Dissolved Oxygen Dynamics in the Dunnville Marsh on the Grand River, Ontario, Canada

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.
I understand that my thesis may be made electronically available to the public.

Abstract

Dissolved oxygen (DO) is one of the most important environmental factors necessary to sustain aquatic life and the overall health of aquatic ecosystems. The Grand River is the largest watershed in southern Ontario. It has been adversely affected by agricultural activities and a growing urban population which has led to periods of the year when oxygen supplies in river waters are extremely low. The southern part of the river near its mouth is unusual compared to upstream reaches by having extensive marsh and open water wetlands along its banks. This study focuses on the Dunnville Marsh, a typical example of wetlands along the southern end of the Grand River. The spatial and temporal variation in dissolved oxygen was studied in the Dunnville Marsh and in a stretch of the Grand River immediately beside it over a one year cycle during 2007 to 2008. Dunnville Marsh exhibited little influence on the oxygen regime of the river. The Grand River; however, could influence the oxygen regime in the marsh during the spring when waters are high but exerts little influence during the rest of the year. There were no great differences in DO between the wetland and the river during the high water spring melt period; however notable differences occurred in the summer and fall.

At most of the river sites, DO data exhibited subsaturation levels in fall 2007, around saturation in spring 2008, and supersaturation in summer 2008.The opposite was the case for most of the wetlands sites in summer 2008 demonstrating subsaturation levels of DO, around saturation in spring 2008, and DO records ranged from subsaturation to supersaturation in fall 2007.

Oxygen stable isotopes and diel O_2 measurements showed that ecological factors probably were influencing the DO cycle in Dunnville Marsh whereas both ecological and weather factors influenced the cycle in the Grand River.

Monthly $\delta^{18}O_{DO}$ data from the river revealed a shift towards atmospheric equilibrium compared to the wetland. These data exhibited less photosynthetic and more respiration activity in the fall and more photosynthetic activity during the summer. The wetland showed higher photosynthetic activities in the summer than the river; however, there was discrepancy between the low $\delta^{18}O_{DO}$ signature and the accompanied low DO saturation levels in some of the wetlands sites especially in the summer of 2008. The ground water input or the small isotopic changes on overlying water of $\delta^{18}O_{DO}$ (small sediment respiration fractionation-factor) could be an explanation for this difference.

Nitrogen input from the agricultural areas was low at most of the time and had minimal influence on the DO in the Dunnville Marsh. Despite low nitrogen input the attenuation ability of the Dunnville Marsh was apparent, presumably due to plant uptake, especially in the northern part of the marsh. The Grand River showed a significant hydrological effect on Dunnville Marsh during the spring when runoff is high. $\delta^{18}O$-water proved to be an effective tool for differentiating river and wetland waters. Based on the $\delta^{18}O$-water signature in late April (after the flood season) it appears river water extended about two-thirds along the main stream well into Dunnville Marsh. River water, probably inundates a significant part of the Dunnville Marsh in early April (flood peak), when water flow was more than 10 fold higher than later in April following the peak flood season.

Total nitrogen (TN) and dissolved organic carbon (DOC) showed the effect of the river on the southern part of the marsh due to the clear difference in concentrations exhibited between the northern part of the marsh and the river. River water intruded into the marsh and brought the DO to similar saturations as in the river in spring. This river influence on DO saturation of Dunnville Marsh happened because of the lack of vegetation in April which can be considered as a major factor influencing the DO in the marsh.

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Dedication

I would like to dedicate this work to:

My lovely family who supported me throughout my life, especially my mother who kept me in her thoughts all the time. Also, I would like to dedicate this work to my new born nephew Ramel "the prince"………… I love you all!

The Grand River and wetland sciences

The souls of my three friends (Omar, Raid, and Mulhim) who could not continue the scientific work and research because their journey of life was ended in Baghdad. Peace be upon their spirits.

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Chapter 1
Introduction

1.1 Introduction

Oxygen, and especially dissolved oxygen, plays a crucial role in sustaining life in aquatic ecosystems, including wetlands (Hampson 1989). DO is an important part of the oxygen cycle in aquatic ecosystems (Figure 1.1). It is found in microscopic bubbles that are mixed in the water and occur between water molecules. DO levels in aquatic systems probably reveal more about ecosystem metabolism processes than any other single parameter. Concentrations reflect the balance between oxygen supply from atmosphere and photosynthesis on one hand, and the metabolic processes that consume oxygen on the other (Kalff 2002). DO measurements provide valuable information about the biological and biochemical reactions going on in water. It is a measure of one of the important environmental factors affecting aquatic life and provides an indication of the capacity of water to receive organic matter without causing problems (Wetzel and Likens 1991).

Because DO concentration is affected by many water quality parameters, it is a sensitive indicator of the overall health of aquatic ecosystems (Manya et al. 2006). Oxygen may be removed from or added to water, by various physical, chemical or biological reactions. The oxygen transfer in natural waters depends on: internal mixing and turbulence due to the velocity gradients and fluctuations, temperature, wind mixing, waterfalls, dams, rapids and surface films (Lopes and Silva 2006), as well as organic activity such as primary production, decomposition of organic matter, and other biological processes (Nelson et al. 1994). The speed at which oxygen can enter and mix through water depends on stirring at the surface, currents in the water and the depth of the water. For example, shallow-flowing streams usually have high oxygen levels while stagnant and deep pools may have low oxygen levels in deeper parts.

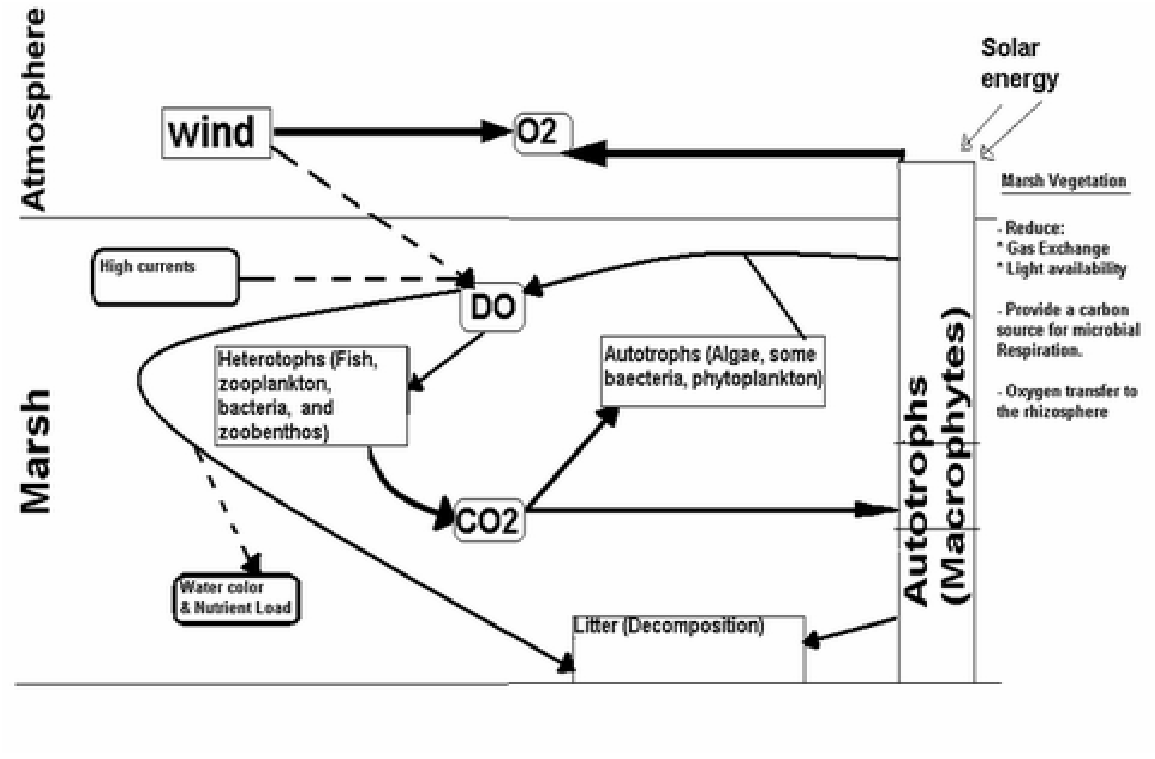

Figure 1.1: Oxygen cycle in a typical marsh. The solid lines going from and to DO represent factors that affect DO directly. The dashed lines represent factors affect DO indirectly.

The concentration of dissolved oxygen in water depends on temperature, pressure, and concentrations of various ions (Wetzel and Likens 1991). Another factor influencing the solubility of oxygen in water is salinity. Sea water and saline lakes with a salinity of about 35,000 mg/ L hold about 20% less DO at saturation than distilled water at the same temperature (Kalff 2002).

In aquatic ecosystems, the DO can be affected by two main metabolic processes: photosynthesis and respiration. DO increases rapidly during the day from photosynthesis of benthic algae, phytoplankton and aquatic vegetation in the presence of sunlight, and decreases after nightfall or on cloudy days when oxygen production ceases but oxygen consumption continues (Manya et al. 2006; Smith and Able 2003). Photosynthesis can be an important contributor of DO, especially in highly productive waters, and is generally reflected in the magnitude of diel fluctuations in DO concentrations (Hampson 1989). Decomposition of organic matter, unlike photosynthesis, takes place both at day and night time and therefore, the influence of organic matter on DO concentration is apparent during the day and night (Manya et al. 2006). The rate of consumption of DO, or oxygen demand, is governed by chemical and biological factors within the water column and bed sediments. The rate is also temperature dependant and can be expected to vary seasonally. Daily mean DO concentrations exhibited marked seasonality with concentrations in the cooler winter months significantly higher than concentrations during the warm summer months. (Hampson 1989). High rates of photosynthesis in dense beds of submerged macrophytes in the littoral zone and wetlands may produce supersaturation on sunny days, but the beds become subsaturated as the result of respiration (Kalff 2002).

