emissions from *Miscanthus x giganteus* and willow were compared to emissions from arable annual crops grown for food production. The study found the N₂O fluxes were significantly smaller for the bioenergy crops, measuring average fluxes

were; $8 \mu\text{g m}^{-2} \text{h}^{-1} \text{N}_2\text{O-N}$ for wheat, $32 \mu\text{g m}^{-2} \text{h}^{-1} \text{N}_2\text{O-N}$ for oilseed rape and $4 \mu\text{g m}^{-2} \text{h}^{-1} \text{N}_2\text{O-N}$ for *Miscanthus* and $0.2 \mu\text{g m}^{-2} \text{h}^{-1} \text{N}_2\text{O-N}$ for Willow (Drewer et al., 2012a).

This chapter is concerned with measuring N_2O and CH_4 emissions from plots of *Salix viminalis* x *schwerinii* (commercially known as ‘Tora’) that have been treated with inorganic (27% CAN) and organic (Biofert) fertiliser over a 20 month period, from October 2008 – August 2010. The experiment was to determine the potential benefits of using a readily available, cheap alternative organic fertiliser, Biofert, on a *Miscanthus* crop. This could then be compared to the inorganic CAN fertiliser and the difference between the N_2O and CH_4 emissions from both treatments as compared to the control i.e. no fertiliser application plots. As such, the hypotheses of this study were, a) an increase in N_2O fluxes after fertiliser application is dependent on fertiliser type, b) fluxes of CH_4 are insignificant and c) there is a greater increase in yield on application of fertiliser than increase in N_2O flux.

3.2 Materials and Methods

3.2.1 Experimental Site

Approximately 20 months of measurements of N_2O and CH_4 emissions were collected from a Willow stand at the Oak Park Research Centre, Carlow, Ireland. Measurements were taken from October 2008 to August 2010, in 2008 the Willow was not fertilized, on 6th June 2009 and 6th June 2010, 150kgN ha^{-1} of Biofert and 150kgN ha^{-1} of 27% Calcium Ammonium Nitrate (CAN) were spread in five block replicates.

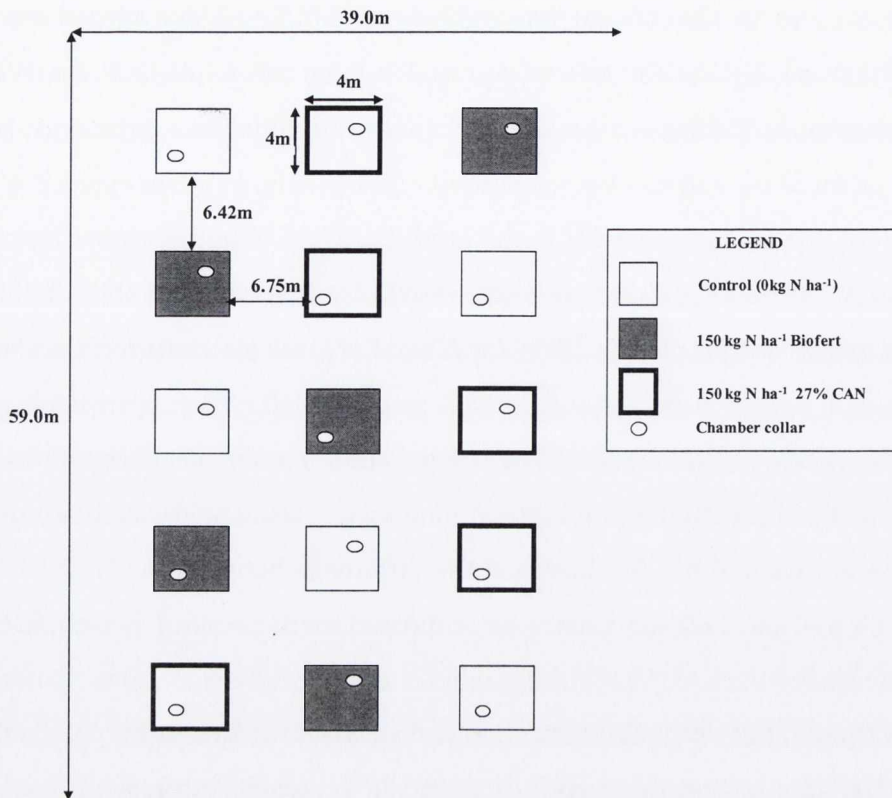


Figure 3.1 Experiment design of fertiliser application on Willow site.

In June of 2010 150kgN ha⁻¹ of Biofert and 150kgN of 27% Calcium Ammonium Nitrate (CAN) were spread in five block replicates (see figure 3.1). Harvesting took place on 27th March 2010 after a two-year growth cycle.

We used short rotation coppice (SRC) Willow, a perennial, fast-growing, high yielding woody crop that is considered suited to Ireland's climatic and soil conditions (Dawson, 2007). Generally, it is harvested every 2-5 years and is managed under a coppice system (Evans et al., 2007). After planting stems are cut back during the winter after their first growing season to allow for coppicing. A rotation length of 2-3 years is usually practiced and should occur with the peak mean annual biomass increment (MAI). In the UK, higher planting densities and more frequent harvesting coincided with higher annual yields (Bullard et al., 2002). However, this requires more intensive management and thereby negating advances in yield increase with increased costs for management (Wilkinson et al., 2007). As such, a three year rotation system was used for our plots.

The site had an elevation of 58m, an annual rainfall in 2008 of 945 mm, in 2009 of 1085 mm and from January to June 2010 of 338 mm and a mean annual maximum air temperature in 2008 of 13.2° C, in 2009 13.1°C and from January to June 2010 of 16.8°C and a mean annual minimum air temperature of 5.6° C in 2008, of 5.4°C in 2009 and 7.6°C in 2010. The soil is classified as sandy loam with a pH of 6.2. The Willow site has been permanent for the past five years.

3.2.2 Measurement of N₂O and CH₄ flux

Fluxes were measured using vented closed flux chambers (Mosier, 1989). N₂O and CH₄ emissions from 5 replicated chambers were measured on a weekly basis. Samples were taken at four times; (t = 0) 0 mins, (t = 1) 10 mins, (t = 2) 20 mins and (t = 3) 30 mins, after the chamber was placed over the collar. Samples were taken using a 60 ml gas-tight syringe after pre-evacuating the 20 ml vials. 20 ml of the sample was then injected into the 20ml gas-tight vial and stored until analysis. Samples were taken as far as possible at the same time of day to minimize the effects of diurnal variation. The tightness of the static chamber was tested by checking the linearity of N₂O gas flux within the chamber. Gas samples were measured at Trinity College Dublin using a gas chromatograph (PerkinElmer Clarus 500 Gas Chromatograph) with Electron Capture Detection (ECD) and Flame Ionization Detector (FID). The equation for closed flux chambers was used for calculating the daily flux of N₂O and CH₄ from each chamber (Smith et al., 1995, Baggs et al., 2003b):

$$\text{Equation 3.1} \quad \text{g N}_2\text{O-Nha}^{-1}\text{d}^{-1} = \frac{\text{Vol. (ml)} \times \text{ppm change (X-X}_0\text{)} \times 28 \text{ (g N)} \times 60 \text{ (mins.)} \times 24 \text{ (h)} \times 10^8}{\text{Area (cm}^2\text{)} \times \text{time closed (mins.)} \times 24000 \text{ (1 mole as ml)} \times 10^6}$$

as adjusted for CH₄:

$$\text{Equation 3.2} \quad \text{g CH}_4\text{ha}^{-1}\text{d}^{-1} = \frac{\text{Vol. (ml)} \times \text{ppm change (X-X}_0\text{)} \times 16 \text{ (g CH}_4\text{)} \times 60 \text{ (mins.)} \times 24 \text{ (h)} \times 10^8}{\text{Area (cm}^2\text{)} \times \text{time closed (mins.)} \times 24000 \text{ (1 mole as ml)} \times 10^6}$$

N₂O emission factors are defined as the amount of N emitted as N₂O per year as a percentage of the total N fertiliser applied. Emission factors (EFs) for N fertilizer were calculated by expressing the cumulative emissions from fertilized plots minus that of the control plots as a percentage of the total N applied after being adjusted for ammonia volatilisation:

Equation 3.3
$$EF = \frac{[(\text{Cumulative flux (fertilizer treatment)} - \text{Cumulative flux (control)}) / (\text{fertilizer applied} \times (1 - \text{Frac}_{\text{GASF}}))] \times 100}{\text{IPCC, 2000}}$$

with cumulative annual N₂O-N loss=cumulative annual N₂O-N loss (with fertiliser or manure input)-cumulative annual N₂O-N loss (zero-N control). *Frac*_{GASF} is the fraction of nitrogen that volatilises as NH₃ and NO_x from applied synthetic fertiliser (*Frac*_{GASF} = 10%).

3.2.3 Soil Temperatures

At each sampling a digital handheld thermometer was used to measure the soil temperature at a depth of 10cm. The Teagasc Oak Park Research Centre weather station also measured the soil temperature at a depth of 10cm every half hour.

3.2.4 Soil Moisture, WFPS and Soil Density

Daily rainfall (mm) was recorded at the Teagasc Oak Park Research Centre weather station. At each sampling 4 soil samples were taken at a depth of 20cm. These samples were weighed (fresh weight) then placed in an oven set at 105°C and dried until they were a constant mass and were then reweighed (dry weight). Their gravimetric Soil Water Content (SWC) was calculated as the difference between the dry weight and the fresh weight (Choudhary et al., 2002);

Equation 3.3
$$SWC (\%) = (D_w / S_w) \times 100$$

SWC = Soil Water Content (%)

D_w = (Fresh weight of soil (g)) – (Dry weight of soil)

S_w = Stable soil dry weight (g)

Total Soil Porosity was calculated using the following equation:

Porosity = $(1 - (\text{bulk density} / \text{particle size}^a)) \times 100$

^a fixed particle size of 2.65cm³

WFPS was calculated by determining volumetric soil water and then dividing volumetric soil water by total porosity.

The soil bulk density was measured at the beginning of the experimental period using methodology outlined in Chapter 2 and was 0.91 g cm⁻³, no significant difference was detected between plots (t-test, $p < 0.05$).

3.2.5 Nitrate and ammonium content of the soil

Once a month during sampling 4 soil samples at a depth of 20cm were taken from the site, during the period of fertiliser application samples were taken weekly.

Nitrate and ammonium concentrations were measured colorimetrically, based on the Armstrong et al., (1976) using a Bran and Luebbe Auto Analyser (Bran and Luebbe, Norderstedt, Germany). Soil samples were homogenised by being sieved through a 2 mm mesh. For each replicate, 20g of soil was taken and added to 100ml of 2 M KCl and was mixed using an automatic shaker for 1 hour. This solution was then filtered through Whatman No.2 filter paper for nitrate analysis. For ammonium analysis the sample was then filtered again through a cellulose acetate membrane with a pore size of 45 µm.

3.2.6 Biomass Yield

Biomass yield was measured in March 2010 after a two year growth period, 4 x 4m plots were cut using clippers. The cut biomass was removed from the

plot and weighed. A sub-sample was then dried to constant weight in order to quantify dry matter content.

3.2.7 Statistics

Emission data was checked for normal distribution and log transformed if necessary. Multiple regression was carried out for flux vs soil temperature, soil moisture, soil nitrate and soil ammonium. 1-way and 2-way ANOVAs were carried out for flux and soil nitrate concentrations. All statistical analysis was carried out using DataDesk (Data Description Inc. New York, USA) and MiniTab (Minitab 15.1.30.0, Minitab Inc.).

3.3 Results

3.3.1 Rainfall and Soil Parameters

Figure 3.2 illustrates the monthly rainfall experienced at the Teagasc Research Centre weather station in Oak Park for 2008, 2009, 2010 and the 30 year mean (1967-1997). This was situated approximately a half a kilometre from the Willow field.

A plot of the 30 year mean monthly rainfall is also included. What is apparent is that the 2008 and 2009 data sets differ significantly from the 30 year mean values when late winters, mid-summer and spring months are considered.

In January of 2010 rainfall increased by 85mm (215%) from 2009 levels, in April and May of 2010 rainfall levels decreased by 61 mm (57%) and 40 mm (26%) from 2009 levels. Rainfall levels in June of 2009 were more than double the 30 year mean at 125mm and rainfall decreased significantly the following year in June by 108mm (86%). There was heavy rainfall in August and September of 2009, 161 mm in August (nearly two and a half times the 30 year mean) and 219 mm in September (nearly three times the 30 year mean).

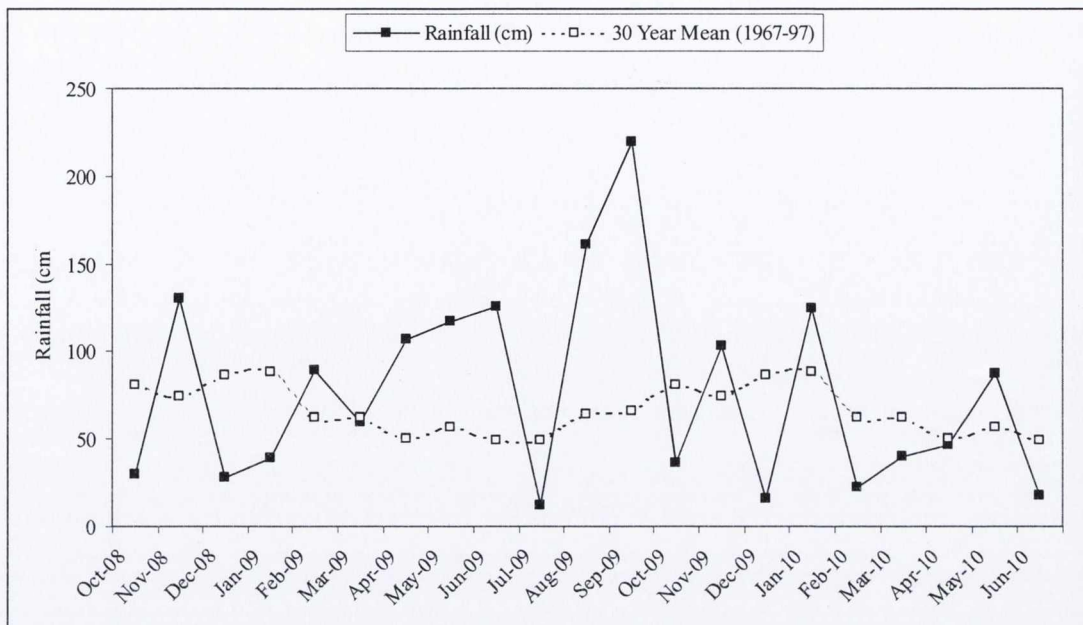


Figure 3.2 Monthly rainfalls for 2008 – 2010 at the Teagasc Oak Park Research Centre, Carlow and the 30 year mean. Symbols indicate rainfall in 2008, 2009, 2010 and the 30 year mean. Data provided by Met Eireann and John Hogan, Teagasc.

Table 3.1 Description of the soil parameters for the Willow site.

Soil Parameter	Willow
Soil Type	Loamy Sand
% Sand	86
% Silt	13
% Clay	0.1
Bulk Density	0.91 g cm ⁻³
Porosity	0.64
field capacity	0.33
Wilting point	0.14
pH	6.7

3.3.2 Soil Temperature

Figure 3.3 illustrates the monthly mean soil temperatures measured for the end of 2008, then 2009 and until July 2010. These temperatures were measured at a depth of 10cm at the Teagasc Research Centre weather station. In December of 2008 the soil temperature was 2°C warmer than the same month in 2010.

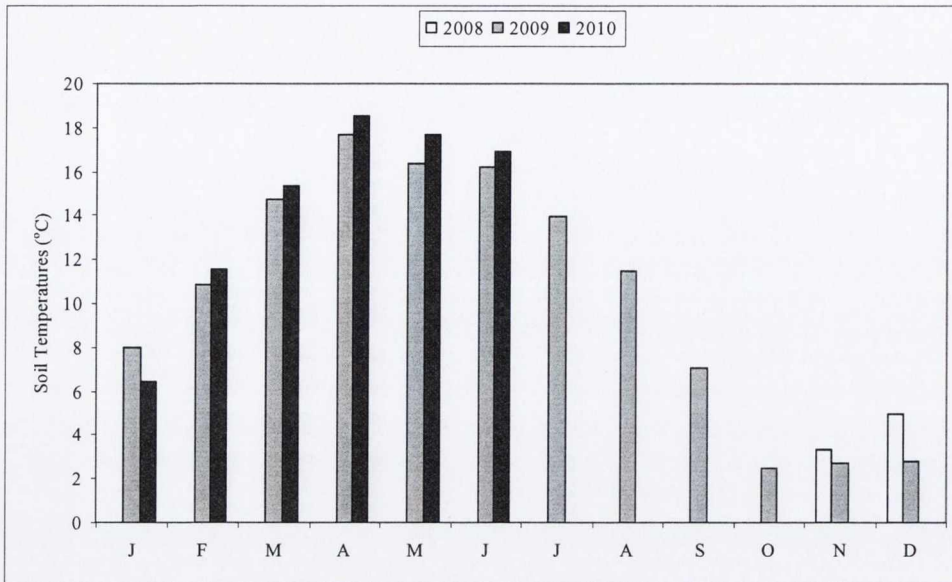


Figure 3.3 Monthly average soil temperatures for November 2008 – July 2010 at the Teagasc Oak Park Research Centre, Carlow. Data provided by Met Eireann.

3.3.3 Soil Moisture and Temperature at the Site

Figure 3.4 illustrates the weekly rainfall data measured at the weather station at Oakpark Research Centre, Carlow and the weekly soil moisture measurements taken when flux sampling was carried out on the Willow site. There is a clear relationship between the two variables.

Low rainfall in the autumn of 2008 resulted in low soil moisture content, 19.5 % which itself related to a WFPS value of 30.3% also due to low rainfall, soil moisture in late October of 2010 resulted in soil moisture levels of 21.2%, relating to a WFPS of 33%. In comparison, very high rainfall in September 2009 led to very high soil moisture content of 38.4% resulting in a WFPS value of 62.1%.

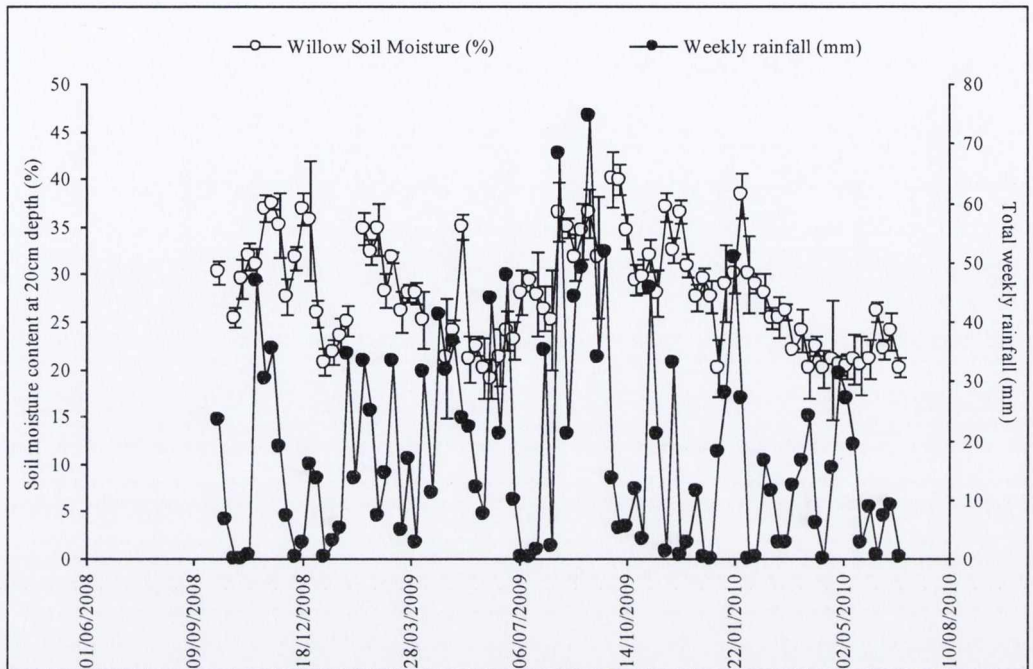


Figure 3.4 Weekly rainfall for October 2008 – July 2010 at the Teagasc Oak Park Research Centre, Carlow and the moisture content at the Willow site. Symbols indicate weekly rainfall and daily soil moisture content.

