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CONTRIBUTION OF DISSOLVED ORGANIC CARBON LEACHING TO THE ANNUAL CARBON BUDGET OF A DAIRY FARM

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Abstract

Soils are the largest terrestrial store of carbon (C) and changes in this store of C can impact on soil quality and atmospheric CO₂ concentrations. Research on C budgets at paddock to national scales has focused most attention on the processes of respiration and photosynthesis in determining the net loss or gain of C from an ecosystem. However, leaching of dissolved organic carbon (DOC) is a potentially important component of the C budget that is rarely measured when developing carbon budgets, and as a consequence, is often estimated or excluded. Much of the literature indicates that while DOC leaching is important, the loss of DOC from the terrestrial ecosystem may only be small. In the vasose zone DOC that is leached may be adsorbed on to soil and stabilised or may be mineralised, effectively preventing it from leaching from the ecosystem.

The objectives of this thesis were to determine if DOC leaching from the soil of a dairy farm was an important contribution to the C budget. To measure this, soil leachate was collected from five paddocks using 100 suction cup lysimeters. These were installed within the footprints of two eddy covariance towers on a dairy farm in Waharoa, Waikato, New Zealand. In general samples were bulked over paddocks, with 10 mL of water from each suction cup contributing to the overall bulked sample. Water extracted from the suction cups was analysed for DOC, total nitrogen, and nitrate. DOC concentration measurements were coupled to the volume of water draining through the soil. The volume of drainage was obtained from a water balance model using measurements of evaporation and precipitation. Leaching from the soil started in mid-May continuing through till mid-November. The total amount of water draining through the soil for the year was calculated to be 990 mm, with a mean concentration of $4.5 \pm 0.8 \text{ mg L}^{-1}$ (mean \pm SE). The mass of DOC leached was $38 \pm 4 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ (mean \pm SE). The concentration of DOC showed no monthly variation, while the mass of DOC showed a strong seasonal trend, with the greatest mass of DOC leaching during the wet winter period. Ultimately the main driver of DOC leaching at this site was the volume of water draining through the soil, because DOC concentration changed very little.

In order to understand the suite of processes that influence the fate of DOC the subsoil, internal cycling process including mineralisation and sorption of DOC were investigated in the laboratory. Results showed that DOC leached to a depth of 0.65 m could be mineralised by soil microbes lower in the profile, converting it to CO₂. The total C respired over a week (12.81 $\mu\text{g CO}_2\text{-C}^{-1} \text{ g soil}^{-1}$) was 11 times greater than the C added (1.18 $\mu\text{g C}^{-1} \text{ g soil}^{-1}$). In a repeat of the same study the amount of CO₂ respired was 25 times greater than the addition of DOC, indicating that fresh additions of DOC to the subsoil can lead to priming. Additionally sorption experiments indicated that the concentration of DOC lost to the groundwater would be less than the concentration of DOC measured at 0.65 m. Soil water solution with a concentration of 7 mg L⁻¹ DOC mixed with subsoil had a 50% reduction in concentration when shaken for four hours with Te Punga soil. Similar results were found in the Piarere soil with a 34% reduction in DOC concentration. In contrast when both soils were shaken with DOC (4 mg L⁻¹) in a second experiment, there was a small amount of net desorption. Overall there was potential for the soils at this site to reduce the concentration of DOC leached from 0.65 m, through adsorption of DOC onto the soil. Subsequently sorption would have caused a reduction in the DOC mass lost. While results from laboratory studies were variable it was clear that both sorption and mineralisation in subsoils will moderate leaching losses of DOC to groundwater.

In the context of a paddock scale C budget, where the atmospheric exchange of C through respiration and photosynthesis (NEE) was about -880 kg C ha⁻¹yr⁻¹, leaching of 38 kg C ha⁻¹ yr⁻¹, represents 4.5% of the total exchange. Compared to the net ecosystem carbon balance (NECB), which included farm inputs and outputs, of a similar intensive grazed system, DOC leaching is equal to 3-15% of the total. However as DOC leaching at 0.65 m does not accurately represent a leaching loss from the system, as sorption and mineralisation can further alter the mass leached, the contribution of DOC loss through leaching to the carbon budget is comparably small and does not represent a significant component of the C budget at this site.

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1 Introduction

1.1 Background

Carbon (C) is an important component of the atmosphere, the land and water; globally it is the fourth most abundant element. The soil C pool is the largest terrestrial C pool, constituting some 2000 Gt of soil organic C (Janzen, 2004), 3.3 times greater than the atmospheric C pool of 760 Gt and 4.5 times greater than the C stored in biota (560 Gt) (Lal, 2008). Soil C is also beneficial to many physical, chemical and biological processes including: structural stability, as it helps bind particles into aggregates (Tisdall & Oades, 1982), fertility, through the release and availability of nutrients (Kalbitz *et al.*, 2000), cation exchange capacity, water movement and water holding capacity (Lal, 2004). Thus losses of soil C can lead to soil degradation causing a reduction in biomass and productivity. C is cycled between the atmosphere the land and the oceans as CO₂, which is an important greenhouse gas. Consequently the uptake and release of CO₂ by terrestrial ecosystems is an important control of the climate system. This highlights the importance of quantifying fully the losses of C from the soil, including how C is stored and cycled, as small changes in stored soil C can have a large effect on the changes in global C cycling and soil quality (Smith *et al.*, 2008).

Much attention has focused on the processes of respiration and photosynthesis for determining the net loss or gain of C from ecosystems, however there are a number of other loss mechanisms, including dissolved organic carbon (DOC) leaching that need to be quantified. DOC inputs are derived from root exudates, soil organic matter and from microbial biomass (Kalbitz *et al.*, 2000) and DOC can be produced from simple leaching of organic materials, through desorption from soil colloids, and from organic matter decomposition (Michalzik *et al.*, 2003). DOC is defined as the component of C that can pass through a 0.45 µm filter and can exist as a wide range of molecules from simple amino acids and sugars to complex humic substances with large molecular weights (Moore *et al.*, 2008). DOC plays an important role in the terrestrial ecosystem, through its role

as a substrate for biological activity, its ability as weathering agent and its effects on the availability of metals and nutrients (Thurman, 1985). DOC is also an important source of C in rivers and lakes. The process of DOC leaching from the surface soil to lower in the profile provides a way to transfer C where it can be sorbed and stored in the vadose zone. And is potentially an important way to sequestering C (Sanderman & Amundson 2009).

In general DOC leaching is a component of the C budget that is not well constrained. Synthesised leaching values from the soil range between 11 and 1690 kg C ha⁻¹ yr⁻¹ (Kindler *et al.*, 2011; Ghani *et al.* 2010). The contribution of photosynthesis to the net carbon budget of grassed ecosystem is in the 10s of thousands, in comparison the mass of DOC leaching is small. However the proportion of this leaching contributing to a loss or gain from the net C budget depends on the internal soil cycling process. Laboratory experiments indicate that most mineral soils have a tendency to adsorb DOC (Münch *et al.*, 2002; Sanderman & Amundson, 2009), with sorption showing a strong positive correlation with soil sub surfaces rich in iron and aluminium sesquioxides (Sanderman & Amundson, 2009; Schneider *et al.*, 2010). Large proportions of DOC also have the potential to be mineralised to CO₂ (Moore *et al.*, 2008). Whether leached DOC is mineralised to CO₂, stored in the soil by sorption on to mineral surfaces or if it is leached to the groundwater will ultimately determine how DOC leaching is accounted for in C budgets.

There have been a number of studies reporting on DOC leaching from forest soils (e.g. Peichl *et al.*, 2007; Sanderman and Amundson 2009), some from unmanaged grasslands (Don & Schulze, 2008) and grazed pastures (eg Mc Tiernan *et al.*, 2001; Harrison *et al.*, 2008). However, there is little published data on leaching from intensively managed pastures that are grazed year round, such as those which are common in New Zealand. Consequently, the magnitude of DOC leaching is rarely represented in conceptual and numerical models and is often not included or is estimated in carbon budgets for grazed pastures (e.g. Mudge *et al.*, 2011).

Grazed grasslands in New Zealand make up some 11.1 million hectares of the total land surface (41% of the land usage). This 11.1 million hectares is divided

into four main uses, dairy farming, sheep farming, beef cattle farming, and mixed sheep and beef cattle grazing (1.9, 3.3, 1.4 and 5.1 million hectares respectively) with other grazing stock making up the rest (Statistics New Zealand, 2007). In the Waikato region of New Zealand, pastoral farming makes up 58% of the total land use with a large proportion of this dairy farming (Statistics New Zealand, 2007). Globally grazed pastures make up 26% of the earth's ice free land surface (FAOSTAT, 2011) and have high naturally high soil C contents (Conant *et al.*, 2001), rendering them an important component of the global C balance. Because pastoral farming represents one of the major land uses, it is important to fully quantify C through measurements of the C cycle, as well as understand the major process controlling these systems.

Methods for measuring DOC leaching are complicated and variable, due to the collection of both DOC leachate and water balance measurement. *In situ* measurements are made difficult due to the impracticality of collecting percolating water from the unsaturated zone in the lower soil profile. While laboratory experiments, can interfere with natural soil drainage. There are numerous ways to sample DOC in the field, as highlighted in the literature, with reviews alluding to which method is best under what conditions (Fares *et al.* 2009, Curley *et al.* 2011). However, the lack of widely accepted method along with the known inherent variability of soils has been found to cause large variations in concentrations and thus the flux of DOC leached (Buckingham *et al.*, 2008). Also as is not always possible to measure drainage, creating a water balance and determining drainage in soil can be quite difficult, and it can be estimated in a number of ways.

The focus of measurements on respiration and photosynthesis for estimating changes of soil C storage can lead to an inaccurate estimation in the changes in C stocks, as below ground process including leaching and sorption can lead to an added unmeasured loss or gain of C respectively. Better understanding of the magnitude of the different C fluxes in pasture systems, and the factors driving fluxes could help identify farm management systems which minimise C losses and maximise C sequestration.

1.2 Thesis objectives

The overall goal of this study was to determine if DOC leaching was a significant component of the C budget of a grazed pasture system. The specific objectives were to:

- 1) To quantify the annual mass and concentration of DOC leaching from a typical dairy farm in the Waikato,
- 2) Determine the fate of DOC leached to the vadose zone
- 3) An ancillary objective was to determine the mass of nitrogen leached below the same pasture.

1.3 Thesis outline

Chapter 2 provides a review on the literature surrounding DOC leaching. The main focus is on DOC leaching from grazed pasture ecosystems, however as this literature is sparse the review includes studies of DOC leaching under grasses, forests and cropped systems, from New Zealand and abroad. A review of methods for sampling DOC is also included.

Chapter 3 describes the full methodology, including site description, sampling, laboratory analysis, sorption and respiration experiments as well as data handling and statistical analysis.

Chapter 4 contains the results and discussion of the study. Included in this section is the contribution of DOC leaching to the annual carbon budget of a dairy farm, as well as in depth discussion and critical analysis. This section is presented in the form of a paper, so therefore includes an introduction, literature review and brief methodology that will be repeated from preceding chapters in a more brief form.

Chapter 5: is the culmination of this thesis and contains a summary, conclusions and direction for future research.

The following information can be found in the appendix

- Appendix A, the evaporation gap filling method
- Appendix B, Shows raw data tables for the two respiration experiments
- Appendix C, contains the raw data for this study, including measured DOC concentrations, DOC leaching, rainfall and evaporation data, grazing frequency for each paddock. Sorption experiment raw results are also located here.

2 Literature review

2.1 Introduction

Carbon (C) is an important component of the terrestrial ecosystem, and is especially important in soils, for structure and productivity (Lal, 2004). Soils are also the largest terrestrial store of C, and contribute to the cycling of C between the atmosphere and land as CO₂ (Janzen, 2004). Much attention has been focused on this above ground cycling of C. Dissolved organic carbon (DOC) leaching may be an important part of ecosystem carbon cycling. However DOC leaching is a process that is rarely measured and is quite poorly understood, particularly in grazed pastoral systems (Kalbitz, 2000). Literature suggests that DOC flux and magnitude can change greatly between ecosystems (Neff and Asner 2008). Therefore DOC leaching measurements are required for a large range of ecosystems. Differences in DOC values are in part due to different measurements techniques and experimental procedures but also due to different, biological, chemical and physical factors that alter the amount of DOC leached. The origin function and fate of DOC is only partially understood. However the importance of DOC movement through the soil is quite well studied (eg. Sanderman & Amundson, 2008). With DOC sorption onto mineral horizons providing a way to store large amounts of C for a potentially long time (Guggenberger & Kaiser, 2003), DOC leaching provides a way to potentially sequester C.

The focus of this literature review is on the mass of DOC leaching from the soil and its role in the ecosystem. The literature review will explore common measurement techniques of DOC leaching; highlight values of DOC flux across a range of ecosystems, including some grasslands. Lastly the internal cycling of C in soil including factors and processes that influence leaching of DOC from grasslands will be discussed.

2.2 Dissolved organic carbon

Approximately 55% of soil organic matter (SOM) is C, with the remaining 45% of SOM being comprised of other elements such as nitrogen, oxygen, phosphorus and hydrogen (Amundson, 2001). Dissolved organic carbon (DOC) is the dissolved fraction, operationally defined as the, organic molecules smaller than 45 μm . Soils are known to contain varying amounts of DOC, originating from accumulated plant matter, soil humus, microbial biomass or root exudates (Kalbitz *et al.* 2000),

Advances in carbon 14 and 13 carbon isotope techniques have allowed easier identification of the potential sources of DOC in soils. Kaiser and Guggenburger, (2005) suggest that DOC is derived from the decomposition of humic substances lower in the soil horizon, and that soil C is broken down and washed away before it can be mineralised fully or incorporated back into the soil through adsorption. Fröberg *et al.* (2007) also identified humified organic matter as the major source of DOC in leachates from forest floor and mineral soils, and stated that a large proportion of fresh leaf litter C was either mineralised or sorbed leaving only a small proportion to leach out of the O horizon. In grassland systems organic layers are small or totally missing so the origin of DOC is not likely to come from recent litter inputs and rather partially broken down humic material lower down the soil profile.

The process of DOC leaching is strongly linked to controls on its production consumption and storage in soil. Michalzik *et al.* (2003) suggested that net production of DOC in mineral soils, while still dependant on surface C inputs and the supply of DOC from the metabolic breakdown of surface C, was mostly controlled by the process of sorption. Don and Shuzle (2008) showed that 40% of subsoil DOC was derived from soil organic C down the profile and not from recently added C inputs at the surface. Leading to the conclusion that DOC export from grasslands and forested sites is not only controlled by the vegetation but by the adsorption capacity of the soils, and the water balance; and only during storm conditions or strong preferential flow may surface DOC reach the subsoil. Further, Gielen *et al.* (2011) argued that while microbial decomposition of organic matter

is important for the release of DOC, desorption of organic substances from soil solids was equally important and that DOC leaving the ecosystem was limited by water drainage rather than site productivity. A more in depth analysis on the controls of DOC flux in soil is presented further along in this chapter.

While there is still some confusion over the origins and fate of DOC in soils it is clear that understanding DOC dynamics requires information on both the origin of DOC and the turnover of DOC in soils. While it is important to measure the sources of DOC input into the soil, it is equally if not so more important to understand the internal cycling processes of DOC (Section 2.5.1) in the soil, as the fate of DOC is not only controlled by its production but also through consumption by microbes, transport in water and also the chemically mediated sorption of DOC into lower soil horizons (Kalbitz *et al.* 2003).

2.3 Methods used to measure soil solution

There are two main types of sampling technique used to sample soil: tension or passive collection. As the name suggests tension samplers exert a tension onto the soil to extract DOC solutions. The main form of tension sampler used is the suction cup lysimeter, however, there are also suction plates. Tension samplers can collect samples at discrete intervals or can be continuous. Passive samplers operate by collecting the water that is free draining from the soil, the main type of sampler used is the barrel lysimeter, additionally, there are also non tension plates that collect free draining water. There is much uncertainty surrounding the reliability of soil solution samplers particularly for the collection of DOC (Buckingham *et al.*, 2008). While studies have compared the sampling methods of DOC, the results are limited by the range of the studies, including sampling replicates, the type and depth of soils compared. Soils are inherently variable therefore some results could be linked to soil heterogeneity, including the placement of samplers particularly suction cups in the surface horizons. In a field based comparison (Reynolds *et al.*, 2004) found a twofold difference in the DOC concentrations between zero-tension and tension collector. Additionally, Buckingham *et al.* (2008) found that tension collectors had lower concentrations than non tension collectors for the same soil.

The following review highlights the main methods, the conditions for use, as well as the potential benefits or limitations of the methods.

2.3.1 Suction cup samplers

In the literature, porous suction cups have been given a variety of names, including: suction cup lysimeters, suction cup, vacuum lysimeter, tension cup lysimeter etc. All these names describe the same common principal, a porous suction cup attached to the end of a probe that uses a vacuum to extract water from the soil. Suction cup samplers are by far the most frequently used method for extracting soil water (Weihermuller *et al.*, 2007). Easy installation and ability to collect samples at different soil depths across ecosystems at spatial and temporal scales with minimal installation and manufacture cost have been the key reasons for the extensive use of suction cups (Close *et al.*, 2004). The technique has been around since the early 1900s (Briggs & McCall, 1904) and has been used constantly right up until present day. Suction cups can be inserted from the soil surface to a specific depth by augering a hole or alternately through a trench at a specific depth.

The extraction of water from the soil can be undertaken using two types of operation, continuous or discontinuous. For continuous samplers the advantages are that sample is collected continuously so data can be obtained for all time periods. Small amounts of sample are collected over an extended time period, which reduces the disturbance to the soil column and also sorption onto the porous cup (Weihermuller *et al.*, 2006). Disadvantages include the creation of a preferential flow path through the soil to the cup. (Buckingham *et al.*, 2008), which alters the natural flow path and the DOC concentration of soil. The discontinuous method requires a tension to be set at discrete intervals to collect a sample for a specific time period (Kindler *et al.* 2011). Advantages of this method are that it is cheaper to run, and that it does not disturb the natural soil water drainage by altering the pore dynamics as a continuous system does (Curley *et al.*, 2011). Tension collectors may not collect a representative sample of the free draining water. Buckingham *et al.* (2008), attributed the lower DOC concentration obtained in tension samplers compared to non tension samplers, to the sampling

of water in small soil pores. Further disadvantages include, possible sorption of minerals onto the porous surface and only point samples of the soil water, which may miss rapid drainage and large rainfall events (Grossmann & Udluft, 1991; Weihermüller *et al.*, 2007)

DOC is specifically adsorbed to metal hydroxides via its carboxyl and hydroxyl groups (Kaiser & Guggenberger, 2005) Many ceramic materials therefore sorb considerable quantities of DOM and are only suitable for determining DOC concentrations after a long period of equilibration (Guggenberger & Zech, 1992) and it is often advised that the first samples be discarded (Curley *et al.*, 2011) Sorption of organic and inorganic compounds onto suction cups has been extensively reviewed in the literature, (McGuire & Lowery, 1992; Weihermüller *et al.*, 2007; Fares *et al.*, 2009; Curley *et al.*, 2011) and many others. Therefore it is recommended that other material be used for suction cup, these can include, stainless steel, glass or Teflon suction cups. However these mediums are much more expensive.

Another issue that has been widely discussed is the use of glues and elastomers in the construction of suction cups, these contain solvents and plastics that are released into the sampled water and can increase the DOC concentration by up to 31 mg C L⁻¹. (Siemens & Kaupenjohann, 2003) therefore advise the construction of suction cups without glues or suction plates that do not require glues or solvents.

