2012

Evaluating Methane Emissions from Dairy Treatment Materials in a Cold Climate

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EVALUATING METHANE EMISSIONS FROM DAIRY TREATMENT CONSTRUCTED WETLANDS IN A COLD CLIMATE

A Thesis Presented

by

Eamon J. Twohig

to

The Faculty of the Graduate College of

The University of Vermont

In Partial Fulfillment of the Requirements for the Degree of Master of Science Specializing in Plant and Soil Science

October, 2012
Abstract

Treating elevated nutrients, suspended solids, oxygen demanding materials, heavy metals and chemical fertilizers and pesticides in agricultural wastewaters is necessary to protect surface and ground waters. Constructed wetlands (CWs) are an increasingly important technology to remediate wastewaters and reduce negative impacts on water quality in agricultural settings. Treatment of high strength effluents typical of agricultural operations results in the production of methane (CH$_4$), a potent greenhouse trace gas. The objective of this study was to evaluate CH$_4$ emissions from two subsurface flow (SSF) CWs (223 m$^2$ each) treating dairy wastewater. The CWs were implemented at the University of Vermont Paul Miller Dairy Farm in 2003 as an alternative nutrient management approach for treating mixed dairy farm effluent (barnyard runoff and milk parlor waste) in a cold, northern climate. In 2006, static collars were installed throughout the inlet, mid and outlet zones of two CWs (aerated (CW1) and a non-aerated (CW2)) connected in-series, and gas samples were collected via non-steady state chambers (19.75 L) over a nine-month period (Feb-Oct 2007). Methane flux densities were variable throughout the nine-month study period, ranging from 0.026 to 33.9 and 0.008 to 165 mg m$^{-2}$ h$^{-1}$ in CW1 and CW2, respectively. The average daily CH$_4$ flux of CW1 and CW2 were 1475 and 552 mg m$^{-2}$ d$^{-1}$, respectively. Average CH$_4$ flux of CW1 was nearly threefold greater than that of CW2 ($p = .0387$) across all three seasons. The in-series design may have confounded differences in CH$_4$ flux between CWs by limiting differences in dissolved oxygen and by accentuating differences in carbon loading. Methane flux densities revealed strong spatial and seasonal variation within CWs. Emissions generally decreased from inlet to outlet in both CWs. Average CW1 CH$_4$ flux of the inlet zone was nearly threefold greater than mid zone and over tenfold greater than flux at the outlet, while fluxes for CW2 zones were not statistically different. Methane flux of CW1 was nearly fifteen fold greater than CW2 during the fall, representing the only season during which flux was statistically different ($p = .0082$) between CWs. Fluxes differed significantly between seasons for both CW1 ($p = .0034$) and CW2 ($p = .0002$). CH$_4$ emissions were greatest during the spring season in both CWs, attributed to a consistently high water table observed during this season. Vegetation was excluded from chambers during GHG monitoring, and considering that the presence of vascular plants is an important factor influencing CH$_4$ flux, the potential CH$_4$ emissions reported in our study could be greatly underestimated. However, our reported average CH$_4$ fluxes are comparable to published data from SSF dairy treatment CWs. We estimate average and maximum daily emissions from the entire CW system (892 m$^2$) at approximately 1.11 and 6.33 kg CH$_4$ d$^{-1}$, respectively, yielding an annual average and maximum flux of 8.51 and 48.5 MtCO$_2$-e y$^{-1}$, respectively.
Acknowledgments

I would like to thank my advisors, Aleksandra Drizo, Leslie Morrissey, and Don Ross for guidance and supervision and for showing patience during this lengthy experience. A special thanks to Aleksandra for her undying drive and motivation, and more importantly, for being not only an advisor but also one of my most trusted friends.

I must thank my colleagues in the Plant and Soil Science Department. Thank you to Josef Gorres for his guidance, friendship and sense of humor. Thank you to Anne-Marie Resnik for being such a good listener and for holding our department together.

Thank you to the graduate students with whom I had the fortune of working alongside as part of our research team. In chronological order, you are: Tom DiPietro, Pete Munoz, Matt Cunningham, Simon Bird, David Weber, Martin Lee, and Dana Allen.

Thank you to Alan Howard for always keeping his door open for me and for being such a willing and patient teacher.

Thank you to Eric Seitz and Peter Spartos who served as dependable companions during many hours of grueling field work, endearing inclement weather, unpleasant odors and stings and bites from a variety of biota – all without too much complaint.

I want to thank my entire family for their encouragement, love and support. Most importantly, thank you to my wife for believing in me and for being my best friend and better half. And thank you to my children for being my ultimate source of happiness and motivation in life.
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Literature Review

1.1. Introduction

The amount of the three primary greenhouse gases, carbon dioxide (CO$_2$), methane (CH$_4$) and nitrous oxide (N$_2$O), has increased globally since the Industrial Revolution by 39, 159 and 19%, respectively (IPCC 2007). Greenhouse gases occur naturally in the atmosphere, trapping infrared radiation from the earth’s surface and increasing the temperature of the earth. During the past century, human-related activities have substantially added to the amount of these gases in the atmosphere and enhanced the natural greenhouse effect (US EPA 2010). The most recent U.S. Inventory of Greenhouse Gas Emissions and Sinks estimates that since 1990, U.S. greenhouse gas emissions have increased by 10.5% (US EPA Agency 2012a). Increases in atmospheric concentrations of greenhouse gases are attributed to anthropogenic sources such as the extensive use of nitrogen fertilizers, clear-cutting and burning forests for use in agriculture, and pollutants released from auto emissions and industrial activities (IPCC 2007).

Methane has a life span between 9 and 15 years in the atmosphere, and has 21 times greater global warming potential than CO$_2$ (US EPA 2012a). Natural sources of CH$_4$ are estimated to produce 37% of the total global CH$_4$ emissions, the largest source being from wetlands; however increasing anthropogenic emissions of CH$_4$ are approximately 1.5 to 2.5 times the magnitude of natural emissions (Forster et al. 2007). In the United States, the largest anthropogenic sources of methane emissions are natural gas and oil systems, ruminant digestion and manure management associated with
domestic livestock, decomposing wastes in landfills and coal mining (US EPA 2012a). In 2010, the agricultural sector was responsible for roughly 6% total US greenhouse gas emissions, with 21% and 8% of total CH₄ emissions directly attributed to enteric fermentation and manure management, respectively (IPCC 2007). Of all domestic animal types, beef and dairy cattle were by far the largest sources of CH₄ from enteric fermentation, while dairy cattle and swine represented the largest sources of CH₄ from manure management. Also included in the IPCC (2007) report on emissions from agricultural were rice cultivation and field burning of agricultural residues, representing only relatively minor sources of CH₄.

Although US dairy animal populations have been generally decreasing, emissions of CH₄ due to dairy cattle manure management increased by 107% from 1990 to 2010 (US EPA 2012a). This trend is attributed to regulations limiting the application of manure and to a shift in dairy and swine populations to larger and more concentrated facilities that rely on liquid manure storage and treatment systems. Manure stored or treated in liquid/slurry lagoons, ponds, tanks or pits, treatment systems with anaerobic conditions promotes the production of CH₄ (US EPA 2012a). While animal operations and agricultural activities are a source of air-transported pollutants, such as ammonia and greenhouse gases N₂O and CH₄, agricultural practices also often lead to ecological impairment of the environment by negatively impacting water quality (Sharpley 2003).

1.2. Impacts of Agricultural Activities on Water Quality

Increased nutrient pollution of streams and lakes from dairy farms and other agricultural activities has been widely recognized across the U.S. and other parts of the
world. Based on a 1998 assessment, the U.S. Environmental Protection Agency listed agriculture as the primary pollution source of rivers, streams, lakes and ponds (USEPA 2003, Ribaudo 2003). As of 2011, approximately 917 million acres of land in the United States is under agricultural production with over 1.2 million livestock operations (USDA 2012). The US EPA estimated in 2003 that about 212,000 animal feeding operations (AFOs), of which approximately 20,000 are confined animal feeding operations (CAFOs), generate approximately 500 million tons of manure each year (USEPA 2012c).

The growing trend in agriculture toward concentrated and confined animal facilities has resulted in an accumulation of animal wastes, facility wastewater, and operation area storm runoff, thereby resulting in elevated nutrients, suspended solids, oxygen demanding materials, and heavy metals concentrations in surface and ground waters (USEPA 2003). Agricultural pollution from farms can include point sources, such as discharges from manure storage pits, tile drains from fields or settling tanks, and contamination during fertilizer broadcast applications (Sharpley et al. 2003). Non-point pollution stems from indirect or non-specific sources, and occurs as the result of many agricultural production facilities and activities, including animal feedlots, irrigation, pastures, dairy farming, orchards, and aquaculture (Ongley 1996). Farming activities are recognized as the largest single contributor of non-point source pollution, not only in the United States, but also in Canada, Europe, and other parts of the world (Du Bowy and Reaves 1998; Geary and Moore 1999, Longhurts et al. 2000).

The pollution potential of agricultural operations will depend on the number and type of animals, farm size, location and layout, facilities and practices used to collect and store wastes, and choice of practices for waste management (USEPA 2003). For
example, dairy farms are often situated in remote areas with no access to centralized treatment systems and milk house effluents are therefore traditionally applied to land and/or discharged in treatment lagoons or below ground infiltration systems (Dubowy and Reaves 1994). In general, the concentration of animal feeding and cropping operations in particular regions of the country results in a volume of manure and nutrients on livestock operations that often exceeds the area of available cropland (Sharpley et al. 2003). Solutions are currently being sought for economically viable practices that would ensure reduction in nutrient loads to surrounding watersheds (Ribaudo 2003, USEPA 2003).

1.2.1. Agriculture Pollution in Vermont

One of the two largest contributors to New England’s total farm receipts is milk sales, and there are over 215,000 dairy cows in New England, producing an average of over 18,000 lbs. of milk per cow per year (USDA 2011). While Vermont dairy farms have been recognized as the largest agricultural revenue generator in the region and a significant contributor to the economy (USDA 2011), treatment of dairy wastewater effluents remains a question of concern. For example, recent research in the Lake Champlain Basin (LCB) shows that while developed land contributes up to four times more nonpoint source phosphorus than average agricultural lands, far more acres of LCB land are in agriculture (Troy et al. 2007). There are important factors influencing such pollution. Vermont agricultural producers have much less arable land available on average when compared to other states (Meeks 1986). The lack of cultivable land, combined with the historical settlement patterns and extensive land requirement for dairy
farming, has led to the establishment of agricultural practices on marginal sites, with farms often situated just feet from streams or rivers (Meeks 1986). Such locations increase water contamination risks from barnyards, pastures, milk houses and manure storage, as well as pesticide and fertilizer handling areas.