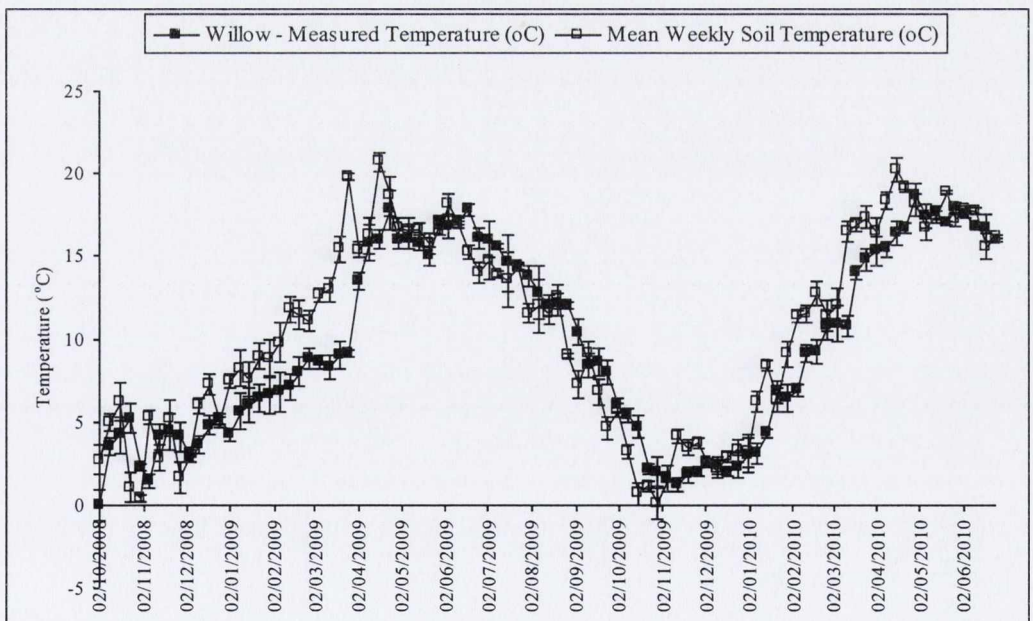


Figure 3.5 Weekly average soil temperature for 2008-2010 at the Teagasc Oak Park Research Centre, Carlow and the daily average soil temperature measured at the Willow site. Symbols indicate average weekly temperature and average daily temperature.

Figure 3.5 illustrates mean weekly soil temperature and measured daily temperature at the Willow site on the days were gas sampling took place. The weekly soil temperatures were measured at the Oak Park Research Centre weather station.

3.3.4 Soil Nitrate and Ammonium content

Figures 3.7 and 3.8 illustrate the changes in the levels of ammonium and nitrate concentration in the soils, respectively. The control, CAN fertilised plots and Biofert fertilised plots are illustrated and the arrows represent the application of fertilisers for 2009 and 2010. The control plots were not spread with any fertiliser.

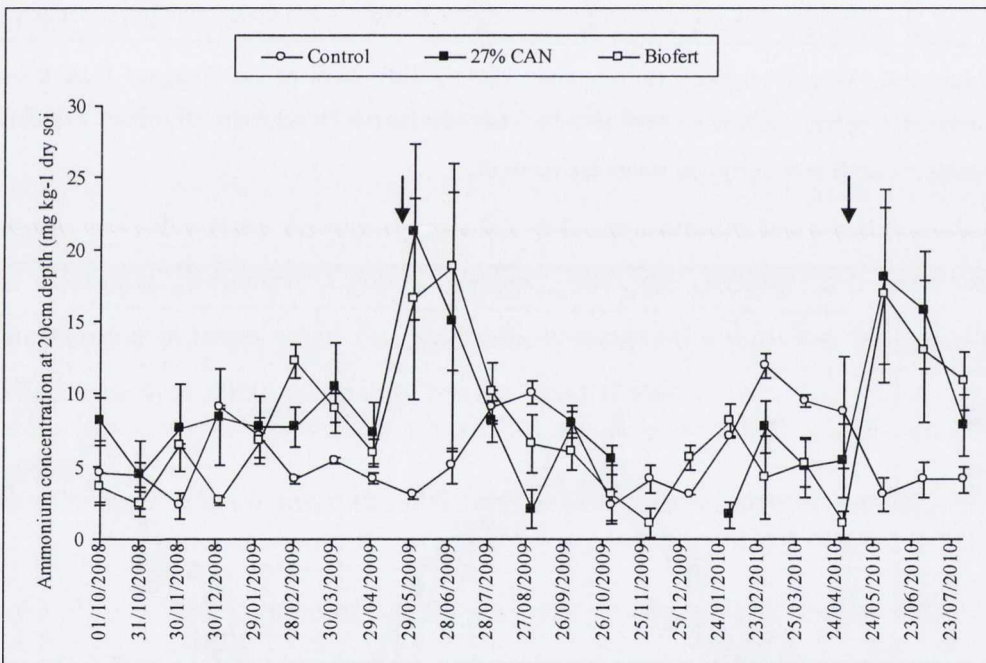


Figure 3.7 Measured soil ammonium in the fertilised and control plots for 2008-2010 throughout the experimental periods. Arrows indicate first measurement following fertiliser application (n = 5). Symbols indicate control plots, CAN fertilised plots and Biofert fertilised plots.

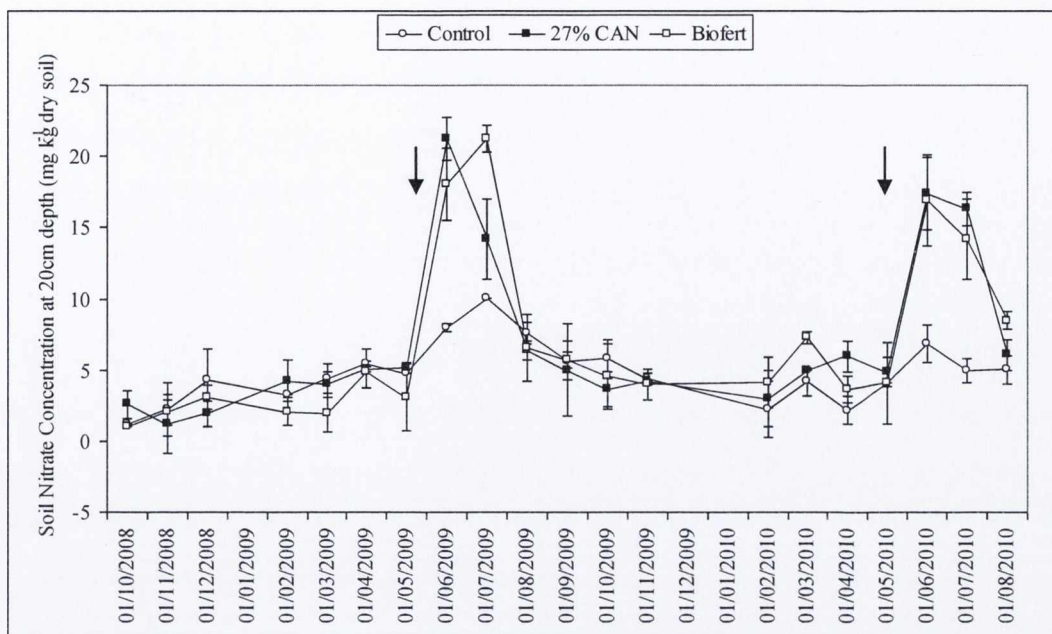


Figure 3.8 Measured soil nitrate in the fertilised and control plots for 2008-2010 throughout the experimental periods. Arrows indicate first measurement following fertiliser application (n = 5). Symbols indicate control plots, CAN fertilised plots and Biofert fertilised plots.

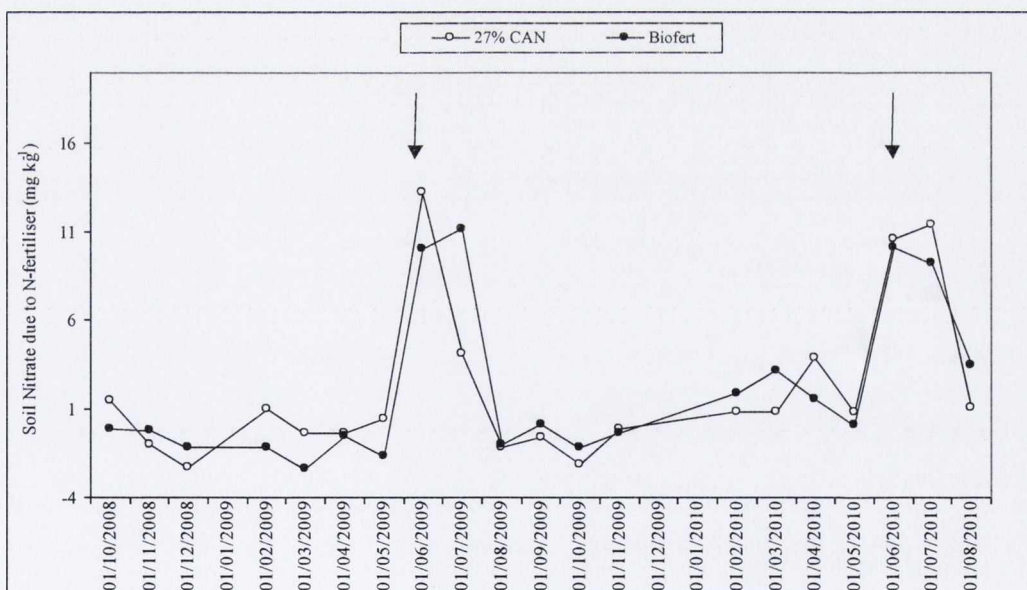


Figure 3.9 Soil nitrate concentration in the Willow site due to fertiliser application in 2009 and 2010. Arrow indicates the first measurement following fertiliser application.

Peak concentrations of soil nitrate corresponded to the application of fertilisers with significant differences between the control and fertilised plots.

This is further illustrated in Figure 3.9 where each point represents the difference between the control and the CAN fertilised plot and the control and the Biofert fertilised plot. It can be observed from the figure that the applied fertiliser was found in the soil for approximately 6 months after application.

Table 3.2 and 3.3 are results from a 2-way ANOVA of the soil N₂O and CH₄ flux data, respectively, where the treatments i.e. addition of 150 kg N of 27% CAN and 150kg N of Biofert fertilisers are a significant determinant of N₂O flux.

Table 3.2 Results of 2-way ANOVA for treatment of Willow plots and soil N₂O flux.

Source	df	Sum of Squares	Mean Square	F-ratio	Probability
Constant	1	18.75	18.75	35.54	≤0.0001
Treatment	2	10.38	5.19	9.84	≤0.0001
Error	225	118.71	0.53		
Total	227	129.09			

The application of fertiliser had no significant treatment effect on soil CH₄ flux on the Willow plots (ANOVA, p >0.05).

Table 3.3 Results of 2-way ANOVA for treatment of Willow plots and soil CH₄ flux.

Source	df	Sum of Squares	Mean Square	F-ratio	Probability
Constant	1	0.725	0.73	12.19	0.0006
Treatment	2	0.106	0.05	0.89	0.41
Error	231	13.745	0.06		
Total	233	13.851			

3.3.5 Nitrous oxide emissions

The experiments on the Willow field were carried out over approximately 20 months. Using this data it is possible to calculate an annual flux of N₂O from a Willow field. Also by recording the environmental variables i.e. soil temperature, soil moisture, rainfall and soil nitrate and ammonium we can use

this data to develop models for N₂O flux. A typical management approach was adopted to represent a typical agricultural regime.

Figure 3.10 represents the daily average N₂O emission rates for 2008 – 2010. During this period two applications of 150kg N ha⁻¹ CAN-nitrogen fertiliser and 150kg ha⁻¹ Biofert was applied on 12th June 2009, the same fertiliser treatments were applied on the 6th June 2010.

During statistical analysis of N₂O data a low number of negative flux values were observed, most of which were observed in the control plots. These were omitted from statistical analysis as data was log transformed for normal distribution and further analysis.

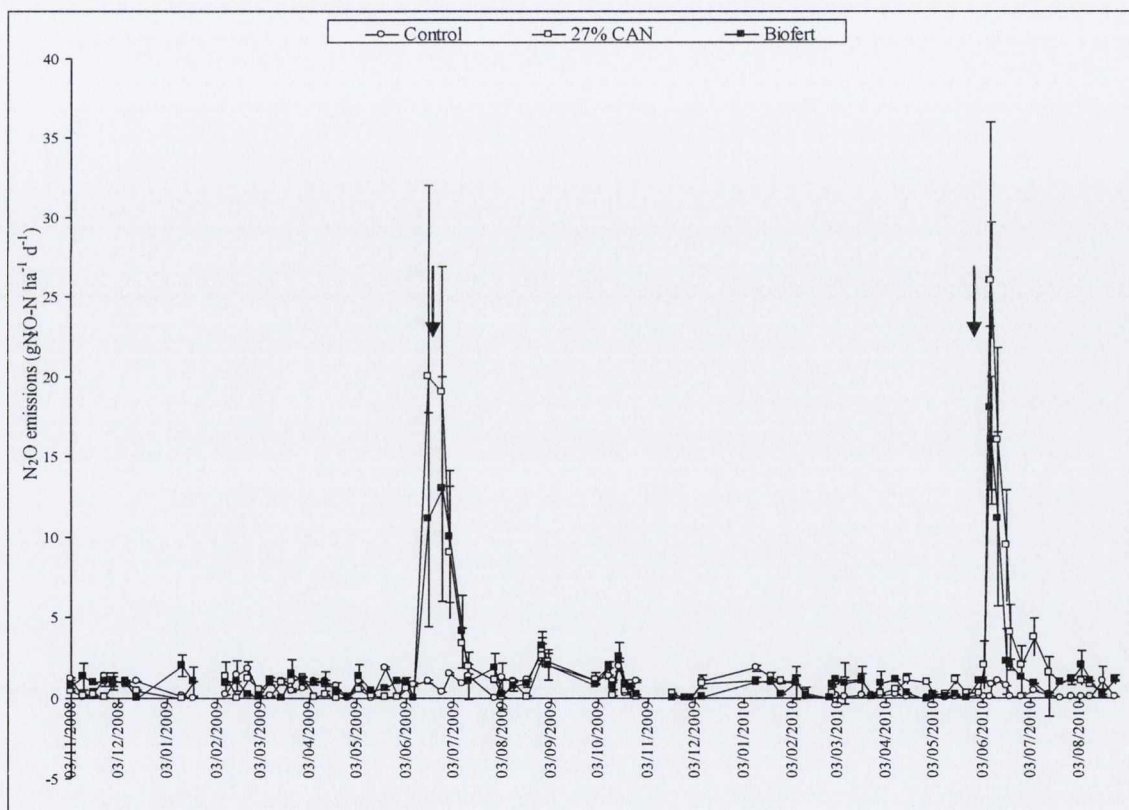


Figure 3.10 Daily N₂O emissions measured on a weekly basis from the Willow site 2008–2010. Arrows indicate fertiliser application time (150kg N ha⁻¹). Symbols indicate treatment at which N₂O flux was measured: Control plots, CAN plots and Biofert plots (each point represents a sample number, n = 5 (±s.e.)).

From 2008 - 2009, the emissions from the control plots were low, ranging from $-0.00052 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ to $2.898 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, there were some peaks around particularly wet periods (see figure 3.10). In 2009, N_2O fluxes from CAN and Biofert plots showed maximum peaks shortly after application of fertiliser. N_2O fluxes from CAN plots reached a maximum of $20.01 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, these levels returned to background low levels approximately 5 weeks after fertiliser application. N_2O fluxes from Biofert plots reached a maximum of $12.9983 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, these levels returned to low background levels after approximately 6 weeks.

In 2010, the emissions from the control plots were low ranging from $-0.015 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ to $1.8392 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ (see figure 4.12). N_2O fluxes from CAN and Biofert plots showed maximum peaks shortly after application of fertiliser. N_2O fluxes from CAN plots reached a maximum of $26.001 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, these levels returned to background low levels approximately 4 weeks after fertiliser application. N_2O fluxes from Biofert plots reached a maximum of $18.008 \text{ gN}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, these levels returned to low background levels after approximately 5 weeks.

Cumulative flux values were calculated for all treatments for the growing season (May – August) of 2009, 2010 and for the entire experimental period (Figure 3.11). For Control treatment plots, cumulative flux values of $0.11 \text{ kg N}_2\text{O-N ha}^{-1}$ for the growing season 2009, $0.02 \text{ kg N}_2\text{O-N ha}^{-1}$ for growing season 2010 and $0.38 \text{ kg N}_2\text{O-N ha}^{-1}$ for the entire experimental period. For 27 % CAN treatment plots, cumulative flux values of $0.41 \text{ kg N}_2\text{O-N ha}^{-1}$ were calculated for the growing season 2009, $0.51 \text{ kg N}_2\text{O-N ha}^{-1}$ for the growing season 2010 and $1.17 \text{ kg N}_2\text{O-N ha}^{-1}$ for the entire experimental season. For Biofert treatment plots, cumulative flux values of $0.33 \text{ kg N}_2\text{O-N ha}^{-1}$ were calculated for the growing season 2009, $0.28 \text{ kg N}_2\text{O-N ha}^{-1}$ for growing season 2010 and $0.88 \text{ kg N}_2\text{O-N ha}^{-1}$ for the entire experimental period.

Using post-hoc Bonferroni analysis we were unable to illustrate a significant difference between the two fertiliser types of 27% CAN and Biofert outside of

the peak N₂O periods immediately following fertiliser application, however they were both significantly different from control treatments (Table 3.4).

Table 3.4 Results for a GLM ANOVA for soil log N₂O flux for Willow ($r^2=0.79$).

Source	df	Sums of Squares	Mean Square	F-ratio	Probability
Date	84	614.212	7.312	19.37	0.000
Treatment (Date)	161	538.939	3.347	8.87	0.000
Rep	4	4.395	1.099	2.91	0.021
Error	855	322.777	0.378		
Total	1104				

We then used grouping information using the Bonferroni method and a 95% confidence interval to determine which dates were significantly different. Using this grouping method, 16 statistically significant groups were illustrated in the data, one group representing the background data outside of fertiliser application period (Table 3.5).

The major peaks for N₂O flux were immediately following fertiliser application in June. 27% CAN had the significantly highest peaks in June 2009 and June 2010, Biofert had its highest peaks at this time too but they were significantly less than CAN fertiliser application peaks. Approximately three weeks post fertiliser application N₂O levels return to background levels.

Willow crop management years are a 2 year cycle of growth with harvest taking place at the end of the second year (Table 3.5).

Table 3.5 Management detail for Willow crop for experimental period.

Date of 150 kg N ha ⁻¹ application	Harvest	Harvest Yield (t DM ha ⁻¹ a ⁻¹)
06/06/09	none	
06/06/10	27/3/10	13.1

When analysed using 1-way ANOVA, treatment was not found to have a significant effect on above ground biomass yield (see Table 3.5).

Emission factors (EF) for both fertiliser treatments were calculated for the growing season 2009 , growing season 2010 and for the entire measurement period. For 27% CAN, in the growing season 2009 EF was 0.22, and for growing season 2010, EF was 0.16 and for the entire measurement period, EF was 0.56. For Biofert, in the growing season 2009, EF was 0.36, for growing season 2010, EF was 0.19 and for the entire measurement period EF was 0.16 (Table 3.6).

Table 3.5 Bonferroni method of grouping of N₂O data for entire experimental period (October 2008 – August 2010) illustrating statistically significant groups and their treatments (150 kg N ha⁻¹ 27% CAN and 150 kg N ha⁻¹ Biofert and a control) for Willow plots.

Date	Treatment	Grouping
08/06/2009	CAN	I
17/06/2009	CAN	I
08/06/2010	CAN	I
09/06/2010	CAN	I
17/06/2009	BF	II
18/06/2010	BF	II
26/06/2010	CAN	III
09/06/2010	BF	IV
18/06/2010	CAN	V
01/07/2009	BF	V
08/06/2010	BF	VI
08/06/2009	BF	VII
21/06/2010	BF	VIII
09/07/2009	BF	IX
28/06/2010	CAN	X
13/07/2009	BF	X
01/07/2009	CAN	XI
19/08/2009	BF	XII
21/06/2010	CAN	XIII
28/06/2010	BF	XIV
28/08/2009	BF	XV

Table 3.6 Total amount of N applied and emission factor for the growing seasons (May – August) for 2009 and 2010 and for the entire experimental period.

Treatment	Emission Factor (%)		
	Growing Season 2009	Growing Season 2010	Entire Measurement Period
150 kg N ha ⁻¹ 27% CAN	0.22	0.36	0.59
150 kg N ha ⁻¹ Biofert	0.16	0.19	0.16

Table 3.7 represents the results of an ANOVA of the N₂O flux versus log soil nitrate, log soil ammonium, log soil moisture and soil temperature data for 2008 – 2010, log soil nitrate has a significant effect on log soil N₂O flux (ANOVA, $p < 0.05$).