DO processes in wetlands, especially marshes and shallow open water wetlands, are somewhat different than in other aquatic ecosystems. These wetlands often exhibit low minimum DO concentrations, wide diel ranges, and experience DO depletion on a diel basis (Mitsch 1989). Differences among wetland types and habitats must be considered when determining appropriate DO conditions within a wetland; wetlands with highly coloured water also are characterized by low water-column DO and show little diel variation. While wetlands vary in terms of their DO dynamics, increased nutrient loads can cause similar trends in DO regardless of habitat type and background DO ranges (McCormic and Laing 2003). The concentration of oxygen in equilibrium with a body of water in contact with the atmosphere varies primarily with temperature. However, non-equilibrium concentrations are typical of wetlands as a result of atmospheric exchange rate and metabolic O_2 consumption and production (Rose and Crumpton 1996).

Little is known about DO oxygen dynamics in coastal wetlands along the shores of the Great Lakes, and even less is known about more riverine wetlands near the mouths of the large rivers flowing into the Great Lakes. This study focuses on one example, the Dunnville Marsh, which occurs near the mouth of the Grand River on Lake Erie. One study on a total of 14 wetland sites located along a 35 km stretch along the southern Grand River between Cayuga and Dunnville showed average DO concentrations of 5.5-9.5 mg/ L, with the highest DO concentration values recorded in wetlands closest to the river (Gilbert and Ryan 2007). Questions emerge about the relationship between the river and the adjacent wetlands. Does the river influence DO concentrations in the wetlands or do the wetlands influence the DO concentrations in the river? The Grand River Watershed is home to about 900,000 people. The rapid increase of population will put more stress on the river; consequently, affect DO which is considered as an indicator of the health of a water body. The Grand River is subject to strong anthropogenic influence including both non point source pollution represented by the agricultural activities within the drainage basin as well as point sources (26 sewage treatment plants); one sewage treatment plant is located in Dunnville approximately 8 km north-east of the mouth of the river.

Stable oxygen isotopic measurements provide a useful tool for assessing the origin and source of the DO. The δ18O measurements can track the sources involved in mixing and the respiratory sink involved in oxygen consumption. The 18O:16O of DO ($\delta^{18}O_{DO}$), like the concentration, is affected primarily by three processes: air-water gas exchange, respiration, and photosynthesis. Gas exchange drives the $\delta^{18}O_{DO}$ toward +24.2 ‰ (vs. SMOW) because atmospheric O2 has a δ18O of 23.5 ‰, and there is a 0.7 ‰ equilibrium fractionation during gas dissolution (Quay et al. 1995). Aquatic photosynthesis produces O2 that is identical to the δ18O of the source water because there is little or no fractionation during photosynthesis. Therefore photosynthetic O2, is depleted in δ18O relative to O2 derived from air-water gas exchange (Wang and Veizer 2000). During respiration, the 16O-16O uptake rate is ~20 ‰ greater than the 18O-16O uptake rate. Thus respiration increases the 18O: 16O of the remaining dissolved oxygen (Kiddon et al. 1993). In the simplest sense, when respiration dominates over photosynthesis, dissolved oxygen will be undersaturated and δ18O > 24. 2 ‰. When photosynthesis exceeds respiration, in contrast, dissolved oxygen will be supersaturated and δ18O will be < 24.2 ‰. When gas exchange dominates over photosynthesis and respiration, as in the surface ocean, dissolved O2 is close to saturation and the δ18O is 24.2‰ (Quay et al. 1993). This technique will be used to understand photosynthesis, respiration, and gas exchange contribution to DO concentration.

Objectives

This project focuses on the Dunnville Marsh because it is a representative example of marshes in the southern part of the Grand River. My thesis has two objectives:

Objective 1 aims to understand the interaction between the Grand River and the Dunnville Marsh; more specifically, to what degree, if any, does the marsh influence DO in the river.

The DO was monitored and compared in and between the Dunnville Marsh and adjacent stretch of the Grand River immediately adjacent to the marsh over one annual cycle. Field measurements were conducted over a one annual cycle on a monthly basis throughout monitored stations in the river and the wetlands. DO concentration and $\delta^{18}O_{DO}$ were measured every month in order to understand the influence of atmospheric O2, photosynthesis, and respiration on DO cycle. A diel study in the marsh and river was conducted once in July 2008 to understand the effect of the day and night time on the DO regime and the link between the river and the wetland.

In order to have better insight regarding the interaction between the river and the marsh, $\delta^{18}O$-water tool was used. The application of this relative new tool was conducted during the dry season (September 2007), the period after the spring flood (April 2008), and the summer (July 2008).

Given the Dunnville Marsh lies in an agricultural area, objective 2 of the thesis aims to assess if there is any nitrogen inputs from agriculture in the marsh and if so, how nitrogen might influence DO. Total nitrogen (TN), nitrate (NO_3^-) and ammonium (NH_4^+) concentrations will be measured at the same time the DO is being measured during the monthly field work in one annual cycle. The nitrogen source that might enter Dunnville Marsh is located along the northern side immediately adjacent to agricultural fields. The nitrogen concentrations immediately at the inflow at the drain that enter the wetland from Maple Creek were used to determine any nitrogen inputs so as to track it in the Dunnville marsh. If present, it would be possible to track the attenuation through the wetland through site W4 (1000m from the drain), W3 (1400m), and W5 (1800m). If there is a high agricultural nitrogen input from the upland from the north side of the marsh then we can see its effect on the oxygen in the wetland itself and in the river.

Chapter 2
Study Site Description

2.1 Location and field site description

The Dunnville Marsh is located at the southern end of the Grand River watershed (42^{o} 53' N, 79^{o} 34' W; ca. 174 m a.s.l.). It is situated about 3 km north of the mouth of Lake Erie, and about 4 km south of the Dunnville dam in the town of Dunnville (Figure 2.1). The Dunnville Marsh covers an area of about 3.35 km^2 and lies south of the Byng Island Conservation Area. Both areas are managed by the Grand River Conservation Authority (GRCA) in partnership with Ducks Unlimited Canada (GRCA 2005).

Wetlands at the southern end of the Grand River from the town of Cayuga to the mouth of the river in the vicinity of the Dunnville Marsh are predominantly marshes characterized by nearly pure communities of *Typha* spp. They are extensive and form wide broad patches along the river. This is in contrast to wetlands farther north along the Grand River where marshes are less extensive, more intermittent and mixed with emergent, floating and submerged aquatics macrophyte communities.

The dam at the town of Dunnville creates a hydrological divide on the river. Water north of the dam may originate from anywhere upstream in the watershed. Water in the river south of the dam is a mix of river water pouring over the dam from sources upstream. Water may back up in the mouth of the river during windy periods and storm events when Lake Erie water is pushed into the river during seiches creating abnormally high water levels and flooding in all the marshes located southern the dam, including the Dunnville Marsh. Artificial drainage channels bring surface drainage waters from surrounding lands into the Grand River. Such a channel connects to Maple Creek on the north-east side and carries water through the Dunnville Marsh into the Grand River. It is also most likely that groundwater discharges into the Dunnville Marsh along its north-east side.

2.1.1 Sampling Stations

A network of nine stations was established in August 2007. The stations were selected so as to include representative habitat conditions in and around the Dunnville Marsh (Figure 2.1; Table 2.1). This study included two stations in the centre of the main channel of the Grand River, immediately upstream and downstream from Dunnville Marsh, one station between the marsh and the river and five stations within the Dunnville Marsh itself (W1, W2, W3, W4, and W5). The last three stations are located along Maple Creek and connected to the Drain station. The Drain station was established at the mouth of Maple Creek where it enters on the northern side of Dunnville Marsh. Maple Creek is connected to an artificial agricultural drainage that collects runoff from the adjacent agricultural fields.

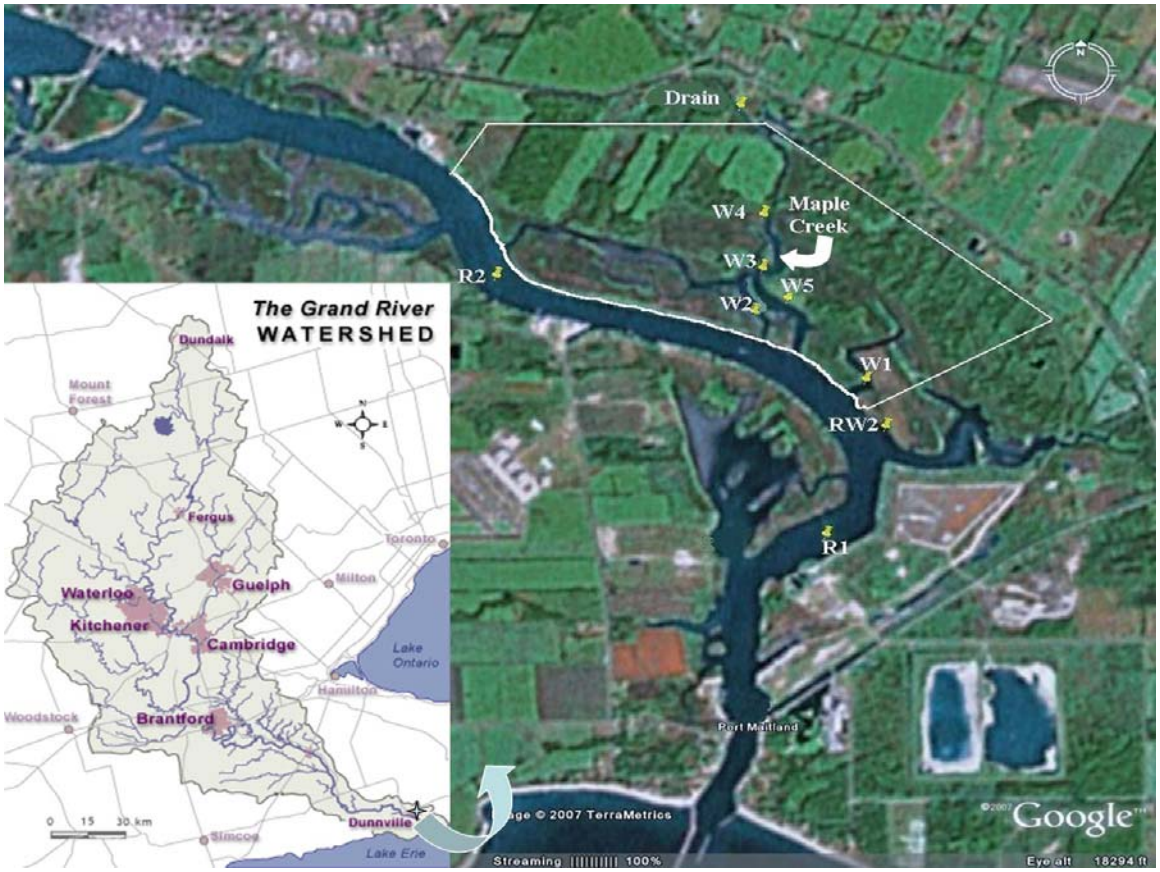

Figure 2.1 An aerial photograph showing the Dunnville Marsh and the Grand River situated between Lake Erie to the south side and the Dunnville Dam to the north-east side. Field sampling stations are represented by yellow spots. The white line represents the border of the Dunnville Marsh property belonging to GRCA. On the bottom left side, a map of the Grand River watershed is presented.