1.2.2. Lake Champlain Water Quality

The LCB comprises a watershed that drains a vast geographic area east of the Adirondack Mountains of New York, west of the Green Mountains of Vermont and north to Quebec, Canada. Over the past decade, Lake Champlain’s water quality has deteriorated significantly, posing a serious threat to the economic vitality of the region, which includes Vermont, New York and Canada (LCSC 2010). Much of Lake Champlain’s pollution problems can be attributed to the influx of non-point pollution from the watershed area. About 95 percent of the total phosphorus load to Lake Champlain is attributed to nonpoint source pollution (Smeltzer et al. 2009). Excess solids and nutrients drain into the lake causing eutrophication and a depletion of oxygen. A lack of oxygen in lake ecosystems harms fish species and, in conjunction with excess nutrients, also promotes optimal conditions for algal and cyanobacteria blooms, a growing problem for Lake Champlain (LCSC 2010). The deterioration of Lake Champlain’s water quality poses a serious threat to the economy of the area, not only at the state level, but also internationally. Consequently, the LCBP seeks alternative and innovative practices to facilitate the protection of and to prevent further degradation of the Lake’s water quality (LCSC 2010).
1.2.3. Reducing Agricultural Water Pollution

Efforts have been made to reduce pollution from agriculture through regulations and the creation of best management practices (BMPs) and accepted agricultural practices (AAPs). With the establishment of the Clean Water Act in 1972, the Environmental Protection Agency created the National Pollutant Discharge Elimination System (NPDES) to regulate point source discharges of pollutants into the nation’s water body’s (US EPA 2006). In addition, all animal feeding operations (AFO) owners and operators must establish a site-specific Comprehensive Nutrient Management Plan (CNMP; US EPA 2003).

In agriculture, a set of methods collectively known as Best Management Practices (BMPs) have been defined to improve both the protection of environmental resources and farm viability. The state of Vermont has defined BMPs as farm practices implemented either voluntarily or as required in order to address water quality problems and to achieve compliance with state water quality standards (AAM 1996). BMPs include a diverse set of farming practices, such as changing tillage practices or cropping techniques, to farm landscape modifications like planting buffer strips of dense vegetation around fields. A commonly recommended BMP in Vermont for diffuse non-point source field runoff treatment is a 10 foot wide vegetated buffer strip on all fields adjacent to surface waters of the state (AAM 2006). Another example of a recommended BMP is a manure storage pit that is often designed to receive barnyard runoff and milk house wastewater (VT ANR 1990). The State of Vermont also adopted the AAP rules, which focus on farming techniques to reduce non-point source pollution. More specifically, AAPs are developed to regulate the management of barnyards and manure storage areas to limit the risk of
discharge of manure or other wastes to streams (AAM 1996). An example of an AAP is the banning of manure spreading on fields between December 15th and April 1st when the ground is generally frozen, and field applied manure could easily be transported into surface waters (AAM 1996).

Commonly funded production area BMPs includes waste storage facilities, silage leachate systems, milk house waste systems, and barnyard runoff collection (VT AAFM 2012). However, waste storage facilities, such as manure storage pits, cannot always control surface runoff losses of nutrients to surface and groundwater (Harris et al. 1997). Reliance on natural wetlands and their inherent remediation processes to treat such nutrient losses is, however, limited due to historic and dramatic losses of natural wetland acreage paired with irreversible degradation of wetland quality due to uncontrolled discharges and incorrect valuations of environmental impact of wastewater. Constructed wetlands (CW) are systems that have been designed with the aim of reproducing natural wetland processes in a more controlled environment and are used around the world to treat agricultural wastewaters (VanderZaag et al. 2010).

1.3. Constructed Wetlands for Agricultural Effluents Treatment

Constructed wetlands have emerged as a promising technology for municipal, industrial, urban runoff, and agricultural effluents treatment over the past 20 years (Hammer 1989, Moshiri 1993, Kadlec and Knight 1996, DuBowy and Reaves 1994, Kadlec et al. 2000, Hunt and Poach 2001, Vymazal et al. 2010). CWs were first developed in Germany during the 1950s by Kathe Seidel (1966) who carried out numerous experiments testing the use of wetland plants for the treatment of various types
of wastewaters. The use of CW systems has been recently reviewed extensively in scientific literature (Kadlec and Wallace 2008). Currently, CWs can be classified according to: vegetation type (free floating, floating leaved, emergent and submerged); hydrology (free water surface (FWS) and subsurface flow (SSF)); and SSF can be further classified according to vertical (V) or horizontal (H) flow direction (Vymazal 2010).

![Figure 1. Cross section of a typical, HSSF CW (source: www.iridra.eu).](image)

Research has demonstrated that CW systems provide an effective treatment alternative for biological oxygen demand (BOD), total suspended solids (TSS), bacteria e.g. *Escherichia coli* and nitrogen (N) (Kadlec and Wallace 2008). Treatment performance, however, depends on the incoming wastewater characteristics and loading, climate conditions, and CW design. In general, CW systems can achieve efficient reduction of BOD (up to 90-98%) and TSS (up to 85-95%), while the removal of total nitrogen (TN) and total phosphorus (TP) are variable (50-90% and 40-90%, respectively) (Kadlec and Knight 1996, Kadlec *et al.* 2000, Kadlec and Wallace 2008, Vymazal 2010).

A main advantage of CW systems is that they are relatively inexpensive to construct and maintain, depending on the strength of water to be treated and the
topography of the terrain (Kadlec and Knight 1996). Compared to conventional treatment plants, most CWs require minimal energy, are easy to install, and unlike other practices, require minimum maintenance (Vymazal, 2010). In addition, the systems are environmentally friendly, pleasant in appearance, contribute to wildlife habitat creation, and the wetland substrate may have the potential to serve as a source of natural fertilizer for crops (Kadlec and Wallace 2008).

The main disadvantage of CWs applications is large land area requirements for treating larger volumes and/or highly concentrated wastewaters, such as agricultural effluents, therefore CWs are more suitable for rural or low density areas (Denny et al. 1997). Pollutant treatment efficiency can also vary dramatically depending on climate conditions, maintenance and CW design. For example, nitrogen removal by CWs is variable depending on system design and phosphorus retention is usually low regardless of CW design. Furthermore, plant uptake only represents temporal storage because the nutrients are released back to the water after plant decay (Vymazal, 2010).

Constructed wetlands are compatible with typical farm operations and have been historically utilized for the treatment of agricultural effluents. In 1998, the Livestock Wastewater Treatment Database (LWDB) included 68 CW sites with 135 separate systems in North America and the large majority of these systems employed a FWS design (Knight et al. 2000). The types of agricultural effluents treated by CWs include dairy manure and milk house wash water, runoff from feeding operations, poultry manure and swine manure. Typical agricultural wastewaters are much higher strength than municipal wastewaters, with BOD, TSS, and ammonia-N often above 100 mg l\(^{-1}\) (Kadlec and Wallace 2008). For example, the CW employed at the University of Vermont Dairy
Farm in 2003 was designed to handle an influent BOD concentration of 4000 mg L$^{-1}$ and a peak flow of 37,500 L d$^{-1}$, with variable flow from barnyard runoff and milk house wastewater ranging from 500 to 10,000 L d$^{-1}$ (Munoz et al. 2006).

Constructed wetland technology has been utilized for centuries for the treatment of wastewater produced by residential settlements and production activities, and these systems are an accepted way to remediate wastewater effluent from agricultural, municipal and industrial systems. For example, HSSF CWs are used to treat wastewater from industry (textile in Australia, tannery in Portugal, chemical in the UK, petrochemical in US and China), agriculture (dairy and pig farm) and aquaculture operations in Australia, Canada, Germany, US and Uruguay, landfill leachate in Poland, and urban and rural runoff in the UK, US and Australia (Vymazal 2010). However, production of potent greenhouse gaseous products such as CH$_4$ and N$_2$O during wastewater treatment in CWs may compromise air quality (VanderZaag et al. 2010). In order to address the question of whether the implementation of CWs to reduce negative impacts on water quality creates a climate-related problem, since the late 1990s, scientists began measuring greenhouse gas fluxes from CWs in order to assess their contribution to atmospheric increases in CH$_4$, CO$_2$ and N$_2$O (Tanner et al. 1997, Fey et al. 1999).

1.4. Methane Emissions from Wetlands

In order to better understand the potential contribution of greenhouse gases to the atmosphere by CWs, it is important to understand the processes and to quantify gas flux from natural wetlands. Although wetlands have traditionally been viewed as major carbon sinks due to their dense vegetation, significant quantities of greenhouse gases, in
particular CH$_4$, are released from wetlands due to anaerobic decomposition (Bartlett and Harriss 1993). An overview of CH$_4$ fluxes from different types of wetlands was recently published by Kayranli et al. (2010) and is provided (Table 1).