Table 3.7 Analysis of variance for Log N₂O flux with soil nitrate, soil ammonium, soil moisture and soil temperature.

Source	df	Sum of Squares	Mean Square	F-ratio	Probability
Constant	1	17.323	17.323	43.61	≤ 0.0001
Log Soil Nitrate	57	49.658	0.871	2.19	0.007
Log Soil Ammonium	3	0.243	0.081	0.204	0.893
Log Soil Moisture	42	9.620	0.229	0.577	0.957
Soil Temperature	1	0.114	0.1134	0.286	0.596
Error	36	14.302	0.397		
Total	213	125.463			

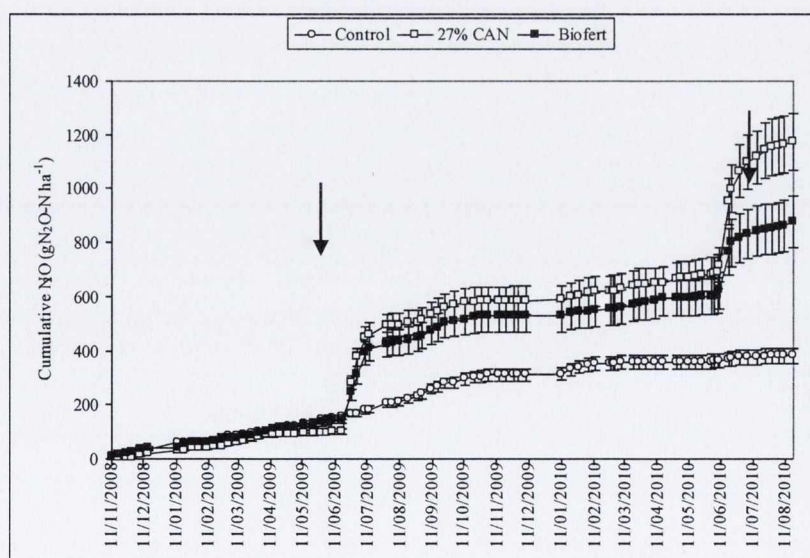


Figure 3.11 The cumulative N₂O emissions for control, 27% CAN fertiliser and Biofert fertiliser treated plots for the entire experimental period. Each point represents the mean ± s.e. of five measurements, arrows represent addition of fertiliser (150 kg N ha⁻¹ y⁻¹).

3.3.6 Methane Emissions

Figure 3.12 illustrates the daily average CH₄ emissions from 2008 – 2010 incorporating the same treatment regime, control plots, 150kg N CAN fertiliser and 150kg N Biofert fertiliser applied in June of 2009 and June 2010.

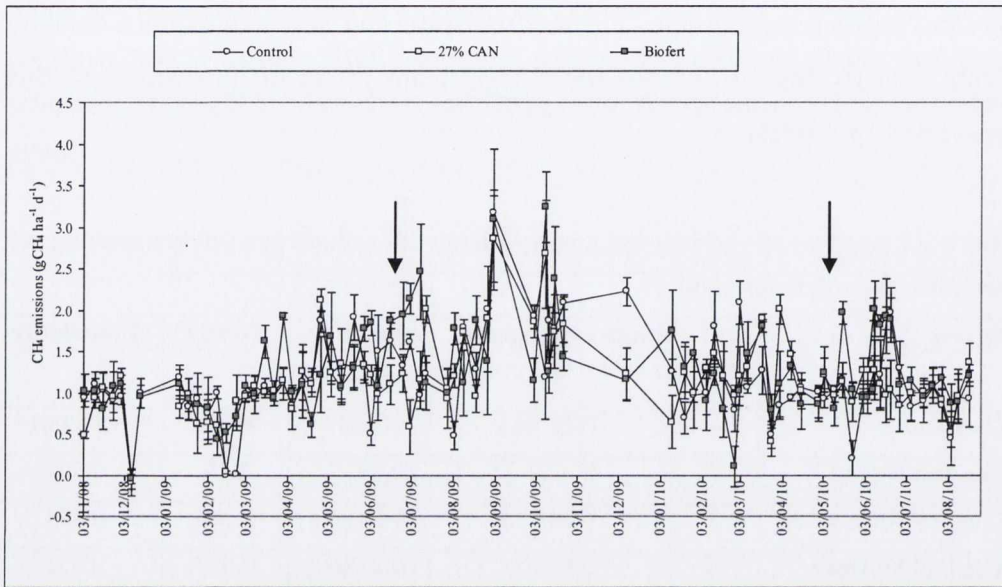


Figure 3.12 Daily CH₄ emissions measured on a weekly basis from the Willow site 2008-2010. Arrows indicate fertiliser application time (150kg N ha⁻¹). Symbols indicate treatment at which CH₄ flux was measured: Control plots, CAN plots and Biofert plots (each point represents a sample number, n = 5 (±s.e.)).

The CH₄ emissions were quite low over the experimental period. From late 2008 to 2009, the emissions from the control plots were low ranging from – 0.007 gCH₄ ha⁻¹ d⁻¹ to 3.11 gCH₄ ha⁻¹ d⁻¹, there were some peaks around particularly wet periods (see figure 3.12).

In 2009, CH₄ fluxes from CAN and Biofert plots showed peaks shortly after application of fertiliser. CH₄ fluxes from CAN plots reached a maximum of 3.001 gCH₄ ha⁻¹ d⁻¹, these levels returned to background low levels approximately 1 week after fertiliser application. CH₄ fluxes from Biofert plots reached a maximum of 3.719g CH₄ ha⁻¹ d⁻¹ after particularly heavy

rainfall in September of 2009 these levels returned to low background levels after approximately 2 weeks.

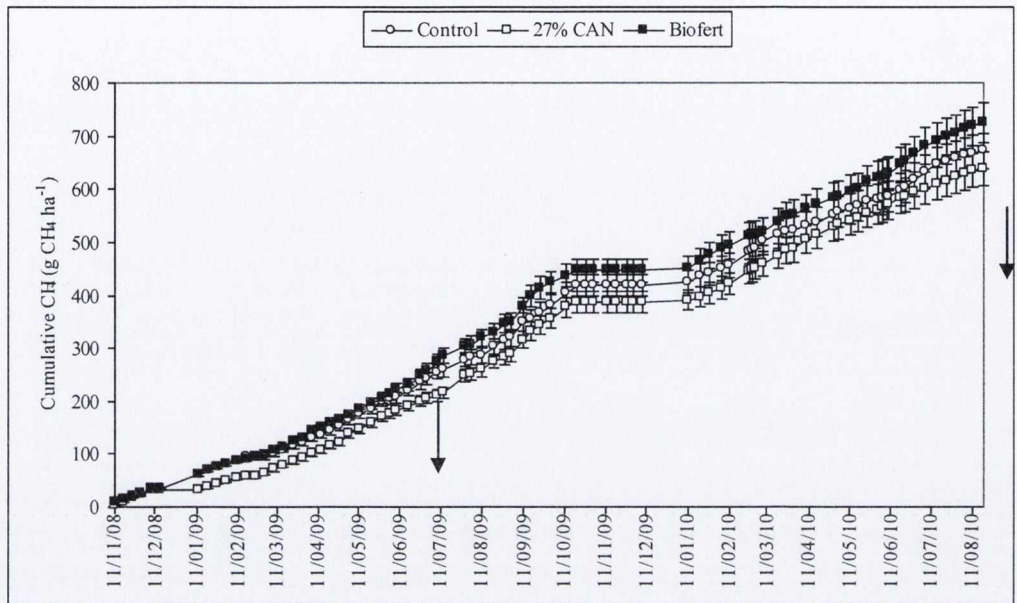


Figure 3.13 Cumulative CH₄ emissions measured from the Willow site 2008-2010. Arrows indicate fertiliser application time (150kg N ha⁻¹). Symbols indicate treatment at which CH₄ flux was measured: Control plots, CAN plots and Biofert plots (each point represents a sample number, n = 5 ±s.e.).

In 2010, the emissions from the control plots were low ranging from 0.091 gCH₄ ha⁻¹ d⁻¹ to 2.05 gCH₄ ha⁻¹ d⁻¹ (see figure 3.12). CH₄ fluxes from CAN and Biofert plots showed maximum peaks shortly after application of fertiliser. CH₄ fluxes from CAN plots reached a maximum of 2.002g CH₄ ha⁻¹ d⁻¹, these levels returned to background low levels approximately 1 weeks after fertiliser application. CH₄ fluxes from Biofert plots reached a maximum of 2.140 gCH₄ ha⁻¹ d⁻¹, these levels returned to low background levels after approximately 2 weeks. Some negative fluxes were observed from control plots and treatment plots on occasion. There was no significant effect of fertiliser treatment on CH₄ emissions over the experimental period.

3.3.7 Multiple Regression Analysis

Table 3.8 illustrates the N₂O flux values with the factors, soil ammonium, soil nitrate, soil temperature and soil moisture content. A multiple regression of

this data was carried out for Log N₂O flux and results are illustrated. Soil nitrate is a highly significant factor ($p \leq 0.001$) as is soil ammonium ($p \leq 0.05$) and soil temperature ($p \leq 0.05$).

Table 3.8 Regression analysis results for Log N₂O versus log soil ammonium, log soil nitrate, soil temperature and soil moisture content (log soil N₂O flux = - 3.40 + 2.85 log soil nitrate concentration - 0.0194 soil ammonium concentration + 0.0860 soil temperature + 0.0229 soil moisture; $r^2 = 0.55$).

Predictor	Coefficient	S.E. of Coefficient	T-ratio	Probability
Constant	-3.397	2.719	-1.25	0.243
Soil Ammonium	-0.01942	0.04072	-0.48	0.645
Log Soil Nitrate	2.8478	0.9529	2.99	0.015
Soil Temperature	0.08599	0.08230	1.04	0.323
Log Soil Moisture	0.02294	0.07686	0.30	0.772
Source	df	Sum of Squares	Mean of Squares	F-ratio
Regression	4	5.3635	1.3409	2.76
Residual Error	9	4.3765	0.4863	
Total	13	9.7399		

A regression analysis was carried out using soil nitrate as a predictor of soil N₂O flux (Table 3.9). The regression equation was log soil N₂O flux = - 0.4205 + 0.1171 Soil Nitrate, $r^2 = 0.65$).

Table 3.9 Regression analysis results for log N₂O versus soil nitrate (log soil N₂O flux = - 0.4205 + 0.1171 Soil Nitrate, $r^2 = 0.65$).

Source	df	Sum of Squares	Mean of Squares	F-ratio	Probability
Regression	1	19.671	19.671	120.70	0.000
Error	66	10.7561	0.1630		
Total	67	30.4271			

A multiple regression of CH₄ data was carried out and results are very weak i.e. variation of the data is related to a value of $r^2 = 7.4\%$. This is due to the nature of the data i.e. very low emissions and high variation.

3.3.8 Relationship of N₂O flux with soil nitrate

Figure 3.13 illustrates a positive linear relationship between N₂O flux and soil nitrate for both fertiliser types, as soil nitrate concentration increases, soil N₂O flux increases. This accounts for 39% and 65% of the variation of the data for 27% CAN and Biofert fertilisers, respectively.

The relationship between soil N₂O flux and soil nitrate concentration due to fertiliser is outlined below in figure 3.14 where it explains 49% of the variation in the data. The level of fertiliser applied positively relates to soil nitrate concentration which in turn positively relates to soil N₂O flux.

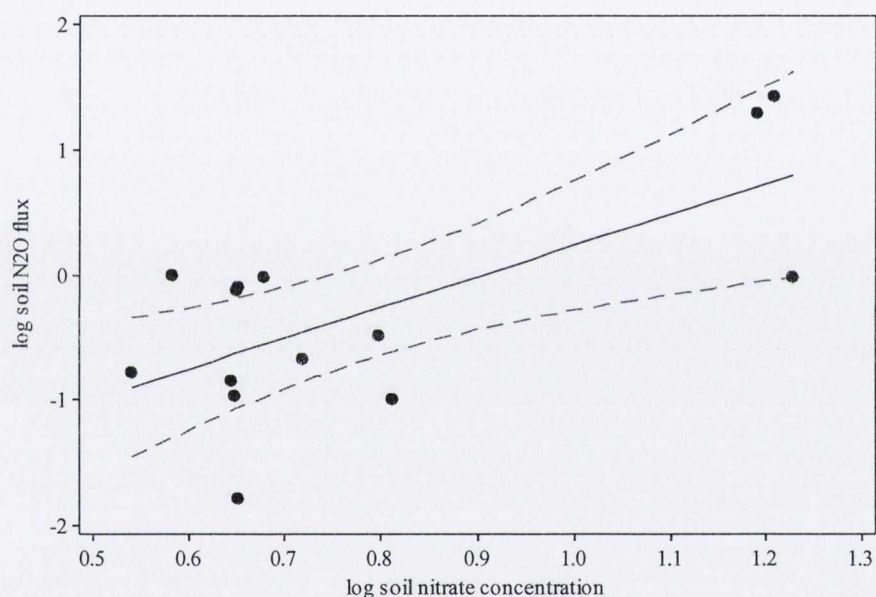


Figure 3.14 Log soil N₂O flux correlated to log soil nitrate concentration, dashed lines representing the 95% confidence bounds (log N₂O flux = -2.238 + 2.474 log soil nitrate concentration: $r^2 = 0.47$).

3.4 Discussion

A low number of negative N₂O flux values were observed, most of which were from control plots. This is considered to be a result of the soil acting as an N₂O sink, particularly when the soil was wet e.g. after heavy rainfall (Flechar et al., 2005). The activity of denitrifying bacteria is controlled partially by O₂ concentration (mainly through soil water content) amongst

other factors e.g. C availability, N availability, pH and temperature. The level of N₂O emissions from soil that is contributed through denitrification is considered to be most significant under sub-oxic conditions where water-filled pore space (WFPS) is greater than 70% and available C and soil nitrate are non-limited (Davidson, 1991b, Bateman and Baggs, 2005). The production and activity of denitrification reductases are suppressed in high O₂ concentration environments (Otte et al., 1996). This is reflected in the increase in the N₂O/N₂ ratio with increasing O₂ concentration (Weier et al., 1993). After being exposed to heavy rainfall i.e. when aerobic soils become anaerobic, the nitrate and nitrite reductases activate quicker than the N₂O reductase so the denitrifier N₂O/N₂ ratio is higher in the immediate days after rainfall (Knowles, 1982). However, when O₂ availability increases after an anaerobic phase all denitrification enzymes except N₂O reductase remain active (Morley et al., 2008). Indeed, negative fluxes have been reported in several systems and controlled environment experiments (Chapuis-Lardy et al., 2007). These negative fluxes can be significant in magnitude (Flecharde et al., 2005) and as such should not be ignored when calculating mean fluxes or seasonal or annual emissions. Upon examining our fluxes, which were not significant in proportion, they may be attributed to experimental, sampling or analysis artefacts.

From this experimental work, support for the concept that cumulative emissions of N₂O from soils are directly related to the addition of fertiliser, particularly in terms of post-fertiliser application concentration of soil nitrate. A plot of N₂O flux derived from fertiliser (treatment – control) against the concentration of soil nitrate from fertiliser (treatment – control) for fertiliser illustrated a positive linear relationship (see figure 3.15). The linear relationship equation was: $\log \text{N}_2\text{O flux} = -0.4205 + 0.1171 \log \text{soil nitrate concentration}$ due to fertiliser application with an r^2 value of 0.65. These figures would suggest that such a strong correlation with soil nitrate concentration that the majority of the N₂O flux is produced through denitrification with a smaller proportion being produced through nitrification. Peaks in N₂O flux were associated with times of fertiliser application.

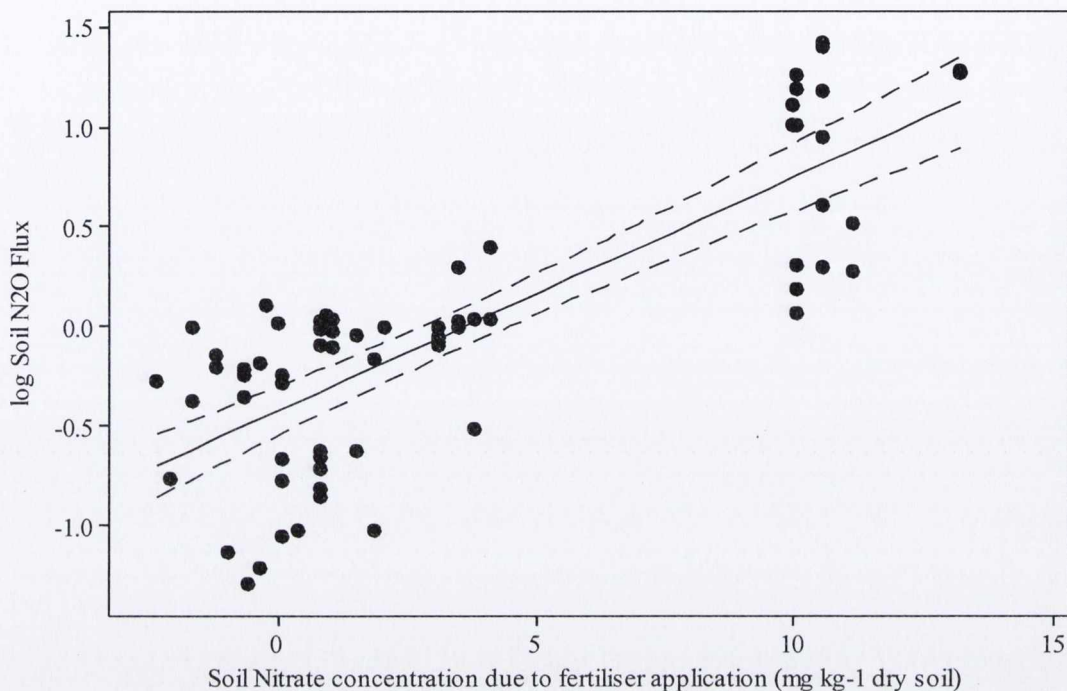


Figure 3.15 Log soil N₂O flux correlated to log soil nitrate concentration due to fertiliser application, dashed lines representing the 95% confidence bounds (log N₂O flux = -0.4205 + 0.1171 log soil nitrate concentration due to fertiliser application: r² = 0.65).

Table 3.10 illustrates the cumulative values for N₂O, CH₄ and their CO₂ equivalents for control plots and the two fertiliser application treatments.

Table 3.10 Cumulative N₂O, CH₄ and CO₂-equivalent values for the entire experimental period for Willow.

Treatment	N ₂ O (kg N ₂ O-N ha ⁻¹)	CO ₂ -equiv. (kg)	CH ₄ (kg CH ₄ ha ⁻¹)	CO ₂ -equiv. (kg)	Total CO ₂ - equiv.(kg)
Control (0 kg N ha ⁻¹)	0.38	118.14	0.67	14.11	132.24
150 kg N ha ⁻¹ 27% CAN	1.17	363.26	0.64	13.41	376.68
150 kg N ha ⁻¹ Biofert	0.88	271.57	0.72	15.22	286.79

From this data N₂O emissions are significantly greater than CH₄ emissions from Willow for the entire experimental period. The control plots have the

lowest CO₂-equivalent values at 132.24 CO₂-equivalents (kg), CAN values are the highest at 376.68 CO₂ equivalents (kg) and Biofert is below CAN at 286.79 CO₂-equivalents (kg).

From figure 2.16(i) this proportion of greenhouse gases is further illustrated, N₂O has higher emissions than CH₄ from Willow where N₂O flux emissions are highest in the two treatments where fertiliser is applied. For the control plots the CH₄ emissions were higher than N₂O emissions. In terms of total CO₂-equivalents in figure 3.16 (ii) CAN fertiliser treatment has the highest CO₂-equivalent value, followed by Biofert and the control plots have the lowest value.