2.3.2 Suction plates

Suction plates are similar in operation to suction cups. The porous plate is inserted in the soil usually through a trench and collects soil water by either using a tension to draw a sample from the soil or a zero tension method, where saturated flow naturally percolates into the plate. Both of these methods have running disadvantages, in the tension method the plate is set to a constant tension, whereas the soil water matric potential is continually changing, therefore the plate will sometimes draw water from a greater area, changing the natural flow path of the water in the soil (Weihermüller *et al.*, 2007) On the other hand the zero tension

plate will not actively draw water in, so a saturated zone will form above the plate and will lead to flow of water away from the plate (Weihermüller *et al.*, 2007). The same issues apply to plates as suction cups in regards to sorption of inorganic and organic compounds, and like suction cups this can be overcome by selecting a different plate medium Siemens *et al.* (2003) recommends the use of a sintered boro-silicate glass suction plate when collecting samples for DOC analysis, as this reduces the potential contamination from glues and elastomers as well as reduces the effects of sorption that can arise when using ceramic samplers. In comparison to suction cups, plates can sample from a larger area, and the origin of the sampled water is better known (as they are a flat 2D surface) as water can only be sampled from above (Allaire *et al.*, 2009). However the use of suction plates is somewhat more expensive due to the installation effort and does not allow for the same sampling intensity spatially

2.3.3 Barrel Lysimeters .

Lysimeters are columns or tubes that contain soil, either disturbed or undisturbed soils. They can be installed in the field (Harrison *et al.*, 2008) over specially designed lysimeter pits, or they can be controlled in a glass house or laboratory (Ghani *et al.*, 2010). When installed in the field, conditions are as close to natural as attempted to be maintained, this is done by levelling the lysimeter with the natural ground surface and reducing the gap between the soil and the lysimeter to keep the lysimeter the same temperature. Solute is collected from the lysimeter base either through suction or through passive through flow. Passive flow uses gravity to draw water out, one disadvantage of this technique is that water pools at the bottom of the lysimeter, forming an aerobic zone where some degradation of the solute may occur (Weihermüller *et al.*, 2007). Suction lysimeters on the other hand are more expensive, they do however overcome the saturation issue, but like plates and cups interaction between the suction and the soil has been noted (Allaire *et al.*, 2009). One of the big setbacks of lysimeters is that they do not account for lateral flow and the boundary of the lysimeter can cause a fringe effect and preferential flow paths (Weihermüller *et al.*, 2007). While it is time consuming and often expensive to install lysimeters, they may be used for several years. Other advantages are that they monitor a relatively large surface area

compared to suction cups, and accurate water and mass balances can be made if the lysimeter is able to be weighed (Allaire *et al.*, 2009).

In summary, there is much evidence supporting the variation in DOC concentration with different sampling methods. This can be due to preferential sampling of pore spaces, ie. Suction samplers draw sample from small pores, whereas passive samplers are representative of the free flowing water in large pores (Buckingham *et al.*, 2008). Additionally they can both alter the natural drainage conditions, through preferential flow paths, and interrupting lateral flow. Unfortunately there is no commonly prescribed method, so it has to be accepted that some variation between samples will arise from the sampling method, and in the end it is cost, sampling intensity, and the main research question that will determine the best method.

2.4 DOC leaching

Values for DOC leaching are derived mainly from studies on temperate forest soils. Although somewhat less abundant, studies on temperate grasslands and cropped soils are also available and even fewer studies have been published on grazed pastures. DOC fluxes and concentrations sampled from a field can have considerable temporal and spatial variation (Zsolnay, 2003). This large variation in DOC across and within ecosystems, and the variation in soil C, needs to be considered when comparing fields from different locations. Consideration should also be taken when comparing doc leaching under different land uses, or when using or interpreting this data in the context of C budgets and management schemes. In this literature review, the emphasis is placed on grazed pasture systems, however, I will compare and contrast different land uses, and measurement approaches to show how DOC varies and why it is important to measure each different land use type.

The definition of DOC leaching in most contexts is the movement of DOC from the upper soil horizons to lower in the soil. Leaching can be measured in the soil at a number of different depths, however DOC leaching cannot always be counted

as a loss of C from the ecosystem, as beyond the extraction depth, DOC could be sorbed or desorbed from soil or mineralised to CO₂. (Siemens & Kaupenjohann, 2003)) looked at DOC leaching at different depths and found that there was a reduction in DOC concentration with depth. The reduction in DOC concentration with depth has been attributed to the sorption and mineralisation of DOC as it moves through the soil. Therefore most authors consider the loss of DOC at 0.9-1m depth represents the DOC export to leaching (Guggenberger & Kaiser, 2003). However even then there is the potential for immobilisation by sorption and mineralisation in the vadose zone.

2.4.1 Measurements of DOC flux

Riverine DOC fluxes have been used to determine the mass of C lost from the terrestrial ecosystem to the oceans when creating large scale C budgets (Schlünz & Schneider, 2000; Cole *et al.*, 2007). Hope *et al.* (1994) created an early literature review of C export in river waters across a range of ecosystems in North America, Europe, and New Zealand, and found that DOC export ranged between 10 and 100 kg C ha⁻¹ y⁻¹ for individual catchments. Three North American temperate grasslands were represented in the review with an average DOC loss of 3 kg C ha⁻¹ y⁻¹. (Alvarez-Cobelas *et al.*, 2012) expanded on this early literature review reporting dissolved organic carbon export from catchments worldwide to be between 2.1 kg C km⁻² yr⁻¹ and 92,474 kg C km⁻² yr⁻¹. Linking riverine C fluxes to the terrestrial ecosystem is difficult because the measurements are incorporated over the whole catchment integrating surface waters, aquifer water, as well often averaging across a number of ecosystems and land uses (Kindler *et al.* 2011). Additionally the internal cycling of DOC in rivers is not often considered, this may be problematic as rivers have their own internal production and consumption of DOC. Thus leaching data from soils is preferred. A literature review by Neff and Asner (2001) presented values for DOC fluxes from the soil and in streams across a range of ecosystems under grass or forest. DOC flux in soil ranged from 20 kg C ha⁻¹ y⁻¹ to 220 kg C ha⁻¹ y⁻¹ under eucalyptus forest and grass, 180 - 840 kg C ha⁻¹ y⁻¹ below a temperate evergreen forest, this compares to the 10 kg C ha⁻¹ y⁻¹ from the stream flux from the same temperate evergreen forest.

There is evidence that the loss of C leaching from soils changes with land use. Neff and Asner (2001) showed that on average DOC flux was greater under forested ecosystems compared to grasslands and croplands. This suggestion agrees with (Sanderman *et al.*, 2008), who measured leaching of DOC below a forest system to be greater than from grassland, with values of DOC leaching at a depth of 40 cm being $74 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ and $17 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ respectively. Another comparison by Kindler *et al.* (2011) looked at leaching losses of DOC from a forest, a grassland and a cropland, reporting little difference in the fluxes, with an annual loss of $35 \pm 13 \text{ kg C ha}^{-1} \text{ y}^{-1}$ for forests, $53 \pm 20 \text{ kg C ha}^{-1} \text{ y}^{-1}$ for grasslands, and $41 \pm 13 \text{ kg C ha}^{-1} \text{ y}^{-1}$ for croplands (mean \pm SE). However, most of these grassland ecosystems were considerably different to the grasslands in New Zealand. Many studies of DOC on grasslands including those by Kindler *et al.* (2011) and Sanderman & Amundson (2009) represent native and prairie grass ecosystems, making them not especially comparable to the intensively managed, grazed pastures that cover much of New Zealand.

Measurements of DOC loss from grazed pasture are rare. McTiernan *et al.* (2001) carried out an investigation into the flux of C leaching on a cattle farm in Devon, England over a period of two months. They found that total C flux varied between 42 and $118 \text{ kg C ha}^{-1} \text{ y}^{-1}$, with larger fluxes being found on soils that were not tile drained and which had received nitrogen fertiliser. Harrison *et al.* (2008) investigated DOC leaching from a grazed sheep farm in the UK, finding DOC fluxes ranging from $32 \text{ kg C ha}^{-1} \text{ y}^{-1}$ – $208 \text{ kg C ha}^{-1} \text{ y}^{-1}$.

As well as vegetation and land use, soil type and mineralogy can also be an important controlling factor when determining DOC leaching. Don and Schulze (2008) looked at DOC leaching from two contrasting soil types (Arenosol vs Vertisol) in an un-grazed grassland in Germany, they found that DOC leaching was negatively correlated to the clay content of the soil with the DOC leaching from the clay-poor Arenosol being $55 \text{ kg C ha}^{-1} \text{ y}^{-1}$, seven times larger than in the clay-rich Vertisol, $8 \text{ kg C ha}^{-1} \text{ y}^{-1}$. The lower leaching from the Vertisol was suggested to be because of retention of DOC on the clay minerals and higher mineralisation. As soils can vary on scales of less than a meter, comparisons

between measurements made across towns and even farms could have considerable differences.

2.4.2 Measurements of DOC flux in New Zealand

Compared to the measurements made across the globe, the numbers of studies measuring DOC leaching in New Zealand are low. However, there has been a greater focus on managed grazed pastures, and the local proximity of the study means that many of the controlling variables including climate have been the same or similar. Parfit *et al.* (2009) measured DOC leaching on two uphill grazed sheep pastures in Taranaki New Zealand, one pasture had no nitrogen input and the other high N input. DOC flux was $228 \text{ kg C ha}^{-1} \text{ y}^{-1}$ and $121 \text{ kg C ha}^{-1} \text{ y}^{-1}$ respectively. Sparling *et al.* (2006) looked at the changes in four different soils following irrigation with secondary treated municipal waste; these results were compared to control soils without effluent irrigation. As part of the study, a number of leached products were measured across the control sites including total organic C. The results of the unirrigated soils showed Recent soils leached the greatest C with $219 \text{ kg C ha}^{-1} \text{ y}^{-1}$, followed by Gley ($51.5 \text{ kg C ha}^{-1} \text{ y}^{-1}$), Pumice ($21.5 \text{ kg C ha}^{-1} \text{ y}^{-1}$) and Allophanic soils ($9.23 \text{ kg C ha}^{-1} \text{ y}^{-1}$).

Ghani *et al.* (2010) undertook a DOC leaching investigation of six pastoral soils in New Zealand. Soil cores were taken from the field placed in a growth chamber and flushed with water to force leaching. DOC leaching from these cores was between 280 and $1690 \text{ kg C ha}^{-1} \text{ yr}^{-1}$. These values were higher than other values in the literature which is likely due to the nature of the experiment. In this same study, Ghani *et al.* (2010) found that DOC leaching was greatest from the Gley soils compared to Allophanic soils. These studies (Ghani *et al.* 2010, Parfit *et al.* 2009, Sparling *et al.* 2006) provide evidence that DOC may be an important loss of C when creating a C budget.

Table 2.1: Values for DOC leaching across a range of studies and vegetation types.

Land use	site	Soil description	average annual rainfall (mm)	average annual temperature (C)	sampling method	Depth measured in soil (m)	DOC flux (kg C ha ⁻¹ yr ⁻¹)	Author
Grasslands								
Unspecified	Mehrsted, Germany	Clay rich Vertisol	547	8	Suction plate	0.65-0.11	8	Don & Shulze (2008)
Unspecified	Kallenborn, Germany	Clay poor Arenesol	566	7.8	Suction plate	0.65-0.11	55	Don & Shulze (2008)
Dairy Grazing, Perennial rye grass clover	Waikato-Taranaki, New Zealand	Rawerawe (Gley)	1320*	14.7*	intact soil column (Laboratory)	0.25	1692	Ghani <i>et al.</i> (2010)
Dairy Grazing, Perennial rye grass clover	Waikato-Taranaki, New Zealand	Te Kowhai (Gley)	1135*	12.5*	intact soil column (Laboratory)	0.25	943	Ghani <i>et al.</i> (2010)
Dairy Grazing, Perennial rye grass clover	Waikato-Taranaki, New Zealand	Bruntwood (Allophanic)	1135*	13.8*	intact soil column (Laboratory)	0.25	281	Ghani <i>et al.</i> (2010)
Dairy Grazing, Perennial rye grass clover	Waikato-Taranaki, New Zealand	Lepperton (Allophanic)	1465*	13.7*	intact soil column (Laboratory)	0.25	56	Ghani <i>et al.</i> (2010)
Dairy Grazing, Perennial rye grass clover	Waikato-Taranaki, New Zealand	Awatuna (Allophanic)	1560*	12.5*	intact soil column (Laboratory)	0.25	445	Ghani <i>et al.</i> (2010)

Dairy Grazing, Perennial rye grass clover	Waikato- Taranaki, New Zealand	Glenn (Allophanic)	1465*	13.7*	intact soil column (Laboratory)	0.25	561	Ghani <i>et al.</i> (2010)
Upland Sheep grazing	Control site:Great Dunn fell, Morelands UK	Brown earth	1451	3.56	suction plate	0.28	34.5	Harrison <i>et al.</i> (2009)
Upland Sheep grazing	Control site:Great Dunn fell, Morelands UK	Acid brown soil micropodzol	1451	3.56	suction plate	0.28	14.8	Harrison <i>et al.</i> (2009)
Upland Sheep grazing	Control site:Great Dunn fell, Morelands UK	Peaty gley	1451	3.56	suction plate	0.28	221.6	Harrison <i>et al.</i> (2009)
Intensive and extensive grazing	Laqueuille (France)	Andosol (silt loam)	1757	6.6	Glass suction cups	0.9	11	Kindler <i>et al.</i> (2011)
Unspecified	Carlow (Ireland)	calcic Luvisol (sandy loam)	2236	9.4	Glass suction cups	0.65	33	Kindler <i>et al.</i> (2011)
Unspecified	Easter Bush (Scotland)	Gleyic Cambrisol (sandy loam) Endogleyic Cambrisol	966	8.1	Glass suction cups	1.0	87	Kindler <i>et al.</i> (2011)
Unspecified	Fruebuel (Switzerland)	(Loamy clay)	2178	6.6	Glass suction cups	1.0	76	Kindler <i>et al.</i> (2011)
Cattle grazed Mixed grassland, High nitrogen undrained	Rowden Moor, Devon, England	Dystric Gleysol (clayey)	373	ND	Drained lysimeters	0.55-0.85	118**	McTiernan <i>et al.</i> (2001)
Cattle grazed Mixed grassland High, nitrogen drained	Rowden Moor, Devon, England	Dystric Gleysol (clayey)	373	ND	Drained lysimeters	0.55-0.85	42**	McTiernan <i>et al.</i> (2001)
Cattle grazed grass clover, organic N Undrained	Rowden Moor, Devon, England	Dystric Gleysol (clayey)	373	ND	Drained lysimeters	0.55-0.85	72**	McTiernan <i>et al.</i> (2001)

Cattle grazed grass clover, Organic N Drained	Rowden Moor, Devon, England	Dystric Gleysol (clayey)	373	ND	Drained lysimeters	0.55-0.85	42**	McTiernan <i>et al.</i> (2001)
Cattle grazed Mixed grassland, Zero nitrogen undrained	Rowden Moor, Devon, England	Dystric Gleysol (clayey)	373	ND	Drained lysimeters	0.55-0.85	56**	McTiernan <i>et al.</i> (2001)
Cattle grazed Mixed grassland, Zero nitrogen drained	Rowden Moor, Devon, England	Dystric Gleysol (clayey)	373	ND	Drained lysimeters	0.55-0.85	61**	McTiernan <i>et al.</i> (2001)
Hill country, sheep grazed farmlet	Ballantrae, NZ	ND	1200		Suction cup sampler and continuous suction cup	0.2 -0.5	228	Parfitt <i>et al.</i> , (2009)
Hill country, sheep grazed farmlet	Ballantrae, NZ	ND	1200		Suction cup sampler and continuous suction cup	0.2 -0.5	121	Parfitt <i>et al.</i> , (2009)
European annual grass and native perennial grass	Northern California, USA	Typic Haplustolls			Ceramic cup and Super quartz tension lysimeter	0.50	17	Sanderman &Amundson (2009)
European annual grass and native perennial grass	Northern California, USA	Typic Haplustolls			Ceramic cup and, Super quartz tension lysimeter	0.65	10	Sanderman Sanderman &Amundson
Upland Grasslands	Great Dunn fell, Morelands UK	Brown earth	3375	8.1	Barrel lysimeter	0.28	27.6	Tipping <i>et al.</i> , (1999)
Upland Grasslands	Great Dunn fell, Morelands UK	Micropodzol	3375	8.1	Barrel lysimeter	0.28	170	Tipping <i>et al.</i> , (1999)
Upland Grasslands	Great Dunn fell, Morelands UK	Peaty gley	3375	8.1	Barrel lysimeter	0.28	926	Tipping <i>et al.</i> , (1999)

Forests	site	Soil description	average annual rainfall (mm)	average annual temperature (C)	sampling method	Depth measured in soil (m)	DOC flux (kg C ha ⁻¹ yr ⁻¹)	Author
Beech forest	Hainich (Germany)	Cambrisol (loamy clay)	1363	7.6	Glass suction cups	75	26	Kindler <i>et al</i> (2011)
Beech forest	Soro (Denmark)	Stagnic Luvisol (loamy sand)	1345	8.2	Glass suction cups	100	83	Kindler <i>et al</i> (2011)
Spruce forest	Laois (Ireland	Stagnosolo (clay)	2594	9.1	Glass suction cups	70	6	Kindler <i>et al</i> (2011)
Pine forest	Loobos (Netherlands)	Haplic Arenosol (sand)	1452	9.5	Glass suction cups	120	22	Kindler <i>et al</i> (2011)
Spruce forest	wetzstein (Germany)	Podzol (sandy loam)	1358	5.6	Glass suction cups	90	47	Kindler <i>et al</i> (2011)
15yo White pine forest	Southern Ontario, Canada	Fine sandy. Brunisolic luvisol	1010	7.8	Porous suction cup sampler	100	23	Peichel <i>et al</i> (2007)
15 y o White pine forest	Southern Ontario, Canada	Fine sandy. Brunisolic luvisol	1010	7.8	Porous suction cup sampler	25	142	Peichel <i>et al</i> (2007)
15 y o White pine forest	Southern Ontario, Canada	Fine sandy. Brunisolic luvisol	1010	7.8	Porous suction cup sampler	50	37	Peichel <i>et al</i> (2007)
Redwood Douglas fir 100 y o	California	Typic Haplustolls			Ceramic cup tensiometer, Super quartz tension lysimeter	55	74	Sanderman and Amundson (2009)
Redwood Douglas fir 100 y o	California	Typic Haplustolls			Ceramic cup tensiometer, Super quartz tension lysimeter	75	10	Sanderman and Amundson (2000)

Cropping	site	Soil description	average annual rainfall (mm)	average annual temperature (C)	sampling method	Depth measured in soil (m)	DOC flux (kg C ha⁻¹ yr⁻¹)	Author
Unspecified	Grignon (France)	Calcaric Cambrisol (Silt loam)	1027	9.9	Glass suction cups	90	28	Kindler <i>et al</i> (2011)
Unspecified	Klingenberg (Germany)	Stagnosol (Silt loam)	1307	7.1	Glass suction cups	75	53	Kindler <i>et al</i> (2011)
Other	site	Soil description	average annual rainfall (mm)	average annual temperature (C)	sampling method	Depth measured in soil (m)	DOC flux (kg C ha⁻¹ yr⁻¹)	Author
Cultivated land left bare (bare soil)		Orthic Luvisol (silt)			Automatic equilibrium tension plate lysimeters	40	49	Mertens <i>et al</i> (2007)
bare soil 10 years	Merzenhausen, Germany	Orthic Luvisol (silt)	689	9.5	Automatic equilibrium tension plate lysimeters	120	24	Mertens et al (2007)

*Experiment carried out in laboratory conditions, with temperatures between 4 and 24 °C and artificial water input.

** Study was conducted over two month period (DOC flux is in units of g C m⁻² two months⁻¹)

2.5 Controls on DOC leaching

Although DOC can be produced from simple leaching of organic materials from root exudates, microbial biomass or recent litter (Kalbitz & Kaiser, 2008), microbial activity is important, both in the uptake from and release to the soil solution of DOC. Microbes contribute to the production of enzymes leading to organic matter breakdown and the processing of humus in the vadose zone (Moore *et al.*, 2008). The proportion of DOC originating from each process is still not fully understood, and the majority of published literature concerns forest soils, which makes it difficult to extrapolate findings to grassed pastures. While some debate that much of the DOC in the subsoil originates from the subsoil its self (Michalzik *et al.*, 2003) and only through preferential flow paths can surface soil DOC directly reach the subsoil (Kaiser & Guggenberger, 2005; Fröberg *et al.*, 2007), others have found that DOC production in the surface horizons is the driving control of DOC leaching (Qualls & Haines 1992). Understanding the proportion of DOC that each process contributes to total DOC leachate can develop understanding about the internal cycling and turnover of C in soils.

2.5.1 Internal cycling

The concentration of DOC in soils is the net result of processes that release and remove DOC from the soil. DOC is removed from soil through adsorption or decomposition by microbes (Figure 2.1). These processes are in turn dependent on internal soil conditions and environmental controls. The primary influence on the flux of DOC within soils is the rate at which DOC is produced and several studies have examined the controls on DOC production (Kalbitz *et al.*, 2000). Laboratory incubations of litter and soils have revealed the influence of the following on DOC production: temperature (Moore & Dalva 2001), soil pH (Andersson *et al.*, 2000), C/N ratio, amount and quality of substrate (Don & Kalbitz, 2005; More & Dalva, 2001), frequency and rate of leaching, oxygenation of the soil, and the microbial biomass/community. Similar influences determine the mineralisation of DOC from soil, with temperature, moisture and the chemical and physical soil properties having the largest influence (See sections 1.2.1 to 1.2.3).