**Table 1.** Overview of CH$_4$ fluxes from different types of natural wetlands, modified from Kayranli et al. 2010.

<table>
<thead>
<tr>
<th>Type of Wetland</th>
<th>Location</th>
<th>CH$_4$ flux (mg m$^{-2}$ h$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riparian Marshes</td>
<td>Ohio, USA</td>
<td>~3.5</td>
<td>Altor and Mitsch 2006</td>
</tr>
<tr>
<td>Swamp forest/marsh</td>
<td>Louisiana, USA</td>
<td>6.08-38</td>
<td>Alford et al. 1997</td>
</tr>
<tr>
<td>Wet meadow tundra</td>
<td>Alaska, USA</td>
<td>0.66-17.75</td>
<td>Bartlett et al. 1992</td>
</tr>
<tr>
<td>Forested swamps/ marshes</td>
<td>USA</td>
<td>3.99</td>
<td>Bartlett and Harris 1993</td>
</tr>
<tr>
<td>Peatlands</td>
<td>Northern USA</td>
<td>5.48</td>
<td>Armentano and Menges 1986</td>
</tr>
<tr>
<td>Peatlands</td>
<td>Florida, USA</td>
<td>25.68</td>
<td>Armentano and Menges 1986</td>
</tr>
<tr>
<td>Peatlands</td>
<td>Central Canada</td>
<td>2.79±0.27</td>
<td>Turestsky et al. 2002</td>
</tr>
<tr>
<td>Peatlands</td>
<td>Central Canada</td>
<td>0-14.84</td>
<td>Moore and Rolet 1995</td>
</tr>
<tr>
<td>Bogs and rich fens</td>
<td>Manitoba, Canada</td>
<td>0.91-9.95</td>
<td>Bellisario et al. 1999</td>
</tr>
<tr>
<td>Fens, bogs, ponds</td>
<td>Northwest Canada</td>
<td>-0.054-10.62</td>
<td>Liblik et al. 1997</td>
</tr>
<tr>
<td>Minerotrophic fens</td>
<td>Northeast Germany</td>
<td>0.6-9.0</td>
<td>Augustin et al. 1998</td>
</tr>
<tr>
<td>Wetlands (flooded)</td>
<td>Sanjiang, China</td>
<td>0.5 ± 0.19</td>
<td>Zhang et al. 2005</td>
</tr>
<tr>
<td>Wetlands (seasonally flooded)</td>
<td>Sanjiang, China</td>
<td>0.18±0.15</td>
<td>Zhang et al. 2005</td>
</tr>
<tr>
<td>Flooded forest and floating grass mats</td>
<td>Brazil (Amazon Floodplain)</td>
<td>8-92</td>
<td>Bartlett et al. 1988</td>
</tr>
<tr>
<td>Flooded meadow, mire bank, lacustrine sedge fen, and reed marshes</td>
<td>Finland (Lake Haposelka, Lake Mekrijarvi)</td>
<td>-0.2-6</td>
<td>Juutilen et al. 2001</td>
</tr>
<tr>
<td>Sub-arctic wetland</td>
<td>Sweden</td>
<td>0.2-36.1</td>
<td>Strom and Christensen 2007</td>
</tr>
<tr>
<td>Bog and forested swamp</td>
<td>North Wales, UK</td>
<td>-0.006-3.14</td>
<td>Kang and Freeman 2002</td>
</tr>
</tbody>
</table>
1.4.1. Natural Wetlands

Wetlands cover approximately 5% of the Earth’s surface and are the largest natural source of CH₄, emitting an estimated 170 Tg y⁻¹ (US EPA 2010). The Intergovernmental Panel on Climate Change (2007) calculated that wetlands are responsible for approximately 80% of all natural sources of global CH₄ emissions and 30% of all sources to the atmosphere. Researchers have known since the 1960s that wetlands produce CH₄ and, as interest in measuring CH₄ emissions from wetlands has grown, the relative importance of these emissions to overall atmospheric levels became clear (US EPA 2010, Bartlett and Harriss 1993).

The dominant factor controlling soil formation and flora and fauna species in wetlands is water saturation, the source of which may be precipitation, subsurface flow from ground water or surface flow from a surrounding watershed. Bacteria in the moist, anoxic wetland soils produce CH₄ as they decompose dead plant material and are therefore affected by many environmental variables (US EPA 2010). The emissions of CH₄ are a result of the balance of the production (methanogens) and consumption (methanotrophs) carried out by different groups of bacteria.

Whalen (2005) recently grouped controls of wetland CH₄ emissions into two categories: process-level and ecosystem-level factors. The climatic setting as well as the plant species present in the wetland controls CH₄ emissions at the ecosystem level, however, the most important ecosystem-level control on CH₄ emissions is the presence of water and the position of the water table because flux is greatly reduced in the absence of water (US EPA 2010). Process-level controls include organic matter quality and quantity, temperature and pH, all of which affect how well bacteria grow. For example, once
anaerobic conditions are established, organic matter supply and temperature may be the primary controls influencing CH$_4$ flux (Valentine et al. 1994).

Methane is released from wetlands via three pathways provided by primary productivity to reach the atmosphere: diffusion through the soil or water profile, plant mediated (aerenchyma), and ebullition when concentrations of CH$_4$ exceed saturation levels. Assessing the importance of ebullition is difficult due to the episodic nature of large gas volume releases (US EPA 2010). Wetland plant aerenchyma can serve as an important transport pathway for CH$_4$ emissions by providing a bypass of the potentially unsaturated surface areas of the wetland where oxidation can occur (US EPA 2010). Several authors have reported on the significance of methane transport through the vascular system of emergent wetland plants (Schutz et al. 1989, Chanton et al. 1992, Whiting and Canton 1992, Whalen 2005).

1.4.2. Constructed Wetlands

Only a few studies have published assessments of potential CH$_4$ emissions from CW systems (VanderZaag 2010). These studies have revealed that CH$_4$ released from CW systems during the treatment of wastewater depends on climate, temporal and seasonal variability (Mander et al. 2005, Inamori et al. 2007, Johannson et al. 2004, Liikanen et al. 2006), strength and type of wastewater (Tanner et al. 1997, Picek et al. 2007), vegetation (Inamori et al. 2007, Maltais-Landry et al. 2009) and system design (Mander et al. 2008, VanderZaag 2010).

Constructed wetlands typically receive a large external supply of carbon from the incoming wastewater. Carbon cycling in CWs is complex and carbon is removed from
wastewater by sedimentation, microbial assimilation, chemical binding and gaseous emissions of CO\textsubscript{2} and CH\textsubscript{4} (Kadlec and Knight 1996). Degradation reactions depend on the wetland environment as both anaerobic and aerobic processes consume carbon compounds (Kadlec and Wallace 2008). Photosynthesis and aerobic respiration dominate aerobic zones where carbon can be oxidized, resulting in CO\textsubscript{2} production. However, because of the anoxic nature of HSSF CWs, anaerobic processes such as fermentation and methanogenesis also occur. During fermentation, organic matter itself becomes the electron acceptor in anaerobic respiration by microorganisms, resulting in intermediates such as ethanol, lactic acid or CO\textsubscript{2}. Methanogenesis occurs when methanogens use CO\textsubscript{2} as an electron receptor to produce CH\textsubscript{4} in extremely reduced conditions (Mitch and Gosselink 2000). It is also important to note that CWs show seasonal variability in organic matter removal, driven by climate, plant biomass cycling, and water temperatures (Kadlec and Wallace 2008).

Reports from CW researchers are somewhat conflicting in terms of CW contribution to global CH\textsubscript{4} emissions. Johansson et al. (2004) reports that CWs are prone to emit CH\textsubscript{4} at similar rates as natural wetland ecosystems with similar vegetation cover and that the conversion of soil areas to wetlands could give rise to dramatic increases in the amounts of CH\textsubscript{4} released. Mander et al. (2005) suggests that although N\textsubscript{2}O and CH\textsubscript{4} emissions from CWs can be relatively high, their global influence is not significant. Going further, the authors suggest that if all global domestic wastewater were to be treated by CWs, the share of global trace gas emissions would still be less than 1% (Mander et al. 2005). Conversely, Maltais-Landry (2009) reported that CWs emitted 2-10 times more GHGs than natural wetlands and Tai et al. (2002) measured CH\textsubscript{4} fluxes
reaching 250 times (5.2 g m⁻² d⁻¹) greater than natural wetlands in CWs treating municipal sewage, demonstrating the potentially high CH₄ emissions from CWs fed with high strength wastewater.

1.5. Measuring GHG Emissions from Wetlands

The US EPA (2010) lists three principal techniques for estimating CH₄ emissions from wetlands: surface flux extrapolation, process modeling, and inverse modeling. Surface flux extrapolation uses actual emission measurements collected with eddy correlation towers or chambers. Chamber systems are widely used to measure soil or wetland GHG fluxes. Chambers placed over soils and/or wetlands is the most direct way, and for many purposes the only means, of measuring trace gas emissions to the atmosphere occurring within the substrate (Livingston et al. 2005, Davidson et al. 2002). Nevertheless, such measurements are subject to many potentially serious and systematic errors (Hutchinson and Livingston 2001).

Norman et al. (1997) reports that soil-surface flux is difficult to measure because of numerous measurement errors associated with various proposed methods. Rayment (2000) compared two methods (open or closed chamber) and determined that fluxes measured with closed systems are often 10% less than those measured with open systems. This result is in accordance with similar findings by Norman et al. (1997) who found a consistent difference of around 10% between closed and open chambers. Other authors suggest that closed chambers prevent the transit of atmospheric pressure to the soil surface, thereby reducing the exchange of air between the soil and the atmosphere and resulting in lower flux rates than would occur naturally (Hutchinson and Mosier 1981).
Rayment (2000) suggest that closed chambers underestimate true flux rates because the chamber volume includes volume of air-filled spaces in the soil and is thus larger than the volume of the chamber alone. Their results indicate an underestimation of flux of up to 30% by closed chambers. It is difficult, however, to quantify volume of air in the soil as it varies between sites, with soil type and with soil moisture (Rayment 2000). Norman et al. (1997) indicates that accurate soil-surface flux measurements are burdened by spatial and temporal variability and by dependence on environmental factors and substrate nutrient characteristics. The authors suggest that the primary source of variability in chamber-based gas measurements is associated with spatial heterogeneity. Results reported by Davidson et al. (2002) support this conclusion, reporting soil respiration rates differing by a factor of 2 between very poorly drained and well drained soils in a forest in Maine. The authors suggest that spatial and temporal heterogeneity can be addressed with appropriate chamber sizes and numbers and frequency of sampling.

Hutchinson and Livingston (2001) focused on problems with vents and seals in non-steady state chambers and suggest that seemingly trivial leakiness of seals between elements of chambers (collar and chamber top) results in significant risk of measurement error and that a leaky seal is a poor substitute for a properly designed vent tube. In addition, the authors report that the depth to which chamber walls are inserted to minimize lateral diffusion of gas is an important consideration, particularly for porous or well drained soils. Chambers must be inserted into the soil to at least a depth that lateral diffusion beneath the side walls will not significantly influence the rate of gas exchange across the covered surface. A well-designed chamber must include a properly sized and
located vent tube, the best possible seal between chamber top and its base, and adequate insertion depth of the base into the soil (Hutchinson and Livingston 2001).