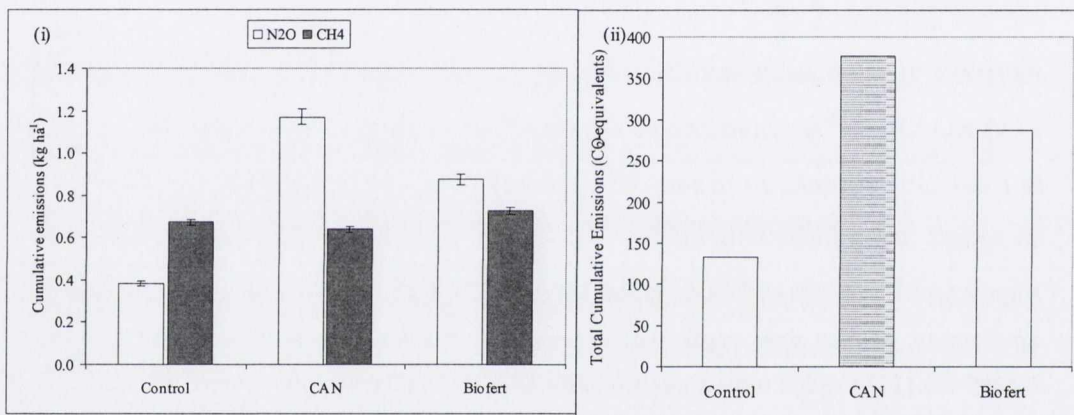


Figure 3.16 Total cumulative emissions during for the entire experimental period for Willow (i) represents the cumulative emissions for N₂O (kg N₂O-N ha⁻¹) and CH₄ (kg CH₄ ha⁻¹) for the three different treatments (n=5, ±s.e.), (ii) represents the total emissions in terms of CO₂-equivalents for the three different treatments.

It is surprising that soil moisture was not a significant factor in the regression analysis, however, a Pearson correlation of the log of soil moisture and soil temperature value of -0.692 illustrates how they are strongly negatively correlated. This would suggest that soil moisture would affect the N₂O flux through its interaction with soil nitrate by affecting the availability of this ion for the process of denitrification. Moisture stimulates denitrification by temporarily reducing the oxygen diffusion into the soil. As such, in order for peak N₂O emissions to occur, soil moisture and soil nitrogen concentration are required.

During fertiliser application periods i.e. May – August of 2009 and 2010 the control plots had a cumulative flux value of $0.277 \text{ kg N}_2\text{O-N ha}^{-1}$ compared to $0.565 \text{ kg N}_2\text{O-N ha}^{-1}$ for 27% CAN and $0.488 \text{ kg N}_2\text{O-N ha}^{-1}$ for Biofert. So, 73% and 67% of the total N_2O flux over the entire 12 month period was associated with the fertilisation period of May – August.

The application of 27% CAN and Biofert fertiliser increased soil nitrate and ammonium concentrations (see figures 3.7 and 3.8), this would in turn effect soil nitrification and denitrification, thus increasing soil N_2O flux.

In order to relate the level of N_2O emissions to the application of fertiliser we calculated an emission factor, whereby the percentage of applied N released via N_2O to the atmosphere can be calculated. We used annual data for the full 12 months of 2009 to determine and calculate the emission factor for the two fertilisers, 27% CAN and Biofert. For both fertilisers, there is a control plot available to use in the calculation for emission factor. Using the 2009 time period and the fertilizer treatment of 150 kg ha^{-1} CAN-nitrogen and 150 kg ha^{-1} Biofert, an emission factor value of 0.22 and 0.16 were calculated, respectively. Currently, an IPCC (IPCC, 1996) default value of 1% is used as a national emission factor, ours is significantly less. There has been criticism of the IPCC default values in over- or under-estimating the N_2O flux from N applied to soil (Laegreid and Aastveit, 2002, Schmid et al., 2001). As such, it is important that a greater database of national greenhouse gas inventories is available thus improving the accuracy of national greenhouse gas inventories.

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Chapter 4 Validation with DNDC-model of field measurements of N₂O emissions.

4.1 Introduction

N₂O production in the terrestrial cycle is mainly biological via nitrate dissimilation (NO₃⁻ reduction to NH₄⁺ and denitrification) and nitrification (ammonia oxidation and nitrifier denitrification) (Davidson, 1991a, Bremner, 1995, Baggs, 2008). Significant factors affecting the emission of N₂O from soil are soil pH, soil water content (water-filled pore space, WFPS), soil temperature, soil concentration of NO₃⁻ and NH₄⁺, microbial activity. Also critical in N₂O emissions are the complicated interactions between soil properties, climatic factors and agricultural management which result in high spatial and temporal variations (Choudhary et al., 2002).

Predictive models are being used to investigate and manage the potential impacts that climate change and agricultural management can have in agriculture under different climate scenarios from different management practices and in different ecosystems. These models simulate denitrification and nitrification using different methodology.

The DayCent (Del Grosso et al., 2000, Parton et al., 2001) model is a widely used ecosystem biogeochemistry model which uses a sophisticated bottom-up approach, it accounts for N inputs, water, temperature, O₂ and labile C availability and plant N demand which would directly influence soil N₂O emissions. The modelled output from DAYCENT is based on soil surface flux measurements.

Expert-N is a development system for the turnover of nitrogen to simulate the N cycle in arable agriculture (Engel and Priesack, 1993). The system uses modular model components for soil heat, crop growth, N transport and soil water flow. These components are made up of standardised model units which represent a single process each for the component as N mineralisation for N transport or root water uptake for crop growth.

The NASA-Ames has developed a NASA-CASA (Carnegie-Ames-Stanford Approach; (Potter and Klooster, 1997)) model version that simulates biogenic trace gas fluxes (e.g. CO₂, N₂O, NO) on a regional scale by merging input datasets of satellite 'greenness' index, radiation, vegetation, climate and soils with simple algorithms for moisture flow and nutrient transformation processes in terrestrial ecosystems (Potter and Klooster, 1997). The soil submodel in the model simulates carbon and nitrogen cycling using a set of compartmental difference equations based on a simplified version of the CENTURY model (Parton et al., 1987, Parton et al., 1992)

Exclusion of nitrifier denitrification or nitrate ammonification as sources of N₂O is a criticism of these models but this would be very difficult due mainly to lack of data relating to the controls of these processes for model parameterisation and then model validation. Also, scale is a major issue with modelling as most experiments conducted are used to improve understanding of underlying processes and are conducted at microscale / plot scale. However, most models depend on aggregated response at field or landscape level. When upscaling a linear relationship is usually applied which then assumes all controlling parameters on N₂O emissions are the same across all scales and the detailed from microscale experiments is then lost (Baggs and Philpott, 2010).

The main aim of this work is to estimate the reliability and validity of the DeNitrification-DeComposition (DNDC) model to accurately assess N₂O emissions from *Miscanthus* from collected field data. We can do this by directly comparing it to actual field measurements taken of N₂O emissions. However, this can be difficult due to large inherent uncertainty associated with N₂O emissions measured from the field (Bouwman, 1996 ; DeVries et al., 2005). Sensitivity analysis of DNDC can be used to quantify the uncertainty arising from model predictions and their input parameters (Giltrap et al., 2010).

DNDC was used for our study as the required input data was readily available, the simulation time is short and it has already been extensively used in modelling ecosystem biogeochemistry to estimate GHG emissions (Smith et al., 2010). The DNDC model has been used on agricultural soils to quantify N₂O (Li, 2000) using a rainfall driven process based model (Li et al., 1992). Good agreement has been shown with DNDC outputs and measured flux values for a similar soil type over a growing season for spring Barley in Carlow, Ireland (Abdalla et al., 2009a, Abdalla et al., 2010b). The DNDC model also simulates the interactions between different soil processes and how changes to a particular parameter will have an affect on other emissions, leaching etc. As such it can be used in policy and planning of mitigation strategies for N₂O in the future and assessing management impacts in the future.

The hypothesis is that DNDC would be a predictive N₂O model for soil under a *Miscanthus* crop using conventional management practice. We aimed to validate DNDC for annual data set of emissions from a *Miscanthus* plot.

4.2 Materials and Methods

DNDC model

The DNDC model itself is a process based computer simulation model of carbon and nitrogen biogeochemistry in agricultural systems. For our data we used DNDC Model Version 9.1. It consists of two parts, the first part predicts soil temperature, soil moisture, soil pH, soil redox potential (Eh) and substrate concentration profiles related to specific drivers e.g. vegetation, soil, climate and anthropogenic activity. The second part predicts NO, N₂O, N₂, CH₄ and NH₃ fluxes by using the soil environmental factors that have been modelled e.g. nitrification, denitrification and fermentation sub-models. Each specific geochemical or biochemical reaction has been parameterised by using basic physics, biology and chemistry laws along with empirical equations based on laboratory work.

As a whole the model works from 4 major ecological components: climate, soil properties (physical), vegetation and anthropogenic activities.

4.2.1 DNDC model validations

Data sets were collected from field measurements of N₂O from the *Miscanthus* plots. Environmental data that was collected from measurement days and also from the Teagasc weather station in Carlow i.e. daily mean maximum and minimum temperature and daily rainfall. This data was used to test the validity of the DNDC model.

The process for DNDC validation was:

- (i) Comparison of field N₂O emissions and DNDC modelled N₂O flux
- (ii) Comparison of field N₂O emission factor and DNDC model emission factor
- (iii) Comparison of field measured cumulative N₂O emissions and DNDC model cumulative N₂O emissions.

An equation was used to calculate the relative deviation (y) of DNDC modelled emissions from measured N₂O field emissions:

Equation 4.1
$$y = \frac{(x_s - x_o)}{x_o} \times 100$$

Where, x_s = DNDC simulated emission, x_o = field measured emission. Simulated daily fluxes from DNDC were used to calculate DNDC annual and seasonal fluxes (Cai et al., 2003).

The root mean square error (RMSE) is also used to calculate the total difference between daily modelled and measured N₂O flux. The RSME was assessed by comparing the value obtained assuming a deviation corresponding

to the 95% confident interval of the measured (RMSE_{95%}). Where \bar{O} is the mean of the observed data, O_i are the observed values, P_i are the predicted values, $t_{(n-2)95\%}$ is Student's t distribution with $n - 2$ degrees of freedom and a two-tailed P-value of 0.05, and n is the number of pair values:

$$\text{RMSE} = \frac{100}{\bar{O}} \sqrt{\sum_{i=1}^n (P_i - O_i)^2/n}$$

Equation 4.2

$$\text{RMSE}_{95\%} = \frac{100}{\bar{O}} \sqrt{\sum_{i=1}^n (t_{(n-2)95\%} \times S_e(i))^2/n}$$

Equation 4.3

An RMSE value less than the RMSE_{95%} indicates that the simulated values fall within the 95% confidence interval of the measurements (Smith, 1997).

Table 4.1 The DNDC model input data for the *Miscanthus* crop.

Site and Climate Data	
Latitude (degree)	52
Atmospheric background NH ₃ concentration (ug N m ⁻³)	0.06
Atmospheric background CO ₂ concentration (ppm)	385
Increase rate of atmospheric CO ₂ concentration (ppm yr ⁻¹)	2
N concentration in rainfall (mg N/l)	1
Soil Properties (0 - 20cm depth)	
Soil Texture	Sandy Loam
Bulk Density (g cm ⁻³)	0.95
Soil pH	6.4
Clay fraction (0-1)	0.09
Field Capacity (WFPS, 0-1)	0.52
Wilting point (WFPS, 0-1)	0.15
Initial soil organic carbon (SOC) content at surface soil (0-5cm) (kg C kg ⁻¹)	0.054
Farming Management	
Slope (%)	0
WFPS at field capacity	0.32*
WFPS at wilt point	0.15*
Depth of water-retention layer (cm)	100*
* Default values	

4.2.2 N₂O emissions from *Miscanthus*

Field measurements for *Miscanthus* were carried out on a weekly basis as outlined in chapter 3. The management process and the treatments carried out on the plots were also outlined.

4.2.3 Calculation of emission factor

The emission factors for N₂O emissions were calculated by subtracting the DNDC N₂O model emissions of unfertilised soils from the DNDC N₂O model emissions of fertilised soils, the result was then divided by the fertiliser N input.

4.2.4 Model sensitivity

In order to demonstrate the DNDC modelling results were consistent with the assumptions and structure of the model we carried out sensitivity analysis as recommended (Li et al., 1992). We changed one parameter and kept the rest of the parameters fixed during model cycles. This then illustrated the response of the sub models and the model as a whole to variations of the relevant parameters.

4.3 Results

4.3.1 Simulation of N₂O emissions from the *Miscanthus* plots

Figures 4.1, 4.2 and 4.3 illustrate the temporal pattern of the model simulated and field measured N₂O fluxes obtained for the control 0 kg N ha⁻¹, 150 kg N ha⁻¹ 27% CAN and 150 kg N ha⁻¹ Biofert fertiliser treatments during October 2008 – August 2010.

In general, a consistent pattern of model output or the two fertiliser treatments was observed in that very small, if any peaks of N₂O emissions were produced during the late summer- winter period. However, two specific

groupings of N₂O peaks were observed for each of the growing seasons. An initial period associated with the time of fertiliser application and a second period of considerably higher emission peaks occurring approximately one month before harvest of the crop. The extent of these latter peaks carried between the two fertiliser types and their growing seasons were not observed from measured data.

Table 4.1 Comparison of daily modelled and measured N₂O data using root mean square error (RMSE) (n = 69).

Treatment	RMSE	RMSE _{95%}
0 kg N ha ⁻¹	759	1485
150 kg N ha ⁻¹ 27% CAN	254	314
150 kg N ha ⁻¹ Biofert	297	427

For the 27% CAN 150 kg N ha⁻¹ fertiliser treatment prominent peaks of approximately 50 g N₂O-N ha⁻¹ d⁻¹ in 2009 and approximately 25 g N₂O-N ha⁻¹ d⁻¹ in 2010 occurred during February of each year. In contrast, two similar peaks of approximately 40 g N₂O-N ha⁻¹ d⁻¹ occurred in both years following application of fertiliser.

For the Biofert fertiliser treatment, prominent peaks of approximately 30 g N₂O-N ha⁻¹ d⁻¹ occurred in February/March of 2009 and 2010. Two significant peaks also occurred following fertilisation application of approximately 42 g N₂O-N ha⁻¹ d⁻¹ in 2009 and 2010.

For both treatments these February peaks were not observed in the measured data. In figure 4.1 these February peaks are also illustrated with values of approximately 11 g N₂O-N ha⁻¹ d⁻¹ and approximately 16 g N₂O-N ha⁻¹ d⁻¹. These peak patterns are not reflected in the measured data, however, from March 2009-December 2010 and April 2010-August 2010 there are similar temporal N₂O emission patterns between the model and observed data.

The RMSE and RMSE_{95%} were carried out to statistically compare the total difference in N₂O data between daily modelled and measured values (Table

4.1). It is illustrated in this figure that the modelled data was in good agreement with measured data from the different treatments as all the values fell within the 95% confidence interval values.

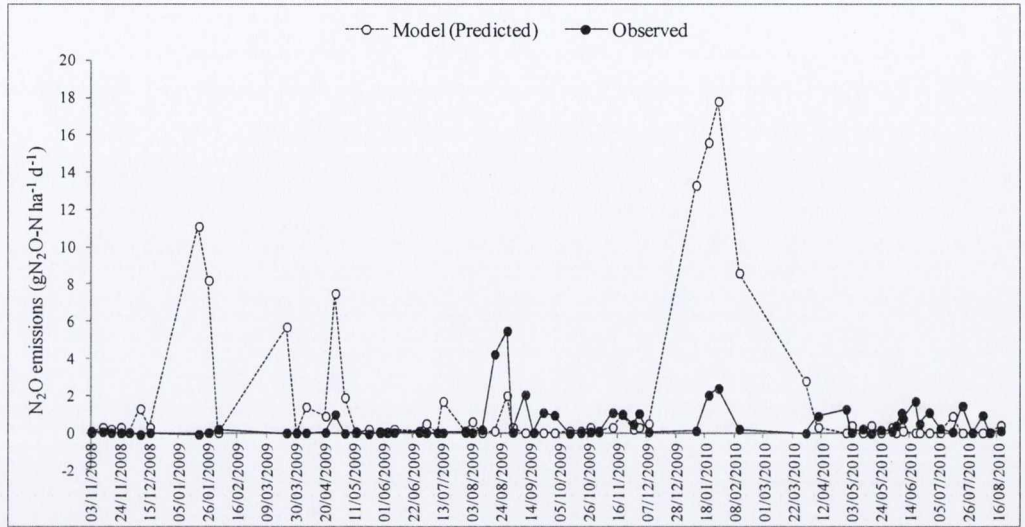


Figure 4.1 Comparison of model-simulated (dashed line, open circle) and field measured (solid line, solid circle) N_2O flux for the control experimental plots where no fertiliser was applied.

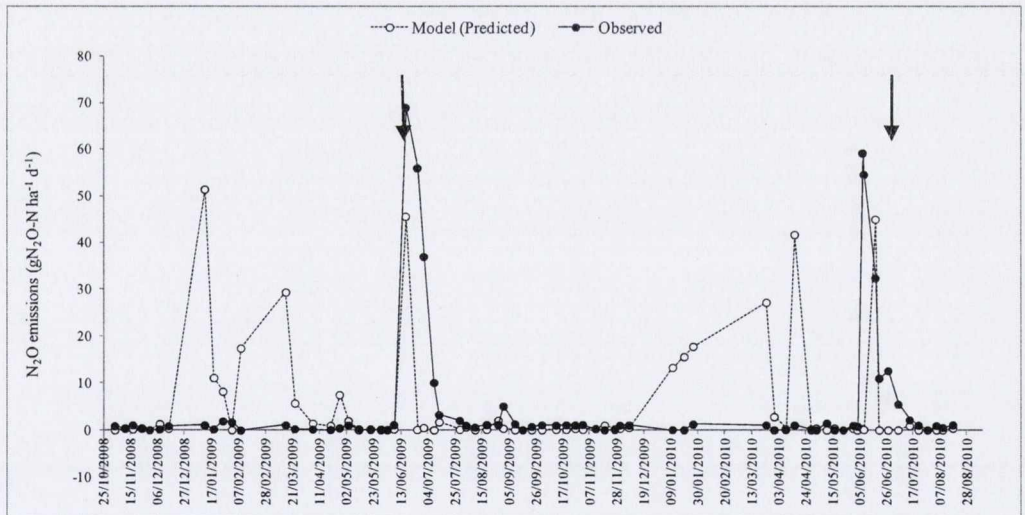


Figure 4.2 Comparison of model-simulated (dashed line, open circle) and field measured (solid line, solid circle) N_2O flux for the 150 kg N ha^{-1} 27% CAN fertiliser application. Solid arrows show time of fertiliser application.

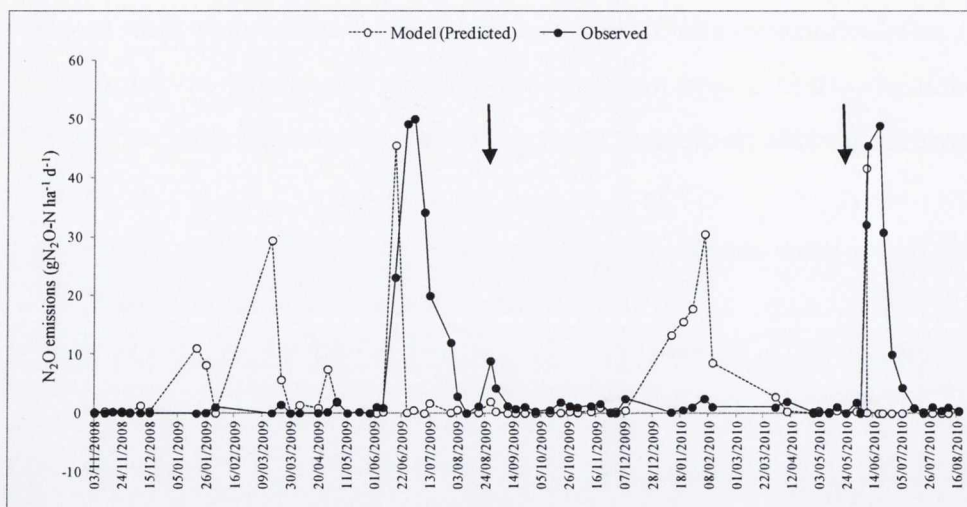


Figure 4.3 Comparison of model-simulated (dashed line, open circle) and field measured (solid line, solid circle) N₂O flux for the 150 kg N ha⁻¹ Biofert fertiliser application. Solid arrows show time of fertiliser application.

4.3.2 Cumulative N₂O fluxes

Figures 4.4, 4.5 and 4.6 illustrate the pattern of cumulative flux for both measured and model output values from control 0kg N ha⁻¹, 150 kg N ha⁻¹ 27% CAN and 150 kg N ha⁻¹ Biofert fertiliser treatment plots. Here cumulative values are calculated for the entire experimental period from October 2008 – August 2010. Also evident during this period is the marked overestimation for the modelled cumulative flux compared to measured values in each treatment. The sharp increase in cumulative fluxes is associated with fertiliser application during the spring of 2009 and 2010.