Table 2.1 A list of the sampling stations describing the location and the range of the water depth observed at each station during the period of this study. Compare with Figure 2.1.

Station	Distance from the river (m)	Range of water depth in 2007 (cm)	Range of water depth in 2008 (cm)	Site location
W1	120	14-25	40-60	Dunnville Marsh
W2	130	16-25	20-39	Dunnville Marsh
W5	320	13-24	42-56	Dunnville Marsh
W3	700	12-18	23-35	Dunnville Marsh
W4	1100	0-18	25-35	Dunnville Marsh
Drain	2100	16-26	55-69	North of the Marsh
R2 (upstream)	In the Grand River	395-425	400-425	2500m down from the Dunnville Dam
R1 (Downstream)	In the Grand River	510-550	440-640	2700m down from the upstream
RW2	on the edge of the wetland	16-27	35-50	Between R1 and W1

2.2Geology and Soils

The southern end of the Grand River below the dam lies on glaciolacustrine clay and silt laid down in Glacial Lake Whittlesey and subsequent glacial lake water bodies that covered the eastern end of the Erie Basin. Much of the area is covered by alluvial sands and silts and some gravels derived from upstream transport in the Grand River and from transport by Lake Erie currents entering the river mouth (Barnett 1991). The small creeks such as Maple Creek in Dunnville Marsh also contribute silt and some sand in suspension during storms and high water periods. The sediments within Dunnville Marsh under the beds of Typha are mineral-rich. The organic content is around 20% fresh weight which is slightly higher than sediment in the marshes above the dam where organic matter content is between 8% and 14%. Shells of gastropods were observed to be especially abundant in some parts of the Dunnville Marsh (Fischer et al. 1995).

Soils in the vicinity of the Dunnville Marsh are classified as orthic humic glysol soils with sand and some silt and clay. They are alkaline, strongly calcareous that generally are poorly drained, with high conductivity, and prolonged saturation period (Presant and Acton 1984). These conditions are most conducive to establishment of mineral wetlands that include the marshes along the Grand River.

2.3 Climate

Mean annual temperature was 15.3 ^{o}C in fall 2007, 10.1 ^{o}C in spring 2008, and 19.5 ^{o}C in summer 2008. Mean annual precipitation was 60.6mm in fall 2007, 66mm in spring 2008, and 130mm in summer 2008 (Environment Canada 2008).

The Year of 2007 (late summer and fall) was very dry compared to the year of 2008 (spring and summer). Precipitation during the months of May, June and July 2008 were very regular. Precipitation occurred on a weekly or more frequent basis. For instance, precipitation in July 2008 was well above the long term average across the watershed. Monthly averages ranged from 95% to 224% of the long-term average. This regular precipitation maintained flows in the river system. On the other hand, precipitation in April 2008 went below the long- term average for April. Monthly averages ranged from 59% to 88% of the long-term average. In addition to light precipitation in April, conditions were warm. It is also important to keep in mind the period from May through November in 2007 was one of the driest in the past 60 years (GRCA Report 2008). The lack of rainfall dating back to late April 2007 has caused stream flows to be well below normal throughout the watershed (GRCA Report 2007).

Lake Erie levels were below the long-term average for the months August, September, and October 2007. It was at the average for May and June 2008 and above the average for April and July 2008 (GRCA Report 2007; GRCA Report 2008).

2.4 Vegetation

Dunnville Marsh is one of the largest and most representative marshes in the southern end of the Grand River. Emergent communities dominated by *Typha* spp. and some *Lythrum salicaria* form the primary vegetation communities of most of the marshes in the area. Occasional submerged taxa such as *Potamogeton pectinatus* and *P. crispus* and floating taxa such as *Nuphar variegatum* and *Nymphaea odorata* are scattered throughout the emergent stands of *Typha*. Low macrophyte diversity is typical (Gilbert and Ryan 2007). It is possible that soil erosion and runoff containing pesticides may have contributed to some decline of macrophyte growth and overall decline in diversity (Fischer et al. 1995). A study of the water in small patches of submerged aquatic vegetation in the *Typha* was found to have high concentrations of suspended sediments. Resuspension of sediments by carp, wind, and waves are responsible for maintaining turbid conditions that are highly unfavorable to submerged aquatic macrophyte growth.

Chapter 3

Methods

3.1 Field Studies

Maps, reports and aerial photographs were inspected prior to field work during which time a general plan was made for establishing field sampling stations. A field reconnaissance trip in July 2007 was made to request permission for access from landowners and gain a general sense of the field conditions in the Dunnville Marsh. Field sampling was performed once a month from August through October 2007 and from April to July 2008 to gain one annual cycle within the study site.

Duplicate samples of water were collected for $\delta^{18}O_{DO}$ at each station. Samples were collected using 160ml pre-evacuated glass bottles containing sodium azide to prevent any biological activity. While held underwater a needle was inserted through the butyl rubber stopper into the evacuated bottles, and the bottle allowed filling. Care was taken to ensure the needles were flushed with sample to avoid atmospheric contamination of the sample. Samples for analysis of $\delta^{18}O_{water}$ were collected using 30 ml Nalgene bottles. Samples were collected for analysis of dissolved organic carbon (DOC), nitrate (NO_3^--N), Chloride (Cl^-), sulfate (SO_4^{-2}), and ammonium (NH_4^+) in 125 ml Nalgene bottles. Dissolved inorganic carbon (DIC), samples were collected using 30ml glass bottles. Care was taken to ensure there was no headspace and samples were preserved with $HgCl_2$ in the field. A YSI multi-probe meter was used to measure dissolved oxygen (DO), pH, salinity, conductivity, and water temperature in the field. The Winkler method for DO was used to compare field meter measurements during the Diel sampling and for DO measurements in June 2008. Water samples for analysis with the Winkler method were preserved in the field using $MnSO_4$ and NaOH-KI and analyzed immediately upon return to the laboratory (Smith 2005). All field samples were packed on ice and transported in a cooler back to the laboratory at the University of Waterloo.

3.1.1 River Flow

River discharge data were collected at the village of York, about 35 km north of the Dunnville Marsh which represents the closest location for which discharge data are collected (provided by John Bartlett, Grand River Conservation Authority). The discharge data presented in this study were collected on the same days as the dates of our sampling.

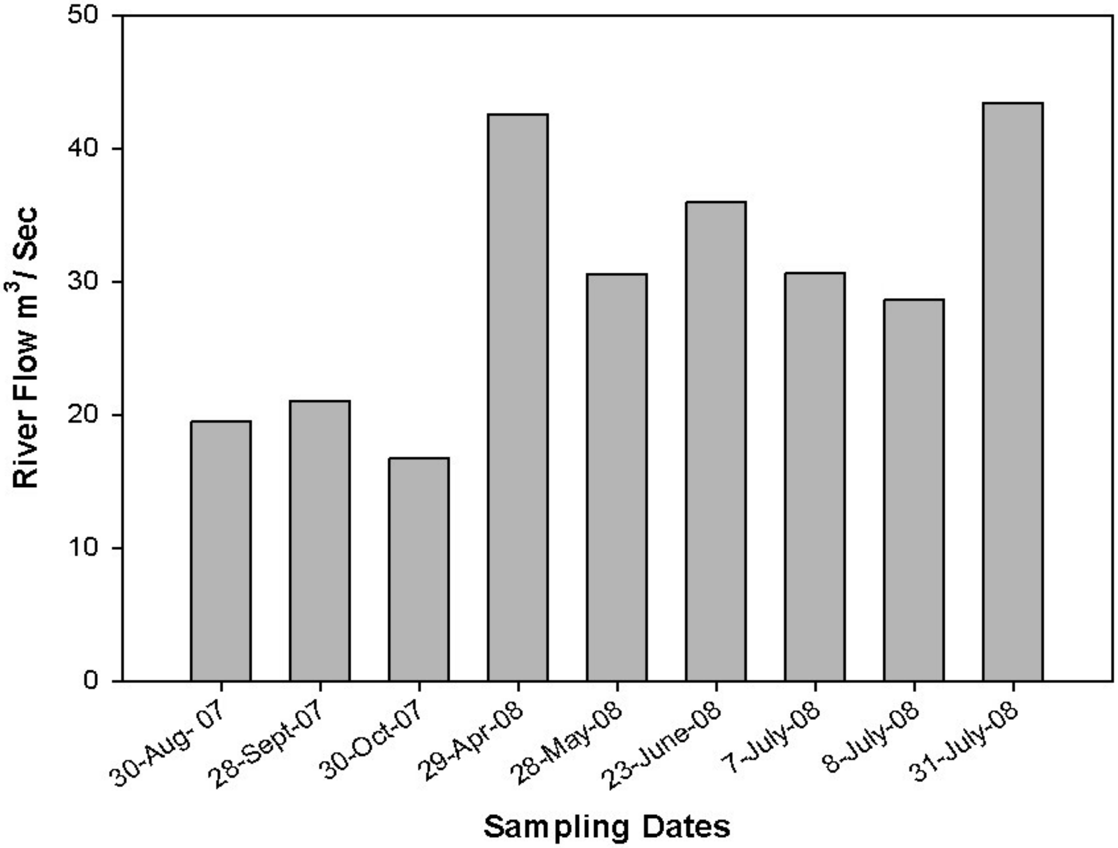

Figure 3.1 This Figure displays the river discharge at York on the same day of the sampling dates.

3.1.2 Diel Sampling

Diel sampling was conducted at three sites over the course of 24 hrs in early July 2008. Two sites in the river (R1 and R2) and third in the wetland (W5) were chosen. A total of 10 samples were collected at each location in the 24 hour period. At each sampling time, samples were collected in order (R1, R2, and then W5). We adjusted two of the sampling times around the sunset and the sunrise. $\delta^{18}O_{DO}$, DO, temperature, and conductivity were measured regularly while $\delta^{18}O_{water}$ samples were collected once on the 7th of July.