Davidson et al. (2002) focused on uncertainties of chamber-based measurements of CO₂ emissions from soils. They report that disturbance of diffusion gradients cause underestimates of fluxes by < 15% and that error can be partially corrected by curve fitting and by using shorter measurement periods. The authors also cite over-pressurization or under-pressurization of the chamber as a potential source of measurement error. For example, in open chamber systems, pressure imbalances may be caused by flow restrictions in air circulating designs can result in large errors but may be avoided with properly sized chamber vents and unrestricted flows. Whenever a chamber is placed on the substrate and the concentration in the chamber headspace gas begins to change, the natural concentration gradient with the soil profile is altered; however these inherent sources of error can be minimized with proper chamber designs, data analyses, and spatial and temporal sampling designs (Davidson et al. 2002).

Constructed wetlands are a challenging place to measure gas flux and emissions data from CWs are scarce (VanderZaag 2010). Previous research on GHG emissions from CWs has primarily reported using non-steady-state or static chambers, although specific methods varied. For example, to study the gases evolved from a HSSF CW treating dairy wastewater, Fey et al. (1999) measured the release of N₂O using open, PVC chambers equipped with vacuum pumps and molecular-sieve traps to collect and absorb the emitted N₂O. Johansson et al. (2004) measured CH₄ and N₂O flux from a SF CW in Sweden using static chambers. During sampling, a polycarbonate chamber equipped with internal cooling fans and removable lids were placed in a static aluminum
frame in the surface water, with an effort to minimize disturbance of vegetation or sedimentation of the wetland. Mander et al. (2005, 2008) measured CH_4 and N_2O emissions from a SSF CW in Estonia treating municipal wastewater. The closed chamber method was used in the field in parallel with intact soil core analysis (He-O method) in the lab. Collars were placed in the soil and chambers were set into the collar and sealed with water during sampling events.

At the Nova Scotia Agricultural College, VanderZaag et al. (2010) measured CH_4 and N_2O released from a series of CWs treating agricultural wastewater using steady-state chambers installed on top of concrete tanks containing the CWs. Air from each sample location was measured continuously with a trace gas analysis system. Similarly, while researching natural wetlands in Europe dominated by Phragmites australis, Kim et al. (1999) used the tunable diode laser spectrometer to measure CH_4 released from the wetland soil.

Ding et al. (2004) estimated the total CH_4 released from China’s natural wetlands using a closed chamber technique. Permanent stainless steel collars were placed into wetland soils and Plexiglas chambers with internal fans were placed atop the collars. Samples were withdrawn from the chambers through a stopper using airtight syringes. A similar experiment in Taiwan by Chang and Yang (2004) used an acrylic chamber with an electric fan, internal thermometer, and an airtight stopper to seal a sampling port placed directly on the soil.
1.6. Methane Emissions from Constructed Wetlands – Previous Investigations

A wide spectrum of greenhouse gas emissions from CWs, measured in a limited number of studies employing flux chamber methods, is published in the literature due to the variety of environmental (climate) and design (wastewater type and strength, CW type, vegetation) factors influencing emissions.

The earliest reports begin in the late 1990s with studies of emissions from SSF gravel (Tanner et al. 1997) and peat (Fey et al. 1999) CWs treating agricultural wastewater. Tanner et al. (1997) reported average CH\textsubscript{4} emissions of <450 mg m\textsuperscript{-2} d\textsuperscript{-1} from vegetated (Phragmites australis) and <1400 mg m\textsuperscript{-2} d\textsuperscript{-1} from unplanted CWs (19 m\textsuperscript{2}) in New Zealand. Methane flux data from CWs treating agricultural effluents is limited to these studies and, studies conducted in temperate climates are limited to our own study and to VanderZaag et al. (2010) who reported average CH\textsubscript{4} fluxes from SF and gravel SSF CWs planted with Typha latifolia as <1235 and <770 mg m\textsuperscript{-2} d\textsuperscript{-1}, respectively, in Nova Scotia.

Only a few studies from Japan published CH\textsubscript{4} emissions from CWs fed with artificial wastewater. Inamori et al. (2007) reported average CH\textsubscript{4} fluxes from vegetated, gravel/sand VSSF CWs as <1080 (Phragmites australis) and <1560 mg m\textsuperscript{-2} d\textsuperscript{-1} (Zizania latifolia). In a similar study, Wang et al. (2008) measured CH\textsubscript{4} flux from gravel/sand VSSF CWs planted with Typha latifolia and Zizania latifolia reported averages of 2540 and 6487 mg m\textsuperscript{-2} d\textsuperscript{-1}, respectively. Average CH\textsubscript{4} flux from the same unplanted VSSF CWs was 654 mg m\textsuperscript{-2} d\textsuperscript{-1}. The relatively high average CH\textsubscript{4} fluxes reported by Wang et al. (2008) are most likely attributed to the high strength of the artificial wastewater.
The majority of publications related to greenhouse gas emissions from CWs concern systems treating municipal wastewater. The first CH$_4$ flux data reported from such systems were by Gui et al. (2000), who measured an average CH$_4$ flux of only <30 mg m$^{-2}$ d$^{-1}$ for a large (4500 m$^2$), vegetated, SF CW in Japan. Johansson et al. (2004) monitored CH$_4$ flux from a SF CW (~1000 m$^2$) treating municipal wastewater and planted with *Typha latifolia*, *Phragmites australis* and *Spyrigyra* sp and reported flux ranges of 0 to 1259, 50 to 1054 and -375 to 1739 mg m$^{-2}$ d$^{-1}$, respectively. Unplanted areas of the FS CW emitted a similar range (0 to 1071 mg m$^{-2}$ d$^{-1}$) of CH$_4$. In Estonia, Mander et al. (2005) measured CH$_4$ from a HSSF CW planted with *Typha latifolia* and *Phragmites australis* and found that fluxes ranged from 40.8 to 12,672 mg m$^{-2}$ d$^{-1}$ over 18 months of monitoring. Using a smaller data set from the same HSSF CW, the same research group later reported a flux range of -0.22 to 8,924 mg m$^{-2}$ d$^{-1}$ (Mander et al. 2008). Sovik et al. (2006) summarized CH$_4$ emissions from SSF, SF, and overland and groundwater flow CWs in Estonia, Finland, Norway and Poland and reported a wide range of fluxes from -32 to 38,000 mg m$^{-2}$ d$^{-1}$ due to the variety of CW designs included in the study. More specifically, the seasonal CH$_4$ flux range from the HSSF CWs in Estonia, Norway and Poland was -1.5 in winter to 670 mg m$^{-2}$ d$^{-1}$ during the summer. Also in Europe (Czech Republic), Picek et al. (2007) reported CH$_4$ emissions of 0 to 2,232 mg m$^{-2}$ d$^{-1}$ in a SSF CW (748 m$^2$) planted with *Phragmites australis*. In Sweden, Strom et al. (2007) reported a CH$_4$ flux range of -377 to 1,387 mg m$^{-2}$ d$^{-1}$ from a SF CW planted with *Juncus effuses*, *Typha latifolia*, and *Phragmites australis*.

Compared to studies of CWs treating municipal wastewaters, there are very few examples in the literature of CWs treating storm water runoff. Liikanen et al. (2006)
reported an average CH$_4$ flux of 140 mg m$^{-2}$ d$^{-1}$ from a large (2.4 ha) SSF CW in Sweden treating peat-mining runoff and vegetated with *Sphagnum* sp and *Menyanthes trifoliate*. Smialek *et al.* (2006) measured low (< 3 mg m$^{-2}$ d$^{-1}$) CH$_4$ flux from a SF CW in Ohio (USA) treating agricultural field and storm water runoff and planted with *Juncus effuses* and *Salix nigra*.

Plant-mediated CH$_4$ transport in CWs has been measured in several studies. Higher emissions of CH$_4$ from vegetated CW sites compared to sites without vegetation is reported as plants may act as conduits for the transport of methane (Sovik *et al.* 2007, Strom *et al.* 2007). However, other researchers have reported higher CH$_4$ flux from unplanted conditions, suggesting that vegetation in CWs may increase oxygenation of sediment and reduce CH$_4$ fluxes (Tanner *et al.* 2007, Picek *et al.* 2007, Maltais-Landry *et al.* 2009). There is also conflicting evidence in the literature regarding species-specific emissions of CH$_4$. For example, *Juncus* has been reported to limit (Smialek *et al.* 2006) and enhance the emission of CH$_4$ in CWs (Strom *et al.* 2007). The variability in CH$_4$ emissions suggests that oxygen transfer capacity among plant species varies (Maltais-Landry *et al.* 2009).

Despite the growing number of studies of CH$_4$ emissions from CWs, very few studies have been conducted on dairy treatment CWs in a North American cold climate (VanderZaag *et al.* 2010, Smialek *et al.* 2006) or more specifically, in the US (Smialek *et al.* 2006).
1.7. Research Objectives

As CWs are an accepted management practice for treating wastewaters, such as agricultural effluents, their potential to mediate or enhance CH$_4$ emissions should be assessed. The main objectives of this research were: (1) to quantify CH$_4$ emission rates in two SSF, cold-climate CWs for dairy effluent treatment; (2) to assess spatial and seasonal variability on CH$_4$ emission rates; (3) to gain better understanding of CH$_4$ emission levels from CWs and their potential to effect global climate change. The research hypotheses were: 1) supplemental aeration will reduce CH$_4$ fluxes from CWs (e.g. the unaerated wetland will have higher CH$_4$ flux of compared to aerated wetland; 2) CH$_4$ flux will differ along the CW transect and is expected to be higher at wetland cell inlet areas (vs. mid or outlet areas), and 3) CH$_4$ flux will be greatest during the summer season (vs. spring or fall).
Evaluating Methane Emissions from Dairy Treatment Constructed Wetlands in a Cold Climate

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Abstract: Constructed wetlands (CWs) are an increasingly important technology to remediate wastewaters and reduce negative impacts on water quality in agricultural settings. Treatment of high strength effluents typical of agricultural operations results in the production of methane (CH₄), a potent greenhouse trace gas. The objective of this study was to evaluate CH₄ emissions from two subsurface flow (SSF) CWs (223 m² each) treating dairy farm effluents. The CWs were implemented at the University of Vermont Paul Miller Dairy Farm in 2003 as an alternative nutrient management approach for treating mixed dairy wastewater (barnyard runoff and milk parlor waste) in a cold, northern climate. In 2006, static collars were installed throughout two CWs (aerated (CW1) and a non-aerated (CW2)) connected in-series, and gas samples were collected via non-steady state chambers over a nine-month period (Feb-Oct 2007). The average daily CH₄ flux of CW1 and CW2 were 1475 and 552 mg m⁻² d⁻¹, respectively. Methane flux densities of CW1 were nearly threefold greater than CW2 (p = 0.0387) across all three seasons, although the in-series design may have confounded results by limiting differences in dissolved oxygen and by accentuating differences in carbon loading. Methane flux densities revealed strong spatial and seasonal variation within CWs. Emissions generally decreased from inlet to outlet in both CWs. Fluxes differed significantly between seasons for both CW1 (p = 0.0034) and CW2 (p = 0.0002) and emissions were greatest during the spring season in both CWs, attributed to a consistently high water table observed during this season. We estimate average and maximum daily flux from the entire CW system (892 m²) at approximately 1.11 and 6.33 kg CH₄ d⁻¹, respectively, yielding an annual average and maximum flux potential of 8.51 and 48.5 MtCO₂-e y⁻¹, respectively. Our reported average CH₄ fluxes are comparable to published data from SSF dairy treatment CWs.