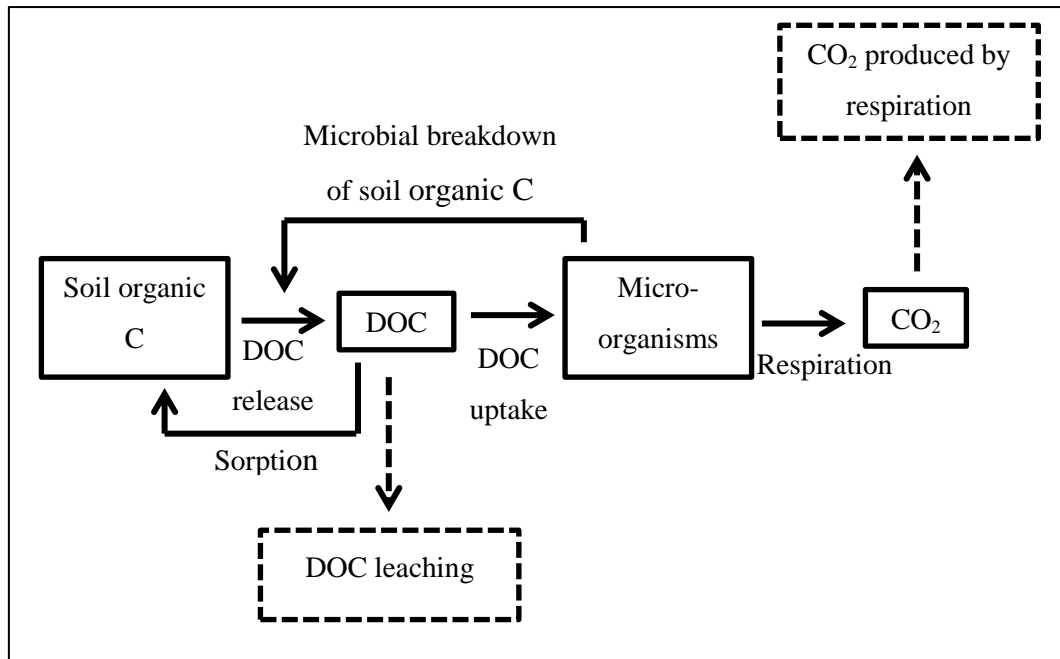


Figure 2.1: Cycling of DOC in soil. Solid lines represent internal transformations, and dashed lines represent losses of C from the system. Figure adapted from Moore *et al.* (2008).

The fate of DOC leached from the surface soil can follow one of three pathways: leaching to the groundwater, mineralisation to CO₂, or sorption and storage in the soil (Figure 2.1). The breakdown of DOC in the soil can be large (Kalbitz *et al.*, 2000; Qualls, 2004), so that much of the DOC produced can be rapidly consumed, being incorporated into microbial tissue, released as CO₂, or sorbed onto soil surfaces. Laboratory experiments typically indicate that most mineral soils have high tendency to adsorb DOC (Kaiser & Guggenburger, 2003). Mineralisation can also be an important pathway of DOC removal, however it usually proceeds at much slower rates than sorption. Qualls and Haines (1992) investigated mineralisation in a forest soil core and found that within 134 days 14-33% of the DOC that was added was decomposed. Also mineralisation is particularly important as DOC can be both created and destroyed by microbes. However, much of the focus of DOC removal surrounds sorption.

(Kaiser & Zech, 2000) showed that 60-90% of DOC added was retained in the soil by mineral horizons within minutes of addition to the soil. Sanderman and Amundson (2009), observed that recently sorbed DOC did not readily desorb back into the DOC pool, and that the bioavailability of DOC in subsoil was low with a

large fraction of DOC having a mean residence time of years to decades. Additionally, Kalbitz *et al.* (2003) created a model which showed that 94% of the DOC leached from a forest floor was stable and had a half-life of 8.6 years. The type of DOC sorbing to soil is also important to bioavailability and its sportive stabilisation. Marschner and Kalbitz (2003) detected that the fraction of DOC in soils that was preferentially adsorbed was the more recalcitrant hydrophobic fraction, thus making it harder to break down. In addition, Fontaine *et al.* (2007) found that much of the DOC sorbed at depth was retained for longer periods, as it bound to soil in a form that microbes cannot access. However, additions of fresh DOC to subsoils can result in priming, where more recalcitrant stores of DOC can be degraded (Fontaine *et al.*, 2007).

In general, when DOC is leached is expected that mineralisation and sorption will make up a greater proportion of the internal cycling than leaching to the groundwater. Kindler *et al.*, (2011) measured a leaching loss of $19 \text{ g C m}^{-2} \text{ yr}^{-1}$ (DIC and DOC) with a concentration of 27 mg L^{-1} but found that due to internal cycling processes the amount reaching the water table and lost to aquifers was often less than 5 mg L^{-1} . Assuming a ground water recharge of $95\text{--}652 \text{ mm yr}^{-1}$ the contribution of DOC to the groundwater is only a small flux ($0.5\text{--}3.3 \text{ g DOC m}^{-2} \text{ yr}^{-1}$), which means about 1-5% of the total surface leachate reached the ground water table. Identification of which process is dominant and the relative proportions of each is critical to developing a C budget for ecosystems.

2.6 Sorption

DOC transport into lower soil horizons where decomposition proceeds at much lower rates (Fontaine *et al.*, 2007) represents a potential way to stabilise and store large quantities of C for a large period of time (Sanderman & Amundson, 2009). Where sorptive retention of DOC occurs, it contributes to carbon accumulation in subsoils by stabilising DOC and preventing mineralisation (Kalbitz & Kaiser, 2008). Values for the amount of DOC contributing to the soil C pool in the vadose zone vary between ecosystem studies; for example, Kalbitz *et al.* (2003) found that 22% of the mineral C stock under a coniferous forest could be attributed to DOC leaching and sorption onto mineral surfaces. Neff and Asner (2001) found a

similar value, attributing 25% of the mineral C stock to stabilisation of DOC. (Sanderman & Amundson, 2009) found that 22% of C inputs below 40 cm soil depth in a coniferous forest could be attributed to the transport and retention of DOC, whereas in the grassland 14% of the C found in the profile below 20 cm was derived from DOC. In Laboratory experiments, the sorption capacity of soils is often high, with many studies finding strong correlation with sorption and the mineral makeup of the soil. The proportion of DOC sorbed in a laboratory experiment by Sanderman & Amundson, (2008) showed that 43-72% of added DOC was retained in soils, and a strong correlation was found with the soil alumina and iron content.

Several studies have shown that DOC concentrations in soil solutions decrease significantly with soil depth and that sorption of DOC to mineral surfaces is more important than the decomposition of DOC (Kalbitz *et al.*, 2000). Tipping *et al.* (1999) showed that the leaching of DOC is greatly affected by the sorption of DOC to mineral horizons. Storage or sorption on to soil surfaces controls the amount of DOC leaching: in the B horizon, sorption onto soil colloids can prevent the DOC moving into deeper soil layers and being leached (Kindler *et al.*, 2011). DOC leaving the B horizon of forest soils have been found to be two orders of magnitude lower than the DOC leaving the O horizon (Michalzik *et al.*, 2001; Neff & Asner, 2001) indicating a high affinity of mineral horizons to sorb DOC. The rate of sorption was thought to decrease with depth but has been found to be constant. (Sanderman *et al.*, 2008) observed that the concentration of DOC in soil water was reduced with depth and this has been attributed to on-going sorption in the soil. Peichl *et al.* (2007) measured the concentration of DOC at different intervals down the soil profile, and results from this study show that the concentration of DOC decreased with depth in the soil profile to values less than 15 mg L⁻¹ at 50 cm depth; however, at 100 cm depth the concentration was slightly higher. Peichel *et al.* (2007) attributed this decrease to sorption of DOC in the soil, and determined that maximum sorption capacity of the soil was reached at 50 cm depth.

2.6.1 Controls on sorption

The effect of mineral surfaces and horizons within the soil and the effects they have on the DOC leaching have been looked at in a number of studies. Don and Schulze (2008) suggest that the high clay content of the mineral horizons promotes DOC adsorption and thus DOC retention. Specifically it has been found in numerous laboratory studies that sorption is strongly positively correlated to the concentration of oxalate extractable iron and aluminium in soil (McDowell & Likens, 1988; Kaiser *et al.*, 1996; Kaiser & Guggenberger, 2000; Kaiser & Guggenberger, 2003; Sanderman & Amundson, 2009; Schneider *et al.*, 2010) and is potentially more important than the total clay content (Kothawala *et al.*, 2008). Oxalate-extractable iron and aluminium are a measure of the concentration of poorly crystalline iron and aluminium oxides that have a high specific surface area in soils (Kindler *et al.*, 2011). The sorption of DOC to soils also depends on the type of DOC compounds (Jagadamma *et al.*, 2012). DOC can be bound to soil by different mechanisms, the process of ligand exchange is especially important when binding DOC to Al and Fe (Guggenberger & Kaiser, 2000).

In general, hydrophobic DOC compounds are more preferentially adsorbed than hydrophilic compounds (Jagadamma, 2012), and it is generally assumed that sorption of hydrophobic compounds is irreversible (Kaiser & Zech, 2000) or remain stable for long periods of time (Guggenberger & Kaiser, 2003). The amount of C sorbing to soil is not infinite, but increases with the number of sorption sites including Fe and Al oxides. However, laboratory studies have found a decrease in the sorption capacity of soils when the solution added had a high pH. pH affects the charge of soil sorption sites and their capacity to retain C and adsorb C (Schneider *et al.*, 2010). Sorption was also lower when there were high sodium and calcium ions in solution. Sodium and calcium can preferentially adsorb to soil microsites and cause the displacement of sorbed organic ions including C (Reemtsma *et al.*, 1999).

Mineralisation

Soil mineralisation is the production of CO₂ from the breakdown of C rich soil organic matter. C which is broken down from plant matter combines with oxygen to produce CO₂ and energy that is used for growth. The term mineralisation is often used and refers to the breakdown of SOM where some of the nutrients are converted to a mineral form of which CO₂ is a by-product, released through respiration. DOC can be broken down by microbes in the soil into CO₂ and released to the atmosphere before it is leached to the lower horizons or the ground water. DOC is a highly bioavailable fraction of C in soils and is therefore readily broken down by microbes (Kalbitz *et al.*, 2000). However sorption and stabilisation in soil usually occurs much faster, than mineralisation often preventing direct breakdown of leached DOC material. Lambie *et al.* (2012) concluded that DOC in soil was a more bioavailable source of C than urine and also suggested that it may lead to priming in soils. Fontaine *et al.* (2007) observed greater mineralisation of C in subsoils following inoculation with fresh DOC, and concluded that near the surface the availability of fresh C is higher which provides a greater energy source for the microbes to decompose other recalcitrant C. Alternatively, in the lower soil profile C is older, and there is little available C to provide energy for mineralisation of the older organic C; however, when DOC is added it causes an increase in the breakdown of ancient C.

2.6.1 Temperature and hydrological controls

The breakdown of organic matter is a chemical reaction, and like all chemical reactions is subject to temperature control (Davidson *et al.*, 2006). Soil respiration has been shown to increase with increasing temperature (Fang & Moncrieff, 2001; Lloyd & Taylor, 1994), so at optimum temperatures more CO₂ is produced. As well as removing DOC from the soil as CO₂, mineralisation is also responsible for the production of DOC in soil through the break down soil organic carbon (SOC). Numerous studies have reported higher concentrations of DOC in summer; this is assumed to be evidence for a greater production of DOC by microbes (McDowell & Likens, 1988). The relationship between respiration and temperature is known to be affected by the moisture content (Lloyd & Taylor, 1994; Fang & Moncreif,

2001; Davidson & Janssen, 2006). In the field there are many contrasting variables including moisture content, soil mineralogy and other soil properties that are likely to influence the production of DOC and the subsequent mineralisation and leaching. Harrison *et al.* (2008) manipulated soil temperature, rainfall and solar radiation in the field and showed that the effect of temperature on DOC leaching was not strong and that leaching was more dependent on the volume of water being leached through the soil.

A number of studies have shown that the concentration of DOC leaching from a soil is strongly related to the volume of rainfall (Harrison *et al.*, 2008; Mertens *et al.*, 2007; Don & Schulze, 2008). Harrison *et al.* (2008) showed that DOC release increased with increasing rainfall in the month of measurement. However, they also found that rainfall in the previous month was negatively correlated with DOC release, with high rainfall levels leading to reduced DOC release. Harrison *et al.* (2008) concluded that the amount of DOC available for leaching is limited, and can be exhausted with higher rainfall and greater water leaching, and that DOC released to the soil for leaching must be slow. During the dry summer months, Mertens *et al.* (2007) showed that there was very little DOC leachate due to the low rainfall and high evaporation preventing the transport of DOC. However, due to lack of dilution the concentration of the leached material was relatively high. This study also showed that the concentration of DOC leachate was highest immediately after rainfall following a dry period, which was attributed to an accumulation of DOC in soil from microbiological detritus during dry periods. In contrast to this, Peichel *et al.* (2007) found no dilution effect of DOC concentration resulting from increased rainfall. This is thought to be due to the predominantly sandy texture of the soils, which have a high proportion of macropores, and may not allow much contact time between sorbed C and water during either heavy or low rainfall periods.

The idea that C and water need to have some extended amount of contact before the C becomes dissolved has been put forward in a number of studies: McTiernan *et al.* (2001) found that DOC leaching was lowest when soil water through flow was rapid, as the speed of the water prevented sufficient contact time between DOC (sorbed onto soil) and water to allow for the DOC to be leached. Therefore

the movement of water through the soil is closely linked to the soil pore space distribution and soil composition. Micropores will retain water longer and allow for greater contact time between compounds and water (Zsomsay *et al.*, 2003).

Pore size and structure of the soil is also important when looking at rates of mineralisation. Buckingham *et al.* (2008) hypothesised that higher DOC concentrations were found in larger pore spaces due to the higher oxygenation and greater rate of DOC production by microbes. Interception of organic material by microbial communities may also prevent higher concentrations of DOC in smaller pores or sorption. (Killham *et al.*, 1993) proposed that microbes on the surface of macroaggregates can intercept most soluble DOC diffusing through the soil, and thus prevent it reaching smaller micropores. In contrast, Mertens *et al.* (2007) found the concentration of DOC in soil to be limited by the water draining in the soil, as the maximum net DOC mobilisation rate in the topsoil was limited. Mertens *et al.* (2007) measured DOC flux at 0.4 m and 1.2 m below a bare agricultural soil in Germany. Annual average DOC fluxes were $4.9 \text{ g C m}^{-2} \text{ yr}^{-1}$ at 0.4 m and $2.4 \text{ g C m}^{-2} \text{ yr}^{-1}$ at 1.2 m depth, with variability in the flux throughout the year arising from differences in leachate volume and speed of water movement, rather than DOC concentration, which remained near constant.

To support this, Kalbitz *et al.* (2000) proposed that low leachate velocities are required to obtain high DOC concentrations. The rate of water movement was found to be correlated with DOC concentration in a study by Münch *et al.* (2002), who found that as the rate of water movement increased, the concentration of DOC in solution decreased due to the reduced solubilisation of C. As water in smaller pore spaces is relatively stable and stored for a long periods of time, it is assumed that smaller pore water stores would have higher concentrations of DOC. However it has also been shown that a wet dry process can produce large amounts of DOC (Lundquist *et al.*, 1999). Drying is known to produce large amounts of water soluble neutral organic matter through the lysis of microbial cells (Christ & David, 1996). This material is highly soluble and can be readily leached when wet (Kaiser & Zech, 1999)

2.6.2 Soil management

2.6.2.1 Nitrogen

As previously mentioned, there are many factors that control the rate of DOC leaching from soils. Kindler *et al.* (2011) investigated the effects of nitrogen in the soil and the C:N ratio of the soil, and found a positive correlation between the C:N ratio and the DOC flux in terrestrial ecosystems. They concluded that DOC leaching from topsoils only occurred when a critical C:N ratio was exceeded, and suggest that above a C/N ratio of eight, there were increasing amounts of soluble C produced. McTiernan *et al.* (2001) also found that increased N inputs increased concentration of DOC leachate and attributed this to increased dry matter production, with a greater dry matter production contributing to a greater amount soluble C produced. Nitrogen inputs also lowered the C:N ratio thus affecting the turnover of organic matter and the contribution of DOC to the soil.

These results are in contrast to Parfit *et al.* (2005) who measured DOC leaching loss between a high input and a low input N fertiliser system. DOC leaching was found to be highest below the low N system which had a DOC: DON ratio of 54 and lowest under the high N input system with a DOC:DON ratio of 16. This was explained in the composition of the DOC, with higher ratios indicating the presence of the more hydrophobic fraction of DOC which is known to readily adsorb to soil mineral surfaces and thus would contribute to a reduced DOC leaching concentration (Marschner & Kalbitz, 2003; Müller *et al.*, 2009).

The average C:N ratio of a typical dairy soil is around 11 (Stevenson *et al.*, 2011). Dairy pastures are characterised by high inputs of N (in the form of urea) equivalent of up to 1000 kg N ha⁻¹ (Di & Cameron, 2002). Furthermore, grazing and grazing intensity can redistribute and cycle N much more rapidly. More information is required about cycling of C and N in dairy pastures. The links between the readily available soil organic C and N fractions need to be established, as well as an increased understanding of the role of microbes, in order to provide a better understanding of C and N dynamics in pastoral soils.

2.6.2.2 *Grazing and urine*

Additions of fertilisers, manures and effluent as well as grazing animals can influence the soil DOC flux in grazed pastures. As well as adding N to the soil, urine also adds large amounts of C. Lambie *et al.* (2011) concluded that a single urine deposition could increase soil C leaching from undisturbed soil cores by up to 10 times that of water-treated soil. While urine in leachate can reach depths up to 0.4 m (Williams & Haynes, 1997). Lambie *et al.* (2011) concluded that the urine caused dissolution of stored soil organic C, potentially due to the high salt content and high pH of urine (Chandra *et al.*, 2002). Urine can however also induce greater soil mineralisation, and additions of urine C may also lead to priming of soil C lower in the profile (Fontaine *et al.*, 2007). The effect of urine on DOC leaching would benefit from further in-field testing.

In summary there are numerous drivers of DOC production, leaching and internal cycling. While there is some literature surrounding these processes, they do not always agree. Additionally much of the work surrounding controls of DOC production and cycling has been carried out in laboratory investigations, without field validation. More often than not the same strong relationship found in the laboratory does not translate to the same strong relationship in the field (Harrison *et al.*, 2008). Also a large proportion of the studies looking at DOC production and cycling, has been surrounding forest soils. Therefore interpretation and extrapolation to grassed ecosystems is difficult. As grasslands make up 25% of the global ice free surface (FAOSTAT 2011), and are a valuable food producing ecosystem, it would be expected that a greater portion of the literature would focus on understanding the soil C cycle including DOC. In future a greater research effort should be directed towards grasslands, particularly grazed pastures.

3 Methods

3.1 Introduction

The focus of this study was to determine whether DOC leaching was an important component of a carbon budget for a typical dairy farm. To measure the DOC leaching, water draining from the soil was collected and analysed for dissolved organic carbon. Outlined below is the general methodology used for this research question.

- Soil water was sampled using ceramic suction cup lysimeters installed at 0.65 m
- DOC and TN concentrations were then determined by analysis on Shimazu TOC analyser
- The mass of DOC leaching was calculated by multiplying the concentration of DOC by the amount of water draining
- The below ground DOC cycle was then investigated by sampling the four main soils at 65 cm and a) measuring the sorption by shaking the soil with DOC solution and b) measuring mineralisation by incubating soils spiked with DOC and measuring the concentration of the carbon respired.

This chapter provides full detail of the methods used in this thesis. These methods are also summarised in Chapter 4. The methodology in chapter 4 is provided in a format more appropriate to a journal paper. Due to this there is some repetition between Chapter 3 and the methods section of Chapter 4.