3.2 Laboratory Analysis

Immediately upon returning to the laboratory from the field, water samples for DOC, Total Nitrogen (TN), anions, and NH_4 analysis were filtered using Glass Microfiber syringe filters (GMF), 0.45µ. The 125 ml water samples were filtered and subsamples collected for DOC, TN, and anions. An additional 40 ml subsample for NH_4 was filtered, and preserved with 20% H_2SO_4 (acidified to pH 4-5). Filtered samples were stored in a refrigerator (4^oC) until analysis. All other samples for analysis including $\delta^{18}O_{water}$ and $\delta^{18}O_{DO}$ were stored in dark refrigeration at 4^oC, until analyzed using Isotope Ratio Mass Spectrometry according to the methods outlined in Wassenar and Koehler (1999). This analysis was conducted at the University of Waterloo in the Earth and Environmental Sciences Department. DIC concentrations were determined using a high temperature TOC analyzer (Dohrmann DC-90, Rosemount Analytical). A high temperature TOC analyzer was used to measure DOC and TN concentrations (Tekmar Dohrmann, Apollo 9000). The analysis of anions (including NO_3^-, SO_4^{-2} and Cl^-) were performed using Ion Chromatograph (ICS-90, DIONEX). Prior to the analyses of SO_4^{-2} and Cl^-, water samples were diluted (10x) with distilled water. NH_4 samples were measured using Chlorometric analyzer (Technicon Auto Analyzer III.). DO titration using the Winkler method was performed within 24 hours of field sample collection.

3.3 Statistical Analysis

One-way ANOVA (Analysis of Variance) was used to test for differences between means of three groups (River, Southern Wetland, and Northern Wetland) for three different months (September 2007, April 2008, and July 2008). Data were checked for normality and variance homogeneity. If the data did not meet such assumption then several kinds of data transformations were performed. If data normality or variance homogeneity did not improve even after any data transformations, non-parametric ANOVA (Kruskal-Wallis) was used. All the statistical analyses were performed using Sigma Plot version 11 (Systat 2008).

Chapter 4

Results

4.1 Dissolved Oxygen and Isotopes

4.1.1 Dissolved Oxygen Saturation

River sites tended to show higher values for % DO saturation compared to sites within the wetland especially during the summer months. In the summer, DO saturation ranged from 103% to 115% in the river, whereas the wetland varied from 37% to 110% (Fig 4.1). Values from the downstream river site were consistently slightly less than values from the upstream river site. DO readings were measured during the morning for the downstream site (R1) and during the afternoon for the upstream one (R2). The highest DO saturation was 115 % at the upstream river site in July 2008. The lowest was 72% at the downstream river site in September 2007 (Fig 4.1). Spring and summer values in the river tended to be slightly higher compared to values from the fall

DO values from the river and wetlands sites varied temporally. In September 2007, DO saturations in the river showed lower range (72% - 87%) compared to the DO saturation range in the wetland (75% -134%). In late fall and spring (October 2007, April and May 2008), DO variations in the River sites were within the range of the DO readings of the wetland sites (Fig 4.1). During these three months the spatial pattern within the wetland showed less variability across all wetland sites. The wetland site on the edge of the river reflected the same pattern as observed in the river sites. The other wetland sites showed some seasonal variability, more in the summer than at other times of the year.

High values of 134% were recorded in September 2007 at the site near the inflow from Maple Creek. This site also exhibited lower DO values compared to most of the wetland and river sites (Fig 4.1).

The W1 site, a wetland site located near an open water channel on the left side of Maple Creek, showed the lowest oxygen readings at most times except during the spring season. The lowest value at this site was of 37% in June 2008 (Fig 4.1). We have to mention that DO samples of June 2008 were measured using Winkler method, while DO measurements of the other months were recorded using DO probe. September values exhibited the greatest variability across the wetland. In general, most of the wetland sites had lowest values during the summer than at any other time of year.

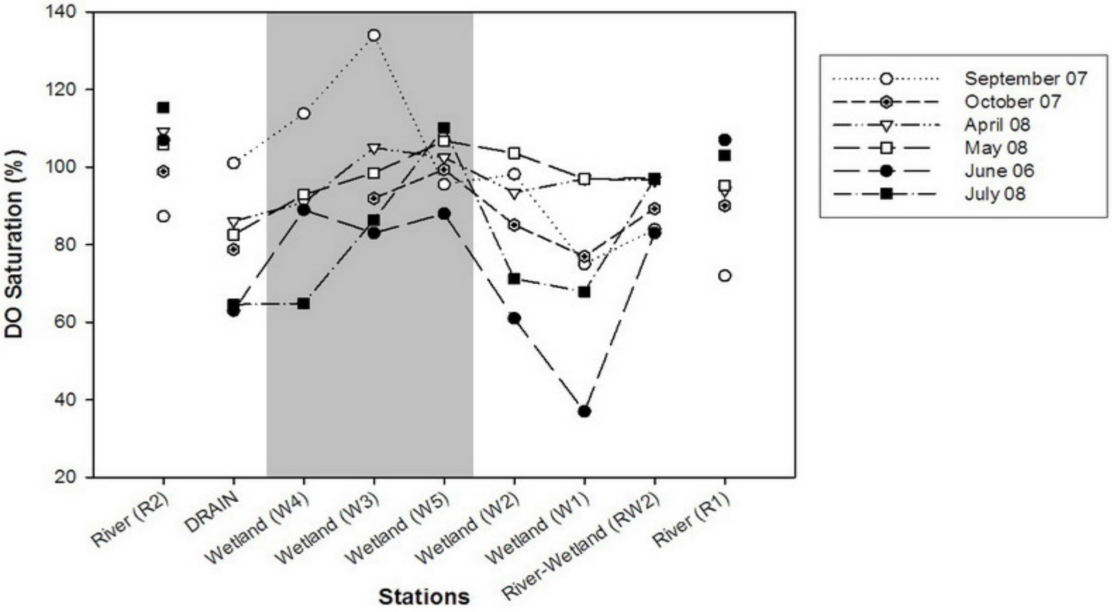

Figure 4.1 Spatial and temporal variations of dissolved oxygen saturation, as percentage, in the Dunnville Marsh and the Grand River. The gray shaded area represents the wetland sites connected to the Maple Creek inflow (Drain site).

4.1.2 Stable isotopes of DO

The seasonal and spatial distribution of δ^{18}O-DO showed that both upstream and downstream river sites were closer to atmospheric equilibrium than the wetlands sites (Fig 4.2). The δ^{18}O-DO values in the most of wetland sites showed a photosynthetic influence. These photosynthetic influences were more affective in the wetland sites located further from the river compared ones close to the river (Fig 4.2).

In October 2007 most of the rivers and the wetland sites were close to the atmospheric equilibrium with lower photosynthetic influence than the other months (Fig 4.2). High oxygen isotopes values were observed in fall 2007 at both the downstream river site and some of the wetlands sites close to the river (Fig 4.2). In spring and summer 2008 there was no big difference regarding the photosynthetic influences. The lowest δ^{18}O-DO values were recorded in May and July 2008 (Fig 4.2).

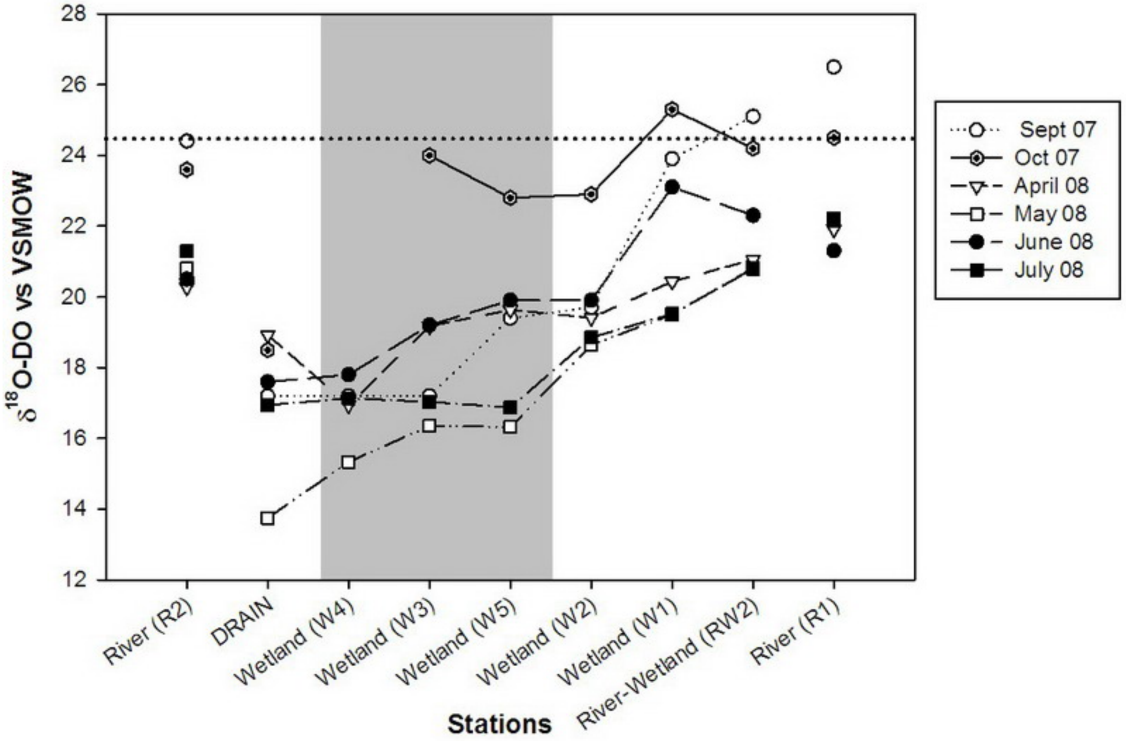

Figure 4.2 This figure displays the changes of δ^{18}O-DO spatially and temporally. The dotted line represents the atmospheric equilibrium point. The gray shaded area represents the wetland sites connected to the Maple Creek inflow (Drain site).