Keywords: methane, constructed wetlands, subsurface flow, cold climate, agricultural wastewater, artificial aeration
2.1. Introduction

The growing trend in agriculture toward concentrated and confined animal facilities has resulted in an accumulation of animal wastes, facility wastewater, and operation area runoff, thereby leading to ecological impairment of the environment by negatively impacting water quality (Sharpley 2003). Treating elevated nutrients, suspended solids, oxygen demanding materials, pesticides and fertilizers in agricultural wastewaters is therefore necessary to protect surface and ground waters. Constructed wetlands (CWs) have emerged as a promising technology for municipal, industrial, urban runoff, and agricultural effluents treatment (Kadlec and Knight 1996, Kadlec et al. 2000, Hunt and Poach 2001, Vymazal et al. 2010). Compared to conventional sewage treatment plants, most CWs require minimal energy, are easy to install, require minimum maintenance (Knight et al. 2000) and are therefore compatible with many farm operations. However, CWs may require large land areas for treating larger volumes and/or heavily concentrated wastewaters and are therefore most suitable for rural or low density areas (Denny et al. 1997).

Typical agricultural wastewaters are much higher strength than municipal wastewaters and CWs treating agricultural effluents typically receive a large external supply of carbon from the incoming wastewater. Degradation reactions depend on the wetland environment and both anaerobic and aerobic processes have been measured to consume carbon compounds (Kadlec and Wallace 2008). Because of the anoxic nature of SSF CWs, anaerobic processes such as fermentation and methanogenesis occur and the resulting production of methane (CH$_4$), a potent greenhouse gas (GHG).
The amount of the CH\(_4\) in the atmosphere has increased globally since the Industrial Revolution by 159\% (IPCC 2007). While natural sources of CH\(_4\) are estimated to produce 37\% of the total global CH\(_4\) emissions, the largest source being from wetlands; increasing anthropogenic emissions of CH\(_4\) are approximately 1.5 to 2.5 times the magnitudes of natural emissions (Forster \textit{et al.} 2007). In 2010, agricultural practices, such as enteric fermentation and manure management, were responsible for roughly 6\% total US GHG emissions, with 8\% of total CH\(_4\) emissions directly attributed to manure management (IPCC 2007).

In order to address the question of whether CWs contribute to atmospheric GHG concentrations during wastewater treatment, scientists have started to assess potential GHG fluxes from CWs. Previous research on GHG emissions from CWs has primarily been reported using non-steady-state or static chambers (Fey \textit{et al.} 1999, Johansson \textit{et al.} 2004; Mander \textit{et al.} 2005, 2008; VanderZaag \textit{et al.} 2010). Chambers placed over soils and/or wetlands is the most direct way, and for many purposes the only means, of measuring trace gas emissions to the atmosphere occurring within the substrate (Livingston \textit{et al.} 2005, Davidson \textit{et al.} 2002).

The earliest studies of GHG begin in the late 1990s with studies of emissions from subsurface flow (SSF) gravel (Tanner \textit{et al.} 1997) and peat (Fey \textit{et al.} 1999) CWs treating agricultural wastewater in New Zealand and Germany, respectively. Methane flux data from CWs treating agricultural effluents is limited to these studies and, research conducted in cold climates is limited to our own study and to VanderZaag \textit{et al.} (2010) in Nova Scotia. Most studies related to GHG emissions from CWs involve systems treating municipal wastewater (Gui \textit{et al.} 2000, Johansson \textit{et al.} 2004, Mander \textit{et al.} 2005; 2008,
Sovik *et al.* 2006, Picek *et al.* 2007, Strom *et al.* 2007). These studies have revealed that CH$_4$ released from CW systems during the treatment of wastewaters depends on climate, temporal and seasonal variability (Mander *et al.* 2005, Inamori *et al.* 2007, Johannson *et al.* 2004, Liikanen *et al.* 2006), strength and type of wastewater (Tanner *et al.* 1997, Picek *et al.* 2007), vegetation (Inamori *et al.* 2007, Maltais-Landry *et al.* 2009) and system design (Mander *et al.* 2008, VanderZaag 2010). Higher emissions of CH$_4$ from vegetated CW sites compared to sites without vegetation is reported as plants may act as conduits for the transport of methane (Sovik *et al.* 2007, Strom *et al.* 2007). However, other researchers have reported higher CH$_4$ flux from unplanted conditions, suggesting that vegetation in CWs may increase oxygenation of sediment and reduce CH$_4$ fluxes (Tanner *et al.* 2007, Picek *et al.* 2007, Maltais-Landry *et al.* 2009).

Research on CH$_4$ emissions from CWs has been steadily increasing, however, only two studies have been conducted in a North American cold climate (VanderZaag *et al.* 2010, Smialek *et al.* 2006) with only one in the U.S. (Smialek *et al.* 2006). As CWs are an accepted management practice for treating wastewaters, such as agricultural effluents, their potential to mediate or enhance CH$_4$ emissions should be assessed. In this study, CH$_4$ emissions from SSF CWs treating dairy effluent in a cold climate were monitored using static chambers for 9 months at the University of Vermont dairy farm. The main objectives of this research were to: (1) quantify CH$_4$ flux rates of an aerated and non-aerated CW connected in-series, (2) compare CH$_4$ flux within CW zones and (3) assess seasonal variability on CH$_4$ emissions.
2.2. Materials and Methods

2.2.1. Study area

The CW Research Center (CWRC) is located at the University of Vermont (UVM) Paul Miller Dairy Farm in Burlington, Vermont (44°14′60″N, 73°11′9″W), 100 m above sea level. Burlington has a mean temperature of -8.7°C in January and 21.4°C in July. The CWRC comprises four, SSF CWs, each measuring 18 m x 12.5 m x 0.6 m deep, having a surface area of 225 m², a total volume of 135 m³ and a pore volume of 58.32 m³, assuming 45% porosity (Figure 1). The CWRC started receiving an influent consisting of combined feedlot runoff (drainage area 1750 m²) and milking operation wastewater from the dairy in October 2003. The UVM dairy herd consisted of 150 milking cows and 110 calves and heifers. The UVM CWs were designed to handle an influent BOD concentration of 4000 mg l⁻¹ and a peak flow of 37,500 l d⁻¹, which represents a storm event that occurs, on average, once every two years (Munoz et al. 2006, Weber et al. 2007, Lee et al. 2010).

Each CW cell has been equipped with an aeration system designed by North American Wetland Engineering LLC, (Forest Lake, MN) consisting of Ametek regenerative blowers (max flow 1.56 m³ min⁻¹) and a 60 m network of bubble aeration tubing, capable of maintaining 1.13 m³ min⁻¹ at 1.0 m of water pressure, placed on the top of an impermeable liner. However, aeration was activated for only two CW cells at a time, in order to test the effect of oxygenation on pollutant treatment performance (Munoz et al. 2006, Drizo et al. 2008).
Figure 2. Process schematic of UVM CW Research Center during 2007 GHG monitoring (modified from Munoz et al. 2006; not to scale).
2.2.2. **UVM Constructed Wetland Operation 2003-2007**

Tracer studies and spatial temperature and dissolved oxygen mapping were carried out during winter of 2004-2005 (covering a period between sub-zero freezing temperatures to the snowmelt that occurred in early March) by Munoz *et al.* (2006) in order to assess the CW hydraulic characteristics in cold climate. The bromide tracer study showed that actual flow rates during this time period ranged between 1 m$^3$d$^{-1}$ and 5 m$^3$d$^{-1}$ and a theoretical retention time range of 5 to 30 days per wetland cell. The results also revealed, however, the occurrence of preferential flows and clogging caused by the configuration of the inlet infiltrator structures.

The operating parameters of the CW cells changed several times over the first 3-year period of system operation between October 2003 and 2006 (Drizo *et al.* 2006, 2008). CW cells 3 (CW3) and 4 (CW4) were planted with River Bulrush (*Schoenoplectus fluviatilis* (Torr.) in 2003 and remained planted throughout the period of investigation. CW cells 1 (CW1) and 2 (CW2) were not vegetated at the time of the system establishment in 2003; however in May of 2004, both CW1 and CW2 were also planted with River Bulrush (*Schoenoplectus fluviatilis* (Torr.). Aeration was supplied to unplanted CW1 and planted CW3 from October of 2003 until May 2004. After planting CW 1 and CW2 in May 2004, the aeration mode was activated in cells CW2 and CW4 and inactivated in CW1 and CW3.

During February of 2005, the concrete splitter wall within the CW inlet distribution tank deteriorated, resulting in uneven distribution of the flow to the CW cells. As a consequence, CW1 received roughly half of the total flow over 107 days. In order to diminish the potential for overloading this cell and to maintain treatment performance,
CW1 and CW2 were connected in-series in March 2005, and have been running connected in series ever since.

In January 2006, aeration was stopped to cell CW2 and supplied to CW1, while cells CW3 and CW4 remained running in the same mode of operation, e.g. CW3 non-aerated and CW4 aerated. During the third growing season (2006), maintenance of all CW cells as river bulrush monocultures was discontinued and a diverse mix of typical wetland vegetation, including *Typha*, *Phragmites*, *Urtica*, and *Solidago*, quickly spread from the adjacent natural wetland areas to the CW and colonized all four CW cells. The mode of aeration and vegetation and have persisted unchanged since.