3.2 Site description

This study was conducted on a dairy farm located 3 km east of the Waikato Township, Waharoa, in the North Island of New Zealand (Figure 3.1). The farm grazes two herds of dairy cows (total 690 cows) on 207.4 hectares at an approximate intensity of 3.3 cows per hectare on a predominantly rye grass and

clover sward. The nearest climate station is 13 km to the south west near Matamata where the 30 year (1981-2010) mean annual temperature and rainfall are 13.3°C and 1249 mm respectively (NIWA). The measurements for this study were made on a small subset of the farm. Two locations at the furthest eastern point of the farm were chosen due to their flatness and scarcity of trees. The two sites were equipped with Eddy covariance towers to measure the surface carbon exchange (as part of wider study for a dairy farm carbon balance). Evaporation, rainfall, soil tension, radiation and humidity were also measured at each site. Site 1 was made up two paddocks measuring 3.08 ha and 3 ha. Site 2 was made up of four paddocks, however, due to the Eddy co-variance measurements being made over a very small part of one of these paddocks, DOC measurements were made in only three paddocks. Paddock 36 measured 2.61 hectares, paddock 33: 2.41 ha and paddock 34: 2.68 ha. The sampling site was made up of a complex of four soils, the Waihou soil, Piarere soil, Te Puninga soil, and Waitoa soil (Figure 3.2) ranging from well drained to poorly drained.

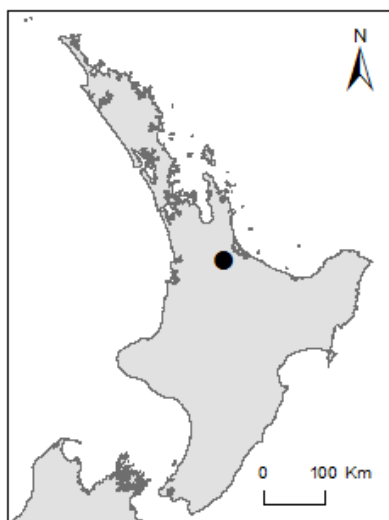


Figure 3.1: Map of the North Island of New Zealand, showing the sampling location (black dot) in Waharoa.



Figure 3.2: Map of farm sampling sites, showing the EC tower, soil pattern, and suction cup installation locations.

3.3 Soils

Waitoa silt loam is a Typic Orthic Gley Soil and makes up the majority of paddock 36. The soil is poorly drained and has a high clay content. Waihou silt loam is a Typic Orthic Allophanic soil, it is found in the top right corner of Paddock 32 and some of paddock 31. The soil has dark topsoil, and a characteristically dark yellowish brown B horizon which is very deep, the soil is also very friable and well drained. The Te Puinga silt loam is a Mottled Orthic Allophanic soil and makes up the majority of paddock 33 and most of 34. The soil has a similar A and upper B horizon as Waihou, however, the deeper B horizon is gley and grey, which causes this soil to be poor-moderately drained. The Piarere silt loam is Typic Orthic Allophanic soil, this soil is found in paddocks 31 and 34, in the higher parts of the paddocks. The soil has a deep A horizon and deep dark B horizons, it differs from the Waihou soil in B horizon colour which is more yellow, and the dark colour is not as deep with light brown colours around 65 cm, and is moderately well drained.

3.4 Samplers

Ceramic suction cup lysimeters were used to collect subsoil water samples. The lysimeter were made of a 60 mm diameter, 70 mm length rounded end, porous ceramic suction cup attached to 450 mm long 60 mm diameter pvc tube. The tube was attached to the ceramic cup by heating and expanding the pvc pipe to which the cup was then forced into, in order to get the best contact between the surfaces and prevent air leaks. The top of the pvc tube was stoppered with a rubber bung which had two 30 mm, 5 mm diameter pvc tubes protruding, one tube extended into the ceramic cup and was used to sample the solution while the other only extended inside the lysimeter 20 mm and is used to apply the suction (Figure 3.3).



Figure 3.3: Picture of ceramic suction cups installed in the field, showing the two pvc tubes the rubber bung and the pvc housing. Lysimeters extended to 0.65 m below the soil surface.

3.5 Sampler installation

100 suction cups were used to sample across the 5 paddocks. Suction cups were housed in groups of four with five groups installed in each paddock. The five paddocks were used as sampling replicates. The location of each group of lysimeters in each paddock was determined based on a stratified random approach with paddocks stratified by soil type (Figure 3.2).

The lysimeters were installed at an angle of 45° from a pit 300 mm below the surface. The holes for the lysimeters were created using a 60 mm diameter auger. To ensure adequate contact between the soil and the suction cup, soil was collected from the bottom of the auger hole, formed into slurry and poured back down the hole before the lysimeters were pushed in. To prevent tubing from being compressed by soil and causing issues with sampling, the lysimeters were left protruding into the 300 mm housing. Due to this the depth to at which the porous cup reached was 650 mm and subsequently this was the sample depth. To protect the tubing and lysimeters from falling soil, a 400 mm by 300mm pvc drainage pipe was placed around the edge of the pit. The pit was then covered with a 25

mm plywood lid pegged into the ground on all four corners to allow cows and farm vehicles to move across.

3.6 Sample collection and analysis

Samples were collected from late April through to the end of October. Sampling time was dictated by soil moisture content with samples collected when soil moisture content exceeded field capacity and leaching was predicted, however, samples were collected no more than twice a month. Samples were drawn into the porous cup through suction. A suction of 30 kPa was applied to the lysimeters using a 60 mL syringe that attached to three way stopcock at the end of the small pvc tube (Figure 3.4)



Figure 3.4: Suction being applied to the suction cup lysimeter following rainfall.

Samples were collected from the lysimeters 24-48 hours after the suction was applied using a 60 mL syringe and stopcock set up attached to the sampling tube. Sample (10 mL) was collected from each of the lysimeters in a paddock and bulked together by paddock. Two times during the sampling period (9 July 2012 and 12 September 2012) samples were bulked per group of suction cups (5 samples per paddock) in order to determine the variation due to the soil order. Also on the 9 July 2012 and 12 September 2012 every individual suction cup in

paddocks 32 and 36 (chosen randomly) were sampled to determine the local variation between cups and the standard error. Any excess sample collected from the lysimeters was discarded or bulked for laboratory experiments. Additionally, the first sample collected from each lysimeter after instillation was discarded, as suggested in the literature (Curley *et al.*, 2011).

Samples were collected into 150 mL Schott bottles and were stored on ice for the duration of time in the field and at 4 °C in a fridge prior to filtering. Samples were filtered using Whatman 45 µm cellulose nitrate 250 mm capsule filters.

The concentration of DOC was measured on a total carbon analyser (Shimadzu TOC-VCSH) fitted with a TNM-1 analyser. The extracts (40 µl) were injected into a detection chamber set at 680°C, where C in the soil solution was combusted and converted into CO₂, which is detected with an infrared gas detector. Three to five injections of a sample were injected until the coefficient of variation was below 2% . TN was also analysed on the TOC machine using the TNM-1 analyser. Analysis for inorganic nitrogen (NO₃⁻ and NH₄⁺) was carried out on the first sample and last 5 samples collected during the sampling period. The concentration of DON in solution was calculated by subtracting the content of NO₃⁻ and NH₄⁺ from the total N contents. The concentration of NO₃⁻ was determined colourimetrically with a Skalar autoanalyser (Skalar Analytical B.V., Breda, the Netherlands). The method involves cadmium reduction of nitrate to nitrite followed by diazotization with sulphanilamide and coupling with N-(1-naphthyl) ethylenediamine dihydrochloride to form an azo dye measured colourimetrically at 540 nm. Simultaneously, on the same equipment, the concentration of NH₄⁺-N in the leachates was also measured. NH₄⁺-N was chlorinated to monochloramine which reacts with salicylate which was then oxidised to form a blue/green coloured complex which is measured colourimetrically at 660 nm.

3.7 Soil water storage

Water holding capacity of the soil was determined in the laboratory following the method of Harding and Ross (1964) Glass wool was packed into the stem of a funnel, 100 g of soil (2 mm sieved and air dried) was placed on top of this, the

bottom of the funnel was stoppered then the soil was then saturated making sure all soil pores were filled with water and carefully tapping out the water. The saturated soils were left overnight. The following day the stopper was removed and the soil was allowed to drain for a further 4 hours (this was assumed to be field capacity). The moisture content of the soil was then determined by weighing a wet sample, drying at 105 °C for 24 hours then reweighing. These values were compared to literature values for field capacity for each soil (McLeod, 1992). Moisture content of the soil was determined in the A horizon 0-200 mm, and for the B horizon 400-650 mm at the start of sampling to create a reference point for the soil water balance. A 100 g sample of soil was carefully removed from the desired depth then stored in an air tight bag. Samples were returned to the laboratory where three replicate samples were weighed out, dried in an oven at 105 °C before reweighing to determine the field moisture content. The field capacity and moisture content data were used to initiate the soil water balance model.

3.8 Soil water balance

As evaporation and rainfall were measured on site, a simple bucket model was used to calculate the volume of water drainage through the soil using Eqn 3.1.

$$Q = P - E - \Delta S \quad 3.1$$

Where Q is discharge or soil drainage (mm), P is precipitation (mm); E is evaporation (mm) and ΔS is change in storage (mm). The model assumes that leaching from a soil layer commenced when the field capacity (FC in mm) was exceeded. The model was initiated using a value for soil water deficit, which was obtained by subtracting the field capacity from the moisture content measured at start of study. When the SWD reached zero, any excess water was assumed to have drained.

Data for measured evaporation was not always available during the sampling period, during this time evaporation was estimated using the FOA 56 equation (Eqn 3.2) (Allen 2004)

$$E_o = \frac{0.408s(Q^* - Q_G) + \gamma \frac{900}{T+273} u_2 D}{s + \gamma(1 + 0.34u_2)} \quad 3.2$$

Where T is the mean daily air temperature (°C), u_2 is windspeed at 2 m height (m s^{-1}) and D is the saturation vapour pressure deficit (kPa), Q^* is net radiation ($\text{MJ m}^{-2} \text{ day}^{-1}$), s is the slope of the saturation vapour pressure vs temperature curve ($\text{kPa } ^\circ\text{C}^{-1}$). The empirical constants relate to the standard values of the canopy and aerodynamic resistance. The evaporation estimate along with the measured rainfall was inputted into the drainage component of Woodward *et al.* (2001) which is a practical model for predicting soil water deficit in New Zealand pastures. The model requires inputs of evaporation and rainfall, as well as initiating variables, bulk density, porosity, field capacity and wilting point for 0-10 cm and 10-50 cm which were obtained from measured data and literature values (McLeod 1992). Two soil layers are modelled: a rapidly recharged and depleted layer and the total plant rooting zone. Evaporation of water from the surface is divided into two components actual evapotranspiration and potential evapotranspiration. Water is added through precipitation to the rapidly recharged zone from here water can be also be evaporated or transported to lower in the soil profile. Evaporation from the surface was limited by the available water holding capacity (water held between field capacity at 10 kPa and permanent wilting point 1500 kPa) actual evaporation was equal to potential evaporation when the soil moisture content was high. However when soils were dried out an added stress component reduces the potential evaporation as the soil plant interface holds water more tightly.

3.1 Evaporation and rainfall instrumentation

Evaporation data were provided by Susanna Rutledge (University of Waikato) which was measured as part of other studies onsite measuring CO_2 and H_2O exchange. In short, fluxes of H_2O were measured using the eddy covariance

technique. The EC setup consisted of a 3-D sonic anemometer (CSAT3, Campbell Scientific Inc.) and a closed path gas analyser (LI-7200, LI-COR Inc., Lincoln, NE, USA) mounted at 1.55 m on the boundary between paddocks 31 and 32 (Figure 3.2). The flow rate was set to 18 L min⁻¹, sample tube length was 600 mm and the tube was heated to avoid condensation from October 2012 onwards. A CR3000 datalogger (Campbell Scientific Inc., Logan, Utah, USA) sampled and stored the high frequency (20Hz) data. Gapfilled fluxes were used to calculate daily sums of evaporation in mm day⁻¹ (see Appendix A for gap filling method).

Rainfall was measured on the boundary of paddock 31 and 32, with a tipping bucket rain gauge (TB3A 0.2, Hydrological Services).

To estimate evaporation measurements further data were required, these were measured at the eddy covariance measurement sites on the boundary of between paddock 31 and 32, and on the boundary between paddocks 33 and 36 (Figure 3.2). Temperature and humidity (HMP 45A, Vaisala, Finland) were measured at 1.5m. From this vapour pressure and saturation vapour pressure were calculated. Net radiation (4-component net radiometer; NR01; Hukseflux, Delft, The Netherlands) was measured at 1.1. m. Soil temperature was measured below the surface at 20 mm and 60 mm using a four junction averaging thermocouple (TCAV, Campbell Scientific Inc.) and at 50 mm with a soil thermistor. Soil heat flux at 80 mm was measured using Soil Heat Flux Plate; (HFP01; Hukseflux, Delft, The Netherlands) and soil moisture was measured using a CS616 (Campbell scientific Inc.) at 50 mm, 100mm and vertically (from 0 – 300mm). All instruments were charged by 12 v batteries powered by 4 solar panels. Measurements are collected at 1 second intervals and totalised or averaged over 30 minutes and stored on a CR3000 (Campbell Scientific Inc) data logger.

3.2 DOC data handling

Dissolved organic carbon concentration data was interpolated across the entire measurement period so that every day during the measurement period had a DOC concentration value. As samples were not collected before May and some leaching occurred during this time, a concentration of DOC was needed for each

day in order to get a yearly mass of DOC leaching. The average of the years concentrations for each paddock was used as the concentration before measurements began. DOC concentration was then multiplied by drainage (as solved in the water balance for each day) to give a value for DOC leaching for each day that drainage occurred. DOC leaching was summed to give a yearly total for leaching from each paddock; this was converted to units of $\text{kg ha}^{-1} \text{ yr}^{-1}$. DOC leaching for the year was the average leaching of all 5 paddocks.

3.3 Soil sampling

Soil samples were collected on the 22 May 2012 from each of the four soils. Samples were collected at 10 cm, 35 cm and 65 cm. Samples from a small pit using a trowel, samples were individually stored in airtight bags. The Piarere silt loam was collected in paddock 31 next to site 5. The Te Punga soil was collected from paddock 33 next to site 2, The Waihou soil, was collected from paddock 32 next to site 5, and the Waitoa silt loam was collected from paddock 36 next to site 1 (Figure 3.2). The moisture content and water holding were measured as the method above. The remaining soil samples were air dried at 4 °C, sieved to 2 mm, and any roots or stones removed.

3.4 Respiration experiment

Soil samples were collected from 65 cm depth and prepared as above. Three replicates of each of the four soils were weighted to 25 g (dry weight equivalent) soil. Leachate was collected and bulked from all of the lysimeter sites analysed for DOC, IC and TN concentration and stored at 4°C. Waitoa and Waihou soils were saturated to their respective field capacity using the bulked low concentration DOC solution (4 mgL^{-1}) (treatment low), a high concentration DOC solution (68 mg L^{-1}) or a water (control). As the soils had varying field capacities to keep the same amount of liquid and the same amount of DOC in each, water and DOC were added at an appropriate ratio. Three replicates of 25 g (dry equivalent) samples of each control and treatment were weighed and sealed in a modified 1000 mL jar with a rubber stopper attachment in the lid. The soil jars were incubated at 20°C for seven days. The CO_2 was measured using an infrared gas

analyser (LI 6262, LI-COR, Lincoln, NE, USA). The soils were further incubated for three weeks with headspace CO₂ measurements made every 7 days.

To confirm the first findings, the experiment was repeated with all four soils and only using the low treatment (4 mg L⁻¹) and control.

3.5 Sorption

To determine the amount of DOC adsorption, the soil samples were each shaken with the bulked DOC solution at 4°C to inhibit microbial respiration. 2.5 g of sieved air-dried soil was added to a falcon tube with 0.025 L of DOC bulked solution or water as a control and was shaken at 50 rpm for 4 hours (Lambie *et al.*, 2010). This was carried out in triplicate for each soil. The soil solution slurry was then centrifuged for 20 minutes at 2500 rpm and then filtered through 45 µm Whatman cellulose nitrate filter. The supernatant was analysed for total C on a Shimadzu TOC-HNTC (as above). Adsorption of DOC onto the soil was then calculated using Eqn3.3. :

$$adsorption = \frac{(a-B)*V}{DW} \quad \text{Eqn 3.3}$$

Where a is concentration (mgL⁻¹) of DOC bulked solution, B is C concentration (mgL⁻¹) of supernatant after shaking and filtering. V is volume of DOC bulked solution (0.025 L) and DW is dry weight of the soil at 105°C. A positive number indicated that DOC had been adsorbed onto the soil where as a negative number showed that DOC concentration of the supernatant had increased therefore there was net desorption from the soil.

3.6 Data Analysis

The design of the sampling was a stratified random layout. One-way analysis of variance ($\alpha = 0.05$) was used to determine differences between soils in DOC, TN, and respiration treatment and controls. These statistical analyses were performed with Statistica Statistical Software (2011). The correlation coefficients between leached DOC with grazing, rainfall, evaporation and drainage were determined by

fitting linear regressions. Linear regressions and correlations were performed with Microsoft Office Excel (2010 Edition).

4 CONTRIBUTION OF DISSOLVED ORGANIC CARBON LEACHING TO THE ANNUAL CARBON BUDGET OF A DAIRY FARM

4.1 Introduction

Soils are the largest terrestrial store of carbon (C) containing some 2000 Pg C in organic matter globally. This compares to atmospheric pool of 760 Pg C and 500 Pg C in plant biomass (Janzen, 2004). Carbon is essential to soil physical, chemical and biological processes, including structural stability (Tisdall & Oades, 1982), fertility, cation exchange capacity, water movement and water holding capacity (Lal, 2004). Therefore losses in soil C can lead to soil degradation, potentially reducing plant biomass and soil productivity. Carbon is cycled continuously as CO₂ between the land and atmosphere. As CO₂ is an important greenhouse gas the uptake and release of CO₂ by terrestrial systems is also an important control on the climate system. Consequently, it is very important to accurately quantify the losses and stores of C in the soil, including how C is cycled, as small changes in stored C can have a large effect on the global C cycling and soil quality (Smith *et al.*, 2008) .

In general, dissolved organic carbon (DOC) leaching is a component of the C budget that is not well constrained, with leaching values from the soil ranging between 42 and 1690 kg C ha⁻¹ yr⁻¹ (McTiernan *et al* 2001, Ghani *et al* 2010). Dissolved organic carbon is operationally defined as the fraction of C that can pass through a 45 µm filter (Moore *et al.*, 2001) (Kalbitz *et al.*, 2000) (Kalbitz *et al.*, 2000) (Kalbitz *et al.*, 2000) (Kalbitz *et al.*, 2000). Although DOC import to

and export from ecosystems is often reportedly small compared to atmospheric C fluxes (respiration and photosynthesis), DOC can represent an important flux of C in global C cycling when C is lost from the terrestrial ecosystem to groundwater or surface waters. While DOC can leach below the topsoil, this is not necessarily a loss of C from the soil; the proportion of leaching contributing to a loss or gain from the net soil C stock depends on the internal soil cycling process of mineralisation and sorption, particularly in the vadose zone.

Dissolved organic carbon is the main form by which C is transported from surface soils to lower in the subsoil. Dissolved organic carbon inputs are derived from root exudates, soil organic matter and from microbial biomass (Kalbitz *et al.*, 2000). Dissolved organic carbon can be produced through the simple leaching of organic materials or derived from the physical and chemical alteration during decomposition of soil organic matter by microbes (Moore *et al.*, 2008). The concentration and leaching loss of DOC in the subsoil is then controlled by processes of adsorption and desorption from soil surfaces and mineralisation to CO₂. Once DOC has leached to the vadose zone, laboratory experiments have indicated that most mineral soils can adsorb DOC (Guggenberger & Kaiser, 2003; Sanderman & Amundson, 2009). In addition, DOC is readily accessible to microbes which can lead to mineralisation of DOC in soil and conversion to CO₂ (Don & Kalbitz, 2005). Additions of DOC from surface litter layers to the subsoil can also cause priming (Fontaine *et al.*, 2007), a process whereby fresh additions of C cause stimulation of microbes and subsequently increase respiration from the subsoil.

As production of DOC is predominantly a microbial process, it is likely that DOC production will be highest under conditions favourable to microbes. Favourable conditions include moist soils (Christ & David, 1996), oxic soils with warm temperatures (Moore & Dalva, 2001), slightly acidic pH (Andersson *et al.*, 2000), Large amounts and quality of substrate (Moore & Dalva, 2001; Don & Kalbitz, 2005) and an active well-structured microbial community.