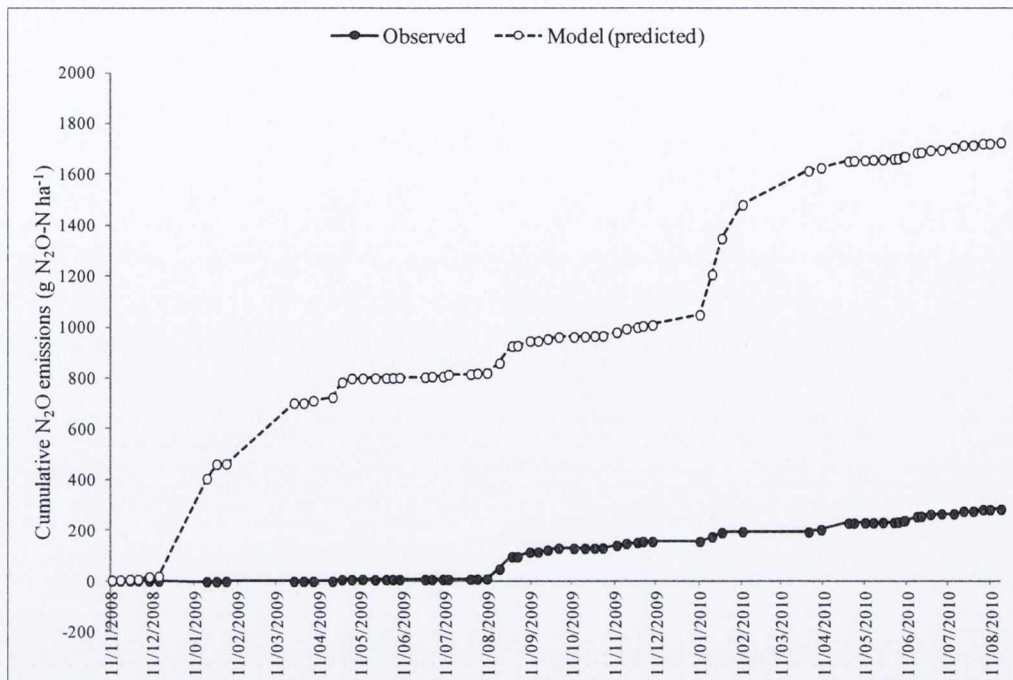


Figure 4.4 Comparison of cumulative model-simulated (dashed line, open circle) and field measured (solid line, closed circle) N₂O emissions from the control experimental plots during October 2008 – August 2010.

Figures 4.7, 4.8 and 4.9 illustrate the patterns of cumulative flux for measured and model output values from control 0 kg N ha⁻¹, 150 kg N ha⁻¹ 27% CAN and 150 kg N ha⁻¹ Biofert fertiliser application treatment plots. Their cumulative values are calculated for the management year February 2009 – March 2010. They exhibit similar patterns of cumulative flux where both fertiliser application treatments result in sharp increases in cumulative fluxes. There is also a marked overestimation of cumulative flux from the model data compared to the measure data in each treatment.

Table 4.2 lists the relevant deviation of the modelled cumulative values with respect to the observed values. From these values, DNDC best describes the management year scenario. Deviation scores varied from -2.2 to 391%. In the entire experimental period deviation scores varied from -13 – 411%. In each case the highest deviation score was a result of control 0kg N ha⁻¹ fertiliser treatment.

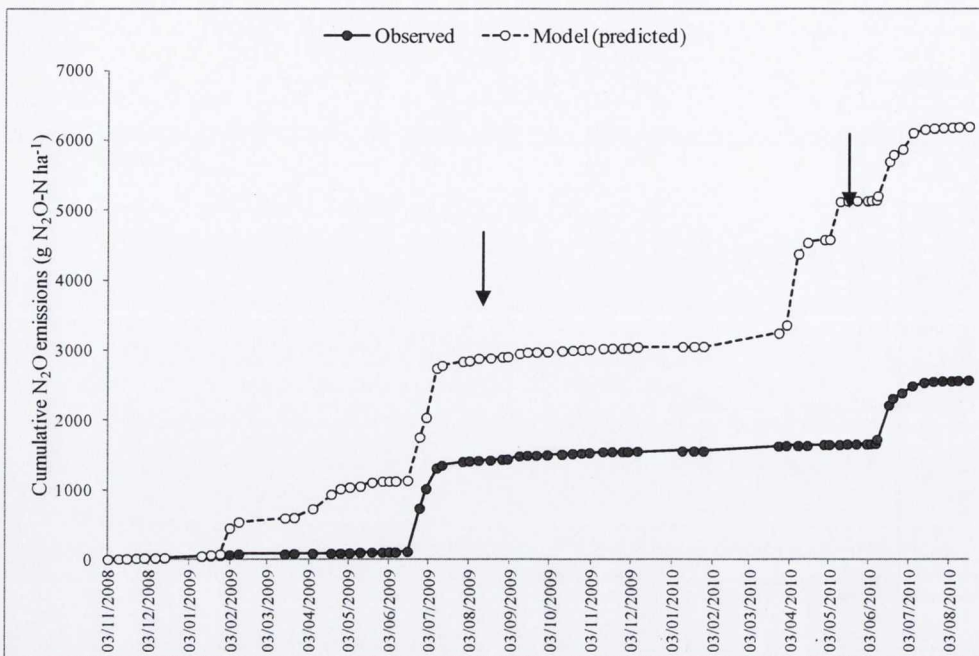


Figure 4.5 Comparison of cumulative model-simulated (dashed line, open circle) and field measured (solid line, closed circle) N_2O emissions from the 150 kg N ha^{-1} 27% CAN fertiliser application applied during October 2008 – August 2010.

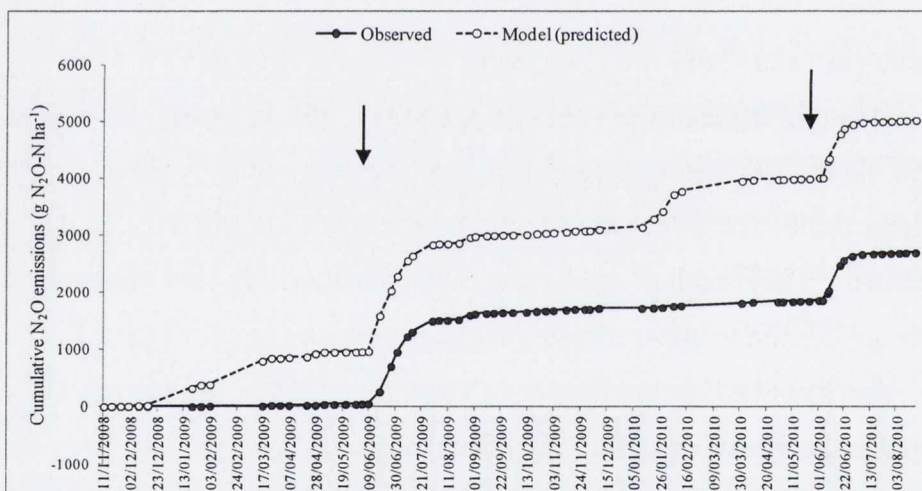


Figure 4.6 Comparison of cumulative model-simulated (dashed line, open circle) and field measured (solid line, closed circle) N_2O emissions from the 150 kg N ha^{-1} Biofert fertiliser application applied during October 2008 – August 2010.

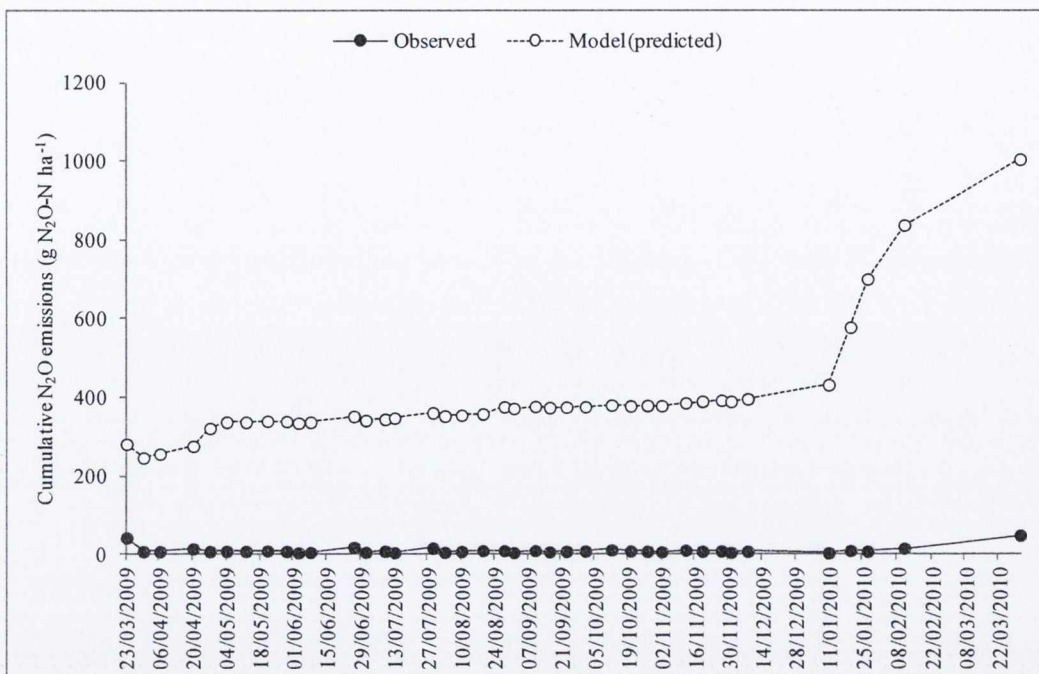


Figure 4.7 Comparison of cumulative model-simulated (dashed line, open circle) and field measured (solid line, closed circle) N_2O emissions from the control plots during the management year February 2009 – March 2010.

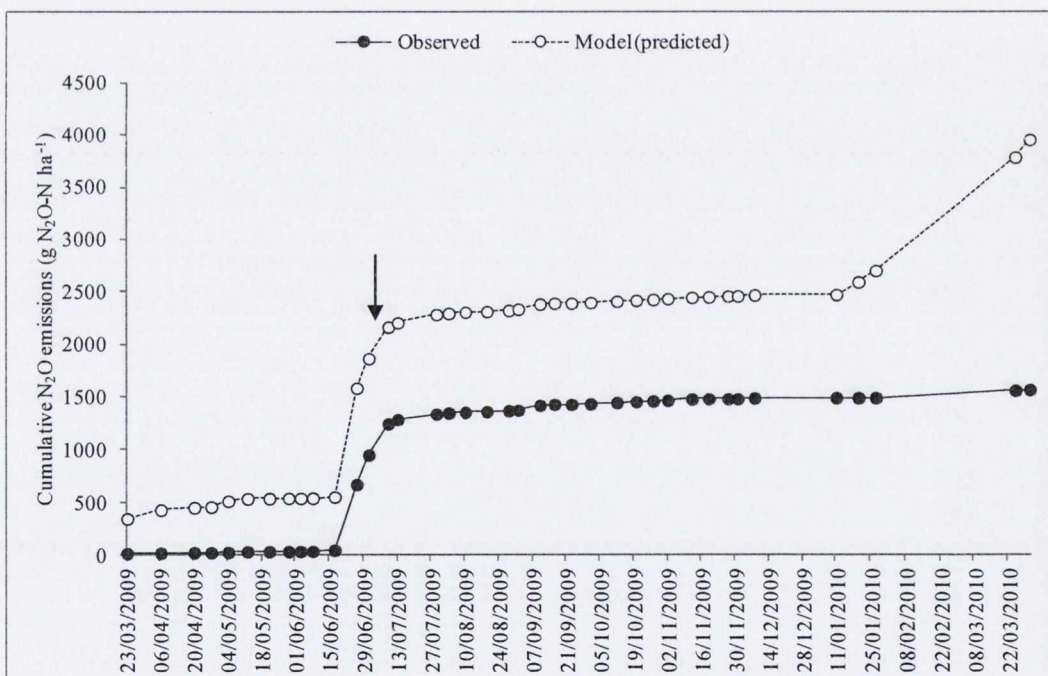


Figure 4.8 Comparison of cumulative model-simulated (dashed line, open circle) and field measured (solid line, closed circle) N_2O emissions from the 150 kg N ha^{-1} 27% CAN fertiliser application applied during the management year February 2009 – March 2010.

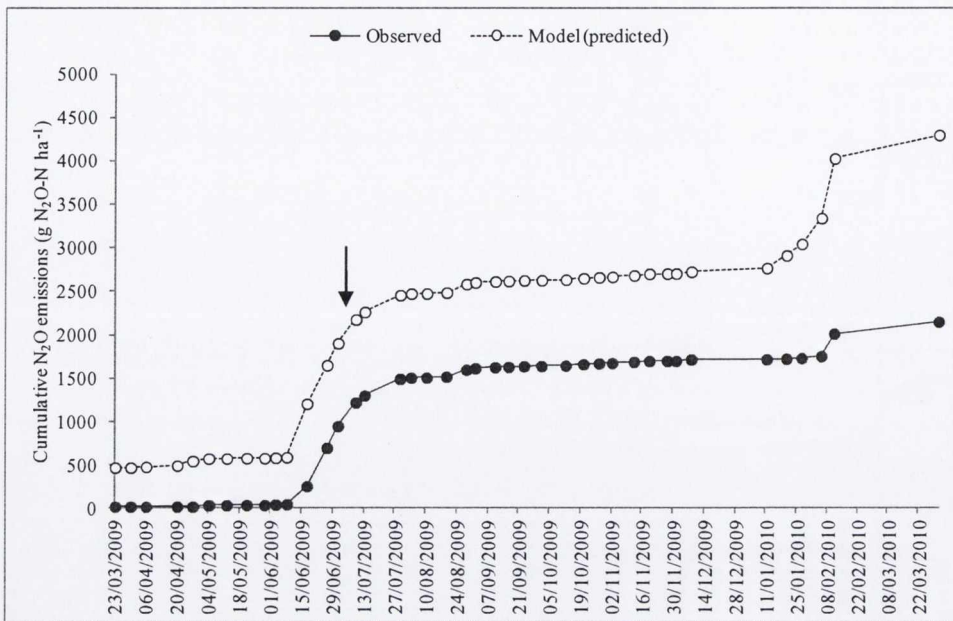


Figure 4.9 Comparison of cumulative model-simulated (dashed line, open circle) and field measured (solid line, closed circle) N₂O emissions from the 150 kg N ha⁻¹ Biofert fertiliser application applied during the management year February 2009 – March 2010.

Table 4.2 Observed and modelled cumulative N₂O emissions from the entire experimental period and from the management year.

Treatment	Cumulative N ₂ O emission (kg N ha ⁻¹)		
	Observation	Model	Relative deviation (%)
<i>Entire experimental period October 2008 – August 2010</i>			
Control 0 kg N ha ⁻¹	282.34	1443.8	411.4
150 kg N ha ⁻¹ 27% CAN	2569.38	3627.3	41.12
150 kg N ha ⁻¹ Biofert	2695.98	2336.40	-13.33
<i>Management year March 2009 – February 2010</i>			
Control 0 kg N ha ⁻¹	194.83	957.3	391.35
150 kg N ha ⁻¹ 27% CAN	1567.03	2388.3	52.4
150 kg N ha ⁻¹ Biofert	1809.01	1774.1	-2.2

4.3.3 Emission Factors

Emission factors for the simulated seasonal N₂O emissions from the Biofert and 27% CAN fertiliser plots were no different from each other so one value was used to represent an overall ‘fertiliser’ treatment. They were very low

values. An emission factor of 0.15% was calculated for the period from August 2009 to August 2010.

4.3.4 Sensitivity to agricultural practices

Table 4.2 illustrates the sensitivity of the DNDC modelled N₂O emissions to changes in soil characteristics, soil farming management and changes in climate.

Increasing soil bulk density resulted in increases in predicted N uptake by the crop, increasing it to 1.8 g cm⁻³ resulted in increases of N₂O flux by the crop of 153% and uptake of N by the soil of 35%.

Decreasing the pH to 4 also resulted in increases in N uptake by the crop of 9%. However, a lower pH of 4 resulted in decreases in N₂O flux of 12%, increase of pH to 8 resulted in further decreases in N₂O flux of 18%.

Table 4.2 Sensitivity of the DNDC model to change in soil characteristics, management and climate at the *Miscanthus* site.

Scenario	N up taken by crop (kg N ha ⁻¹ y ⁻¹)	Annual flux (kg N ha ⁻¹ y ⁻¹)			Ratio (N ₂ O : N ₂ O + N ₂)
		N ₂ O flux	N ₂ flux	N ₂ O + N ₂	
<i>*Baseline</i>	270.6	1.7	11	12.7	0.13
Bulk Density (g cm ⁻³)					
1	279.0	1.8	11.2	13.0	0.14
1.6	356.5	3.4	14.7	18.1	0.19
1.8	365.5	4.3	14.2	18.5	0.23
Soil pH					
4	294.5	1.5	0.6	2.1	0.71
6	272.9	1.8	9.9	11.7	0.15
8	273.1	1.4	9.4	10.8	0.13
Initial Soil Organic Carbon (kg C kg ⁻¹)					
+ 20%	283.1	2.2	16.4	18.6	0.12
- 20%	258.4	2.0	6.9	8.9	0.22
Fertiliser Amount (CAN kg N ha ⁻¹)					
75	163.2	1.0	10.5	11.5	0.09
200	342.2	2.3	10.9	13.2	0.17
Fertiliser Type					
Urea	266.5	1.9	11.0	12.9	0.15
Ammonium bicarbonate	249.2	1.8	10.9	12.7	0.14
Ammonium sulphate	268.2	2.5	11.0	13.5	0.19
Fertiliser timing					
6 th April	269.7	1.7	11.1	12.8	0.13
6 th May	270	1.7	11.0	12.7	0.13
26 th May	270.4	2.0	10.9	12.9	0.16
Rainfall					
+ 20 %	270.7	3.4	34.9	38.3	0.09
- 20%	266.8	3.8	24.9	28.7	0.13
Air Temperature					
+ 20%	270.0	4.3	37.8	42.1	0.10
- 20%	270.9	3.0	19.0	22.0	0.14
Scenario	N up taken by crop (kg N ha ⁻¹ y ⁻¹)	Annual flux (kg N ha ⁻¹ y ⁻¹)			Ratio (N ₂ O : N ₂ O + N ₂)
		N ₂ O flux	N ₂ flux	N ₂ O + N ₂	
<i>*Baseline</i>	270.6	1.7	11	12.7	0.13
Bulk Density (g cm ⁻³)					
1	279.0	1.8	11.2	13.0	0.14
1.6	356.5	3.4	14.7	18.1	0.19
1.8	365.5	4.3	14.2	18.5	0.23
Soil pH					
4	294.5	1.5	0.6	2.1	0.71
6	272.9	1.8	9.9	11.7	0.15
8	273.1	1.4	9.4	10.8	0.13
Initial Soil Organic Carbon (kg C kg ⁻¹)					
+ 20%	283.1	2.2	16.4	18.6	0.12
- 20%	258.4	2.0	6.9	8.9	0.22
Fertiliser Amount (CAN kg N ha ⁻¹)					
75	163.2	1.0	10.5	11.5	0.09
200	342.2	2.3	10.9	13.2	0.17
Fertiliser Type					
Urea	266.5	1.9	11.0	12.9	0.15
Ammonium bicarbonate	249.2	1.8	10.9	12.7	0.14
Ammonium sulphate	268.2	2.5	11.0	13.5	0.19
Fertiliser timing					
6 th April	269.7	1.7	11.1	12.8	0.13
6 th May	270	1.7	11.0	12.7	0.13
26 th May	270.4	2.0	10.9	12.9	0.16
Rainfall					
+ 20 %	270.7	3.4	34.9	38.3	0.09
- 20%	266.8	3.8	24.9	28.7	0.13 172
Air Temperature					
+ 20%	270.0	4.3	37.8	42.1	0.10
- 20%	270.9	3.0	19.0	22.0	0.14

Baseline scenario: Bulk density 0.95 g cm^{-3} , soil pH 6.4, SOC 0.054 kg C/kg , fertiliser applied and application date (150 kg N ha^{-1} CAN on 6th June), average annual maximum temperature 13.1°C , average annual minimum temperature 5.4°C , average daily precipitation 0.30cm , soil tillage to 22cm depth in February.

A 20% increase in SOC resulted in increases of 5% in N uptake by the crop and a 29% increase in N_2O flux. A 20% decrease in SOC resulted in a 5% decrease in N uptake by the crop and a decrease of 18% in N_2O flux. Decreasing the fertiliser amount by 50% resulted in a 41% decrease in N_2O flux, while increasing fertiliser amount by 25% resulted in a 35% increase in N_2O flux. The different types of fertiliser had an increased effect of 12% on N_2O flux when Urea was applied. Ammonium sulphate application as the fertiliser resulted in a 47% increase in N_2O flux.

An increase in rainfall of 20% resulted in a 100% increase in N_2O flux, a decrease of 20% resulted in a 124% increase in N_2O flux.