### 2.2.3. Trace Gas Measurement

Trace gas measurements were made using two-part non-steady state chambers (Livingston and Hutchinson 1995) 0.25 m in diameter. Chambers were constructed of ABS plastic fitted to PVC collars via a gas-tight Fernco seal. Collars were inserted into the substrate to a standardized depth of 15 cm to ensure penetration of the collar into the water table of the wetland cell. A spade was used to cut through the surface layers to minimize disturbance. The resultant chamber volume when deployed (assuming the water table was below the surface of the substrate) was 19.75 L.

In the fall of 2006, nine permanent collars were installed in the CW1 (aerated) and CW2 (non-aerated) CW cells, creating a total of eighteen sampling sites. A stratified random experimental design was chosen in which both wetland cells were partitioned into nine zones of equal area (24.8 m²) to represent the inlet (zones 1-3), mid (zones 4-6) and outlet (zones 7-9) areas of each CW (Figure 2). Collars were then placed at random
within each zone and vegetation removed from within the collars. To allow for reestablishment of the microbial community, gas sampling was not initiated until the spring of 2007.

**Figure 3.** Process schematic and selected GHG sampling locations (1-9) and zones

Precautions were taken in order to minimize disturbance of the wetland cell surface during placement and sampling of gas chambers. Wooden bridges were constructed and spanned over the width of each CW cell to allow access to sampling sites without disturbing the surface of the wetland. Any new vegetation was removed from inside collars immediately post sampling to allow fourteen days before the next sample.
event. In addition, municipal fresh water was added to the CW system beginning in the summer (June 15) of 2007 and continued bi-weekly until early fall (Sept 4) in an effort to maintain the position of the water table above the bottom of the chamber collars (Figure 4a,b). During initial attachment of the sample chamber to the collar, the vent on the lid was left unsealed in order to keep the internal chamber pressure equal to ambient conditions. Samples were collected through a 1 m polypropylene tube (0.080” ID) attached to the chamber lid to further minimize the potential for disturbance.

2.2.4. Sample Allocation

Three gas sampling chambers were assigned to each CW for sample events, i.e. one chamber was attached to one of three randomly selected collars within each cell’s inlet, mid, or outlet areas, such that a total of six chambers were sampled. Once connected to a collar, chamber vents were sealed using a rubber stopper, the sample line was cleared by withdrawing 60 ml of air from the chamber, and an ambient air sample was immediately taken using a 60 ml plastic syringe equipped with a nylon stopcock. Four, 20 ml gas samples were manually withdrawn from the chamber at 20 min standard time intervals over one hour, starting with time 0. The gas sample was then immediately transferred by injection into two, replicate 10 ml, pre-evacuated 20 mm glass headspace vials (Restek) with metal seal PTFE/silicon crimp caps (MicroLiter). Gas samples were stored in racks within a cardboard box for roughly two hours in the field and then transported to the laboratory and immediately analyzed. Chambers were removed from the permanent collars post sampling and stored until the next sample event. The sampling and analysis procedure was carried out bi-weekly during the 2007 growing
season (March to November). Limited field observations were also made, including air
temperature and water table height.

2.2.5. Gas Analysis

Gas samples were analyzed for methane (CH$_4$) concentration in the UVM Plant
and Soil Science Department laboratory on a Shimadzu GC-17A (Columbia, MD, USA)
greenhouse gas analyzer equipped with flame ionization detector (FID) and Shimadzu
AOC-5000 autosampler. Water vapor was removed from samples via a 1.0 m Poropak-
Q column (Supelco) and a 2.0 m Hayesep D column (Supelco) was used for sample
separation, with nitrogen (~25 ml min$^{-1}$) as the carrier gas. The GC oven, injection, and
FID temperatures were maintained at 60°C, 150°C, and 250°C. GC analysis was
completed within 24 hours of sampling. All standards were created in the laboratory by
injecting known concentrations of gas into the same pre-evacuated, 10 ml vials as used
for samples. A five-point linear calibration curve was created by serial dilutions of a
custom mixed (5000 mg l$^{-1}$), certified standard (Airgas, Salem, NH). Working quality
control standards were made via serial dilutions of a Scotty 14 custom mix (1000 mg l$^{-1}$)
cylinder (Scott Specialty Gases, Plumstead, PA) and analyzed every 12 samples. In
addition, field blanks were created in the laboratory by evacuating sample vials and
injecting with nitrogen gas. Field blanks were carried throughout the sampling
procedure, analyzed with samples, and compared to known ambient CH$_4$ concentrations
(NOAA 2008). Samples of ambient air taken at time zero were compared to known
ambient CH$_4$ concentrations to check for initial disturbance of the substrate. The mean of
replicate sample concentrations was used to calculate a coefficient of variance and values > 10% were reexamined.

2.2.6. **Flux Modeling**

Modeling gas flux data was achieved by employing either a linear or quadratic regressions for each chamber deployment depending on the linearity of the data. Diffusion was presumed the dominant process driving gas emissions between the surface and the atmosphere under most conditions; therefore flux density was first estimated by fitting an assumed linear model of chamber headspace concentration with time to the observed data. Residual sum of squares was calculated to compare the observed vs. estimated linear fit.

Empirical modeling of time-dependent chamber concentrations often underestimate emissions because they do not account for the effect of the chamber on the gas exchange process (Livingston et al. 2005, 2006). The linear model can severely underestimates flux and only applies if the chamber measurement intervals and environmental parameters are such that it can be assumed that emissions are constant over the period of chamber deployment (Livingston et al. 2006). Theoretical and numeric simulation studies indicate that the quadratic model more accurately estimates emissions than does the linear model in almost every situation (Wagner et al. 1997, Kutzbach et al. 2007, Forbich et al. 2010). Therefore, a quadratic regression was employed (n = 57) rather than a linear fit for all cases except when the concentration curve was concave (n = 23). Flux calculations were discarded (n = 3) for regressions
indicating disturbance of the substrate. Slope, the first derivative at $t_0$, was then used to calculate CH$_4$ flux density for each chamber as follows:

\[
\text{Flux density (mg m}^{-2} \text{ h}^{-1}) = \text{slope (mg m}^{-2} \text{ h}^{-1}) * \text{chamber height (m)}
\]

2.2.7. Statistical Analysis

Two-way ANOVA tests of CH$_4$ flux with interaction (cell and zone, cell and season, cell and zone for each of the three seasons) was performed using SAS 9.2 (SAS 2008). CH$_4$ flux data were transformed to log values due to the wide range of flux values across the data set and least square means were calculated due to unbalanced sample sizes of the treatments. All statistical analyses assumed a confidence interval of 95% ($\alpha = 0.05$). In order to investigate the effects of seasonal variation to CH$_4$ fluxes, the data set was divided into three seasons: March-May (spring, season 1), June-August (summer, season 2), and September-November (fall, season 3). In addition, paired t-tests were performed to compare the summarized CH$_4$ flux data to biological oxygen demand (BOD$_5$) loading rate data collected at the CWRC from 2004 to 2007 (Figure 8, Appendix) and on ammonium (NH$_4$) removal efficiency data collected at the CWRC during 2007 (Table 3, Appendix).

2.3. Results

Methane fluxes averaged 1475 and 552 mg m$^{-2}$ d$^{-1}$ for aerated CW1 and non-aerated CW2, respectively over the nine month period of emissions monitoring. Flux densities were variable throughout the nine-month study period, ranging from 0.026 to 339 and 0.008 to 165 mg m$^{-2}$ h$^{-1}$ in aerated CW1 and non-aerated CW2, respectively.
(Figure 4a,b). Methane flux densities of CW1 was nearly threefold greater than CW2 ($p = .0387$) averaged across all three seasons (Table 2).

**Figure 4.** Methane flux densities (mg m$^{-2}$ h$^{-1}$) measured throughout the nine-month study period are shown for the inlet, mid and outlet zones of aerated CW1 (a) and non-aerated CW2 (b), as well as total precipitation (cm) for the seven days preceding flux measurement and dates of freshwater addition to the CW system.
Table 2. Mean CH$_4$ flux and standard errors (mg m$^{-2}$ h$^{-1}$) for CW1 and CW2 inlet, mid and outlet zones and their seasonal averages. Fluxes were reported as means ± standard error to account for differences in sample size (n).

<table>
<thead>
<tr>
<th></th>
<th>CW 1</th>
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<th>CW 2</th>
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<tr>
<td></td>
<td>Inlet Mid</td>
<td>Outlet</td>
<td>Avg</td>
<td>Inlet</td>
</tr>
<tr>
<td>spring</td>
<td>182(4)</td>
<td>46.0(2)</td>
<td>45.5(4)</td>
<td>100(10)</td>
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<tr>
<td>± SE</td>
<td>75.7</td>
<td>9.97</td>
<td>33.8</td>
<td>37.7</td>
</tr>
<tr>
<td>summer</td>
<td>32.9(5)</td>
<td>5.38(5)</td>
<td>3.77(5)</td>
<td>14.0(15)</td>
</tr>
<tr>
<td>± SE</td>
<td>18.9</td>
<td>2.93</td>
<td>1.51</td>
<td>6.91</td>
</tr>
<tr>
<td>fall</td>
<td>159(4)</td>
<td>106(4)</td>
<td>0.276(4)</td>
<td>88.4(12)</td>
</tr>
<tr>
<td>± SE</td>
<td>83.2</td>
<td>58.3</td>
<td>0.141</td>
<td>36.5</td>
</tr>
<tr>
<td>3 seasons</td>
<td>117(13)</td>
<td>49.3(11)</td>
<td>10.4(13)</td>
<td>61.5(37)</td>
</tr>
<tr>
<td>± SE</td>
<td>37.4</td>
<td>24.1</td>
<td>11.0</td>
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</tbody>
</table>

Average flux for the CW1 inlet zone was over four times greater ($p = .0205$) than CW2 inlet zone, but mid and outlet zones were not statistically different between CWs. Flux densities generally declined from inlet to outlet within both CWs, with higher fluxes measured at the CW inlet zones and the lowest fluxes measured at the outlet zones (Table 2, Figure 5). The average fluxes for CW1 zones were different ($p = .0003$), with average inlet zone flux being nearly three and tenfold greater than mid ($p = .0520$) or outlet ($p = <.0001$) zones and with mid zone flux being four fold greater than the outlet ($p = .0247$). Fluxes for CW2 zones were not statistically different ($p = .4516$).
Average CH$_4$ flux also generally declined from inlet to outlet across all three seasons in CW1 but was variable in CW2 (Table 2). During the spring season, average CH$_4$ fluxes within CW zones were not significantly different in CW1 ($p = .1849$) or CW2 ($p = .5234$). During the summer, however, flux of CW1 zones were different ($p = .0091$), declining from the inlet to the outlet zone and with the inlet averaging three to eight times greater than mid ($p = .0088$) and outlet ($p = .0041$) zones. Similarly during the fall, fluxes between CW1 zones were different ($p = .0009$) as flux declined across zones with inlet ($p = .0008$) and mid ($p = .0006$) zones greater than outlet. As with spring season, fluxes of CW2 zones were not statistically different during the summer ($p = .5559$) or fall ($p = .5770$).
Figure 6. CW1 and CW2 average CH$_4$ flux and standard error (mg m$^{-2}$ h$^{-1}$) for three seasons of GHG monitoring with season total precipitation (cm). Similar letters represent mean values that are not statistically different. ($p < .05$).