The proportion of DOC leaching to the groundwater, adsorbed or mineralised, is also controlled by many of the same factors controlling production, since

microbes are responsible for removing DOC from the soil through mineralisation. The chemical and physical properties of the soil are important controls on sorption, with sorption showing a strong positive correlation to soil subsurface rich in iron and aluminium oxide (McDowell & Likens, 1988; Kaiser *et al.*, 1996; Kaiser & Guggenberger, 2000; Kaiser & Guggenberger, 2003; Sanderman & Amundson, 2009). Sorption is also found to be highest under slightly acidic soils, whereas in more alkaline soils desorption will dominate (Guggenberger & Kaiser, 2003). The release of DOC is also linearly related to the velocity and residence time of water in the soil, with DOC concentrations decreasing with increasing water through flow velocity (Münch *et al.*, 2002; Mertens *et al.*, 2007). As the water velocity increases sorption decreases, as does the ability of water to pick up soluble C due to increased bypass flow. Thus the mass of DOC leached is ultimately controlled by the amount, rate and residence time of water in soil. Whether DOC is leached to groundwater, mineralised to CO₂, or stored in the soil by sorption will finally determine how DOC leaching needs to be accounted for in C budgets.

Dissolved organic carbon leaching is known to vary on temporal and spatial scales with rates of DOC leaching differing between soils under the same vegetation, across vegetation types and in different climatic zones (Kalbitz *et al.* 2000). There have been numerous studies reporting DOC leaching from forest soils (Don & Kalbitz, 2005; Peichl *et al.*, 2007; Moore *et al.*, 2008; Fujii *et al.*, 2009; Sanderman & Amundson, 2009; Fröberg *et al.*, 2011) and some from native pastures, unmanaged grasslands (Don & Schulze, 2008) and croplands (Kindler *et al.*, 2011). In contrast, there are comparatively few studies focusing on intensively managed temperate pastures (McTiernan *et al.*, 2001), that are grazed year round, such as those in New Zealand. As a consequence DOC leaching is excluded or estimated when C budgets are made for grassed systems (eg. Mudge *et al.*, 2011). DOC leaching may also be important when quantifying C stocks, as measurements made in the surface soils may misrepresent the actual C storage of the soil, as DOC leaching is commonly assumed to be a significant means of transporting carbon lower into the subsoil where it could be stabilised (Michalzik *et al.*, 2003). Grazed grasslands in New Zealand make up some 11.1 million hectares, which equates to 41% of the total land usage (Statistics New Zealand 2007). Globally, grazed pastures make up a quarter of the earth's ice free land

surface (FAOSTAT, 2011), therefore understanding how C is cycled in these ecosystems is essential to global C budgeting.

Dissolved organic carbon leaching from soils has been found to be a significant pathway of C loss in some grassed ecosystems (Ghani *et al.*, 2010), however it is generally in forests or peatlands where DOC leaching to the groundwater is considered an important loss. In these ecosystems DOC is primarily derived from the organic rich surface layers that are often absent from grasslands (Michalzik *et al.*, 2001). Neff and Asner (2001) reviewed the literature comparing DOC leaching from a range of ecosystems demonstrating generally larger losses of DOC from forests than grasslands. They found that DOC leaching through soil ranged from 20 kg C ha⁻¹ yr⁻¹ to 220 kg C ha⁻¹ yr⁻¹ under eucalypts forest and grass complex and between 180-840 kg C ha⁻¹ yr⁻¹ below a temperate evergreen forest. (Sanderman & Amundson, 2009) measured DOC leaching below a grassland and a forest and found that leaching below the forest was greater than the grassland with 74 kg C ha⁻¹ yr⁻¹ and 17 kg C ha⁻¹ yr⁻¹ respectively. Measurements of leaching in New Zealand are limited, however several studies have been carried out which consider DOC leaching in different soils or under different conditions. Parfitt *et al.* (2009) measured DOC leaching under a New Zealand steep land pasture grazed by sheep. In this study, DOC leached was 228 kg C ha⁻¹ yr⁻¹ where no nitrogen was added and 121 kg C ha⁻¹ yr⁻¹ under high nitrogen input treatment. Sparling *et al.* (2006) measured DOC leaching in four contrasting soils, and found that the mass of DOC leached varied between soil orders (Recent soil leached 219 kg C ha⁻¹ yr⁻¹, Gley soil 51 kg C ha⁻¹ yr⁻¹, Pumice soil 136.5 kg C ha⁻¹ yr⁻¹, and Allophanic 9.2 kg C ha⁻¹ yr⁻¹). In another New Zealand study, Ghani *et al.* (2007) measured much higher leaching from six different soils cores under pasture. The lowest leaching was from an Allophanic soil (280 kg C ha⁻¹ yr⁻¹) and the highest from a Gley soil (1690 kg C ha⁻¹ yr⁻¹).

Due to the variability of DOC leaching data, further information on annual DOC losses are important for understanding C cycling in pasture and contribution to the C budget. The main objective of this thesis was to measure the annual mass of dissolved organic carbon and nitrogen leaching from a New Zealand pasture grazed by dairy cows. The fate of DOC in the subsoil was explored in a laboratory

study where both mineralisation and sorption were investigated to determine the contribution of DOC to the carbon budget of a grazed dairy pasture.

4.2 Methods

4.2.1 Site

This study was conducted on a dairy farm located 3 km east of the Waikato Township, Waharoa, in the North Island of New Zealand (Figure 4.1). The farm grazes two herds of dairy cows (total 690 cows) on 207.4 hectares at an approximate intensity of 3.3 cows per hectare on a predominantly rye grass and clover sward. The nearest climate station is 13 km to the south west near Matamata where the 30 year (1981-2010) mean annual temperature and rainfall are 13.3 °C and 1249 mm respectively (NIWA, 2012). The measurements for this study were made on 5 paddocks of the farm. Two locations at the easternmost point of the farm were chosen due to their flatness and scarcity of trees. The two sites were equipped with Eddy covariance towers to measure the surface carbon exchange (as part of wider study for a dairy farm carbon balance) (Figure 4.2). Evaporation, rainfall, soil tension, radiation and humidity were also measured at each site.

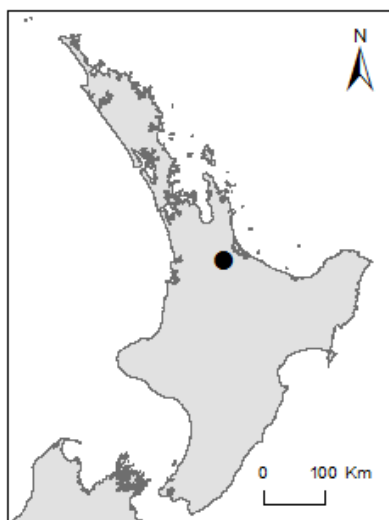


Figure 4.1: Map of the north island showing location of the farm site in the Waikato



Figure 4.2: Map of farm sampling sites, showing the EC tower, soil pattern, and suction cup installation locations.

4.2.2 DOC sampling and analysis

In total, DOC leaching concentrations were measured in five paddocks within the footprint of the Eddy co-variance measurements. Sampling of DOC leachate was made between 0.6 m and 0.65 m depth using suction cup lysimeters. Lysimeters were installed in groups of 4 on a 45° angle from a 0.3 m deep central house. The location of each house of samplers was chosen using a stratified random approach where the paddocks were stratified by soil type. The soil across the paddocks were a complex of four soils: the Te Puninga silt loam, Pairere silt loam, Waitoa silt loam and Waihou silt loam with some modification for drainage channels and farm roads (Figure 4.2). Each paddock contained 5 houses and 20 individual samplers. In total, 100 suction cup lysimeters were used to collect DOC leachate at this site.

Soil water samples were taken approximately bimonthly when the soil water balance showed the soils were above field capacity and therefore drainage was likely. In total, DOC leaching was measured 11 times from May through to October. Samples were usually bulked for each paddock, however to determine the variation between suction cups, houses and soils, all suction cups were sampled on two occasions. Samples were collected by applying a tension of 30 kPa to the suction cup lysimeters using a syringe. Samples were bulked in the field with 10 mL of sample from each suction in a paddock. Samples were first filtered through a 0.45µm cellulose nitrate membrane filter, before the concentration of DOC was measured on a total carbon analyser (Shimadzu TOC-VCSH fitted with a TNM-1 analyser, Shimadzu Corporation, Melbourne, Australia). The extracts (40 µl) were injected into a detection chamber set at 680°C, where C in the soil solution was combusted and converted into CO₂, which is detected with an infrared gas detector. 3-5 injections of a sample were injected until the coefficient of variation was below 2%. Total N in the soil extracts was also determined by a Shimadzu TOC-VCSH analyser fitted with a TNM-1 analyser. Analysis for NO₃⁻ and NH₄⁺ was carried out on the last 5 samples collected. The concentration of dissolved organic nitrogen (DON) in soils was calculated by subtracting the content of NO₃⁻ and NH₄⁺ from the total N contents. The concentration of NO₃⁻ in the soil extracts and leachates was

determined colorimetrically with a Skalar autoanalyser (Skalar Analytical B.V., Breda, the Netherlands). The method involves the cadmium reduction of nitrate to nitrite followed by diazotization with sulphanilamide and coupling with N-(1-naphthyl) ethylenediamine dihydrochloride to form an azo dye measured colorimetrically at 540 nm. Simultaneously, on the same equipment, the concentration of NH_4^+ -N in the leachates was measured colorimetrically by the salicylate-nitroprusside method.

4.2.3 Meteorological measurements and water balance

Fluxes of dissolved C were calculated by multiplying concentrations of DOC and TN with the volume of leached water, which was derived from a soil water model, using a simple water balance where the soil is treated as bucket (Eqn 4.1).

$$Q = P - E - \Delta S \quad 4.1$$

Where Q is discharge or soil drainage (mm); P is precipitation (mm); E is evaporation (mm) and ΔS is change in storage (mm). The model assumes that leaching from a soil layer commenced when the field capacity (FC in mm) was exceeded. Water was input through measured rainfall (TB3A 0.2 Hydrological Services) and water removed through evaporation. Soil water deficit was used in the model as the field capacity of the soil minus the water content at the start of measurement. When the soil water deficit reached zero, any excess water was assumed to have drained. The soil water model was solved using both measured evaporation from a closed path infrared gas analyser (model LI-7200, LI-COR Inc., Lincoln, NE, USA) and also using FAO-56 evaporation using Eqn4.2.

$$E_o = \frac{0.408s(Q^* - Q_G) + \gamma \frac{900}{T+273} u_2 D}{s + \gamma(1 + 0.34u_2)} \quad 4.2$$

Where T is the mean daily air temperature ($^{\circ}\text{C}$); u_2 is windspeed at 2 m height (m s^{-1}); D is the saturation vapour pressure deficit (kPa); Q^* is net radiation ($\text{MJ m}^{-2} \text{ day}^{-1}$) and s is the slope of the saturation vapour pressure vs. temperature curve ($\text{kPa } ^{\circ}\text{C}^{-1}$). The empirical constants relate to the standard values of the canopy and

aerodynamic resistance (Allen *et al.*, 1998). Measurements for temperature and humidity (HMP 45a) were measured at 1.5 m. From this vapour pressure and saturation vapour pressure were calculated. Net radiation (4-component net radiometer; NR01; Hukseflux) was measured at 1.1 m. Soil temperature at 50 mm was measured using a four junction averaging thermocouple (TCAV, Campbell Scientific Inc.) and at 100 mm with a soil thermister. Soil heat flux at 80 mm was measured using Soil Heat Flux Plate (HFP01; Hukseflux) and soil moisture at 300 mm using a soil Tensiometer.

4.2.4 Respiration experiment

Soil samples were collected from 65 cm depth from each of the 4 soils. Samples were air dried at 4 °C, sieved to 2 mm, and then stored at 4 °C until needed. Three replicates of each of the four soils were weighted to 25 g (dry weight equivalent) soil. Leachate was collected and bulked from all of the lysimeter sites analysed for DOC, IC and TN concentration and stored at 4°C. Waitoa and Waihou soils were saturated to their respective field capacity using the bulked low concentration DOC solution (4 mgL⁻¹) (treatment low), a high concentration DOC solution (68 mg L⁻¹) or a water (control). As the soils had varying field capacities to keep the same amount of liquid and the same amount of DOC in each, water and DOC were added at an appropriate ratio. Three replicates of 25 g (dry equivalent) samples of each control and treatment were weighed and sealed in a modified 1000 mL jar with a rubber stopper attachment in the lid. The soil jars were incubated at 20 °C for seven days. The CO₂ was measured using an infrared gas analyser (LI 626, LI-COR Inc., Lincoln, NE, USA). The soils were further incubated for three weeks with headspace CO₂ measurements made every 7 days.

To confirm the first findings, the experiment was repeated with all four soils and only using the low treatment (4 mg L⁻¹) and control.

4.2.5 Sorption experiment

Sorption measurements and experimentation was carried out using the methodology described in Lambie *et al.* (2012). 2.5 g of sieved air-dried soil was

added to a falcon tube with 0.025 L of DOC bulked solution at low concentration (4 mg DOC L⁻¹), high concentration (7 mg DOC L⁻¹) or water (control). The falcon tube was shaken at 50 rpm for 12 hours at 4°C to inhibit microbial respiration. This was carried out in triplicate for each soil. The soil solution slurry was then centrifuged for 20 minutes at 2500 rpm and then filtered through 45 µm Whatman cellulose nitrate filter. The supernatant was analysed for total C on a Shimadzu TOC-HNTC (as above). Adsorption of DOC onto the soil was then calculated using Eqn 4.3.

$$adsorption = \frac{(a-B)*V}{DW} \quad 4.3$$

Where a is concentration (mgL⁻¹) of DOC bulked solution, B is C concentration (mgL⁻¹) of supernatant after shaking and filtering, V is volume of DOC bulked solution (0.025 L) and DW is dry weight of the soil at 105°C. A positive number indicated that DOC had been adsorbed onto the soil where as a negative number showed that DOC concentration of the supernatant had increased and therefore there was net desorption from the soil.

4.2.6 DataAnalysis

The design of the sampling was a stratified random layout. One-way analysis of variance ($\alpha = 0.05$) was used to determine differences between soils in DOC, TN, and respiration treatment and controls. These statistical analyses were performed with Statistica Statistical Software (2011). The correlation coefficients between leached DOC with grazing, rainfall, evaporation and drainage were determined by fitting linear regressions. Linear regressions and correlations were performed with Microsoft Office Excel (2010 Edition).

4.3 Results

4.3.1 DOC leaching

Annual rainfall for the year 2012 as measured at the farm was 1770 mm. Measured annual evaporation was 749 mm which, using the water balance equation, lead to a drainage of 990 mm past a soil depth of 65 cm. FAO estimated evaporation was higher than the measured evaporation at 931 mm leading to a drainage of 748 mm (Figure 4.3). As the measured and estimated evaporation were similar, the DOC leaching produced using either measured or estimated evaporation was similar. The measured evaporation and consequent drainage are reported here.

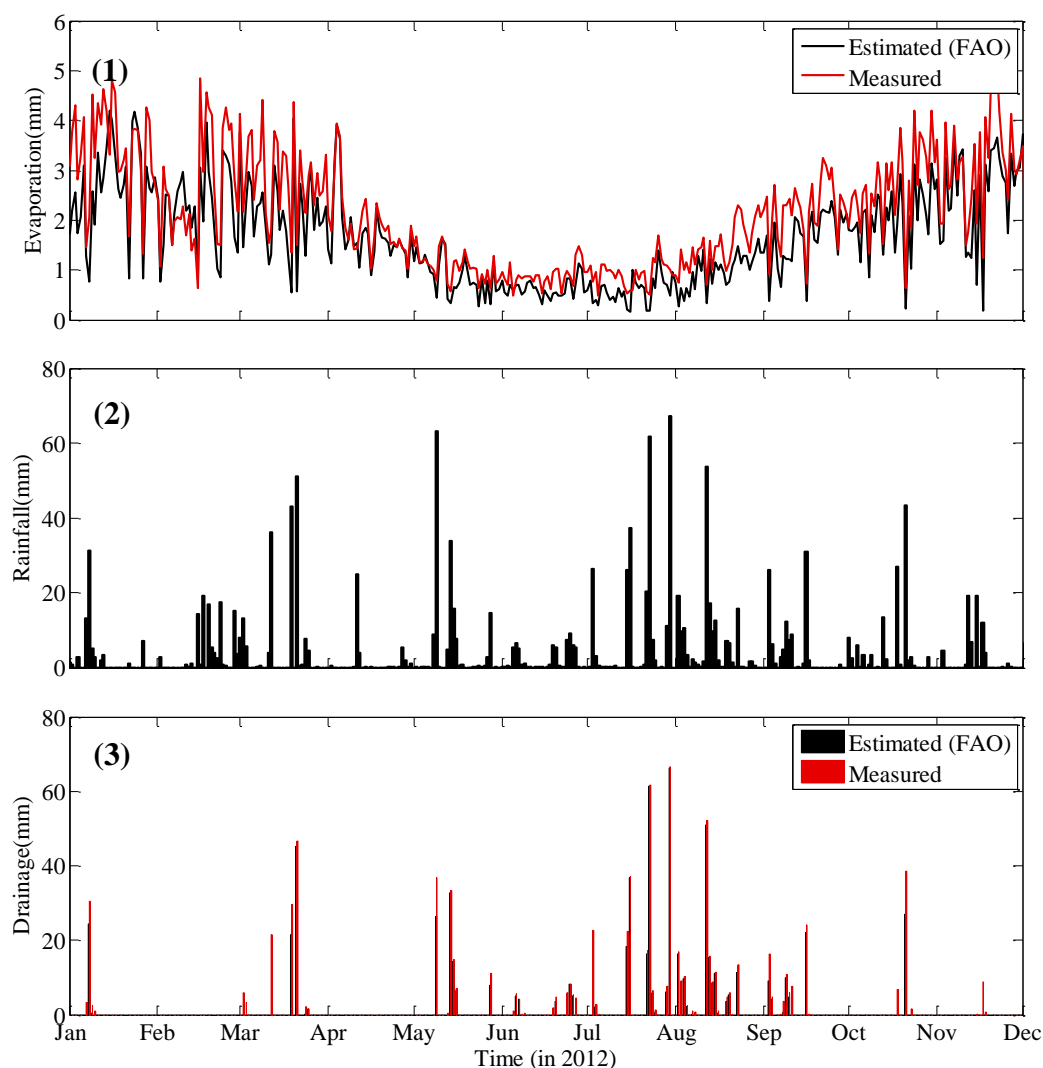


Figure 4.3: (1) Annual daily average of measured and FAO estimated evaporation; (2) Annual daily rainfall; (3) Annual daily average of drainage from measured and FAO estimated evaporation

DOC concentration was measured 11 times throughout the year with a total of 55 samples collected across the five paddocks. DOC concentration generally ranged between 0.5 mgL^{-1} and 9 mgL^{-1} (Figure 4.4), however the DOC concentration in paddock 32 ranged between 39 mg L^{-1} to 0 mg L^{-1} in June. As tested by ANOVA, the DOC concentration showed no significant variation ($p < 0.05$) throughout the year.

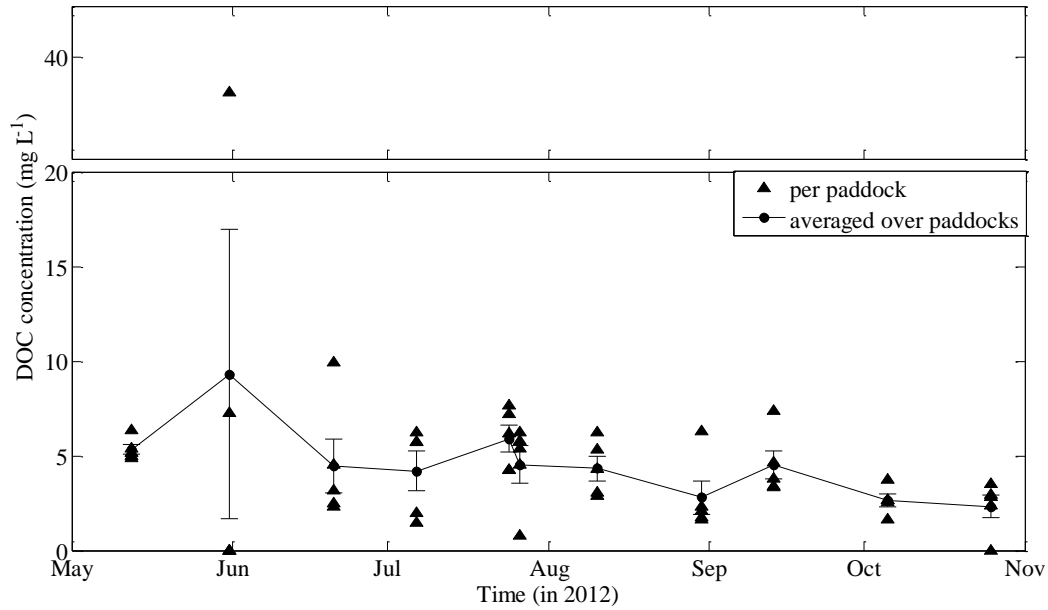


Figure 4.4: Measured daily DOC concentration, average daily DOC concentration. Triangles represent the individual measurements of bulk samples of DOC from each of the paddocks. The filled circle represents the DOC concentration averaged across each of the paddocks (error bars represent standard error).