A 20% increase in air temperature resulted in a 153% increase in N_2O flux, a 20% decrease in air temperature resulted in a 76% increase in N_2O flux.

4.4 Discussion

The results from this chapter are used to assess the reliability of the DeNitrification-DeComposition (DNDC) model in estimating the N_2O flux from *Miscanthus* plots by comparing them to field measurements of N_2O . Also, the model was used to estimate the impact of changes in soil parameters e.g. pH, bulk density, agricultural management practices e.g. date of fertiliser application, levels of fertiliser used, and climatic change e.g. changes in rainfall and temperature, would have on N_2O emissions and also on the resultant emission factors.

For comparison of N₂O fluxes in the *Miscanthus* plot we have a data set which dates from October 2008 until August 2010, approximately 18 months of data. During which there were two separate application of fertiliser in June of each year. In calculating emission factors we used a full year from August 2009 until August 2010. We have also looked at comparison between fertiliser treatments during the management year. The model worked particularly well for Biofert fertiliser application in both the entire experimental period and during the management year period when compared to observed data. It overestimated the cumulative emissions over the management year and entire experimental period for the control plots.

Seasonal emissions of N₂O were not well described by DNDC over the whole experimental period. The DNDC model data did show some seasonality of the data set, however, large peaks in February of each year greatly overestimated the field observed/measured data. This is due to the tillage effect of the model data being displayed. It could be argued that to produce a true reflection of a long-term established plot, this may not be an issue and as such might not be entered into the model. However, in order to analyse all possible emission cause factors we kept it in our model, they did however greatly increase flux data peaks: control plots resulted in DNDC modelled data cumulative fluxes of approximately 11 and 18 kg N₂O-N ha⁻¹ d⁻¹ compared to values closer to 0.3 kg N₂O-N ha⁻¹ d⁻¹ for observed data, Biofert fertilised plots resulted in DNDC modelled data peak fluxes of 28 and 15 kg N₂O-N ha⁻¹ d⁻¹ compared to 2 and 1.5 kg N₂O-N ha⁻¹ d⁻¹ and 27% CAN fertiliser treated plots resulted in DNDC modelled data peak fluxes of 28 and 30 kg N₂O-N ha⁻¹ d⁻¹ compared to 1.3 and 2.5 kg N₂O-N ha⁻¹ from observed fluxes.

As can be seen from the figure 4.2, in 2009 and 2010, the effect of fertiliser was detected by the model during the seasonal period i.e. fertiliser application period. In 2009 the CAN fertilised plots were underestimated by the model but the peak was picked up (figure 4.2). In 2009 and 2010, the modelled data for CAN fertiliser gave relative deviations from the observed cumulative data

(Table 4.2). In the management year, the modelled data for CAN fertiliser gave relative deviations from the observed data of 52.4% (Table 4.2).

The Biofert fertilised plot peaks were picked up by the model but the slower return to background levels was not picked up by the DNDC data (figure 5.3). In 2010, neither of the fertiliser plots peaks were picked up by the DNDC model (figure 5.2 and figure 5.4), thus greatly underestimating the N₂O emissions during this period of 2010. For Biofert fertilised plots, the modelled data in 2009 gave relative deviations from observed data of 9.6 and -71% (figure 5.3). In 2010, the modelled data for Biofert fertiliser gave relative deviations from the observed data of -9.8 and 56% (see figure 5.4).

Differences between the modelled data and the observed seasonal emissions for both fertiliser treatments ranged from -1.12 to 0.37 kg N ha⁻¹ (Table 5.1). The average relative variation for all fertilised treatments was 99%.

Control plot N₂O emissions were poorly described in 2009 by the DNDC model: relative deviations of the simulated from the observed ranging from -4.13 to 45.6 (see figure 5.5). In 2010 the DNDC estimated emissions and resulting relative deviations were better described: data values ranged from -1.7 to 0.85, but, the average deviation was still very high at 82% (see figure 5.6). However, these ranges are dealing with low N₂O flux levels.

Fertiliser is a large driver of N₂O emissions in soil, with amounts of fertiliser applied causing resultant significant effects on N₂O flux from soil (as outlined in chapter 3 and chapter 4). In using the DNDC model, these affects of fertiliser are further highlighted. Increasing the fertiliser amounts by 25% resulted in a 35% increase in N₂O flux, conversely, decreasing fertiliser applied by 50% resulted in a 41% decrease in N₂O flux. The type of fertiliser used also produced a significant increase in N₂O flux i.e. 12% increase when Urea was applied and a 47% increase when ammonium sulphate was applied.

pH had a significant effect on the model data output, a pH of 4 resulted in decreases in N₂O flux of 12%, increase of pH to 8 resulted in further decreases in N₂O flux of 18%.

Soil tillage had a very significant affect on N₂O emissions of our modelled data. The experimental site was well established as a crop and tillage only takes place in the first year of establishment. As such, it is reasonable to assume that the levels of N₂O flux illustrated in the model data greatly overestimate the actual observed N₂O flux data of an established crop.

For 2009 and 2010, the DNDC model greatly overestimated the N₂O emissions. For both 2009 and 2010, the model was able to pick out many of the peaks of the observed N₂O data and observed a similar seasonal pattern. However, there were two large peaks during February of both 2009 and 2010 which had a significant effect and corresponding overestimation of cumulative N₂O emissions.

Cumulative N₂O emissions are also greatly influenced in the model by soil organic carbon (SOC). The SOC value for the soil that was used in the model was 0.054kg C kg⁻¹ dry soil at the site. A 20% increase in SOC resulted in a 29% increase in N₂O flux in the model data output and a 5% increase in soil N uptake by the crop. A 20% decrease in SOC resulted in a significant 18% decrease in N₂O flux and a 5% decrease in soil N uptake by the crop.

The model data was used to calculate emission factor (EF) values for both 27% CAN and Biofert fertilisers. These values were not significantly different and as such the data was grouped together to calculate an EF value for 'fertiliser' treatment. An emission factor of 0.15% was calculated using the period from August 2009 to August 2010 as an agricultural management year. The EF values vary in Ireland, depending on soil type, climate, year, land management, grassland ranges are from 0.7% (Carlow), 3.4% (Cork), 4.7% (Wexford)(Hsieh et al., 2005, Hyde et al., 2006, Flechard et al., 2007). The use of DNDC on Irish soils requires calibration of the soil parameters to prove effective for optimum simulation of DNDC (Rafique et al., 2011b).

In regards to changes in climate, some changes and their corresponding affects are difficult to interpret, an increase in rainfall of 20% resulted in a 100% increase in N₂O flux, a decrease of 20% resulted in a 124% increase in N₂O flux. Air temperature also had a significant effect on N₂O flux, a 20% increase in air temperature resulted in a 153% increase in N₂O flux, a 20% decrease in air temperature resulted in a 76% increase in N₂O flux. These discrepancies may be explained by the large peak exhibited in February of both years and as such may impact the effects on N₂O.

In conclusion, the DNDC has been able to show similar patterns to observed data during fertiliser application periods of the *Miscanthus* plots. Further work would be required in order to parameterise the DNDC for the soil where there were poor correlations between measured and estimated results e.g. February peaks. In order to further improve the model, a wider data base for *Miscanthus* with more intensive measurement periods i.e. more than once a week and better input data such as the soil organic carbon would be very useful in further refining model output for *Miscanthus*. For the purposes of predicting N₂O emissions, our modelled data was reasonable in comparison to the measured data. However, the level of complexity and the detail in that is necessary for the input data were reliant on estimates from separate data from the literature. As *Miscanthus* is not a default crop on the DNDC programme these estimates will need further refinement from data available. It must also be noted that with improvements in the model versions there is still significant spatial and temporal variability in emissions and interactions between the driving variables which challenge our ability to predict emissions (Calanca et al., 2007).

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Chapter 5 General Discussion

Introduction

This chapter will discuss a number of important elements; the GHG emissions in Ireland and how they relate to other countries and the policies introduced in order to reduce them; the economics of biomass energy crop production in Ireland; the observations from the experimental work with a comparison of *Miscanthus* crop growth versus Willow and the factors involved; the growers of biomass crops and final conclusion.

Greenhouse Gases and Policy

Agriculture releases significant amounts of CO₂, CH₄ and N₂O (Cole et al., 1997, IPCC, 2001, Paustian et al., 2004), in Ireland, it remains the single largest contributor of greenhouse gas emissions at 30.4% of the total ahead of energy (21.7%) and transport (19.1%). Agricultural emissions increased from 2009 to 2010 by 0.2% (0.04 Mt CO₂eq), this is the first increase since 2003 (EPA, 2010a) (increases in gasoil use on farms and lower prices for nitrogenous fertiliser resulted in greater sales are primarily responsible). As outlined by the IPCC the following are methods of reduction:

Reducing emissions

The fluxes of these gases can be reduced by improving management efficiency of carbon and nitrogen flows in agricultural ecosystems.

Enhancing removals

Agricultural soils act as large carbon sinks (IPCC, 2001). It has been evaluated that more than 50 PgC has been lost from these sinks (Paustian et al., 1998, Lal and Bruce, 1999, Lal, 2004b). But improved practices that increase the photosynthetic input of carbon and or slows the return of stored carbon to CO₂ via respiration, fire or erosion will increase carbon reserves,

i.e. sequestering carbon / building carbon sinks. Significant levels of carbon can be stored in soils through practices suitable to local systems (Lal, 2004a). Significant amounts of vegetative carbon can also be stored in perennial plantings on agricultural lands (Albrecht and Kandji, 2003). In Carlow, field measurements were used to predict the potential of *Miscanthus* to sequester carbon. *Miscanthus* plantations were considered to store between 2 and 3 Mg C ha⁻¹ y⁻¹ subject to crop yield and the initial soil organic C level (Dondini et al., 2009).

Avoiding / displacing emissions

Biomass crops grown on agricultural land can be used as a source of direct fuel (Schneider and McCarl, 2003, Cannell, 2003). The CO₂ that is released when these crops are combusted is of recent atmospheric origin i.e. photosynthesis and is not carbon emitted from fossil fuels. In essence, the net benefit of these biomass crops as GHG sources is equal to the fossil-derived emissions displaced, subject to any emissions from producing, transporting and processing. It has also been demonstrated that biomass crops *Miscanthus* and SRWC can be economically competitive and provide low GHG emission energy sources (Styles et al., 2008, Styles and Jones, 2008).

Ireland's limit set by the terms of the Kyoto Protocol are 314.18 Mt CO₂eq for 2008-2012. In order to be compliant, Ireland's emissions for this period must be below the Kyoto limit at the end of the time period, less any offsets from approved forest sinks which is allowed under Article 3.3 of the Protocol as well as use of purchased Kyoto Protocol credits. In December of 2008, the European Council and Parliament agreed the 'climate and energy package' which became law in June 2009. Ireland must also meet EU compliance targets for 2020 for emissions outside the emissions trading scheme (ETS) i.e. agriculture, transport, residential and waste. Under EU Directive 2009/28/EC, Ireland must deliver a 20% reduction in non-ETS greenhouse gas emissions by 2020 relative to 2005 levels. Ireland also has binding limits over the 2010-2020 period to ensure a gradual move towards their targets. Ireland has committed to reductions with 20% of energy coming from renewable

resources and a reduction of 20% in primary energy usage through greater energy efficiency (EuropeanCommission, 2008b). Ireland's reductions towards meeting the Kyoto Protocol targets and the 2020 target is looking positive towards compliance. However, this is primarily a direct result of the current economic recession and immediate short-term economic outlook. The global economy since the end of 2008 has experienced a massive crisis unseen since the great depression in 1929. Indeed, for the EU 20-20-20 targets, a Gross Domestic Product (GDP) growth of 2.2% until 2010 was used and a rate of 2.3% between 2010 and 2020 (EuropeanCommission, 2008a). Opinions are divided on how well the economy will recover and is illustrated in Figure 5.1 for future growth projections. Indeed according to the EPA's projections (EPA, 2011), Ireland is on course for meeting its targets due to economic output reduction of 10-15% (ESRI, 2010) which underpin our energy demands (SEAI, 2010) thus resulting in a knock-on effect on EPA projections.

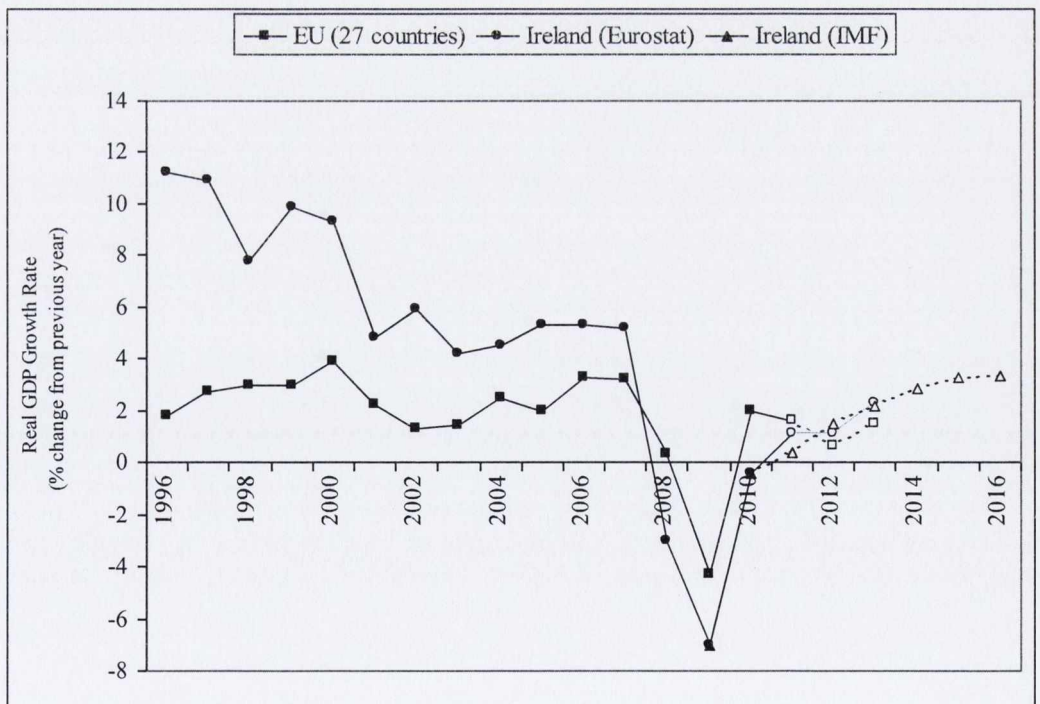


Figure 5.1 GDP growth for EU-27 and Ireland up until 2010 with forecasts from 2010-2013 from Eurostat and IMF (2011-2016) as % change (dashed lines and symbols with no fill represent forecasts for future growth).

How this affects biomass crops? An opinion that is often discussed is that climate policy is out of place as the capital and funds required to deal with climate change is too costly and that European industries should not be hampered by such as they struggle to cope with a worldwide fall in demand for goods and products and major financial restrictions. Another common opinion is that with the economic downturn and reduction in industrial activities that GHG emissions will decrease so no effort is required to comply with EU targets.

It has been recognised that half of global GHG emission reductions are to be achieved through energy efficiency measures as shown in the WEO 2009 (EEA, 2010a). This means a global energy demands must be met by less traditional fossil fuel combustion. This also would have the additional benefit in reduction emissions of air pollutants such as SO₂, NO_x and particulate matter (PM) (IEA, 2009). In order for the EU to obtain significant drops in CO₂ emissions in the energy sector there need to be gains in energy efficiency and increased share of low-carbon energy sources in the energy mix (Kerebel, 2009). From 1996 – 2007 there were massive decreases in European energy intensity, due mainly to restructuring of European economies in the 1990s following the end of the Soviet era, resulting in an impressive drop in energy consumed per unit of GDP (EEA, 2010b). It is highly important for Europe to reduce its energy intensity and use less energy across the board in all sectors per unit of activity, as the recession has simply decreased the activity but not the amount of energy consumed per unit of activity. In terms of units of carbon used per unit of energy, i.e. carbon dependence, this is quite difficult to decrease. There are significant policies required and major investment required to transform the fuel mix. The share of low-carbon energies i.e. renewables in the primary energy market is a major factor in carbon dependence. Wind and solar energy were significantly developed over the 2000s, from a very low starting point and on a European scale represent approximately 7% of the European energy mix (TREN, 2008). In order to further reduce European carbon dependence a greater proportion of energy must come from renewables. “Clean” energy sources must make up a far greater proportion of the energy mix in Europe. While the economic crisis

has reduced GHG emissions due to less industrial activity it provides a new difficulty in funding the investments required to increase the proportion of renewables in the energy mix as large investments are required in energy producing countries.

In May 2010, the Minister for Communications, Energy and Natural Resources announced price supports for bioenergy under REFIT. The supported technologies are Anaerobic Digestion CHP, Biomass CHP and Biomass Combustion including a provision for 30% co-firing of biomass at the three State owned peat power stations. This can offer opportunities for the agriculture sector to provide long term sustainable markets for bioenergy crops. The Bioenergy Scheme 2010-2012 which is 50 % co-funded under the rural Development Programme of Ireland was launched to build on the Exchequer funded pilot Bioenergy Scheme 2007-2009. Approximately € 0.6 million in establishment grants was paid to farmers under the Bioenergy Schemes in 2010 and approximately 350 hectares of crops were established under the 2010 scheme (Department of Agriculture, 2010).

However, Ireland has agreed to reduce greenhouse gas emissions by 20% of 2005 levels by 2020 as part of the EU Climate and Energy Package for the post-Kyoto period 2013-2020. As part of the Copenhagen Accord (which was the main output from the December 2009 UNFCCC Climate Change negotiations in Copenhagen which was noted by Parties) in a joint letter the EU reiterated a conditional offer of increasing the EU 2020 emission reduction target to a conditional offer of 30% reduction in the event of a comprehensive agreement on global emissions reductions (EU, 2010). This could potentially increase the Irish reduction target to a reduction level of 30%, this would mean a reduction of 5.87 million tonnes from 19.58 in 2005 to 13.71 in 2020.

According to the EPA between 2009 and 2010 emissions from agriculture increased by 0.2% (0.04 Mt CO₂ eq). This is the first time there has been an increase since 2003 and is largely connected to cheaper prices for fertiliser

and the knock on increase in sales and the increase in gasoil use on farms (EPA, 2010a).

Economics of Biomass Production & Agriculture in Ireland

Many factors affect the economics of *Miscanthus* crop production e.g. yield, farmer-producers profit margin, propagation method, production chain chosen, years of production, annual or overall costs, transport and land-use costs, cost of land (Lewandowski et al., 2000). Economic analysis based on Danish conditions suggested that production costs for *Miscanthus* are comparable to other annual and perennial energy crops approximately € 70 t⁻¹ or € 4.10 GJ⁻¹, making it marginally economically viable if agricultural set-aside payments are included (this assumes a 10-12 year rotation to absorb establishment costs)(Lewandowski et al., 2000, Jorgensen and Venendaal, 1997). In Ireland, Willow and *Miscanthus* have been demonstrated to be economically competitive with current agricultural land uses (Styles et al., 2008).

Within Ireland, dairy and tillage farm systems have the highest proportion of economically viable farm business, however, across the other farming systems, only just over 36% of farms were classified as economically vulnerable. Less than 10% of cattle rearing farms were considered to be economically viable businesses (Hennessy et al., 2010b).

***Miscanthus* and Willow as Biomass Production Crops**

Methane from enteric fermentation and manure management composes up to 70% of agricultural GHG emissions with nitrous oxide from application of fertiliser and animal deposition making up the remainder (EPA, 2010b). *Miscanthus* has considered agronomic advantages such as low management input with low fertiliser and low pesticide crop (Lewandowski et al., 2000) with carbon emissions lower than those of livestock production and annual tillage crops. As recent data stands, 56% of farm systems in Ireland are cattle-

based, 17% sheep-based and 16% dairy-based, tillage accounts for 6% and mixed livestock for 5% (Hennessy et al., 2010b). As such *Miscanthus*, as a biomass crop, provides possibilities of reducing GHG emissions by displacing CH₄ / N₂O emissions associate with farm management practices and by increasing soil organic carbon sequestration (Jorgensen and Jorgensen, 1996, Clifton-Brown et al., 2007, Biewinga and van den Bijl, 1996).