No significant differences in CH$_4$ fluxes were observed between CWs or within CW zones during the spring season. Methane flux of CW1 was nearly fifteen fold greater than CW2 during the fall, representing the only season during which flux was statistically different ($p = .0082$) between CWs (Table 2, Figure 6). Fluxes differed significantly between seasons within both CW1 ($p = .0034$) and CW2 ($p = .0002$). The greatest average CH$_4$ fluxes were measured in the spring season. Average CH$_4$ flux measured during the spring was statistically greater than summer and fall for both CW1 ($p = .0008$, $p = .0050$) and CW2 ($p = .0331$, $p = <.0001$).

Average flux within inlet zones during the spring were not statistically different in CW1 ($p = .2604$) or CW2 ($p = .1348$). Flux in CW1 mid zone was lower during the summer than in spring ($p = .0089$) and fall ($p = .0008$) and flux in CW2 mid zone was greater in the spring than in summer ($p = .0172$) and fall ($p = .0154$). Average fluxes of
outlet zones were different across seasons in both CW1 ($p = .0008$) and CW2 ($p = .0709$) with greatest average flux occurring during the spring in both CW1 and CW2.

2.4. Discussion

2.4.1. Methane Emissions and Context

Emissions from SSF CWs reported in the literature for a variety of wastewaters, including domestic (Mander et al. 2005, 2008 and Picek et al. 2007) and dairy effluents and for different temperate climates ranging from subtropical New Zealand (Tanner et al. 1997) to maritime Nova Scotia (VanderZaag et al. 2010) range from ~20 to ~3000 mg m$^{-2}$ d$^{-1}$. The CH$_4$ emissions observed in this study are most comparable to that reported by VanderZaag et al. (2010) (< 770 mg m$^{-2}$ d$^{-1}$) for a SSF CW planted with *Typha latifolia* and treating dairy wastewater. An overview of CH$_4$ fluxes from different types of CWs is provided in Kayranli et al. (2010) and VanderZaag et al. (2010).

Assuming that CW3 and CW4 perform similar to those observed in this study (CW1 and CW2) and computing emissions per CW surface area, we estimate average daily emissions from this UVM facility (892 m$^2$) at approximately 1.11 kg CH$_4$ d$^{-1}$ and an annual average flux of 8.51 MtCO$_2$-eq y$^{-1}$. Extrapolating from the range of emission for CW1 and CW2, the potential maximum daily and annual fluxes from the UVM CW facility were 6.33 CH$_4$ d$^{-1}$ and 48.5 MtCO$_2$-eq y$^{-1}$. These estimates assume CW operating parameters similar to those employed during 2007 GHG monitoring: aerated CW1 connected in series with non-aerated CW2, and non-aerated CW3 and aerated CW4 each operating independently.
2.4.2. Flux Variation between Constructed Wetlands

Our first research hypothesis, that the CH$_4$ flux in the non-aerated wetland CW2 would be greater than that in the aerated wetland CW1, was rejected since the average CH$_4$ flux from aerated CW1 was nearly threefold greater than (p = .0387) non-aerated CW2 (Table 2). These results were somewhat surprising since methanogenesis is an obligatory anaerobic process (Knight and Wallace, 2008) and methanotrophy was expected in the aerated substrate and overlying waters. The degree of oxygenation was thus expected to be a principal factor driving CH$_4$ fluxes from CWs. For example, Maltais-Landry et al. (2009) monitored CH$_4$ production from CW mesocosm located in a greenhouse environment at the Montreal Botanical Gardens, Montreal, Quebec demonstrating that artificial aeration employed to increase dissolved oxygen (DO) levels and to boost treatment performance of a CW creates aerobic conditions inhibiting methanogenesis and reducing CH$_4$ fluxes. However, Wagner et al. (1999) showed that methane can be generated from aerated marshland and model soils.

Dissolved oxygen levels within CW cells were not measured during the GHG monitoring period, however, oxygen was consistently supplied to CW1 via supplemental aeration at a potential max flow of 1.56 m$^3$ min$^{-1}$. Previous studies at the UVM CWRC showed that aeration supplied to CW cells increased DO content of the treated water up to as much as 6 mg l$^{-1}$ compared to DO concentrations of ~1 mg l$^{-1}$ in non-aerated cells (Munoz et al. 2006). Ammonium (NH$_4^+$) and nitrate (NO$_3^-$) concentrations of CW inlet and outlet water were analyzed weekly (Lachat QuikChem methods 12-107-06-2-A, 12-107-04-1-B) during the GHG sampling period. Nitrification, indicated by NH$_4^+$ removal and NO$_3^-$ production, would indicate that DO was present within CWs. Nitrate
production, although variable throughout the nine-month monitoring period, occurred in CW1 but was not observed in CW2 (Figure 9, Appendix). Ammonium removal within the aerated CW1 and CW4 averaged 43.8% and 61.9%, respectively, versus -2.1% for non-aerated CW3. Ammonium removal in non-aerated CW2, although high (70.8%), was not statistically different from aerated CW4 (Table 3, Appendix). Since CW1 and CW2 were connected in-series, it is possible that aeration supplied to CW1 elevated DO levels that persisted into CW2, resulting in higher NH$_4^+$ removal efficiency.

2.4.3. Spatial Variation in Flux within Constructed Wetlands

The CH$_4$ emissions data in general supports the hypothesis that CH$_4$ flux will differ along the CW transect, with greater flux at inlet areas (vs. mid or outlet areas). Average CH$_4$ fluxes from the CW1 inlet area were nearly threefold greater than from the mid zone and over eleven times greater than observed at the CW1 outlet area. In addition, CH$_4$ fluxes were consistently higher at CW1 inlet for all three seasons and, although highly variable, over the entire nine month period of study. Methane fluxes averaged for CW1 and CW2 combined showed that flux from inlet areas was over five times greater ($p = .0003$) than from outlet areas. These findings are consistent, for example, with Tanner et al. (1997) who reported higher CH$_4$ emissions at gas sampling sites closest to wastewater inflows on SSF CWs treating agricultural wastewater in New Zealand. Sovik et al. (2006) also reported large spatial variation in CH$_4$ fluxes, but again with highest emissions from inlet sections of HSSF CWs in Estonia, Norway and Poland treating municipal wastewater. Similarly, Picek et al. (2007) found 64% of the total CH$_4$ emissions were emitted from unvegetated inflow zones of SSF CWs treating municipal
wastewater in the Czech Republic. Chiemchaisri et al. (2009) monitored CH$_4$ flux from a SSF CW treating young landfill leachate in Thailand and reported highest emissions from inlet zones, a reduction in flux to less than 10% of original value at the mid zone, and no detection of CH$_4$ at the outlet zone.

Previous research has shown that DO levels are not homogeneous within the wetland zones and that generally DO levels in CWs decrease from inlet to outlet (Kadlec and Reddy, 2001). However, tracer studies performed by Munoz et al. (2006) on an aerated, UVM CW cell indicated higher DO levels at CW outlet zones, possibly due to the occurrence of preferential flows and formation of dead zones caused by the configuration of the inlet infiltrator flow structures. Higher DO levels at CW outlet zones would explain higher CH$_4$ emissions observed at the inlet zones. In addition, higher DO concentrations at CW1 outlet zone could be maintained at similar concentrations as water flowed into CW2 in series, therefore inhibiting methanogenesis in CW2. However, without direct DO measurements, it is unknown if aeration affected the differences in CH$_4$ flux observed between cells and zones.

2.4.4. Seasonal Variation

Our hypothesis that CH$_4$ flux would be greatest in the summer was also rejected. The results from this study showed that CH$_4$ fluxes on average were higher in the spring compared to summer and fall fluxes in both CW1 and CW2. These results differ from expectations and other studies from CWs that reported highest CH$_4$ fluxes during the summer months (Johansson et al. 2004, Mander et al. 2005, Inamori et al. 2007, Sovik et al. 2006, Maltais-Landry et al. 2009). Several factors relating to seasonal changes,
including water level, organic load, temperature, and vegetation as outlined below may account for the disparity between seasonal CH$_4$ flux patterns in CWs measured in this study and in previously reported data.

2.4.5. Water Table and Seasonal Variation

The rate of methanogenesis in the lower sediment layers of CWs, particularly in SSF CWs, relative to consumption by aerobic bacteria (methanotrophs) in aerated and/or unsaturated areas above the water table determines net CH$_4$ flux (Kadlec and Wallace, 2008, Strom et al. 2007, Dinsmore et al. 2009). Therefore, as water tables drop, the potential for CH$_4$ production decreases and CH$_4$ consumption in the upper layers of the CW gravel bed increases.

To measure CH$_4$ emissions with minimal disturbance, permanent collars were installed 15 cm into the CW gravel bed to the depth of the water table at the time of installation. However, if the water table drops below the surface of the substrate, the upper layers of the CW gravel bed may become sufficiently aerated that CH$_4$ consumption may reduce net CH$_4$ flux.