4.1.3 DO Saturation vs. DO Stable Isotope

Wetlands sites showed lower oxygen isotope values than the river sites especially during spring and summer 2008. The lowest oxygen isotope value in spring 2008 was 20.3 ‰ in the river and 15.3 ‰ in the wetland, whereas the lowest value in summer 2008 was 20.5 ‰ in the river and 16.9 ‰ in the wetland (Fig 4.3). River sites were closer to the atmospheric equilibrium points of both DO saturation (100 %) and δ^{18}O-DO (24.2 ‰) than the wetland sites (Fig 4.3).

In fall 2007 a higher oxygen isotope values were observed in the river sites and some of the wetland sites. The maximum δ^{18}O-DO value in fall 2007 was 26.5 ‰ in the river and 25.3 ‰ in the wetland (Fig 4.3). The δ^{18}O-DO values showed higher variability in fall compared to other seasons within the wetland sites which is reflected clearly on the DO saturation of these sites.

Spring data were around the atmospheric equilibrium of DO (100 %) for both wetland and river sites, but river sites were more shifted towards the δ^{18}O-DO atmospheric equilibrium point (24.2 ‰) than the wetland sites (Fig 4.3).

Summer records revealed super-saturation levels for the river sites and sub-saturation levels for most of the wetland sites. Wetland sites; however, showed lower oxygen isotope values than the river sites (Fig 4.3).

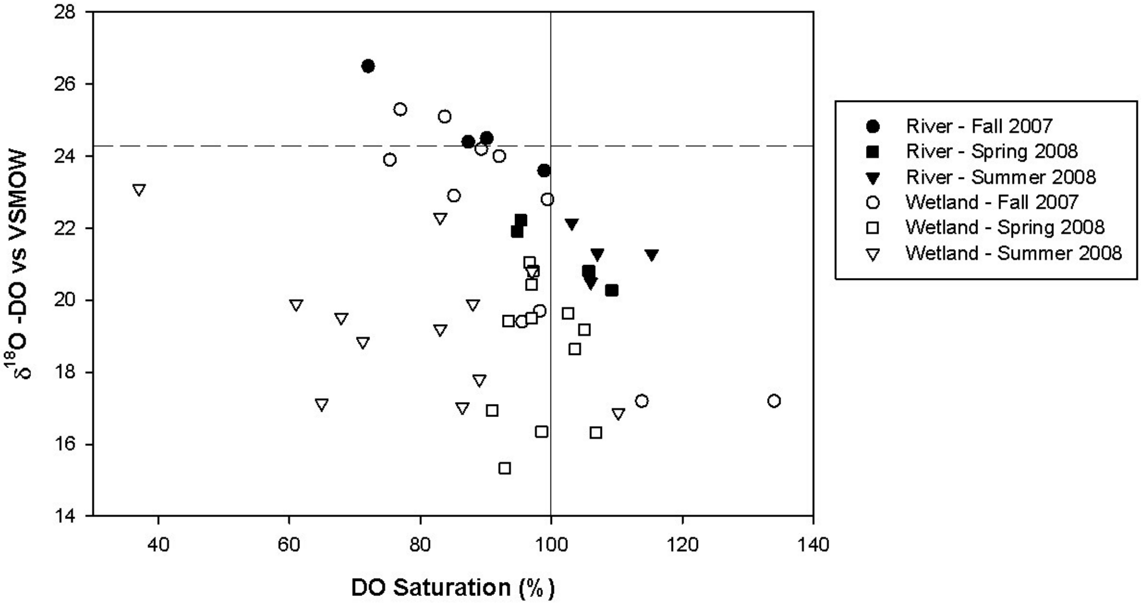

Figure 4.3 A graphical depiction of the DO saturation vs. δ^{18}O-DO of fall (September and October) 2007, spring (April and May) 2008, and summer (June and July) 2008 in Dunnville Marsh and the Grand River. The straight line represents the atmospheric equilibrium for DO saturation while the dashed line represents the atmospheric equilibrium for δ^{18}O-DO.

4.2 Stable Isotopes of Water

Three different periods were chosen for sampling. These were the dry season (September 2007), the period after the spring flood (April 2008), and the summer (July 2008). These time intervals exhibited different trends in the δ^{18}O-water signature. April samples were much more depleted of δ^{18}O-water than the other time periods with no obvious differences between river and wetland sites. The isotope signature of April 2008 varied between -9.12 ‰ and -10.29 ‰ (Fig 4.4). The most enriched δ^{18}O-water value in the wetland (-6.37 ‰) was observed in September 2007 at the northern side of the wetland while the most depleted δ^{18}O-water signature (-10.32‰) was detected in April 2008 at the southern side of the wetland close to the river (Fig 4.4).

Samples from across the wetland sites were more enriched closest to the Maple Creek inflow compared to samples in the wetland closest to the river sites. Not unexpected, water samples in the southern wetland sites and the river had similar signatures (Fig 4.4).

Spatially, April and July values of δ^{18}O-water revealed similar patterns. However, in September, there was a considerable isotopic variability with δ^{18}O-water signatures; more enriched closest to the inflow at Maple Creek (-6.37‰) compared to values farther away and closest to the river (-9.04‰) (Fig 4.4). A sample of Lake Erie water collected in July 2008 was quite enriched (-6.79‰) compared to any of the values from water samples collected in the river and the wetland (Fig 4.4).

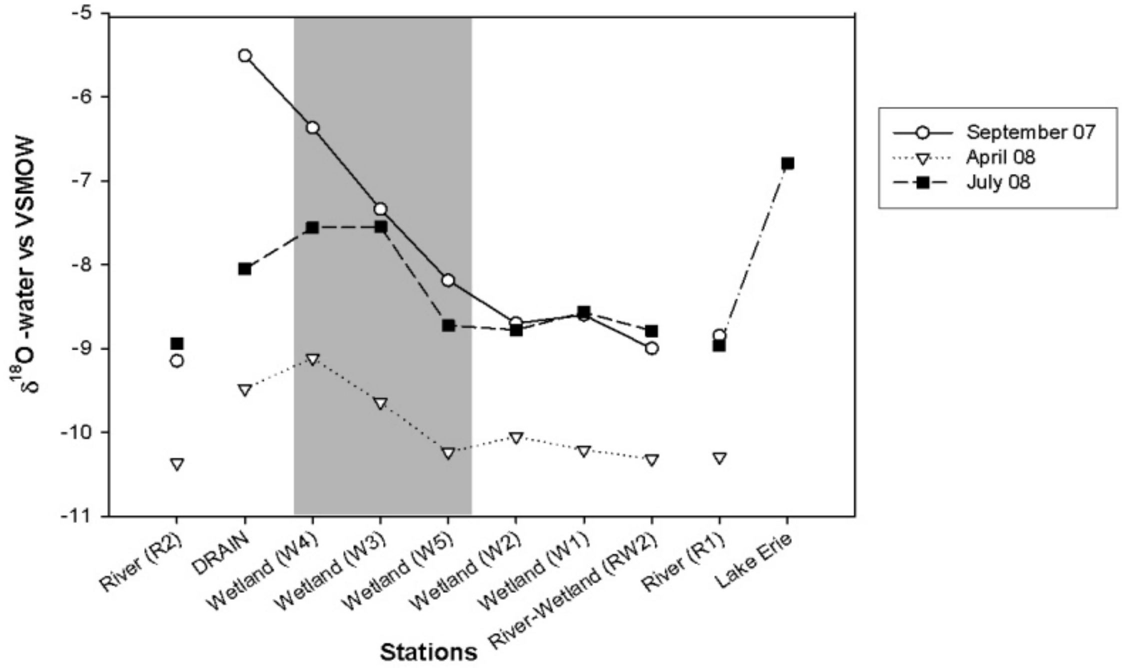

Figure 4.4 Spatial and temporal variations of $\delta^{18}O$-water signature, as permil, in the Dunnville Marsh and the Grand River.

4.3 Diel DO Saturation and Oxygen Stable Isotopes

4.3.1 Diel DO Saturation

Oxygen saturation was monitored over a 24 hour period in summer to determine how oxygen content varies between night and day. The two river sites (R1 and R2) and one site within the wetland (site W5) were chosen for study largely because of the logistics available to make the measurements. Both river sites showed supersaturated oxygen levels during the whole sampling period. The highest DO saturation was at 18:00 hrs (DO% 200) and the lowest was recorded at 9:00 hrs (DO% 121) (Fig 4.5). The greatest differences occurred in the upstream site (R2) compared to the downstream site (R1).

The wetland site exhibited consistently lower diel oxygen values compared to the two river sites. The highest DO record in the wetland was at 15:00 hrs (DO% 141) and the lowest was at 5:15 hrs (DO% 80) (Fig 4.5). %DO was undersaturated during the night compared to daytime when values were higher. In these three sites (R1, R2, and W5) the DO saturations were slightly higher at the noon of the 7th of July compared to the same time on the 8th (Fig 4.5).

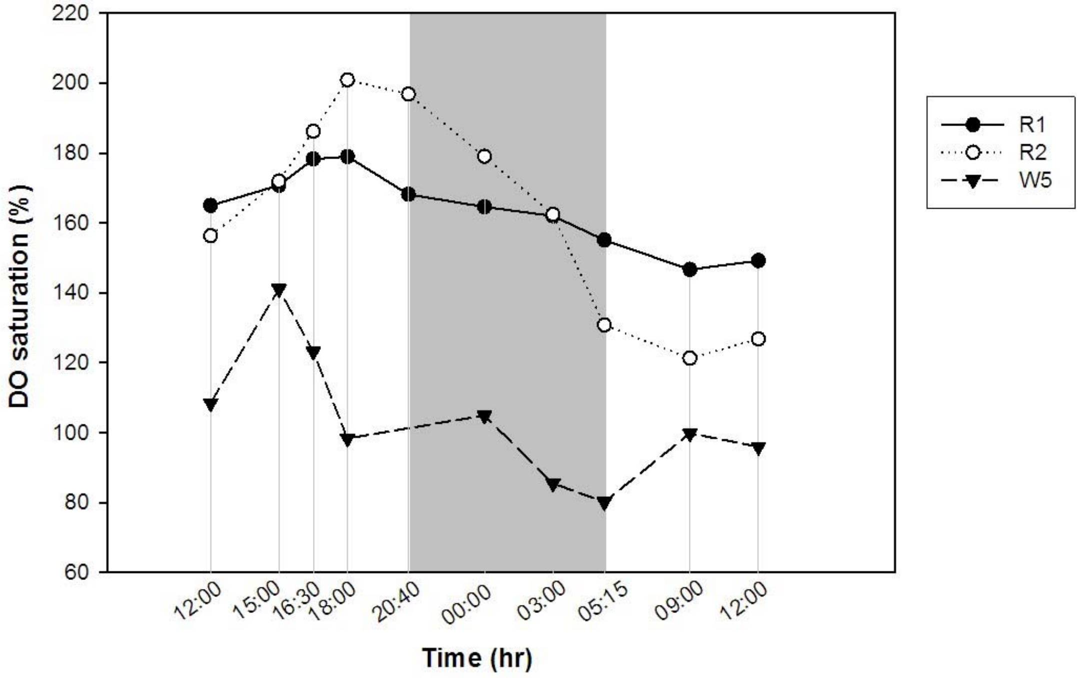

Figure 4.5 Diurnal variations of oxygen Saturation, as percentage, at one marsh site represented in W5 and two river sites represented in the upstream river site (R2) and the downstream river site (R1) in the Grand River. Samples were collected on the 7th and the 8th of July 2008. The gray shaded area represents the night time.