GHG emission reduction are also dependent on whether *Miscanthus* production takes place on arable land or stocked pasture. Increased levels of stored C pools in the soil are a result of the relatively large quantities of rootstock below ground and enhanced soil organic matter content. There is a continuum of below ground C pool from living root biomass and leaves that have undergone senescence and root material through to recalcitrant soil humic fractions (Clifton-Brown et al., 2007). The slower rates of turnover of the humic fraction mean that the greatest long-term benefits arise from sequestration in the more recalcitrant soil C pools (Jones and Donnelly, 2004). Where *Miscanthus* displaces arable land, C sequestration will increase as croplands are net emitters of CO₂ of between 1-3 tCO₂ ha⁻¹ yr⁻¹ where most of the C loss occurs via ploughing and extended fallow periods (Davis et al., 2010). Conversion of arable land into biomass production increases soil C input by approximately 2.8-4.1 tCO₂ ha⁻¹ yr⁻¹ for *Miscanthus* (Rowe et al., 2009b) based on 2-3 years post-establishment to reach these rates (Hansen et al., 2004).

Agriculture has been widely accepted as being a major source of N₂O (Denman et al., 2007) and it has a Global Warming Potential (GWP) of 296 times larger than the mass of CO₂ (Prather et al., 2001). In an attempt to reduce dependence on fossil fuels and increase use of 'carbon-neutral' energy crops, an increase in N₂O may occur as a direct result of N-fertilisation (Crutzen et al., 2007).

This study was designed to investigate N₂O and CH₄ fluxes from a *Miscanthus* and Willow plot as a function of fertiliser type and application.

Furthermore DNDC modelling was carried out on the data for *Miscanthus* to test and validate its output for a series of environmental and soil parameters.

Results obtained from chapter 2 show that there was no yield effect on application of fertiliser to the *Miscanthus* plots. In terms of meeting renewable energy contributions from bioenergy crops, Ireland will have limitations in regard to biomass production based on our current land-use, this is also the case in the UK (Rowe et al., 2009a). Indeed Irish grasslands are forecast to become more intensively managed (Irish Department of Agriculture, 2011) Indeed in order to meet required biomass targets, fertiliser would be required to increase yield. However, in our study we found fertiliser to have no significant effect on yield i.e. N fertilisation does not improve yields as has also been observed in several other studies (Himken et al., 1997, Clifton-Brown et al., 2007, Danalatos et al., 2007). Addition of fertiliser can aid in the establishment phase of planting a *Miscanthus* crop (Drewer et al., 2012b), however it appears to be low N-demanding compared with other crops due also to nutrients returning to the soil as litter where only the stems are harvested and litter remains on the soil. Also there is evidence of high N re-translocation of aboveground tissues to belowground, prior to senescence (Beale and Long, 1997, Beuch et al., 2000). However, there are nutrients removed with every harvest so the long-term requirements for fertiliser application would have to be assessed (Drewer et al., 2012b).

Results from chapter 3 also showed no yield increase or effect with fertiliser application for the Willow plots. That the use of fertiliser on the crops may not be beneficial as there was an increase in cumulative emissions of N_2O , however, 27% CAN fertiliser had lower cumulative emissions than Biofert fertiliser over the management year for *Miscanthus*. For Willow there was also an increase in cumulative emissions of N_2O , however, 27% CAN had higher cumulative emissions than Biofert fertiliser. There was a treatment effect for CH_4 emissions for *Miscanthus* but regression analysis could not isolate any particular variable as observed data was very low and there was high variability. Willow showed no effect of fertiliser application on CH_4 emissions, which were generally low with high variability. These large

inherent variations, particularly in soil N₂O emissions were observed in our study in both daily and cumulative emissions. Choudhary maintains that these variations reflect the natural heterogeneity of soils and that these 'hot spots' may have high concentrations of organic matter, nitrate level and soil conditions (Choudhary et al., 2002).

For the two biomass crops studied within this thesis, it is difficult to directly compare them as the management for both crops is different. The *Miscanthus* crop is grown over a calendar year and is annually harvested. Willow is grown over a two year period and harvested at the end of this time. As such direct comparisons are not entirely valid.

Table 5.1 illustrates the energy content from different biomass fuels contains values for *Miscanthus* and short rotation Willow coppice. From this table it illustrates that both *Miscanthus* and Willow have competitive levels of energy content with other biomass crops.

Table 5.1 Energy content from different biomass fuels at 0% moisture content (Source: Teagasc).

Biomass Fuel	GJ t ⁻¹	KWh t ⁻¹
Soft Wood (spruce)	18.8	5.222
Hard wood (beech)	18.4	5.111
<i>Willow (short rotation coppice)</i>	<i>18.4</i>	<i>5.111</i>
Straw of cereals	17.2	4.778
Straw of corn	17.7	4.917
Cereals, seeds	17	4.722
Rape, seeds	26.5	7.361
Rape, cake	20	5.556
Cereals, whole plant	17.1	4.75
<i>Miscanthus</i>	<i>17.7</i>	<i>4.917</i>
Hay	17.1	4.75

For our management year for *Miscanthus* a yield of 10.1 t ha⁻¹ is compared to the Willow yield of 13.1 t DM ha⁻¹ a⁻¹. This would give Willow a significantly higher yield per annum. We found higher yields amongst

fertilised plots but they were not statistically significant, this has been found in studies investigating application of organic wastes (Quaye et al., 2011). The use of pelleted sludge in studies has shown linear relationship between fertiliser application and biomass production with the ability to absorb Cd and Zn from the sludge into the crop (Labrecque et al., 1995). Also, this was the first 3-year growth cycle for this plot and as such soil nutrient supply may have been sufficient. Increases of 50% in biomass in willow plantations were observed following application of 600 kg N ha⁻¹ in sewage sludge (Nielsen, 1994). In the UK and Canada applications of different rates of sewage sludge (some with lime application) resulted in significant increases of willow stem biomass production (Hodson et al., 1994, Labrecque et al., 1998). However, with growth of willow, it has been reported that annual stem biomass production of 15-22 Mg ha⁻¹ removed 75-86, 10-11, 27-32, 52-79 and 4-5 kg ha⁻¹ yr⁻¹ of N, P, K, Ca and Mg, respectively (Adegbidi et al., 2001). Ericsson observed that whole plant N, P and K accumulations of 270, 42 and 200 kg ha⁻¹ (roots, leaves and stems respectively) for a total biomass of 22.4 Mg ha⁻¹ in 3 year old *Salix viminalis* plantations (Ericsson, 1994). In order to produce high yielding crops of biomass application of adequate nutrients is necessary (Adegbidi et al., 2003). Swedish recommendations for a four-year rotation are 45, 100-150 and 90-120 kg N ha⁻¹ in the second, third and fourth years respectively (Danfors et al., 1998). Application of 60 kg N ha⁻¹ in the planting year followed by 80-120 kg N ha⁻¹, 30 kg P ha⁻¹ and 80 kg K ha⁻¹ is recommended by Ledin (Ledin, 1986).

Fertiliser Use

Miscanthus is considered to be an N-efficient crop and requires between 50-100 kg N ha⁻¹ (Styles and Jones, 2007b) which would be approximately 100 kg N ha⁻¹ less than arable crops. Soil type is a major determinant in N₂O emission mitigation as there is high variability between heavy soils and sandy soils. Another obvious saving is that the production of synthetic fertiliser is reduced through decreased demand.

The Biofert fertiliser utilised in this experiment was dried pasteurised cake granules produced at the Ringsend Waste Water Treatment Plant (WWTP) in Dublin. Estimates of 55-65% of organic matter from the sludge is converted to biogas of which approximately 65% of which is CH₄ and 35% is CO₂. Biogas is used in a gas engine to generate electricity and also fired directly into the steam boiler at the latter part of the treatment process. However the level of biogas production could counterbalance GHG use in this plant in treating sludge, thus potentially reducing overall GHG emissions from Biofert production (subject to a comprehensive life cycle assessment). This WWTP treats 36,000 tonnes of dry sludge per year and produces up to 4MW electricity through its production of Biogas on site, indeed Eirgrid contracted Ringsend Waste-to-Energy converter to provide 72 MW of energy by the end of 2010 (EIRGRID, 2009). The use of Biofert as a fertiliser product would have the potential to provide significant plant nutrients with low or negative cost for the farmer. Waste-water treatment on SRCW for biofiltration could potentially increase production profitability and gross margins for farmers (Styles et al., 2008). Biofert is in good supply and could meet the needs of a burgeoning biomass production market. Figure 5.2 illustrates the market prices for fertiliser in Ireland broken down into fertiliser type. Despite a drop in prices in 2010, they have all exhibited significant upward increases over the last 5 years and are a significant input cost for farmers. This is quite important as fertiliser is an important component of the economics of energy crop production and can account for 20-30% of the costs (Johansson and Rosenqvist, 1995, Kelkjoer, 1995, Strauss, 1995).

In New York state fertiliser can account for 10-20% of the cost of willow biomass crop production over seven rotations (Buckholz and Volk, 2010). In the US, N fertiliser input has been estimated to account for 37% of non-renewable fossil energy input into willow production systems (Heller et al., 2003). By using commercial N fertilisers the fossil fuel demand and GHG emissions mitigated by producing these crops is negated significantly (Buckholz and Volk, 2010, Volk et al., 2004).

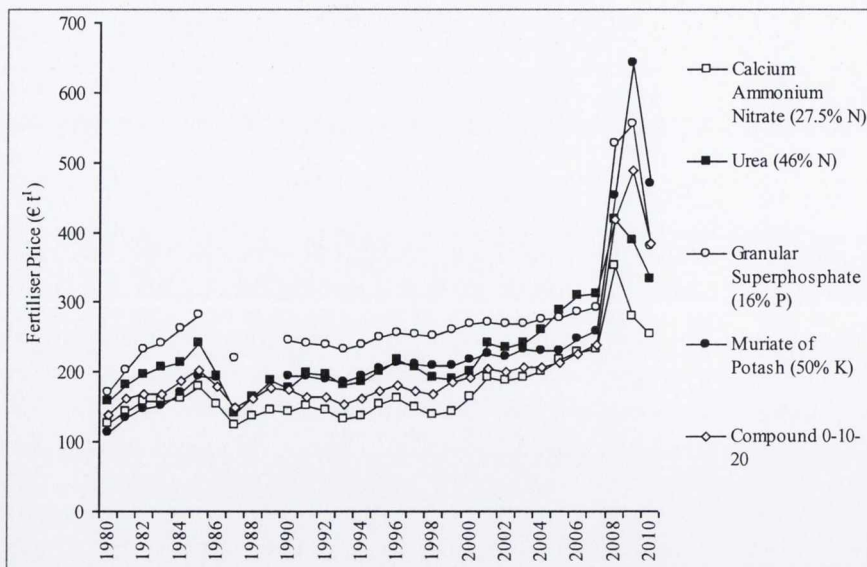


Figure 5.2 The price for fertiliser as an input in Ireland (Source: Central Statistics Office, CSO 2011).

As mentioned previously, there is difficulty directly comparing the two crop systems as they have different management regimes and growth cycles. From Table 5.2 the cumulative flux for Willow plots under the three treatments are observed. From this CAN fertiliser has the highest over the entire experimental period at $1.17 \text{ kg N}_2\text{O-N ha}^{-1}$. For *Miscanthus* over the management year Biofert was observed to have the highest cumulative flux at $1.7 \text{ kg N}_2\text{O-N ha}^{-1}$ over CAN at $1.5 \text{ kg N}_2\text{O-N ha}^{-1}$.

Table 5.2 Cumulative Flux for Willow plots for three different treatments for growing seasons 2009 and 2010 and the entire experimental period.

Treatment	Growing Season 2009 (kg N ₂ O-N ha ⁻¹) ¹⁾	Growing Season 2010 (kg N ₂ O-N ha ⁻¹) ¹⁾	Entire Experimental Period (kg N ₂ O-N ha ⁻¹) ¹⁾
Control, 0 kg N ha ⁻¹	0.11	0.02	0.38
150 kg N ha ⁻¹ 27% CAN	0.41	0.51	1.17
150 kg N ha ⁻¹ Biofert	0.33	0.28	0.88

Our management year emission factor values of 0.47 and 0.55 for CAN and Biofert treatment regimes for *Miscanthus*, respectively and 0.59 and 0.16 for CAN and Biofert treatments for Willow are still substantially lower than those mentioned from Irish studies. It is important to note though soil

characteristics are different and we have not quantified any loss of N through leaching, run off etc. as outlined in the 'Nitrogen Cascade' (Galloway and Cowling, 2002) from chapter 1. Potential negative impacts of *Miscanthus* cultivation are environmental hazards which may occur in its production and emissions. Nitrate leaching occurs mainly in the year of planting which would have serious effects on the soil and local water conditions (Christian and Riche, 1998). From year three after initial planting, leaching of 3-30 kg ha⁻¹ N (without N fertiliser, and with application of 120 kg ha⁻¹ N) was close to recorded values for intensely managed grassland (Christian and Riche, 1998).

A partial solution to emission reductions is change from ruminant agricultural systems to crop based systems as generally there are fewer GHGs in production than ruminant systems. However, arguments made are that changes in land-use can potentially lead to losses in soil organic carbon thus significantly affect global soil organic carbon (SOC) storage (Trumbore, 1997). In regard to *Miscanthus* and Willow crops, this is partly due to the life cycle analyses that have been carried out where the net benefits associated with its growth are not fully taken into account (McLaughlin and Walshe, 1998, Lemus and Lal, 2005, Lettens et al., 2003) and *Miscanthus* has been observed to potentially increase carbon sequestration in soils (Dondini et al., 2009).

Other environmental factors and impacts are increased leaching and decreased biodiversity. There is also the issue of cross compliance obligations associated with the Single Payment Scheme which requires the ratio of permanent grassland and total agricultural area in any EU Member State should not decrease to the detriment of permanent pasture by more than 10%. This puts a limit on the maximum increase in tillage area but it does give Ireland scope for rotating arable land within the limit as 90 % of agricultural land in Ireland is under permanent pasture (Agriculture, 2004).

In Ireland 91% of agricultural land is under grass with 6.7% used for cereals and less than 3% for other crops where in the EU approximately 62% of agricultural land is under arable farming.

Modelling

If we are to consider adopting any future management practices in order to reduce N₂O emissions from a crop it is very important to be able to predict the effects of these practices on future climate scenarios. So we can predict emissions from changes of management, different climate scenarios, different ecosystems etc. For this purpose in this study we have made use of modelling software, DNDC (Li et al., 1992). DNDC is a biogeochemical model based on environmental and ecological drivers (Li, 2000). In this study in chapter 4, DNDC model was tested against field measurements and there was good agreement. This then will be beneficial for estimating N₂O flux for *Miscanthus* crops in Ireland. However, accuracy of the model data depends on the provision of the SOC measurements and available N inputs. Rainfall and air temperatures can be significant drivers of uncertainty in DNDC outputs. As such, local weather data is vital for precision.

Unfortunately as yet, most predictive models consider nitrification and anaerobic denitrification as sources of N₂O only and ignore the contribution of nitrate ammonification (Smith et al., 2010). This is mainly due to lack of data on the controls of these processes for model parameterisation or validation (Smith et al., 2010). An important issue regarding modelling is that scale is a major consideration, where our experimental work is based on a plot scale versus the prediction of emissions and policy decisions are made on regional / national / global scales potentially very different to the smaller plot scale used to understand underlying processes (Standing et al., 2007). It also assumes that the relationships between the controlling N₂O parameters remain the same for all scales i.e. micro-, plot- and macro-scale. For these reasons integration of the plot-scale data with modelling data is very important in order to test the reliability and robustness of modelled data.

Growers of Biomass Crops

The capacity for using biomass crops such as *Miscanthus* and Willow are dependent on the level of adoption by Irish farmers. This in turn will be affected by economic factors such as input costs e.g. rhizome purchase, N input, pesticide, harvesting etc. and the impact these factors have on the value of output. The adoption of some emission abatement practices is subject to market forces like those listed and determines take up by farmers (O'Mara et al., 2007). There is also consideration towards functions of sociological and / or personal factors which influence take up of new crops and technologies (Breen and Donnellan, 2009) e.g. farmer age, education, tradition, farm scale, farmers risk preferences, attitude towards the environment (Clancy et al., 2009). There needs to be a simultaneous improvement on farm profitability and reduction in annual GHG emission through production of biomass crops. Figure 5.3 illustrates the fluctuating prices over the last two decades for different farming systems, this is the economic reality for farmers in the marketplace. The real key is to offer farmers a viable option of farming biomass crop systems.

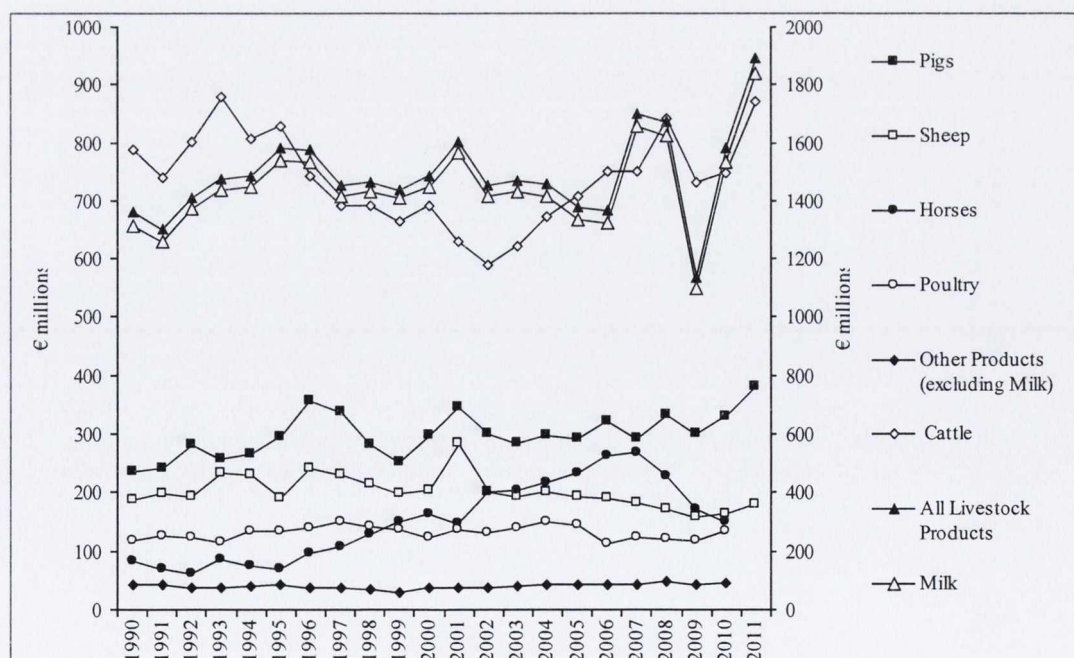


Figure 5.3 Value at current prices for output, input and income in agriculture for livestock in Ireland (All livestock products, Milk and Cattle are based on the right hand side secondary axis, all of the other factors are measured on the primary left hand side axis) (Source: CSO 2011).

According to Teagasc's 2010 National Farm Survey, average farm income increased 46% from €12, 190 2009 to € 17, 771. But this is only an increase of 5% from 2008 and a decline of 10% on 2007 (Hennessy et al., 2010b). However, there is large variation within farm incomes based on farm type. Almost a third of farms earned a Family Farm Income per Farm (FFI) of less than € 3, 500 in 2009, this decreased to 25% in 2010. However, in 2010, three quarters of farm incomes stood at less than € 20, 000. This is a result of the majority of Irish farms being part-time farms i.e. 29% of farms in 2010 were classified as 'full-time' farms by Teagasc. From the same data, 36% of Irish farms were considered 'economically vulnerable' in 2010.

Within the Irish agricultural systems, dairy and tillage farm systems have the highest proportion of economically viable farm businesses. Of the other systems of farming, more than 36% of farms were classified as economically vulnerable with less than 10% of cattle rearing farms being considered economically viable (Hennessy et al., 2010b).

For dairy farms, income increased substantially from a very poor 2009 to 2010, due mainly to increase of 20% of gross output with milk prices increasing by 29% from 2009. The average income on cattle rearing farms increased by 8% from 2009 to 2010. Of these cattle rearing farm systems, 40% earned equal to or less than € 3, 500 in 2010 with less than 3% earning € 20, 000 or more. With these low incomes, over two thirds of farmers earned income off the farm.

Of the other cattle farm systems, market based gross output increased by 6% from 2009 to 2010, however a 4% decline in direct payments combined with a decrease of 2% on input expenditure resulted in an increase of 4% on farm income from 2009 to 2010 to € 9, 679. For the mixed livestock system, many farms benefited from the increase in milk prices and also increases in grain prices. Income from these farms increased 55% from 2009 to 2010.