Inflow to the CW system from dairy parlor operations and precipitation events affect CW water levels as storm water from the dairy feed lot is directed to the CW system (Figure 1). Precipitation total for the seven days prior to CH$_4$ sampling dates are shown in Figures 4 and 6, however, a relationship between sample event associated precipitation and CH$_4$ flux is unclear. Total precipitation for spring, summer and fall seasons was similar (21.3, 26.7 23.2 cm, respectively) and slightly greater during the summer, and therefore does not explain the seasonal variation in CH$_4$ fluxes (Figure 6).
However, during the summer months, increased plant growth and warmer temperatures resulted in higher evapotranspiration rates and declining CW water table heights. Average CH$_4$ flux for CW1 inlet zones was lowest during the summer season (Table 2, Figure 5). Maintenance logs indicate that municipal water was added to the CW inlet tank on 6/15, 6/28, 8/1/, 8/15, and 9/4/07 in response to low water table levels (Figure 4a,b). These dates correspond to the lower CH$_4$ fluxes within CW1 inlet zone, specifically at sample dates 6/13 and 6/27, 8/8 and 9/1/07. The additional fresh water would dilute incoming wastewater to the CW and, in turn, reduce microbial processes and CH$_4$ emissions. A falling water table during the summer is the most likely explanation for the lower CH$_4$ fluxes measured during the summer season.

Weekly inflow to the CW system reveal greater flow to the CW system in the spring as compared to summer and fall, leading to the assumption of a consistently high water table and anaerobic substrate during the spring season (Figure 7, Appendix). A large flow event did occur during the summer season; however, this was primarily driven by precipitation, which may have diluted incoming wastewater. In addition, maintenance logs from the spring (Mar-Apr) of 2007 indicate a steadily high water table and on occasion, a water table above the substrate of the CW1 inlet zone. During the spring of 2007, average CH$_4$ emissions in CW1 were significantly higher than summer and fall seasons (Table 2, Figure 6). Furthermore, no significant differences in CH$_4$ fluxes were observed between CWs or within CW zones during the spring season, supporting the occurrence of a more homogeneous water level throughout the CWs during this time period.
2.4.6. Biochemical Oxygen Demand Loading

Variability in carbon loading to the CW cells should also be considered because methanogenesis occurs frequently in the lower sediment layers of horizontal subsurface flow (HSSF) systems that receive high loads of biological oxygen demand (BOD) (Kadlec and Wallace, 2008). In HSSF CWs, the wastewater is treated via filtration and microbial breakdown as it flows from CW inlet to outlet. Therefore higher concentrations of carbon and higher process rates would be expected to occur at the inlet zones (Sovik et al. 2006). Chiemchaisri et al. (2009) reported both anaerobic and aerobic conditions prevailing over the entire length of the CW but deeper anaerobic zones at the inlet due to high organic loading.

Sovik et al. (2006) reported higher CH$_4$ flux related to higher BOD in inlet waters. The observed difference in CH$_4$ flux between CW1 and CW2 (e.g., greater CH$_4$ emissions from CW1) may be attributed to differences in organic matter loading. Since CW1 and CW2 were connected in series, any treatment achieved in CW1 would reduce the load to CW2. The average BOD concentration of the incoming dairy wastewater was ~3000 mg l$^{-1}$ and the BOD loading to both CW cells was monitored since 2004 (Figure 8, Appendix). The BOD loading rate to CW1 was two times greater ($p < .0001$) than to CW2 during the three years (2004-06) leading up to gas measurements. Furthermore, during the three seasons of gas emissions monitoring in 2007, the BOD load to CW1 was eight fold greater ($p = .0003$) than to CW2. The large disparity in BOD loading rates to CW1 and CW2, both leading up to and during gas monitoring may therefore be an important factor contributing to the greater CH$_4$ emissions observed in CW1. BOD
loading to CW1 in spring, summer and fall seasons, however, were not different \((p = .0989)\), and therefore do not explain seasonal variations in \(\text{CH}_4\) flux.

### 2.4.7. Temperature and Seasonal Variation

Rates of methanogenesis are directly related to temperature (Schutz et al. 1989). Previous research has indicated that water temperature is a good predictor of \(\text{CH}_4\) emissions from CWs (Stadmark and Leonardson, 2005). In the UVM CW, temperature of incoming and intra-CW wastewater depends on the season ambient air temperature and also on the source. Dairy parlor wastewater leaves the milking house at a higher temperature than ambient air, particularly in colder seasons, before combining with barnyard runoff and then entering the CWs. Tracer studies carried out at the UVM CWRC from November to May 2004-05 indicated an average temperature difference between the CW inlet and outlet zones of up to 5 °C (Munoz et al. 2006), possibly contributing to observed higher \(\text{CH}_4\) emissions in CW1 inlet zone. The difference in \(\text{CH}_4\) flux between inlet and outlet zones was greater during cooler spring and fall seasons, lending further evidence of the potential effect of incoming wastewater temperature on inlet zones. Less difference between inlet and outlet \(\text{CH}_4\) fluxes observed during the summer may be due in part to warmer ambient air temperatures and smaller differences in temperature between inlet and outlet zones.

### 2.4.8. Vegetation and Methane Flux

Although plants were excluded from monitoring of GHGs at the UVM CW due to chamber size limitations, it is important to consider that the presence of vascular plants
may also be an important factor influencing CH$_4$ flux. Morrissey et al. (1993) documented the first evidence of stomatal control of CH$_4$ flux by plants (Carex). Previous research estimates that between 50-90% of all CH$_4$ generated from a vegetated, natural wetland is transported through the vascular system of emergent plants (Boon 1999). Therefore, the potential CH$_4$ emissions reported from in our study could be greatly underestimated.

The presence and species composition of vascular plants can affect CH$_4$ exchange between wetlands and atmosphere (Whiting and Chanton 1993). Higher emissions of CH$_4$ from vegetated CW sites compared to sites without vegetation is expected as plants may act as conduits for the transport of methane (Liikanen et al. 2006, Strom et al. 2007).

At the UVM CW, planted areas were more robust at the outlets zones of the cells, particularly in CW1, where much of the inlet zone did not sustain emergent plants, yet CH$_4$ flux was greatest at inlet areas of the CW. The role of many wetland plants in carbon turnover and CH$_4$ emissions has been somewhat conflicting in the literature. Tanner et al. (1997) reported higher CH$_4$ emissions from unvegetated CW sites and Picek et al. (2007) measured highest CH$_4$ flux in unvegetated inlet zones of HSSF CW planted with Phragmites australis. Maltais-Landry et al. (2009) also reported higher CH$_4$ flux from CW mesocosms with non-aerated, unplanted conditions and Dinsmore et al. (2009) found that the presence of aerenchyma-containing vegetation may reduce CH$_4$ fluxes. There is also conflicting evidence in the literature regarding species-specific emissions of CH$_4$ (Wang et al. 2008). For example, Juncus has been reported to both limit (Smialek et al. 2006) and enhance the emission of CH$_4$ (Strom et al. 2007). The variability in CH$_4$
emissions suggests that oxygen transfer capacity among plant species varies (Maltais-Landry et al. 2009).

2.5. Conclusions and Recommendations

1) On average, CH$_4$ flux was higher in aerated CW1 than in the non-aerated CW2 throughout the three seasons of investigation, primarily due to the higher fluxes occurring at the inlet zone of CW1. The in-series CW design may have confounded differences in CH$_4$ flux between CWs by limiting differences in DO and by accentuating differences in carbon loading. Future CH$_4$ flux studies must include measurements of DO content of water throughout the CWs.

2) As expected, CH$_4$ flux differed along the CW zones, being significantly higher at inlet areas than mid or outlet zones.

3) CH$_4$ flux was highest during the spring season, attributed to a consistently high water table and/or fluctuating water table levels within CWs occurring in the summer and fall seasons. Future studies must include water table measurements to aid in explanation of CH$_4$ flux observations.

2.6. Acknowledgements

We wish to thank Senator Jeffords Office for their financial support via United States Department of Agriculture (USDA) research grant: “CWs Center for Research, Education and Outreach at the University of Vermont: pollutant removal processes and mechanisms” and Dr. Gerald Livingston (Altos Imaging) for providing field methods, equipment, and for guidance with data analysis.
2.7. References


NOAA. Annual Greenhouse Gas Index (AGGI), NOAA Earth System Research Laboratory, Boulder CO. http://www.esrl.noaa.gov/gmd/aggi/aggi_2008.fig2.png


Comprehensive References


DuBowy, P.J. and R.P. Reaves (eds.) Constructed Wetlands for Animal Waste Management: Proceedings of Workshop sponsored by the Conservation Technology Information Center, USDA, SCS, EPA and Purdue University, April 4-6, 1994, Lafayette, Indiana.


Gaseous Fluxes from Subsurface Flow Constructed Wetlands for Water 
Treatment. Journal of Environmental Sciences and Health, 40: 1215-1226.

Gaseous Fluxes in the nitrogen and carbon budgets of subsurface flow constructed 

VT.


Control on Methane Release from Carex-dominated Wetlands. Chemosphere, 

Lewis Publishers, Boca Raton, FL.


Norman, J.M., Kucharik, C.J., Gower, S.T., Baldocchi, D.D., Crill, P.M., Rayment, 
carbon dioxide fluxes. Journal of Geophysical Research-Atmospheres, 102(D24): 
28771-28777.

NOAA. Annual Greenhouse Gas Index (AGGI), NOAA Earth System Research 
Laboratory, Boulder CO. http://www.esrl.noaa.gov/gmd/aggi/aggi_2008.fig2.png

Ongley, E.D. (1996). Control of water pollution from agriculture. FAO Irrigation and 
Drainage Paper 55.

to increase pollutant removal efficiency of CWs in cold climate. 

Peel, M.C., Finlayson, B.L., and McMahon, T.A. (2007). Updated world map of the 
Koppen-Geiger climate classification. Hydrology and Earth System Sciences, 11(5), 
1633-1644.

weitland – plants as important sources of carbon. Ecological Engineering, 31(2): 98- 
106.


Appendix

Figure 7. Weekly inflow (m$^3$) to the CW system and precipitation (cm) throughout the nine-month study period.

Figure 8. Average BOD loading rate (g m$^{-2}$ h$^{-1}$) and standard error for CW1 and CW2 during years leading up to and including GHG study (2004-2007), years preceding study (2004-2006), 2007 overall and separate seasons of GHG study.
Figure 9. Nitrate (\(\text{NO}_3^-\)) concentrations (\(\text{mg l}^{-1}\)) in CW1 and CW2 outflow throughout the nine-month study period.

Table 3. Average ammonium (\(\text{NH}_4^+\)) and biological oxygen demand (BOD) removal efficiency (%) by CW1, CW2, CW3 and CW4 for each of and throughout the three seasons of investigation (A= aerated, NA= non-aerated, I= CW independent, S= CW connected in-series).

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<th>BOD Removal (%)</th>
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