DOC concentration (mg L^{-1}) and water drainage (L m^{-2}) were multiplied to determine daily DOC leaching from each of the paddock (Figure 4.5). Daily DOC leaching was sporadic ranging from $0 \text{ kg C ha}^{-1} \text{ day}^{-1}$ when there was no drainage to $4.6 \text{ kg C ha}^{-1} \text{ day}^{-1}$ during the peak of winter rainfall (paddock 34). The largest cumulative mass of DOC leaching was from paddock 36 with $47. \text{kg C ha}^{-1} \text{ yr}^{-1}$, while the smallest was from paddock 31, with $23 \text{ kg C ha}^{-1} \text{ yr}^{-1}$.

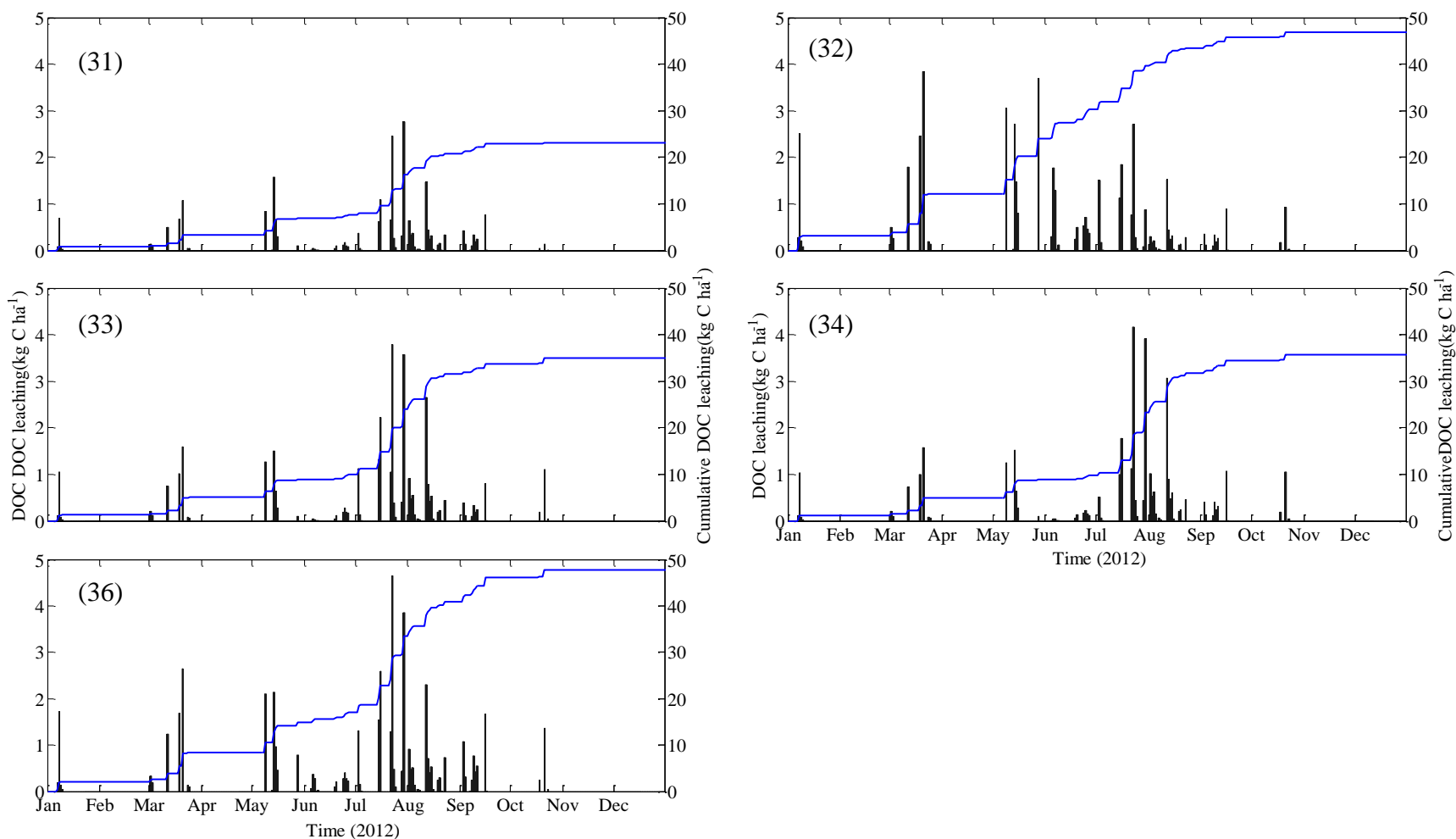


Figure 4.5: Daily average DOC leaching (bars) for the year plotted with cumulative DOC leaching (lines) for each of the paddocks.

DOC leaching and DOC concentration showed no significant variation between paddocks ($p < 0.05$). DOC leaching and DOC concentration showed no significant differences between soil types or sampling sites ($p < 0.05$). The overall annual average DOC concentration with standard error was $4.5 \pm 0.82 \text{ mg L}^{-1}$, ranging between $2.52 \pm 0.47 \text{ mg L}^{-1}$ in paddock 31 and $7.15 \pm 3.30 \text{ mg L}^{-1}$ in paddock 32. The total annual DOC leaching ranged from $23.14 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ in paddock 31 to $47.71 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ in paddock 36. The overall annual average DOC leaching was $37.67 \pm 4.156 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ (Table 4.1).

Total nitrogen concentrations were low and showed no significant variation ($p < 0.05$) between paddocks (Table 4.1). The annual average nitrogen concentration and standard error was $2.13 \pm 0.87 \text{ mg L}^{-1}$, ranging between $0.83 \pm 0.18 \text{ mg L}^{-1}$ in paddock 36 and $5.57 \pm 1.96 \text{ mg L}^{-1}$ in paddock 32. The total annual average nitrogen leaching was $16.28 \pm 3.64 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, ranging from $7.14 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in paddock 36 to $36.744 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in paddock 32 (Table 4.1).

Table 4.1: Summary table of average dissolved organic carbon concentration and total dissolved organic carbon leaching for the year for each of the paddocks and total annual average total nitrogen concentration and total nitrogen leaching for each of the paddocks.

Paddock	Average DOC concentration (mg L^{-1})	Average DOC leaching ($\text{kg C ha}^{-1} \text{ yr}^{-1}$)	Average TN concentration (mg L^{-1})	Average TN leaching ($\text{kg N ha}^{-1} \text{ yr}^{-1}$)
31	2.52 ± 1.71	23.14	1.23 ± 0.44	13.08
32	7.15 ± 3.30	48.68	5.57 ± 1.96	36.744
33	3.73 ± 0.59	34.90	1.66 ± 0.45	14.32
34	3.72 ± 0.68	35.67	1.13 ± 0.44	10.13
36	5.76 ± 0.45	47.71	0.83 ± 0.18	7.15
Overall average	4.5 ± 0.82	37.67 ± 4.15	2.06 ± 0.58	16.28 ± 3.64

4.3.2 Respiration

Soil respiration was measured in two separate experiments. In the first experiment two soils were inoculated with either a high DOC concentration (68 mg L^{-1}) or a low DOC concentration (4 mg L^{-1}) and incubated for 4 weeks at 20°C . The results shown are for the first week of respiration (for the rest of the data refer Appendix B). Soil respiration in the Te Pungia soil was found to be significantly higher than the control (water, 0 mg L^{-1}) in both the high ($p=0.001$) and low ($p=0.046$) inoculation experiments. Soil respiration in the Waihou soil was found to be significantly different than the control in the high inoculation experiment ($p=0.028$). However, soil respiration was not found to be significantly different between the control and the low inoculation experiment ($p>0.05$). For the Te Pungia soil in the low inoculation experiment, the amount of C respired (control adjusted) was nearly 11 times greater than the amount of C added (Figure 4.6). For the Te Pungia soil in the high inoculation experiment, the amount of C respired was 74.5% of the C added. In the high inoculation experiment, the Waihou soil respired 51% of the added C (See Appendix B). The pH of all four soils was measured in a 1:2.5 solution. All four soils were slightly acidic with the Waihou soil having the lowest pH of 5.3, followed by the Waitoa soil with a pH of 5.5, the Piarere soil with a pH of 5.8 and the Te puninga soil with a pH of 6.2.

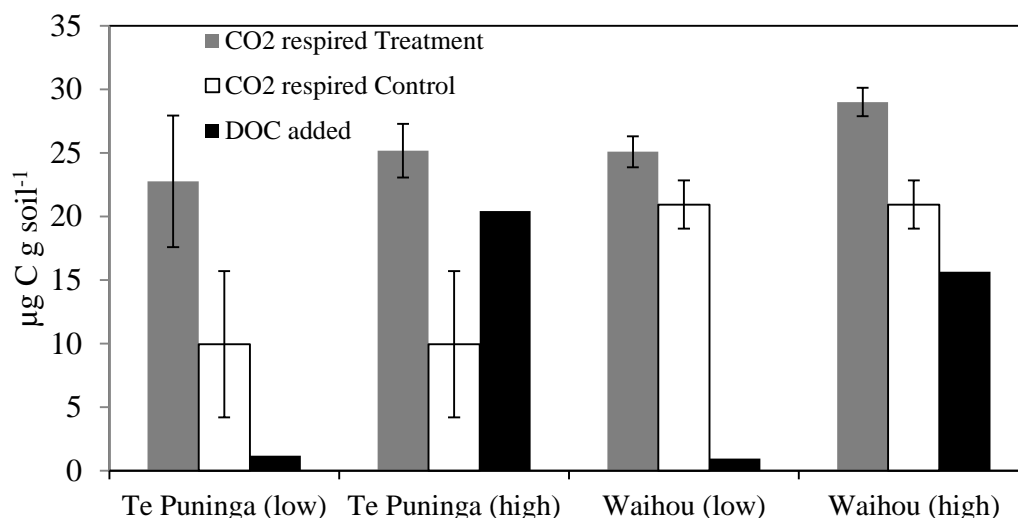


Figure 4.6: Respiration experiment results after one week, for the Te Puninga and Waihou subsoils (0.65 m), using soils wetted to field capacity and amended with solutions of high (68 mg L^{-1}) and low (4 mg L^{-1}) DOC concentration.

To see if the same priming effect was present across all of the soils, the same respiration experiment was repeated using the low (4 mg L^{-1}) DOC concentration. The addition of DOC to the Waihou, Waitoa and Piarere soil had no effect with no significant differences found between the Waitoa soil treatment and control ($p=0.413$), the Waihou soil treatment and control ($p=0.987$), and the Piarere soil treatment and control ($p=0.855$). The Te Puninga soil, however, showed a significant difference between the treatment and control ($p=0.019$) with respiration 15 times greater in the treatment than the control (Figure

4.7). The amount of C respired from C added was calculated in the Te Puninga soil, as it is the only soil where control and treatment were significantly different. Results showed that the addition of DOC resulted in the respiration of 25 times more C than the amount of DOC added (for full results see Appendix B).

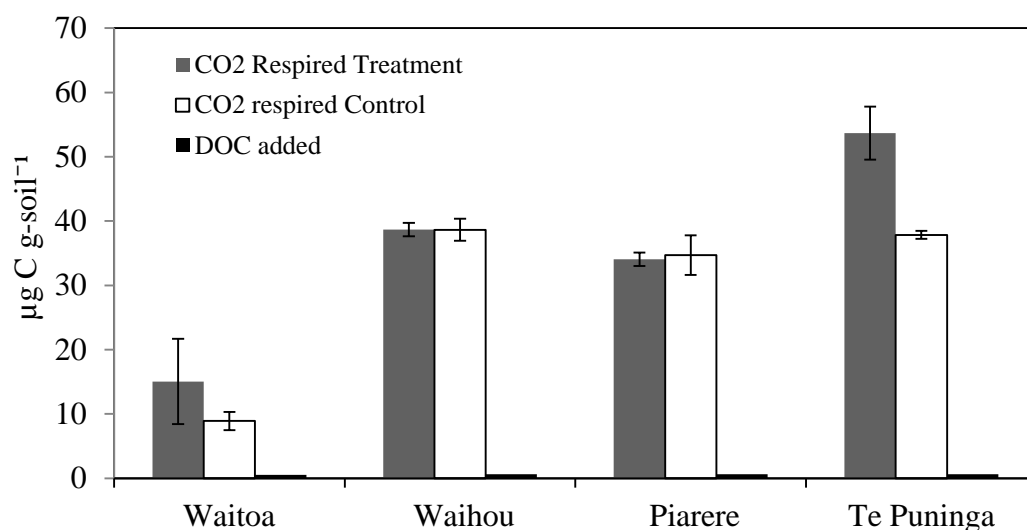


Figure 4.7: Respiration experiment results after one week for the Te Punga and Waihou subsoils (0.65 m), using soils wetted to field capacity and amended with solutions of high (68 mg L⁻¹) and low (4 mg L⁻¹) DOC concentration.

4.3.3 Sorption

Water extraction resulted in net desorption of DOC from the soil in both Te Punga and Piarere soils. The Te Punga soil had greater sorption (0.0531 mg C g soil⁻¹) than the Piarere soil (0.0296 mg C g soil⁻¹) when mixed with a higher concentration (7 mg L⁻¹) DOC solution. When the soil was mixed with the low concentration (4 mg L⁻¹) DOC solution there was net desorption in both the Piarere soil (0.0339 mg C g soil⁻¹) and Te Punga soil (0.0091 mg C g soil⁻¹) (Table 4.2).

Table 4.2: Table of sorption results for the Te Puninga and Piarere soils.

		Te Puninga soil			Piarere soil		
Treatment		High	Low	Control (water)	High	Low	Control (water)
DOC concentration (mg L ⁻¹)	(a)	7.945	4.024	0.742	7.945	4.024	0.742
DOC concentration (mg L ⁻¹)	(b)	3.488	4.786	3.804	5.218	7.143	4.267
Average net sorption (mg C g ⁻¹ soil)	(c)	0.053 ±0.0000	-0.009 ±0.0013	-0.037 ±0.0095	0.030 ±0.0022	-0.033 ±0.0013	-0.038 ±0.0011

(a) is concentration (mgL-1) of DOC bulked solution,

(b) is C concentration (mgL-1) of supernatant after shaking and filtering.

(c) calculated using Eqn 4.1

4.3.4 Controls on DOC leaching

4.3.4.1 Grazing

The timing of grazing of each of the paddocks was recorded by the farmer for the year 2012 (Appendix C). No correlation was found between time since grazing and the DOC concentration for paddocks 31, 32, 33 and a poor correlation was found in paddocks 34 and 36 (Figure 4.8).

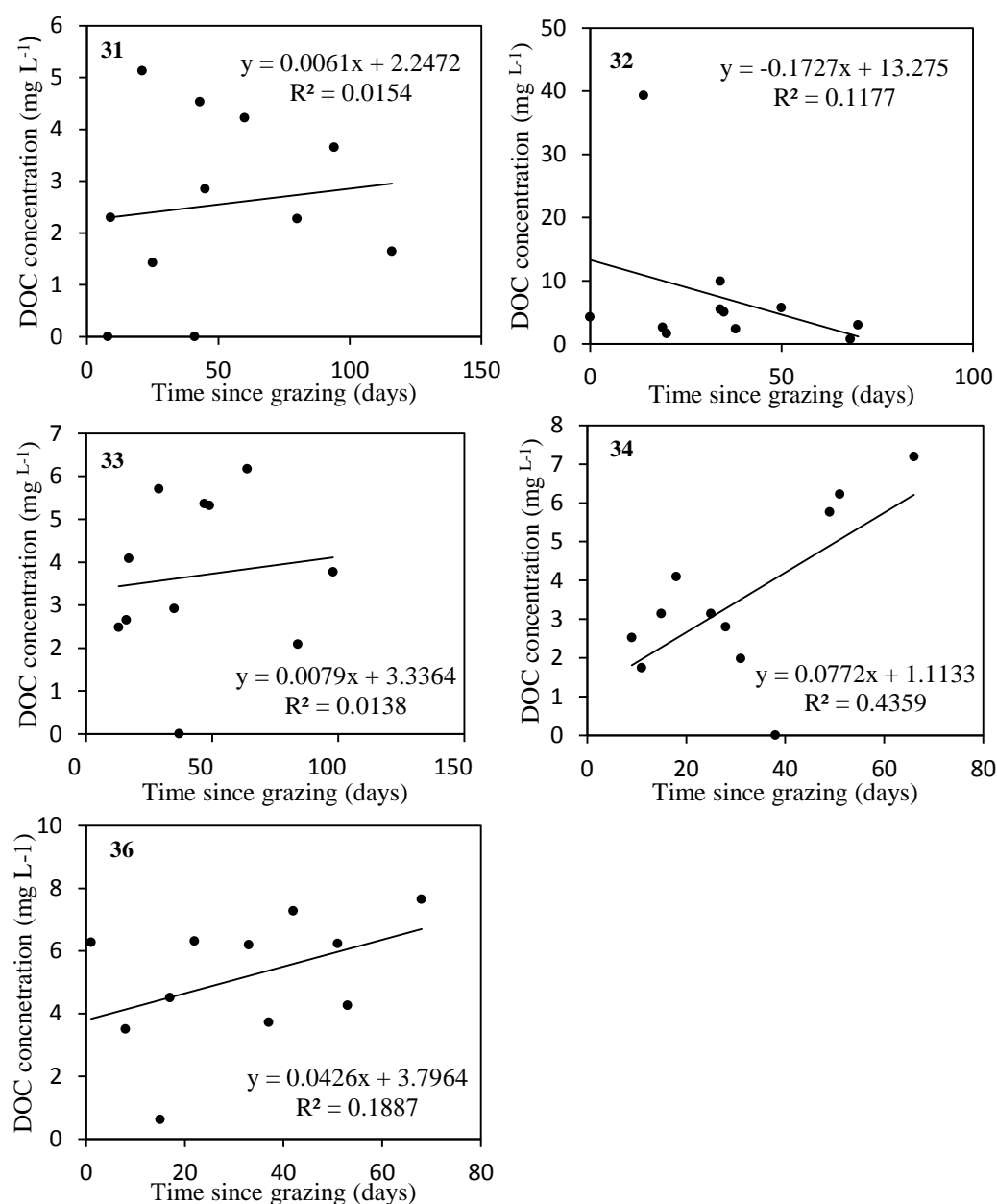


Figure 4.8: Plot of dissolved organic carbon concentration and time since grazing for each of the paddocks, fitted with a linear regression.

4.3.4.2 Rainfall, Evaporation and Drainage

A strong correlation was found between DOC leaching and the monthly average precipitation ($R^2 = 0.86$) and between DOC leaching and the measured evaporation ($R^2 = 0.88$). The strongest correlation was between DOC leaching and drainage in the same month (Figure 4.9).

In contrast, no relationship was found between time since drainage and the concentration of DOC leached (Figure 4.10).

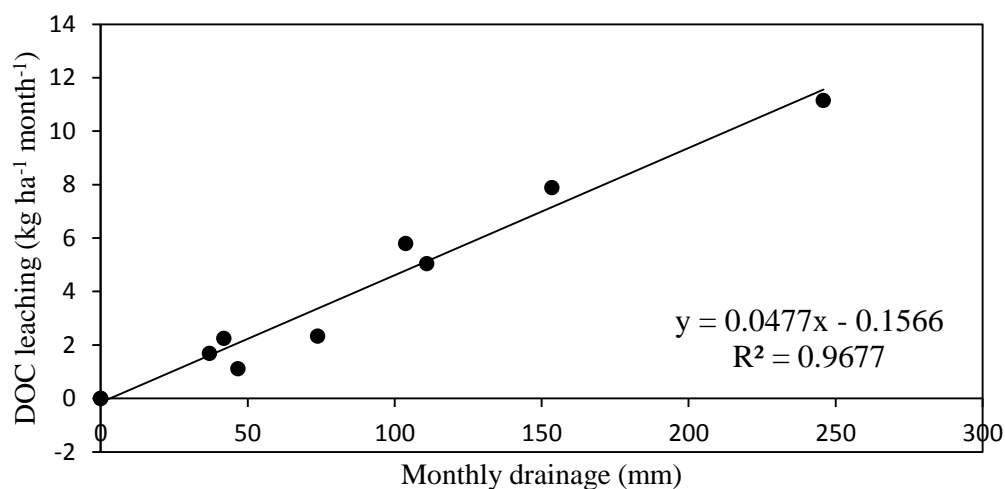


Figure 4.9: Plot of total monthly dissolved organic carbon leaching (mm) and monthly drainage for the year 2012, fitted with a linear regression.