4.3.2 Diel DO Saturation and Oxygen Stable Isotope for the river site (R1)

The % DO showed a clear decrease starting from the sunset on the 7th of July towards sunrise until 9:00 sampling time on the 8th of July. The opposite trend was noticed for the $\delta^{18}O\text{-}O_2$ readings for the same period of time (Fig 4.6). The $\delta^{18}O\text{-}O_2$ data revealed that the photosynthetic influence at 12 noon on the 8th of July (17.7‰) was slighter than the influence at the same time on the 7th of July (15.9‰) (Fig 4.6).The highest DO saturation (179%) was recorded at 18:00 and the lowest (147%) was at 9:00. However, one of the lowest $\delta^{18}O\text{-}O_2$ signatures was noticed at 18:00 and the highest was at 9:00 (Fig 4.6).

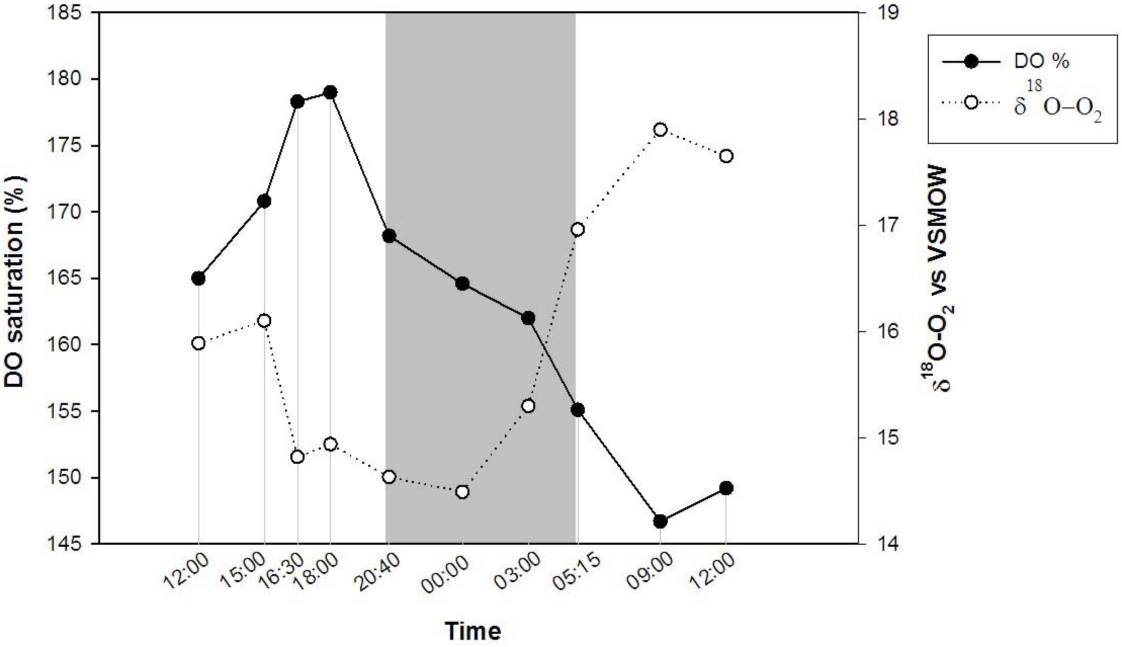

Figure 4.6 This Figure displays the dissolved oxygen saturation and the $\delta^{18}O\text{-}O_2$ diel cycles at the river site (R1) during the 7th and the 8th of July 2008. The gray shaded area represents the night time.

4.3.3 Diel DO Saturation and Oxygen Stable Isotope for the river site (R2)

The highest DO saturation was at 18:00 (DO% 200) and the lowest was at 9:00 (DO% 121) (Fig 4.7). Therefore, DO % remained supersaturated throughout the 24 hour measurement. The opposite was shown for the $\delta^{18}O\text{-}O_2$ signature. The lowest signature (12.8‰), highest photosynthetic influence, was noticed at 18:00 and the highest signature (22.1‰), more towards the atmospheric equilibrium, was noticed at 9:00 (Fig 4.7). Night time data revealed clear decreasing trend in the DO % and another clear increasing trend in the $\delta^{18}O\text{-}O_2$ signature. At the noon of the 7th of July the (DO%; 156) was higher then the (DO%; 127) at the noon of the second day. The opposite case was noticed for the $\delta^{18}O\text{-}O_2$ signature for the time mentioned earlier (Fig 4.7).

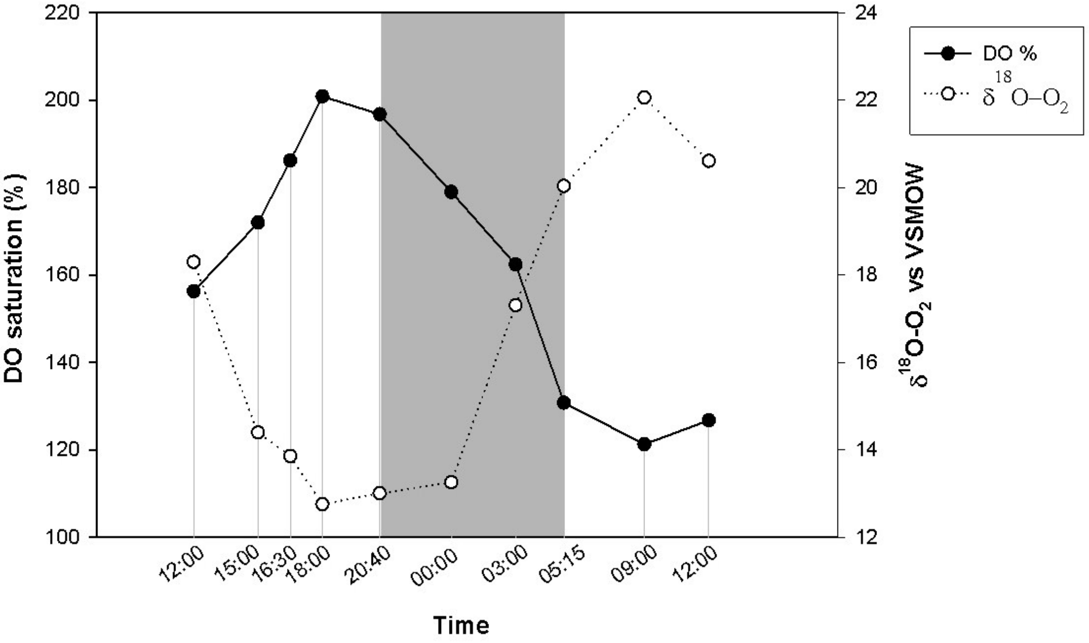

Figure 4.7 This Figure displays the dissolved oxygen saturation and the $\delta^{18}O\text{-}O_2$ diel cycles at the river site (R2) during the 7th and the 8th of July 2008. The gray shaded area represents the night time.

4.3.4 Diel DO Saturation and Oxygen Stable Isotope for the Wetland Site (W5)

The $\delta^{18}O\text{-}O_2$ signature showed a clear increase trend starting from 16:30 (14‰) until 3:00 (19.8‰) after midnight revealing lowest photosynthetic influence after the midnight and during the sunrise. On the other hand, the highest photosynthetic influence (14‰) was noticed during the afternoon at 16:30 (Fig 4.8). The DO % trend though didn't show a clear trend of decrease after the evening time because of the DO % increase at the midnight. The highest DO record in the wetland site was at 15:00 (DO% 141) and the lowest was at 5:15 (DO% 80) (Fig 4.8). The oxygen readings were undersaturated during the night time. The DO recovery was obvious after the sunrise. This recovery was reflected in the decrease of the $\delta^{18}O\text{-}O_2$ signature (Fig 4.8).