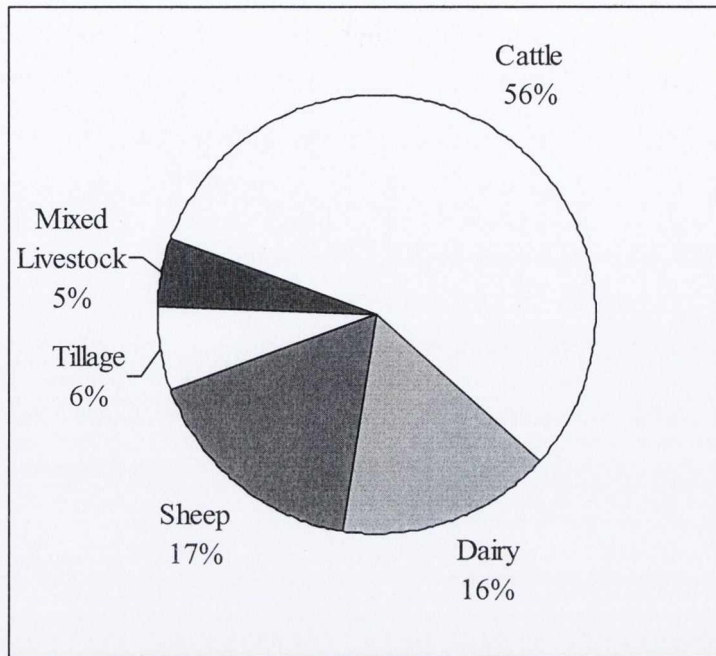


Figure 5.4 Distribution of farm population by systems: all farms (Source: Teagasc (Hennessy et al., 2010a)).

Almost 30% of farms in this system earned an income of €40, 000 or more in 2010. For sheep farm systems, income increased by 15% from 2009 to 2010 with lamb prices increasing by 17% in the same period. In tillage farm systems, income increased 141% from 2009 to 2010 due to a particularly poor year in 2009. Market based gross output increased 55% from 2009 to 2010 and yield ha⁻¹ increased on average 5% with price t⁻¹ increasing 56%.

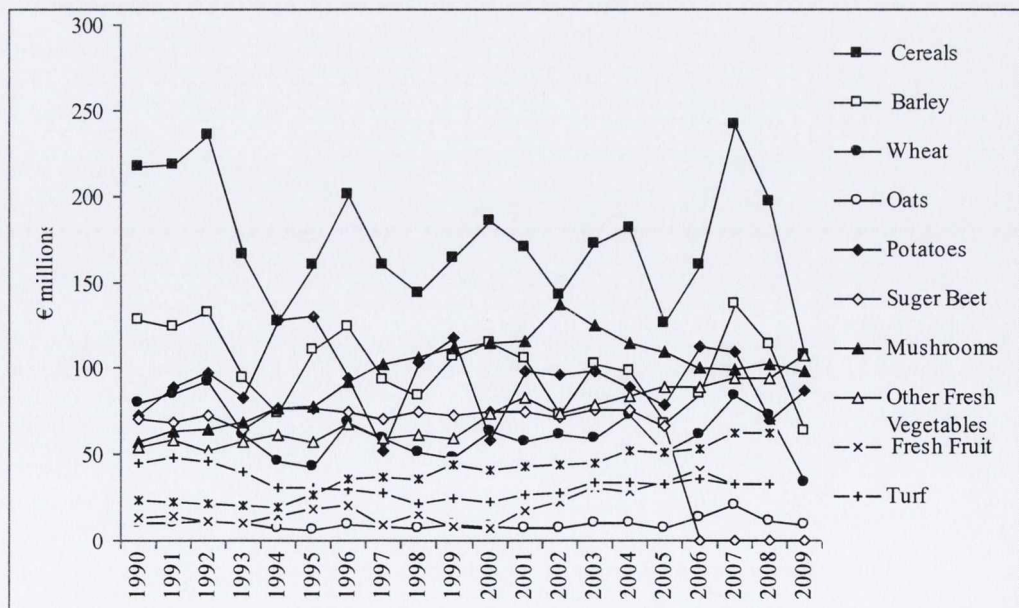


Figure 5.5 Values at current prices for output, input and income in agriculture for crops in Ireland (Source: CSO 2010).

Figure 5.5 illustrates the price fluctuations for Irish crops over the last two decades. After the cessation of sugar beet crops production in 2006, there are marked increases in cereals, barley, wheat and potatoes. From June 2010 to June 2011 there was an 8.3% (22, 900 ha) increase in land planted with cereal crops, wheat increased by 20.5% (15, 900 ha) and oats increased 7.9% (1, 600 ha) and barley increasing by 3.3% (5, 700 ha). This increase is considered to be due to strong prices and renewed optimism in the sector, with Irish prices increasing 89% between 2009 and 2010. Overall total cattle decreased 1.7% and total sheep increased 3.5% (CSO, 2011).

According to Teagasc's Road Map for Tillage 2011 the area devoted to energy crops is expected to increase by up to 46% by 2018 (Teagasc, 2011) (Table 5.4). This would mean a very substantial increase of 2233% over a nine year period in the land grown for energy crops e.g. *Miscanthus* and Willow.

Table 5.4 The hectares of crops grown in Ireland throughout the period of 2007-2009 and the projected increase and decreases in crops for 2018.

Crops	('000ha)		Change (%)
	2007-2009	2018	
Wheat	90.7	120	32
Barley	178.2	200	12
Oats	21.6	30	39
Total Cereals	290.5	350	20
Maize	24	40	67
Oilseed rape	3.7	20	441
Perennial bio-energy crops	3.0	70	2233
Potatoes	12.2	10	-18
Other crops	10	10	0
Total non-cereals	52.9	150	184
Total crops	343.3	500	46

Also within this road map is the projection of establishment costs for *Miscanthus* being reduced by 30% through the home production of planting stock from € 2, 900 ha⁻¹ to € 2, 000 ha⁻¹. The cost of willow chip drying is

also targeted to be reduced to below € 10 tonne⁻¹ from € 30 tonne⁻¹ as part of their technical efficiency improvements (Teagasc, 2011).

Conclusion

While the cultivation of *Miscanthus* and Willow with the application of Biofert as an N source to increase yield provides positive yields for biomass combustion etc. it is part of a mosaic of solutions (Lanigan, 2008) for Ireland's GHG reduction in agricultural emissions. It would be ill-considered to suggest that it would drastically reduce agricultural emissions as a multitude of solutions are required for an overall reduction in GHGs (Helm and Pearce, 1991).

Documents outlining and setting future targets are not fulfilling any important role unless there is a rigorous plan set out which combines fiscal, financial and regulatory measures to achieve these targets at the grass roots level (IrishFarmers'Journal, 2011). The 30% target set out for peat stations to co-burn biomass is going to prove to be a challenge due to scarcity of biomass and also major problems caused by corrosion at the two ESB plants at Shannonbridge and Lanesboro (although following a major overhaul in 2011 they are expected to function at 90% by the end of 2012 (ESB, 2012)). In order to meet National RE Action Plan use of up to four million tonnes of biomass for energy purposes by 2020 is required. Current planting levels of *Miscanthus* and Willow in Ireland are quite insignificant in relation to these levels of biomass. A major problem in attracting crop take-up by farmers is that the short-term markets are very weak for these crops which means growers are taking a big risk despite good long-term market prospects (Burke, 2011). This is being dealt with by REFIT programme offering prices for these plants to resolve this problem. However, there is little chance of the area of land being planted out with these crops being in production by 2020. So, potentially Ireland is looking at importing large quantities of these crops. While it is important to meet our political targets set out by EU etc. there is a potential opportunity to realise national benefits in biomass crop production.

Issues like rural employment, potentially high import prices as we get closer to 2020 and fuel supply security are all important to take into account.

If we are to do this then Ireland needs to greatly increase our indigenous fuel production. Germany, France and Sweden have had success in increasing fuel production through different government incentives.

Commercial enterprises e.g. JHM Crops Ltd. have taken the opportunity to develop reliable local supply of biomass crops for co-firing in ESB power stations and were the first to test *Miscanthus* in the Edenderry Power Station in 2008. It is endeavouring to exploit markets for *Miscanthus* in animal bedding, for co-firing in power stations, as a fuel for Combined Heat and Power (CHP) and the production of *Miscanthus* logs.

The major markets for biomass fuel currently are for heating both commercially and domestically (Figure 5.6). Commercially a market for the equivalent of three million tonnes of oil is in demand where wood chips as boiler fuel would be the most likely substitute.

Ideally the target market would be large buildings with constant heating demands e.g. hotels, government buildings, swimming pools. This market has been affected by the current economic downturn however. Domestically there is an oil, gas and coal equivalent of two million tonnes of approximately five million tonnes of biomass. This market could be met using biomass briquettes / logs / pellets.

As has been observed in this study, the method used for measuring N₂O has major and significant effects on the results. In Cork, eddy covariance techniques were used (Scanlon and Kiely, 2003) and also in Carlow for the *Miscanthus* site for CO₂ measurement. These systems give continuous measurements over a large footprint and are less labour intensive, static chambers are highly labour intensive and potentially miss many N₂O peaks. However, they are dependent on wind speed, direction and power supply to these systems often causes system downtime where significant gaps occur in

the data which then require back-filling. Another significant factor is the expense of these systems versus the robust system used in this study and a high level of maintenance is required.

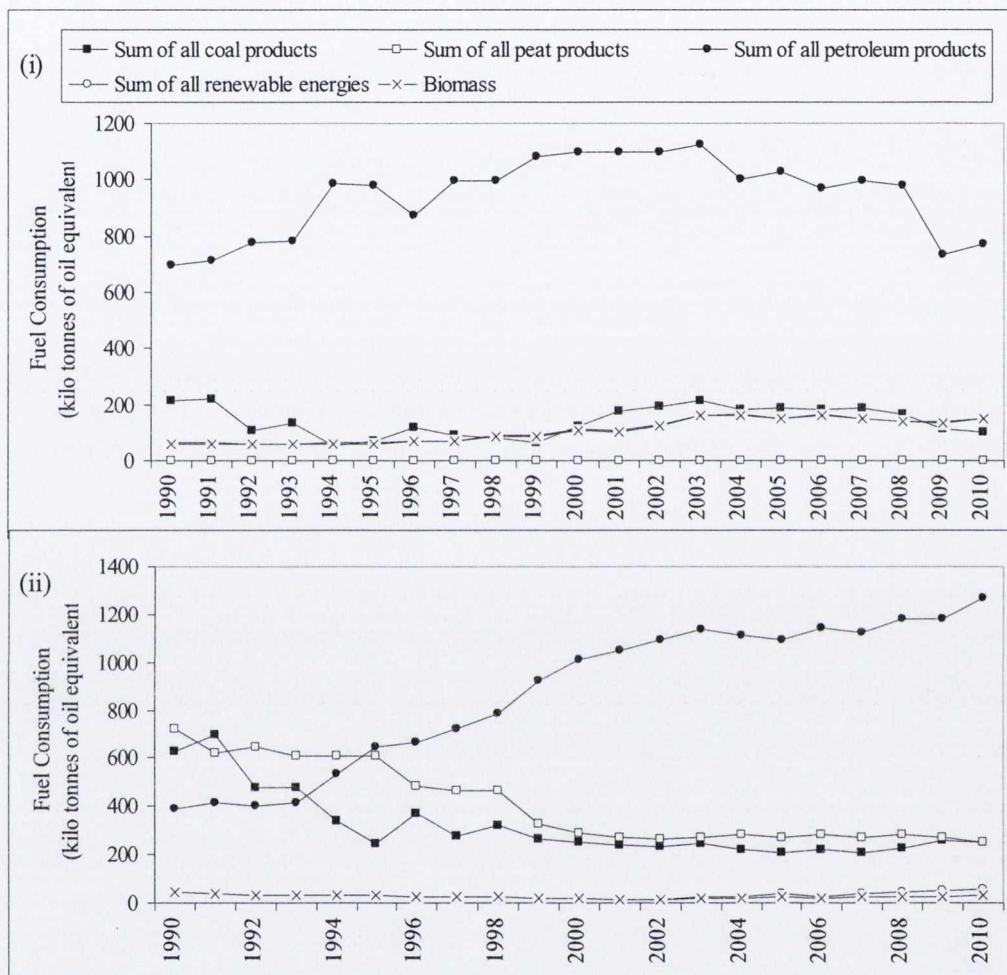


Figure 5.6 Fuel consumption (kilo tonnes of oil equivalent) for (i) Industry, (ii) Domestic demand over the last two decades by fuel type (Source:(SEAI, 2012)).

Ideally, a continuous automated chamber with good replication would be used particularly during short events e.g. fertilisation, freeze-thaw cycles where N_2O peaks are produced over short periods of time.

In order to get a greater picture of N_2O emissions, losses through different pathways e.g. leaching, runoff, atmospheric deposition and greater investigation into the microbial pathways of N_2O would give a greater overall picture of the N-cycle of the crop. Indeed understanding how the changes in

the number and diversity of the microbial communities producing or reducing N_2O in response to agricultural practices are related to N_2O fluxes is key to understanding how we can better control and reduce process rates and microbial sources of N_2O particularly in application of organic fertilisers e.g. Biofert.

Main Findings

- Results from this thesis concern the calculation of annual fluxes and emission factors of the greenhouse gas nitrous oxide from two agricultural crops, *Miscanthus x giganteus* and Willow, *Salix viminalis x schwerinii* ('Tora') in Co. Carlow, Ireland. Two fertilizer types were applied, 150 kg N ha⁻¹ 27% CAN and 150 kg N ha⁻¹ commercial 'Biofert'.
- For *Miscanthus x giganteus* the total cumulative flux for the management year for the control was 0.2 kg N₂O-N ha⁻¹ y⁻¹, for the CAN fertiliser application of 150 kg N ha⁻¹ a value of 1.5 kg N₂O-N ha⁻¹ y⁻¹ was observed and a value of 1.7 kg N₂O-N ha⁻¹ y⁻¹ was observed for Biofert fertiliser application of 150 kg N ha⁻¹.
- From late 2008 to 2009, the emissions from the control plots were low ranging from - 0.003 gCH₄ ha⁻¹ d⁻¹ to 4.201 gCH₄ ha⁻¹ d⁻¹. CH₄ fluxes from CAN plots reached a maximum of 4.20 gCH₄ ha⁻¹ d⁻¹. CH₄ fluxes from Biofert plots reached a maximum of 5.204g CH₄ ha⁻¹ d⁻¹.
- In 2010, the emissions from the control plots were low ranging from 0.0979 gCH₄ ha⁻¹ d⁻¹ to 1.929 gCH₄ ha⁻¹ d⁻¹. CH₄ fluxes from CAN plots reached a maximum of 2.008g CH₄ ha⁻¹ d⁻¹. CH₄ fluxes from Biofert plots reached a maximum of 3.445 gCH₄ ha⁻¹ d⁻¹.
- For the control plots, total CO₂ equivalents were 79.28 kg CO₂, for 150 kg N 27% CAN 473.61 kg CO₂, for 150 kg N Biofert 530.58 kg CO₂.
- Emission factors for the management year for 27% CAN fertiliser was 0.47% and for Biofert fertiliser was 0.55%.
- For *Salix viminalis x schwerinii* ('Tora') control treatment plots, cumulative N₂O flux values of 0.11 kg N₂O-N ha⁻¹ for the growing season (May-August) 2009, 0.02 kg N₂O-N ha⁻¹ for growing

- season 2010 and $0.38 \text{ kg N}_2\text{O-N ha}^{-1}$ for the entire experimental period.
- For 27 % CAN treatment plots, cumulative flux values of $0.41 \text{ kg N}_2\text{O-N ha}^{-1}$ were calculated for the growing season 2009, $0.51 \text{ kg N}_2\text{O-N ha}^{-1}$ for the growing season 2010 and $1.17 \text{ kg N}_2\text{O-N ha}^{-1}$ for the entire experimental season.
 - For Biofert treatment plots, cumulative flux values of $0.33 \text{ kg N}_2\text{O-N ha}^{-1}$ were calculated for the growing season 2009, $0.28 \text{ kg N}_2\text{O-N ha}^{-1}$ for growing season 2010 and $0.88 \text{ kg N}_2\text{O-N ha}^{-1}$ for the entire experimental period.
 - Emission factors (EF) for both fertiliser treatments were calculated for the growing season 2009, growing season 2010 and for the entire measurement period. For 27% CAN, in the growing season 2009 EF was 0.22, and for growing season 2010, EF was 0.16 and for the entire measurement period, EF was 0.56. For Biofert, in the growing season 2009, EF was 0.36, for growing season 2010, EF was 0.19 and for the entire measurement period EF was 0.16.
 - In 2009, CH_4 emissions from the control plots were low ranging from $-0.007 \text{ gCH}_4 \text{ ha}^{-1} \text{ d}^{-1}$ to $3.11 \text{ gCH}_4 \text{ ha}^{-1} \text{ d}^{-1}$. CH_4 fluxes from CAN plots reached a maximum of $3.001 \text{ gCH}_4 \text{ ha}^{-1} \text{ d}^{-1}$. CH_4 fluxes from Biofert plots reached a maximum of $3.719 \text{ g CH}_4 \text{ ha}^{-1} \text{ d}^{-1}$.
 - In 2010, the CH_4 emissions from the control plots were low ranging from $0.091 \text{ gCH}_4 \text{ ha}^{-1} \text{ d}^{-1}$ to $2.05 \text{ gCH}_4 \text{ ha}^{-1} \text{ d}^{-1}$. CH_4 fluxes from CAN plots reached a maximum of $2.002 \text{ g CH}_4 \text{ ha}^{-1} \text{ d}^{-1}$, CH_4 fluxes from Biofert plots reached a maximum of $2.140 \text{ gCH}_4 \text{ ha}^{-1} \text{ d}^{-1}$.
 - The control plots have the lowest CO_2 -equivalent values at 132.24 CO_2 -equivalents (kg), CAN values are the highest at 376.68 CO_2 equivalents (kg) and Biofert is below CAN at 286.79 CO_2 -equivalents (kg).
 - Comparisons of measured and modeled fluxes were carried out using the process-based model, DNDC, for *Miscanthus x giganteus*. Good agreement was found for the crop.

Conclusions

- Application of fertiliser leads to significant increases in soil N₂O fluxes.
- There was no significant difference between type of fertiliser on soil N₂O fluxes.
- There was no significant fertiliser effect on biomass crop yield for *Miscanthus* or Willow.
- CH₄ fluxes for both crops were insignificant.
- N₂O fluxes for both energy crops were significantly small when no fertiliser was applied.
- If fertiliser needs to be applied to a bioenergy crop i.e. one with a poor soil N concentration, early stages of crop establishment, Biofert is the fertiliser to use as it is effective and economic as a fertiliser.
- There needs to be continuous and long-term measurements of the field GHG footprint of bioenergy crops before they can be properly evaluated.
- This study shows that the two bioenergy crops emit low levels of N₂O if they do not receive any N fertiliser.
- However, if bioenergy crops require constant N-fertiliser application this will potentially offset the GHG balance more and the GHG savings in comparison to imported fossil fuel derived energy would be significantly reduced.

Recommendations for future research

- The N₂O fluxes were well quantified in our study, however we used an application rate of 150 kg N ha⁻¹. It would be an improvement on studies to investigate the agro-specific requirements for *Miscanthus* and Willow growth which would improve estimates for N-fertiliser application requirements.
- We used the chamber technique to quantify N₂O and CH₄ fluxes, which may introduce possible bias if integrating the estimates to

ecosystem level when the measurements were at plot scale over soil. The use of N₂O flux estimates and eddy covariance i.e. chamber vs eddy covariance would be useful information. Also the possible use of an extending chamber i.e. one that increases as the crop height increases throughout the season would take into the whole crop.

- The DNDC model performed reasonable in estimating general trends of annual N₂O flux but overall performed poorly. Further work is required to improve the input data particular to *Miscanthus*.
- The use of the chamber technique gave discrete measurements i.e. infrequent measurements. The use of eddy covariance in comparison to DNDC results would be advised to improve the output.
- A full life-cycle assessment of Willow and *Miscanthus* combined with Biofert fertiliser e.g. energy inputs/outputs, Biogas production, presence of PPCPs in soil, N leaching etc. would be very useful information and give a whole picture of biomass crop agronomy.
- We used Biofert as our organic fertiliser, it would be useful to use other wastes as fertiliser to compare the emissions observed.
- Establishment of an Irish GHG working group for graduate students would be a highly useful exercise in terms of knowledge sharing and practical advice on GHG measurements.
- The effect of Biofert fertiliser on soil condition and the effect of Biofert on soil microbial communities and earthworms. If there is any correlation to changes in numbers and community dynamics within a soil and how they are related to N₂O soil fluxes. Microbial growth after Biofert application was observed on the soil particularly on Willow plots.
- As energy crops such as *Miscanthus* have an approximate 20 year life-cycle, seasonal and interannual variations (soil and climate) require continuous measurements long-term before the site specific GHG footprint of the crop can be evaluated comprehensively.

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