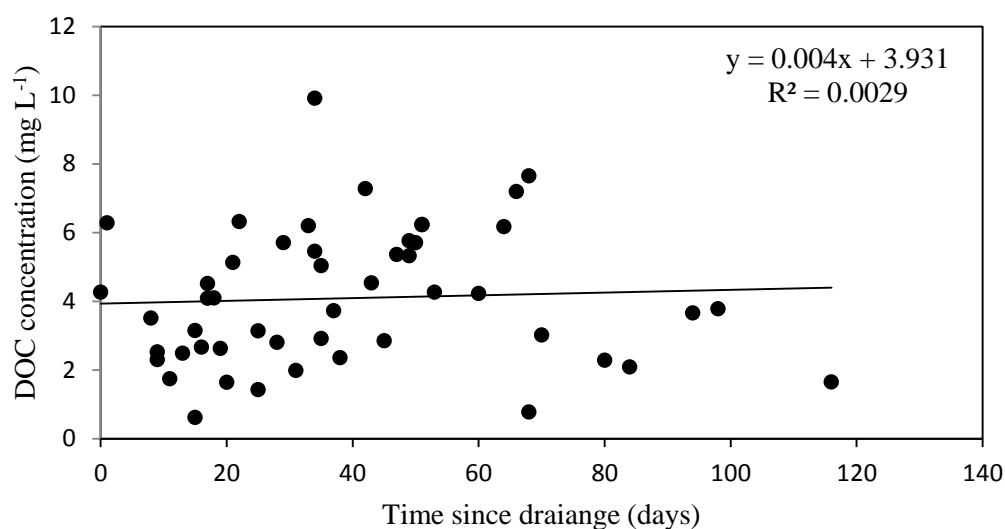


Figure 4.10: Plot of dissolved organic carbon leaching (mm) and time since drainage, fitted with a linear regression.

4.3.4.3 **Nitrogen**

No relationship was found between DOC leaching and total nitrogen leaching ($R^2=0.0517$). For the 5 measurements of inorganic nitrogen and organic nitrogen concentration made in each of the paddocks there was no relationship with DOC concentration ($R^2= 0.034$ and 0.016 respectively). Also, total dissolved nitrogen showed no correlation with total organic carbon ($R^2=0.079$).

4.4 Discussion

4.4.1 Mass of DOC leached

The annual mass of DOC leaching below 0.65 m at this site was $38 \pm 4 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ (mean \pm SE). DOC leaching was in the middle of the range of literature values for DOC leaching in grassed ecosystems, but much lower than studies within New Zealand (Table 4.6). For example Ghani *et al.* (2008) reported a DOC leaching loss between 280 and 1690 $\text{kg C ha}^{-1} \text{ yr}^{-1}$ and Parfitt *et al.* (2009) measured leaching of between 121-228 $\text{kg C ha}^{-1} \text{ yr}^{-1}$. However, the annual rainfall and the subsequent drainage were higher at this site (1771 mm and 990 mm, respectively) than many previous studies (Table 4.3). Ghani *et al.* (2008) estimated drainage from sites in the Waikato to be between 404 mm and 670 mm, similar to 526 to 791 mm measured leaching by (2005). The mentioned studies have lower leaching volumes than those measured in this study; therefore, in order to produce such high DOC leaching the concentration of DOC in solution must be much higher than those measured in this study.

The mass of DOC leaching is important when constructing ecosystem scale C budgets which are often measured using the eddy covariance technique. However, the contribution of DOC leaching to these budgets is often not measured (Mudge *et al.*, 2011). Eddy covariance measures net ecosystem exchange (NEE) which is the balance between respiration (carbon loss from the ecosystem) and photosynthesis (gain of carbon to the ecosystem). Comparisons can be made between the size of DOC leaching to respiration from this site, which is 22,378 $\text{kg C ha}^{-1} \text{ yr}^{-1}$ (S.Rutledge, *pers. comm.*, February 2013). However, not much insight can be gained from comparing this number, as respiration is balanced by the return of C to plants through photosynthesis (gross primary production), and the subsequent return of C to soil by plant root exudates and plant death. The balance of respiration and primary productivity (NEE) at this site for 2012 was -833 $\text{kg C ha}^{-1} \text{ yr}^{-1}$ (S.Rutledge, *pers. comm.*, February 2013). The measured DOC leaching of 37 $\text{kg ha}^{-1} \text{ yr}^{-1}$ represented only 4.6 % of NEE.

Table 4.3: DOC leaching mass from grassed ecosystems, including soil texture, instrumentation and measurement depth.

Author	Location	Drainage (mm)	DOC leaching (kg C ha ⁻¹ yr ⁻¹)	Soil Texture	Collection method and depth (mm)
Barton <i>et al.</i> , (2005)*	New Zealand	616	25***	Loamy sand	0.7
		791	56***	Clay loam	Barrel
		526	8***	Silt Loam	lysimeter
		776	252***	Sand	
Ghani <i>et al.</i> , (2010)	New Zealand	505	1692	Clay loam	0.25
		404	943	Clay loam	Laboratory
		404	281	Silt loam	barrel lysimeter
		695	560	Silt loam	
		644	445	Silt loam	
		644	561	Silt loam	
Harrison <i>et al.</i> (2008)	Wales	Nd	18-35	Clay loam	0.25
					Barrel lysimeter & Zero tension lysimeter
Kindler <i>et al.</i> (2011)	South France	486	11	Sandy loam	0.3-0.9
					Ceramic suction cup
Parfitt <i>et al.</i> , (2009)	New Zealand	791	121	ND	0.2 and 0.5 Ceramic suction cups
		526	228		
Sanderman and Amundson (2009)	North California USA	590	10	Clay loam	0.5
					Quartz tension lysimeter
Sparling <i>et al.</i> , (2006)**	New Zealand	776	21.4	Loamy sand	0.7
				Clay loam	Barrel lysimeter
		745	51.5	Silt Loam	
		550	9.2	Sand	
		725	219		

* Annual mm and mass obtained by averaging from 2 years of data

** Annual mm and mass obtained by averaging from 4 years of data

*** TOC

NZSC- New Zealand Soil Classification (Hewitt 1998)

Sparling *et al.*, 2006 and Barton *et al.*, 2005 are effluent irrigation studies, the results displayed are controls.Ghani *et al.*, 2010 and Parfit *et al.*, 2009 are both from grazed pastures.

NEE exchange only included respiration and photosynthesis measurements. However, on a farm other inputs and exports need to be accounted for. Mudge *et al.* (2011) measured the net ecosystem carbon budget (NECB) of an intensively grazed dairy farm in the Waikato. NEE was measured using an eddy covariance system and other C imports (feed) and exports (milk, methane, and harvested biomass) were calculated from farm production data. Measurements were made over 2 years with contrasting climates: 2008 was characterised by a severe drought, and 2009 had no drought and plenty of summer rainfall. For both years DOC leaching was estimated from literature values to be $50 \text{ kg C ha}^{-1} \text{ yr}^{-1}$, the NECB was $-199 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ and $-1014 \text{ kg C ha}^{-1} \text{ yr}^{-1}$, respectively. Compared to measurements of NECB for a grazed dairy system, DOC leaching of $37 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ is equal to 15% and 3% of NECB for the two consecutive years. Kindler *et al.* (2011) measured DOC leaching at an intensively grazed site to be 5% of NECB over a multi-year period. Even if DOC leaching occurred, respiration data from this site suggests a large component will be degraded to CO_2 , which will be captured by eddy covariance measurements (for full discussion see section 4.2.4.2).

4.4.2 DOC concentration

Concentrations of DOC leaching measured across the site and throughout the year were low, with an average concentration of 4.5 mg L^{-1} . Measurements of DOC concentration in subsoils are typically low (Michalzik *et al.*, 2001; Sanderman & Amundson, 2009; Kindler *et al.*, 2011). Mertens *et al.* (2007) measured average leachate DOC concentrations of 17 mg L^{-1} (0.4 m) and 9 mg L^{-1} (1.2 m) under a bare soil system. Similarly, Kindler *et al.* (2011) measured an average DOC concentration of 9 mg L^{-1} from the subsoil of a grassed system. While both these measurements were considered low, the concentrations were still slightly higher than the average 4.5 mg L^{-1} measured at this site. Sorption in the lower mineral horizons decreases the concentration of DOC from the topsoil to the subsoil (Tipping *et al.*, 1999; Kaiser & Guggenberger, 2000; Guggenberger & Kaiser, 2003; Sanderman & Amundson, 2009). Although DOC concentrations at this site were not measured in the surface soil, there was strong evidence that the low

concentrations measured at 0.65 m were due to the depth of measurement and the sorption capacity of the overlying soil.

It is widely accepted that in soils with substantial clay content, DOC concentrations decrease down through the soil profile (Kaiser & Guggenberger, 2000; Kaiser & Guggenberger, 2003; Michalzik *et al.*, 2003) with a suggested 50-90% reduction in DOC concentration between surface organic and mineral horizons (Neff and Asner 2001). All four soils at this site were of a loamy texture, with three of the four soils classified as Allophanic and therefore containing the mineral allophane. Allophane is a short-range order clay mineral containing silica, alumina and water (Hewitt, 1998). Ghani *et al.* (2008) hypothesised that the presence of allophane lead to a decrease in the amount of DOC leached due to the large surface area and high sorption potential of the mineral. Additionally, Sparling *et al.* (2006) and Barton *et al.* (2005) found lower leaching of DOC from Allophanic soils in comparison to the other three soil orders investigated (Table 4.5). Mineralisation of DOC to CO₂ also plays an important role in the reduction of DOC concentrations lower in the soil (Kalbitz *et al.*, 2000). The fate of DOC is examined further in section 4.2.4

4.4.2.1 *Seasonal difference in DOC leaching mass*

Dissolved organic carbon leaching showed a strong seasonal pattern, with higher DOC leaching mass in July and August for all of the paddocks except paddock 32, which had the highest mass of leaching between April and May due to a high DOC concentration from a single sample in collected in May (Figure 4.4.) DOC concentration showed a strong correlation with volume of water drainage in soil. As the concentration of DOC did not vary significantly throughout the year, during drier periods when the volume of water flowing through the soil was low there was less mass of DOC leached. The mass of DOC leaching at this site is ultimately controlled by the volume of water drainage. The correlation between DOC leaching and drainage may be a potentially useful tool in determining the future mass of DOC leaching at this site, assuming the concentration of DOC remains within the same range.

While the idea that DOC export is strongly related to the hydrological conditions is strongly supported in the literature (Harrison *et al.*, 2008; Gielen *et al.*, 2009), the lack of difference in DOC concentration, seasonal or otherwise at this site, is contradictory to many studies (for example Tipping *et al.*, 1999).

Much of the literature points to an increase in DOC concentration following an extended dry period as soluble C builds up the soil during times when leaching is not occurring (Tipping *et al.*, 1999; Kaiser *et al.*, 2001; Harrison *et al.*, 2008). However, at this site, no correlation was found between DOC concentration and time since drainage (Figure 4.10). An explanation for the lack of high DOC concentrations following an extended dry period could be due to the wetter than normal summer in 2011/2012 with few extended dry periods. Drainage from soil is not typically expected in the Waikato between the months of November and April due to the low rainfall and the negative balance of the soil water storage. However, during the summer 2011-2012 there was enough rainfall to cause drainage in November (9 mm) and December (74 mm) of 2011 as well as in January (37.1 mm) and March (111 mm) of 2012. Samples were not collected during this period, as drainage was not expected and suction cup samplers were not in place at this time.

In part, the lack of seasonality at this site may be explained by the rate of water moving through the soil. DOC leaching is limited by the water draining and the maximum net DOC mobilisation rate in the topsoil is limited (Mertens *et al.*, 2007). To support this, Kalbitz *et al.* (2000) proposed that low leachate velocities are required to obtain high DOC concentrations, thus the low concentrations in winter can be explained by the relatively rapid movement of water through the soil. Münch *et al.* (2002) found that as the rate of water movement increased, the concentration of DOC in solution decreased due to the reduced solubilisation of C. For much of the winter, the soils were constantly at field capacity, so any new water additions were leached rapidly. However, the process of increasing DOC concentrations with slower water movement does not explain why the concentrations in summer were low. While water movement plays an important role in DOC leaching, the production of DOC is very important. In autumn higher

temperatures coupled with the relatively moist soil conditions due to the wetter months may have led to increased respiration, removing much of the DOC produced before it reached 0.65 m. Apart from the study by Mertens *et al.* (2007), much of the work around temperature and water drainage has been conducted in forested systems, both in the field (Gielen *et al.*, 2009) and laboratory (Christ & David, 1996), and as such the same seasonal variation may not apply in temperate pastures.

The low DOC concentration may also be a product of sampling strategy. Samples taken during the year were collected during times when DOC leaching was estimated to be occurring or when soils were at field capacity, thus requiring only small tensions in the suction cups to withdraw samples. To collect samples during drier periods when leaching was not occurring would have required much higher tensions in the suction cups. Samples collected with high tensions, are not usually representative of the soil water that will drain, as they preferentially extract water from micro-pores (Zsolnay, 2003). However, during drier periods, water still remaining in larger pore spaces will be influenced by the time spent there, and may gain more DOC (Kalbitz *et al.*, 2000; Münch *et al.*, 2002; Mertens *et al.*, 2007; Harrison *et al.*, 2008; Gielen *et al.*, 2009). In contrast a study by Buckingham *et al.*, (2008) on the methods used to extract DOC solution in soil, attributed low DOC concentrations in suction cups to their innate ability to remove small pore waters, and claimed that smaller pores had a lower DOC concentration. The method used in this study was used to determine the concentration of leachates and not the ambient soil DOC concentration. However, as a consequence of the discrete sampling method, fluxes in DOC concentrations may have been missed during the beginning of leaching events and thus may have underestimated the potential seasonal variation in DOC concentration. Therefore, there may be some underestimation in the mass of DOC leached for this site.

In general, sampling in summer would not be considered as there is no leaching, however, during the summer of 2011/ 2012 there was sufficient rainfall to cause drainage and some DOC leaching was likely to have been missed. If barrel lysimeters were used the rate of drainage could be directly measured and the

effects of drainage rate on DOC concentration could be investigated, both in the field and in the laboratory.

4.4.3 Controls on DOC leaching

4.4.3.1 *DOC concentration and soil type*

Significant differences in DOC concentration between different soils has been one of the key findings throughout the literature. Don and Schulze (2008) found that DOC leaching was seven times greater in a clay-poor Arenesol than in a clay-rich Vertisol. Dissolved organic carbon concentrations were also found to be different between soils in numerous other studies (Sparling *et al.*, 2006; Harrison *et al.*, 2008; Ghani *et al.*, 2010; Kindler *et al.*, 2011). In the present study, DOC concentrations were not significantly different between the four soils although the p-value for possible difference was 0.076. The lack of certainty of the differences between the soils may be due to imperfect soil classification. Some of the soil sites were hard to classify, particularly in paddocks 36 and 32 due to modification of the soil to allow better drainage and access during wet months (Figure 4.2). Therefore, some of the sites may not be accurate representations of the natural soil and thus affect the concentration of the DOC leached. In addition, further replication of measurements may have allowed for the detection of differences, as measurements for individual soils were made only twice.

Due to the sampling of all four soils being completed only twice, the accurate estimation of DOC leached from each of the soils could not be made. Therefore, definite conclusions cannot be drawn about the effect of soil type on the mass of DOC leaching. An additional limitation was the error associated with the measurement of evaporation and precipitation to estimate leaching. Evaporation and precipitation measurements were made across the entire sampling area which included different soils with different water holding capacities, drainage and water storage properties that can influence drainage volumes. The use of *in situ* barrel lysimeters to measure drainage may have been a better option as spatial variation could have been captured more accurately and individual soil water balances could be solved using drainage water from the barrel lysimeter. Suction cup lysimeters provided a cheaper alternative to barrel lysimeters and could be

installed in greater numbers and sampled more regularly, allowing for greater measurement replication. Additionally at this site measurements were already being made for evaporation (as part of a wider study) therefore making it appropriate to use measured evaporation.

4.4.3.2 *Grazing*

There is very little information available on the management practices associated with grazing on the leaching of dissolved organic carbon or organic matter. Factors that may require consideration include: grazing intensity, effluent quantity and frequency, plant type, and soil compaction or treading by animals.

In the studies by (Ghani *et al.*, 2010) and (Harrison *et al.*, 2008), the experimental design involved the removal of grazing animals for three weeks prior to soil sampling, or the exclusion of animals for the duration of measurements. The stated purpose of this was “to avoid any influence of fresh animal excreta on DOM and soil respiration rates” (Ghani *et al.*, 2010). So while these studies were concerned with grazed pastures, they have less ability to determine the effects of grazing on DOC leaching.

In the present study, the sites were grazed on a whole farm rotation with each paddock being grazed approximately one to two times a month (Appendix C) for the entire sampling period. No correlation was found between time since grazing and DOC concentration (Figure 4.8). This result was unexpected, as dung and urine from grazing animals contain high concentrations of carbon and have been found to leach to depths of up to 0.4 m in macropore flow (Moir *et al.*, 2011). Urine also contains high concentrations of salts, and is alkaline (Lambie *et al.*, 2012), which may influence the solubility of C in solution (Kaiser & Guggenberger, 2003; Sparling *et al.*, 2006) (see section 4.2.4.1 for more on pH).

Comparisons have been made between the losses of C in soils of Dairy farms and adjacent dry stock farms (Schipper *et al.*, 2010; Barnett, 2012) with results showing significantly less C in the A horizon of dairy soil compared to dry stock soils, as well as a decrease in the C stock of dairy soils through time. A key difference between dry stock and dairy farms is the amount of excreta deposited

by dairy cows in comparison with dry stock farms, and this has been suggested as the reason for differences in C content.

Lambie *et al.* (2012) explored the solubilisation of soil C following treatment with cow urine in the laboratory as a means of explaining C loss in dairy pasture. Results showed that cow urine caused significant amounts of C solubilisation in soil. In a four year study by Sparling *et al.* (2006), soil irrigated with effluent was found to have decreased C content in surface horizons. The decrease in C content was attributed to the high salt content of the soil causing some dissolution of soil organic matter, as well as an increase in the mineralisation of C due to the enhanced nutrients and moisture. In the current study, no increase in DOC concentration was found at 0.65 m following grazing. With urine patches covering about 25% of paddocks per year (Moir *et al.*, 2011) presumably some of the suction cup lysimeters would have been installed directly below urine patches. It is therefore surprising that with soil subsurfaces likely in direct contact with DOC, and an increased solubilisation of soil C with urine that there was not a greater range of DOC concentrations measured. This suggests that much of the added C in cow urine and the solubilised C it produces is removed through mineralisation before it reaches the lower subsoil (0.65 m). The release of C that was previously inaccessible may enhance respiration rates (Fontaine *et al.*, 2007). Evidence for priming was also found in lower horizon soils. When available C was added it caused an increase in the mineralisation of soil C.

4.4.3.3 **Nitrogen and DOC**

As N is predominantly covalently bonded to C in soil organic matter, it was expected that C and N leaching would show some correlation. Kindler *et al.* (2011) found a positive correlation between DOC production and the C:N ratio of soil organic matter, and found that nitrogen poor organic matter seems to result in the production of a greater proportion of soluble C. Parfitt *et al.* (2009) also found that in soils with a low nitrogen fertiliser loading, a greater mass of DOC was leached. Interestingly, in this study there is no relationship between organic N and organic C leaching concentration.

4.4.4 Fate of DOC in subsoil

Dissolved organic carbon leaching is a process that is loosely defined in the literature. The loss of DOC through leaching can only be considered a loss from the soil once it has reached the groundwater. However, measurements for DOC leaching are generally made in the subsoil, and therefore do not necessarily represent a loss of DOC from the soil. The processes of sorption and mineralisation are regarded as very important controls on DOC leaching loss. Before reaching the groundwater, DOC may be adsorbed onto soil surfaces and stored in the soil or DOC may be converted to carbon dioxide where it can be measured as an above ground loss.