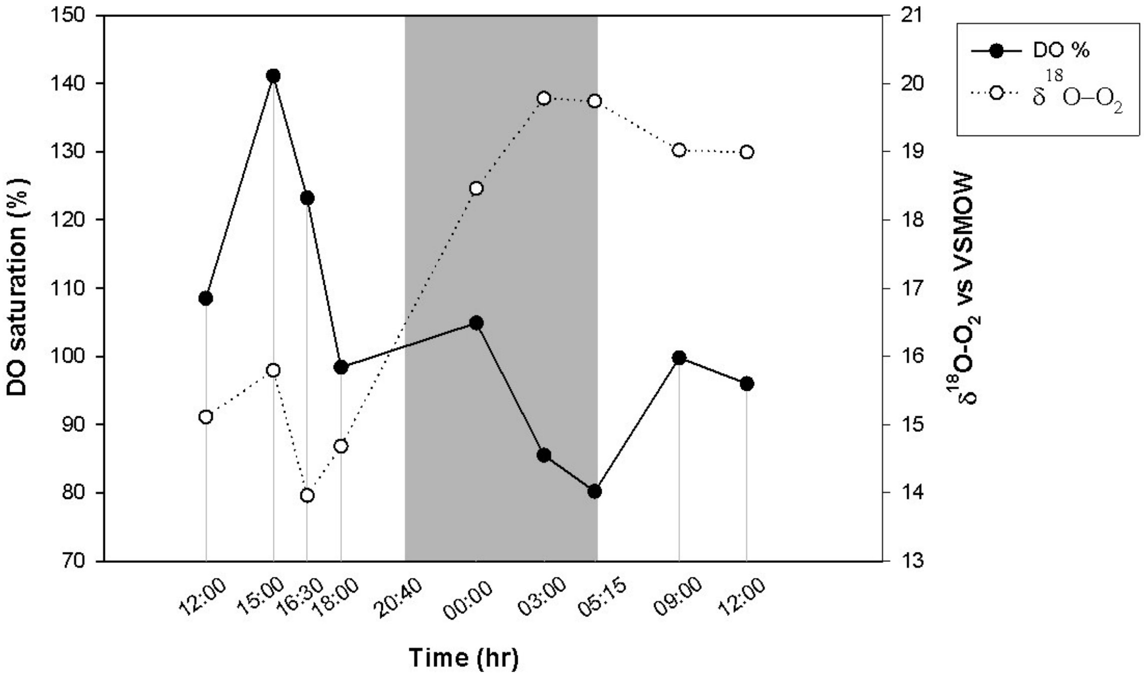

Figure 4.8 This Figure displays the dissolved oxygen saturation and the δ^{18}O-O$_2$ diel cycles at the wetland site (W5) during the 7th and the 8th of July 2008. The gray shaded area represents the night time.

Table.4.1 This table shows the diel data including DO saturation, oxygen isotope values, temperature, conductivity, and 18O-water measurements. Two river sites (R1 and R2) and one wetland site (W5) were sampled. Data were collected on the 7th and 8th of July 2008.

Station	**Diel Data**				
	DO range (%)	**δ18O-DO range (‰)**	**Temperature range (^{0}C)**	**Conductivity range µs/cm^2**	**δ 18O-water (‰)**
River (R1)	146 - 179	14.5 -18	26 - 27.5	645 - 654	-8.97
River (R2)	121 - 200	13 - 21	26 - 28	636 - 680	-8.94
Wetland (W5)	80 - 141	14 - 20	26.5 - 29	663 - 681	-8.73

4.4 Nitrogen

4.4.1 Nitrate

The highest nitrate concentrations occurred at the river sites and the wetland sites closest to the river where values as high as 2.78 mg/L and as low as 0.98 mg/L were recorded (Fig 4.9). Seasonally, NO_3^- concentrations were highest during the spring and progressively were lower in summer and fall.

Next highest values were observed near the inflow from the Maple Creek drain, again with higher values in the spring compared to the summer and fall. The highest NO_3^- value at the inflow was 1.22 mg/L in April 2008, whereas values were non-detectable in August, September, and October of 2007.

The wetlands sites showed differences in the NO_3^- concentrations according to their proximity to the river. Wetland sites closest to the river revealed higher NO_3^- concentrations compared to the wetland sites located farther away from the river. The highest NO_3^- concentration in the wetland was 2.63 mg/L and the lowest was below detection (Fig 4.9). The northern wetland sites (W4 and W3), which are located closest to the Maple Creek inflow drain exhibited values below detection during summer and fall 2007 (Fig 4.9) which coincides when conditions were dry and water levels in the river were low. Most other times, NO_3^- concentrations from the Maple Creek inflow site and at wetland sites close to the inflow point, were higher (Fig 4.9).

Overall, NO_3^- values were highest during the spring across most of the wetland sites and were close to the values detected in the river or at the Maple Creek drain inflow.

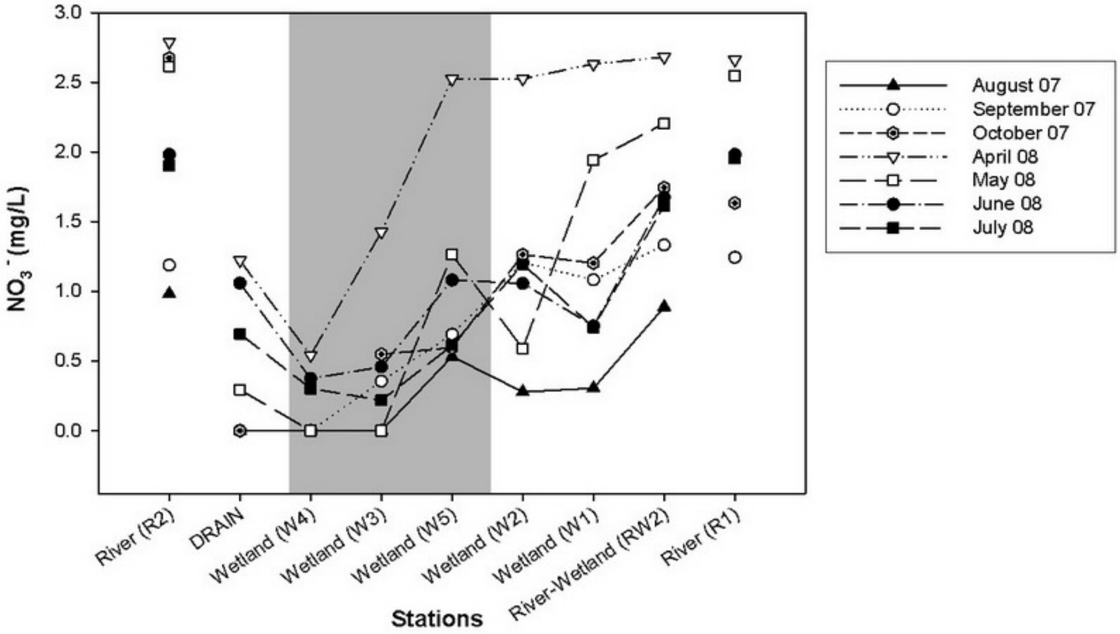

Figure 4.9 Spatial and temporal variations of nitrate, as mg/L, in the Dunnville Marsh and the Grand River. The gray shaded area represents the wetland sites connected to the Maple Creek inflow (Drain site).

4.4.2 Total Nitrogen

TN readings followed similar spatial and temporal patterns as observed for nitrate measurements. High values of 3.2 mg/L were recorded in spring 2008 at the river while the lowest was 1.6 mg/L in summer 2008 (Fig 4.10). In the wetland, the highest value was 3 mg/L in spring 2008 and the lowest was 0.6 mg/L in the summer and fall of 2007 (Fig 4.10).

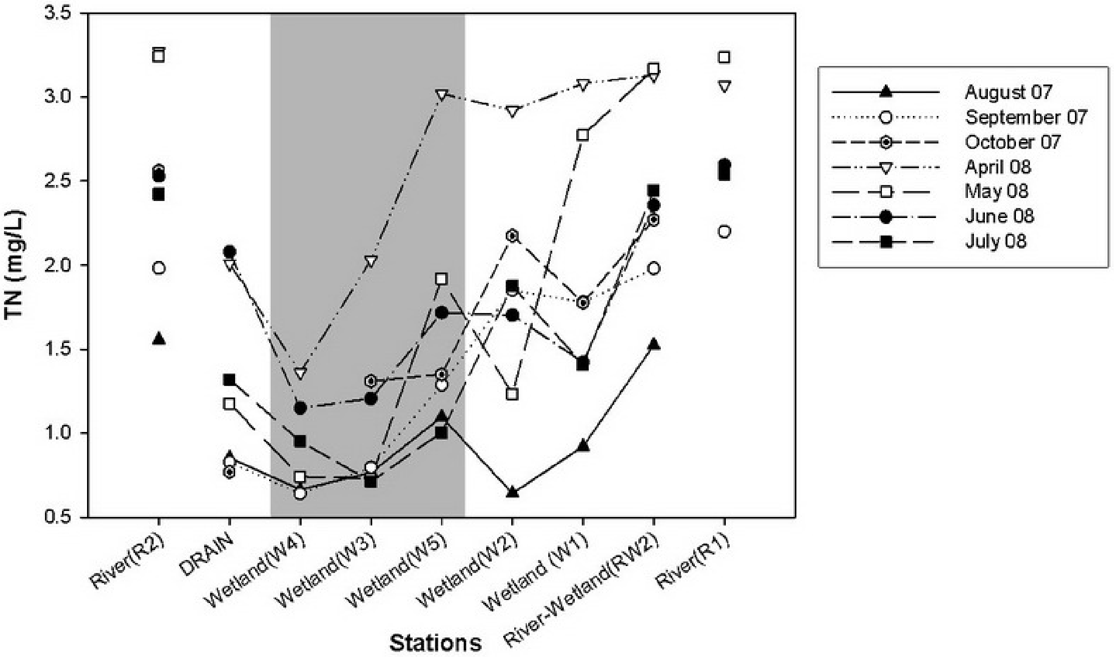

Figure 4.10 Spatial and temporal variations of total nitrogen (TN), as mg/L, in the Dunnville Marsh and the Grand River. The gray shaded area represents the wetland sites connected to the Maple Creek inflow (Drain site).

4.4.3 Ammonium

Ammonium concentrations were very low compared to nitrate concentrations. NH_4^+ concentrations were the same or higher in the river or near the inflow from Maple Creek compared to values from the wetland sites (Fig 4.11). The highest NH_4^+ concentration in the river was 0.212 mg/L in September 2007 and the lowest record was 0.017 in May 2008. NH_4^+ records in September 2007 were relatively higher than other months in both the wetland sites near the river and in the river sites. The highest NH_4^+ concentrations in the river were in September 2007 and April 2008 with values of 0.212 mg/L and 0.096 mg/L, respectively (Fig 4.11).

The site at the inflow from the Maple Creek exhibited higher than or about the same concentrations as wetland and river sites most of the time. The highest recorded

NH_4^+ concentration at the inflow site was 0.230 mg/L in October 2007. September values were lower at the inflow compared to most of the wetland sites and the two river sites. The highest NH_4^+ concentration at the Maple Creek inflow was 0.23mg/L in October 2007 and the lowest record was 0.023 in August 2007 (Fig 4.11).

NH_4^+ concentrations were low or below detection for most times in the wetland. The exception was during September and October when values were high. The highest NH_4^+ concentration in the wetland was 0.213mg/L in October 2007 (Fig 4.11). The fall season (September and October 2007) revealed higher NH_4^+ concentrations compared to the spring and summer. NH_4^+ concentrations were noticeably low in the wetland immediately adjacent to the inflow from Maple Creek.