4.4.4.1 Sorption

Sorption of DOC was measured in the laboratory following the method of Lambie *et al.* (2012). Results for this experiment showed some evidence of sorption of the DOC leachate below 0.65 m. DOC leachate with a concentration 4 mg L^{-1} did not show net adsorption at all to either of the two soils tested, instead causing a small amount of desorption in both of the soils analysed. At higher DOC concentrations adsorption to the soils occurred with over half of the 7 mg L^{-1} solution of DOC added, adsorbing to the Te Punga soil and 37% sorbed in the Piarere soil. The ionic strength of a solution relates to the concentration of ions, and solutions with high ionic content are known to cause desorption of C (Reemtsma *et al.*, 1999). The ionic strength of the DOC solutions was not known and may have contributed to the desorption of the soils. pH is also important when considering sorption. Sorption was found to be highest under slightly acidic conditions, whereas at an alkaline pH desorption will dominate (Guggenberger & Kaiser, 2003). pH of the two soils tested was known to be slightly acidic, however the pH of the DOC solution was unknown. The DOC solutions used in the experiment was a bulk of samples taken from lysimeters at 0.65 m, and therefore represent the DOC that is being leached in the field. While the 4 mg L^{-1} solution did not show sorption, the fact that the 7 mg L^{-1} solution did provided evidence that the soils at 0.65 m are able to adsorb carbon out of solution. All four subsoils at the site were slightly acidic, which should aid in the sorption of DOC. Additional sorption of DOC was strongly related to the finer fraction of soil, specifically the clay content and iron

and aluminium oxide content (Kaiser & Zech, 2000; Kothawala *et al.*, 2008; Schneider *et al.*, 2010; Kindler *et al.*, 2011). All four soils in this study contained clays and were classed as loams, which would also have contributed to sorption.

Solutions used in experiments where the sorption of DOC onto soils is determined typically use laboratory made solutions, with constant pH, ionic strength etc. (Guggenberger & Kaiser, 2003; Kaiser & Guggenberger, 2003; Sanderman & Amundson, 2009; Schneider *et al.*, 2010). *In situ* the DOC solution is not always uniform, and these properties may vary. In this study the use of DOC solutions collected from the field was prescribed so that the proportion of leached DOC adsorbing could be determined. To amend this experiment, further replication of the study is needed as well as use of a wider range of concentrations. In addition to this, some investigation into the sorptive capacity of the overlying soils may have been beneficial in aiding the explanation of the low DOC concentrations measured at this site. Furthermore, investigation into the mineralogy, including the relationship between allophane and DOC sorption, should be conducted.

4.4.4.2 *Respiration*

While mineralisation of DOC is usually regarded as the lesser of the two internal cycling processes (Kalbitz *et al.*, 2000), in this case it was shown that the DOC leaching through the soil was an available source for microbial respiration, which was potentially greater than sorption. Under the right conditions, microbes in the subsoil can breakdown a large proportion of the DOC leaching with estimates that an average of 47% of DOC is biologically available below 0.6 m (Neff & Asner, 2001). Additionally, dissolved organic carbon from aboveground litter can cause priming where microbes break down more recalcitrant C lower in the profile (Park *et al.*, 2002; Fontaine *et al.*, 2007). The priming effect was measured in the Te Puinga soil, with 11 and 25 times more carbon being respired than was added to the soil as DOC.

Mineralisation in the subsoil usually proceeds at much slower rates than in the surface soil (Sanderman *et al.*, 2008a). However, under laboratory conditions soils were sieved, giving microbes a greater aeration and access to a greater portion of C that may have been bound in aggregates. Also, the soils were kept at a constant

temperature of 20°C, which is higher than field conditions and is likely to have increased respiration rates (eg. Lloyd and Taylor, 1994). While mineralisation removed DOC from soil through respiration, increased mineralisation may also lead to greater production and leaching of C through the incomplete breakdown of very old SOC in subsoil (Fontaine *et al.*, 2007). Although this experiment provides an indication of the availability of DOC to microbes, and the activity of microbes, measurements of soil respiration would be best made under field conditions to better determine microbial behaviour under natural conditions. However, there are many confounding variables when measuring respiration in the field and the respiration of subsoil is difficult to measure.

4.5 Conclusion

DOC concentrations were low throughout the year, and showed little variation. Therefore, subtracting evaporation from rainfall was the main technique used to determine the volume of DOC leached. The mass of DOC leached from 0.65 m was also low in comparison to previous studies of DOC (Barton *et al.*, 2005; Sparling *et al.*, 2006; Parfitt *et al.*, 2009; Ghani *et al.*, 2010), with DOC leaching at 0.65 m equivalent to 4.5% of the net ecosystem exchange for this site and 3-15% of NECB for a similar intensive grazed pastoral system (Mudge *et al.*, 2011). Therefore, DOC leaching represents an important component of the carbon budget, if it was assumed to be a loss of DOC. However, leaching from 0.65 m cannot always be regarded as a loss of C from the soil, as, below this depth, soils have the capacity to further adsorb DOC and/or to mineralise DOC. Adsorption of DOC onto soil surfaces can result in C storage and the removal of DOC from solution for potentially long periods of time (Kaiser & Guggenberger, 2000). Both the Te Puninga and Piarere soil were capable of removing DOC from solution when at high concentrations (7 mg L⁻¹), with a 56% and 34% reduction of DOC in solution. The ability of soils to adsorb DOC is related to the proportion of aluminium and iron oxides, clays and the cation bridging ability of the soil, as well as the pH and ionic strength of the DOC solution (Kaiser *et al.*, 1996; Zech *et al.*, 1996; Kaiser & Zech, 2000; Guggenberger & Kaiser, 2003; Kothawala *et al.*, 2008; Schneider *et al.*, 2010). Three of the four soils were of the Allophanic soil order, which was

shown to have lower DOC leaching potentially due to higher sorption (Ghani *et al.*, 2010). The pH of all four soils at 0.65 m was also slightly acidic which is also beneficial to sorption (Kaiser & Guggenberger, 2003). Removal of DOC by mineralisation is possible at 0.65 m with microbes in the Te Puinga soil respiring up to 25 times more C than was added, with respiration 11 to 15 times greater in the DOC treatment soil than the water control.

For DOC leaching to be regarded as a loss from the soil, DOC needs to be lost to the groundwater. However, the movement of DOC from subsurface horizons was not necessarily a loss, but may represent a mechanism by which to store C lower in the soil profile. The movement of C from surface horizons to lower in the soil through DOC leaching is potentially important when quantifying soil C stocks. While the IPCC quantifies C stocks to 0.3 m and other studies have measured C to 0.6 m and beyond (Schipper *et al.*, 2010), only measuring C in the surface soils may not accurately quantify soil C losses and gains, as surface C can be transported as DOC to lower horizons. Therefore care must be taken when selecting a depth to measure losses of C. Consequently, leaching of DOC as a loss may only be important in tile drained and artificial drainage systems or shallow sandy or gravelly soils where DOC reaches the waterways more directly without the same travel distance or time through soil.

5 Conclusions and Future Research

5.1 Conclusions

Soils are the largest terrestrial store of carbon (Lal 2008), losses of soil C can lead to soil degradation causing a reduction in biomass and productivity, C is also cycled between the atmosphere the land and the oceans as CO₂. CO₂ is an important greenhouse gas and so, the uptake and release of CO₂ by terrestrial ecosystems is an important control of the climate system. This highlights the importance of quantifying fully the losses of C from the soil, including how C is stored and cycled in soil, as small changes in stored soil C can have a large effect on the changes in global C cycling and soil quality (Smith *et al.*, 2008). Much attention has focused on the process of respiration and photosynthesis for determining the net loss or gain of C from an ecosystem; however, there are a number of other loss mechanisms, including dissolved organic carbon (DOC) leaching that need to be quantified. In general, DOC leaching is a component of the C budget that is not well constrained, and as a consequence is not often accounted for in carbon budgets (eg Mudge *et al.*, 2011).

The main objective of this thesis was to determine whether DOC leaching was an important component of a carbon budget for a grazed pastoral system. This was carried out in replicate for 5 paddocks at a Waikato dairy farm, that had a complex of four soils. Measurements were made for 7 months from April through to October, 2012. Concentrations of DOC were collected from the soil using ceramic suction cup lysimeters, installed to a depth of 0.65.m Samples were analysed for DOC concentration, which was multiplied with soil water drainage to determine the annual mass of the DOC leaching. Dissolved organic carbon leaching at 0.65 m was $37.6 \pm 4.2 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ (mean \pm SE). The mass of DOC leaching at this site was low in comparison to other studies on grassed ecosystems (McTiernan *et al.*, 2001; Barton *et al.*, 2005; Sparling *et al.*, 2006; Sanderman *et al.*, 2008; Ghani *et al.*, 2010). Net ecosystem exchange (NEE) for this site was $-880 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ (S.Rutledge, *pers. comm.* February 2013), and DOC leaching at this site represented about 4.5 % of the total NEE. Compared to the net ecosystem carbon

balance (NECB) (measured at a different location in a similar study: Mudge *et al.*, (2011) the mass of DOC leaching represents between 3 and 15% of the NECB. Kindler *et al.*, (2011) measured the NECB for a grazed pasture and found DOC leaching to represent 5% of NECB.

While, DOC leaching represented a loss of C from the topsoil, this leaching may not represent a C loss from the system. DOC leaching in this study and many others (eg. Mertens *et al.*, 2001; Sanderman and Amundson 2009; Kindler *et al.*, 2011), measured DOC leaching to the subsoil. For DOC to be counted as a loss from the system, DOC be transported away from the site. While DOC leaching within the soil profile is representative of the potential DOC loss, sorption and mineralisation of DOC may act to reduce the concentration of DOC before reaching the groundwater. To fully determine the contribution of DOC leaching (from 0.65 m) to the NECB, the internal cycling of DOC in the vadose zone also needs to be measured. Determining the cycling of DOC in the vadose zone was the second aim of this thesis.

Results from the laboratory sorption experiment indicated that the concentration of DOC leaching to the groundwater can be lower than the concentration of DOC measured at 0.65 m. The average DOC concentration collected in the suction cup lysimeters of this study was 4.5 mg L⁻¹ however DOC concentration ranged between paddocks from 2.5 mg L⁻¹ and 7.15 mg L⁻¹. Laboratory analysis of two soils collected in this study showed a high capacity for sorption of DOC. Soil water solution with a concentration of 7 mg L⁻¹ DOC, reduced in concentration by over a half when shaken for four hours with the Te Puniga soil. Similar results were found in the Piarere soil with a 34% reduction in DOC concentration. In contrast, when both soils were shaken with DOC at lower concentration (4 mg L⁻¹) there was only a small amount of net desorption. Both experimental concentrations fall within the range of concentration observed in field collections, meaning there could have been some reduction in the concentration of DOC leached below the 0.65 m sampling depth and subsequently a reduction in the DOC mass lost

Mineralisation of DOC was also investigated in a laboratory study. Subsoils from 0.65 m were collected, air dried at 4 °C then inoculated with DOC leachates collected from 0.65 m. Respiration rates of DOC treated samples were significantly higher than the water amended controls for the Te Puinga soil and the Piarere soils. When inoculated with a 4 mg L⁻¹ solution, after correction for the water control the Piarere soil respired 74% of the amount of DOC added, while the Te Puinga soil showed substantial evidence of priming, with CO₂ respiration being 11 and 25 times greater than the DOC addition in two separate studies. These high respiration rates provided evidence that the majority of DOC leached to 0.65 m could be mineralised. A higher respiration of CO₂ – C than DOC-C added was also indicative of priming, where additions of DOC to the subsoil may cause an increase in the mineralisation of more recalcitrant soil organic carbon.

In conclusion, at this site, while DOC leaching from 0.65 m may be a significant component of the cycling of soil C, DOC as loss from the ecosystem was likely not a significant component of the carbon budget. Sorption and mineralisation likely reduce the mass of DOC leaching below 0.65 m and ultimately reduce the mass lost from the ecosystem. Kindler *et al.*, (2011) concluded that DOC leached from a grazed pasture was an important component of a carbon budget, that while comparatively small, it represented a consistent loss of C from the ecosystem. Due to the already small mass of leaching at this site and the likely reduction, DOC leaching as a loss from the carbon budget was not large. However, over long time scales DOC leaching may be a significant loss of C from the soil.

Concentrations of DOC at this site were consistently lower than reported literature for similar land uses and climates (Parfitt *et al.*, 2009; Ghani *et al.*, 2010; Kindler *et al.*, 2011). DOC concentrations showed little variation throughout the year, and was persistently low; as a consequence the volume of water draining through the soil was the main driver of the mass of DOC leaching. The concentration of DOC in soil can be explained by the rate of production of DOC, the solubility of C in soil, and the internal cycling of C (sorption and mineralisation) all of which require further investigation. Overall the results found in this study highlight the variation in DOC leaching across ecosystems, climates and measurements.

The controls on the concentration of DOC leaching were briefly investigated, these included time since drainage, nitrogen leaching, soil type and grazing. No correlation was found with DOC concentration and time since drainage. The lack of variation in DOC concentration could be due to the discrete sampling times, or rate of water flow through the soil. Nitrogen concentration (total and organic) of the leachate showed no relationship with DOC. There was no variation in DOC concentration across the four soil types, even though the soil structure and drainage classes varied. However due to the sampling method the mass of DOC leaching from each soil could not be determined independently. Surprisingly, the time since grazing did not correlate well with DOC leaching concentration suggesting that additions of C in urine, and solubilised C from urine were mineralised, and not detectable at 0.65 m.

Ceramic suction cups were used to sample soil water solution. An obvious limitation of ceramic suction cups is the discrete sampling time and point samples; this means that potential fluxes of DOC may be missed between sampling times, and at the start of drainage, which may have led to a lack of seasonal variation in DOC concentration. Another limitation of suction cup samplers is they do not allow for the quantification of soil drainage and drainage velocity which is potential important in detecting leaching mass changes between soils. A further limitation was the disturbance of soils at this site. Soils could not be properly classified and therefore detection of changes between soils may not be accurate.

5.2 Future research

There are few studies reporting on DOC leaching from grazed pastoral systems, and these have reported substantial differences between sites. As grazed pastures make up a quarter of the land's ice free surface it is important to quantify fully the loss and cycling of C in the soils of these systems. The comparison between this study and others highlighted the need to better quantify the losses of C from the soil including an investigation into the depth at which C budgets and C stocks are accounted for in the soil.

There is very little research into the processes controlling DOC leaching on grazed pastoral systems, including production, cycling, and farm management. Comparing DOC leaching at this site to the international literature provided little insight, as few of the studies focus on such intensive farming systems, or do not look at grazing at all. Future in depth study into controls on DOC leaching from intensively farmed systems, including farm management factors would contribute greatly to understanding and potential to reducing the mass of DOC leaching from these highly managed systems. Urine deposition and its cycling in the soil is one example of a factor important in intensively managed farms that may contribute to DOC leaching and cycling. Urine deposition has been shown to solubilise soil organic C (Lambie *et al.*, 2011). Further investigation into the cycling of urine in soil and its contribution to mineralisation and leaching is important particularly for dairy farms.

Priming of soil C was found in the subsoil of this study. In one of the soils investigated up to 25 times more CO₂ was respired than was added to the soil (control adjusted). Priming is potentially a way to cause losses of C in the soil. Further investigation into the role DOC leaching plays in priming would be interesting and would help in the relatively poorly understood DOC internal cycling process.

The discrete sampling of leachates using ceramic suction cups is not likely the best method to determine the mass of DOC leaching. However, it was appropriate for this study, as a large number of samples could be taken over an extended area. Comparing DOC leaching from suction cups to samples obtained from an instu barrel lysimeter where drainage could be collected continuously would be valuable in determining the possible flux of DOC missed by suction cups. Barrel lysimeters would also be valuable for determining the volume of water draining through the soil, providing the ability to compare water movement through the soil and DOC concentration. Also barrel lysimeters would allow for drainage to be calculated for each sample, so the potential difference in DOC leaching between soils could be investigated.

A synthesis of literature on DOC leaching has shown that DOC concentration and mass can be highly variable. While DOC leaching at this site for the year 2012 is likely not a significant component of the carbon budget for this year, changes in the internal cycling and production of DOC may mean that in other years DOC leaching is an important component of the carbon budget. Changes in farming practices may increase C solubilisation, or reduce mineralisation; additionally, changes in the net gain or loss of C from the system depend on climate and management. At this site if rainfall is increased (or reduced) the mass of DOC leached has the potential to change significantly, and as shown in drought years NEE could be greatly reduced (Mudge *et al.*, 2011) which would make DOC leaching more important to the carbon budget.

6 References

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Appendix A

Corrected fluxes were calculated using EddyPro (LI-COR Inc.) in ‘Advanced’ mode, which calculated half-hourly fluxes from the mixing ratio of H₂O (Burba *et al.*, 2012), applied double coordinate rotation (Wilczak *et al.*, 2001), compensated for time lags between anemometer and gas analyser using automatic time lag optimisation and applied frequency response corrections (for high pass filtering effects (Moncrieff *et al.*, 2004), low pass filtering effects (Ibrom *et al.*, 2007) and instrument separation (Horst & Lenschow, 2009)).

Quality control of H₂O fluxes included removing of fluxes when, i) friction velocity was below 0.11 ms⁻¹ indicating low turbulence conditions ii) the automated gain control (AGC) signal outputted by the IRGA deviated from the ‘baseline’, indicating that high humidity may have affected the IRGA readings iii) the IRGA or anemometer reported warnings, iv) out-of-range values were calculated for the flux ($LE < -100$ or $>700 \text{ W m}^{-2}$) or v) no fluxes were calculated due to instrument malfunction or power outage. The percentage of good data remaining after quality control was 55%. Gaps in the dataset were filled using the online software described by Reichstein *et al.* (2005) which is based on the “covariation of fluxes with meteorological variables and the temporal autocorrelation of fluxes”.

Appendix B

Te Punga soil	Treatment	Total respiration ($\mu\text{g CO}_2\text{-C/g soil}$)	Standard error	Control corrected ($\mu\text{g CO}_2\text{-C/g soil}$)	DOC added ($\mu\text{g doc/g soil}$)	% DOC- to CO_2	priming (a)
week 1	water (control)	9.95	0.46				
	low	22.76	5.17	12.81	1.18	1087.20	11.63
	high	25.17	2.10	15.21	20.42	74.50	
week 2	water	11.17	0.67				
	low	22.58	4.71	11.41	1.18	968.54	10.23
	high	28.04	3.31	16.88	20.42	82.65	
week 3	water	17.17	0.89				
	low	27.14	0.93	9.97	1.18	845.77	8.79
	high	36.79	0.57	19.62	20.42	96.07	
week 4	water	26.02	1.30				
	low	35.28	1.41	9.26	1.18	785.65	8.08
	high	44.61	0.07	18.59	20.42	91.01	

Waihou soil	Treatment	Total respiration ($\mu\text{g CO}_2\text{-C/g soil}$)	Standard error	Control corrected ($\mu\text{g CO}_2\text{-C/g soil}$)	DOC added ($\mu\text{g doc/g soil}$)	% DOC- to CO ₂	priming (a)
week 1	water (control)	20.94	1.89				
	low	25.08	1.22	4.15	0.95	434.19	3.19
	high	28.99	1.12	8.05	15.66	51.44	
week 2	water	27.77	2.87				
	low	29.22	0.71	1.46	0.95	152.58	0.50
	high	32.62	2.80	4.85	15.66	30.99	
week 3	water	34.85	2.04				
	low	35.22	0.52	0.37	0.95	38.90	
	high	38.78	0.43	3.94	15.66	25.14	
week 4	water	41.42	2.61				
	low	42.59	0.94	1.17	0.95	122.48	0.21
	high	45.52	0.44	4.11	15.66	26.24	

(a) Priming is calculated as the control adjusted CO₂ respired, divided by the amount of DOC added. Negative numbers indicate no priming/control respiration was higher than the treatment respiration.

		Treatment	Total respiration (µg CO ₂ -C/g soil)	Standard error	Control corrected (µg CO ₂ -C/g soil	DOC added (µg doc/g soil)	% DOC- to CO ₂	priming (a)
Waitoa soil	Week 1	Control (water)	8.90	1.41		0.00		
		Low	15.04	6.64	6.14	0.55	1123.01	5.59
	Week 2	Control (water)	15.76	1.52		0.00		
		Low	21.57	6.89	5.81	0.55	1063.67	5.27
Te Puninga	Week 1	Control (water)	37.84	0.62	15.84	0.00	2527.39	15.21
		Low	53.67	4.12		0.63		
	Week 2	Control (water)	52.95	1.29		0.00		
		Low	71.09	3.92	18.15	0.63	2895.97	17.52
Piarere	Week 1	Control (water)	34.68	3.08		0.00		
		Low	34.05	1.02	-0.63	0.65	-97.57	-1.28
	Week 2	Control (water)	50.94	4.89		0.00		
		Low	50.09	0.97	-0.84	0.65	-1.31	-1.49
Waihou	Week 1		38.65	1.72		0.00		
			38.68	1.05	0.03	0.62	5.61	-0.58
	Week 2		54.21	1.77		0.00		
			54.06	1.00	-0.15	0.62	-24.94	-0.77