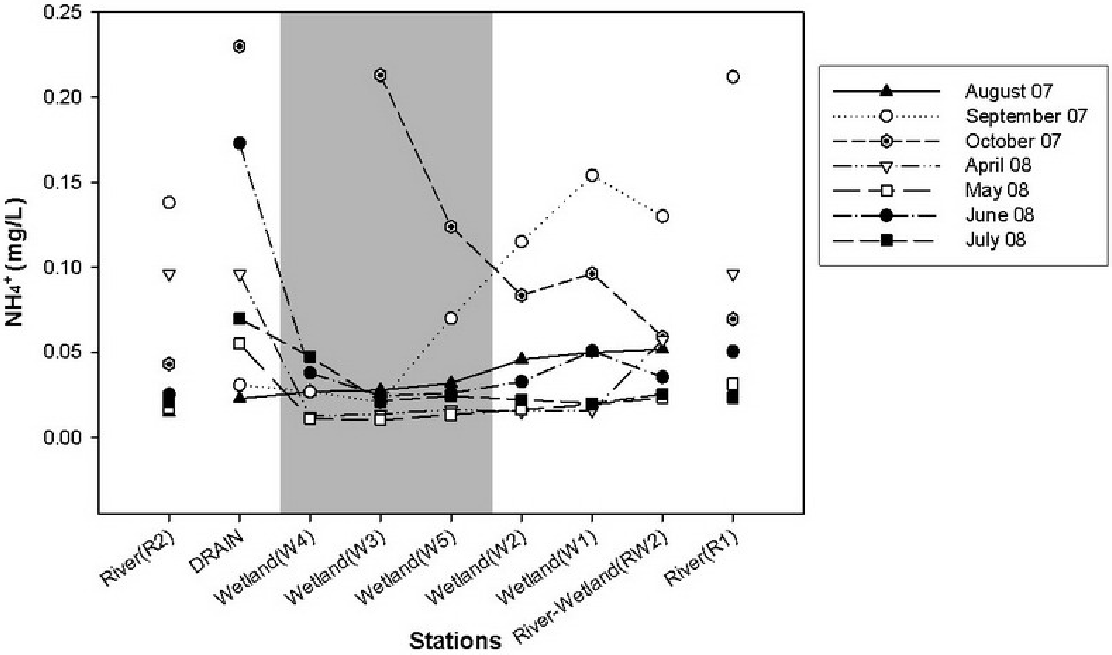

Figure 4.11 Spatial and temporal variations of ammonium, as mg/L, in the Dunnville Marsh and the Grand River. The gray shaded area represents the wetland sites connected to the Maple Creek inflow (Drain site).

4.5 Other Parameters

4.5.1 Dissolved Organic Carbon

DOC concentrations were lowest in the river compared to the wetland sites, especially the wetland sites located farther from the river. In the river, The highest DOC concentration was 8 mg/L in July 2008. The lowest was 4.7mg/L in May 2008 (Fig 4.12). DOC concentrations were about the same in both river sites.

The wetland sites showed higher concentrations than the river sites. Despite the higher DOC concentrations, a gradual decreasing trend is obvious from the sites farther away from the river and decrease closest to the river. Highest DOC concentrations of 13.6 mg/L were observed in April 2008 and the lowest was 5.4 mg/L in October 2007 (Fig 4.12).

The Maple Creek drain site and wetland sites closest to it had higher DOC concentrations than in the rest of the wetland or the river sites, especially in the dry year of 2007. The highest recorded DOC value at the inflow site was 13.71mg/L in September 2007 (Fig 4.12). DOC concentrations were highest during most of the summer, especially on the northern side of the wetland.

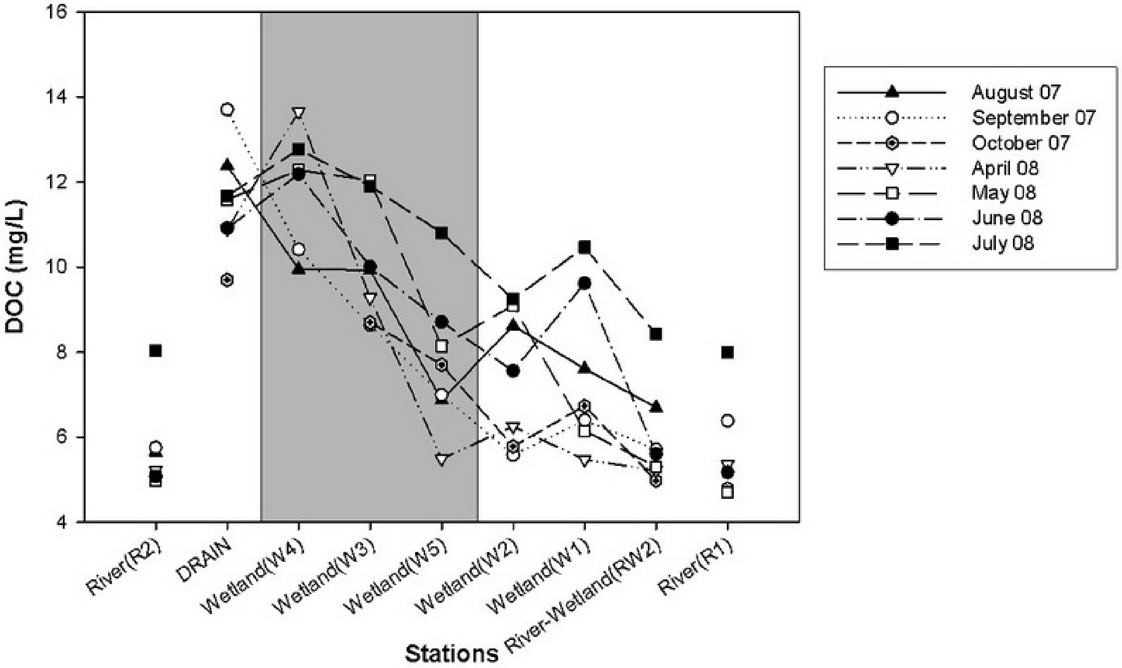

Figure 4.12 Spatial and temporal variations of Dissolved Organic Carbon (DOC) concentrations, as mg/L, in the Dunnville Marsh and the Grand River. The gray shaded area represents the wetland sites connected to the Maple Creek inflow (Drain site).

4.5.2 Sulfate

Sulfate concentrations varied between the wet summer of 2008 and the other months especially the dry summer in August 2007. River values were as high as 38.9 mg/L in October 2007 and as low as 19.2 mg/L in July 2008 (Fig 4.13).

There were not big differences observed across the wetland, with perhaps a slight increase at some sites and a much larger increase at other sites closest to the river particularly during the spring season. The highest value observed in the wetland was 41 mg/L and the lowest was 10.5 mg/L (Fig 4.13). In general, The SO_4^{-2} concentrations in the wetland sites, especially closest to the Maple Creek inflow were lower than the river sites. SO_4^{-2} concentrations tended to be low at the Maple Creek inflow site. Overall, summer months of 2008 had much lower SO_4^{-2} compared to other months (Fig 4.13).

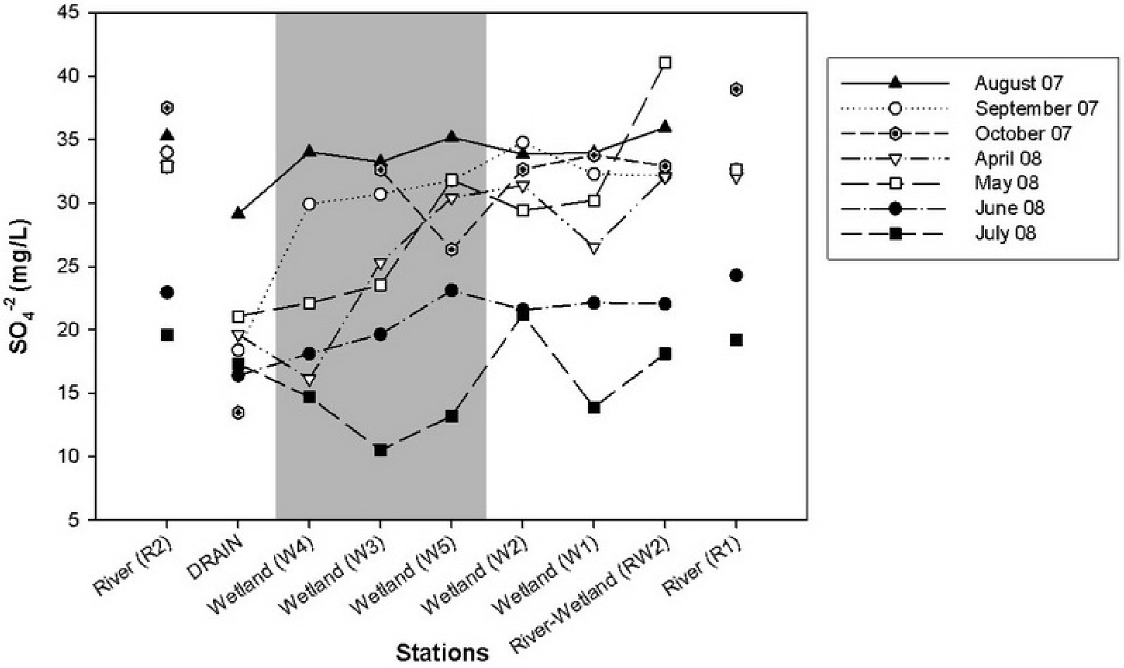

Figure 4.13 Spatial and temporal variations of Sulfate concentrations, as mg/L, in the Dunnville Marsh and the Grand River. The gray shaded area represents the wetland sites connected to the Maple Creek inflow (Drain site).

4.5.3 Temperature

Temperatures showed clear variations in different months but very slight difference between the river sites and the wetland sites. The highest temperatures were recorded during the summer of 2007 and 2008, especially in August 2007 and July 2008. The highest temperature was 26 ^{0}C in August 2007 (Fig 4.14); however, we have to mention that the highest temperature was 29 ^{0}C during the diel work in July 2008 (Table 4.1).

The lowest temperatures were noticed during late fall (October 2007) and early spring (April 2008). The lowest temperature was 7 ^{0}C in October 2007 (Fig 4.14).

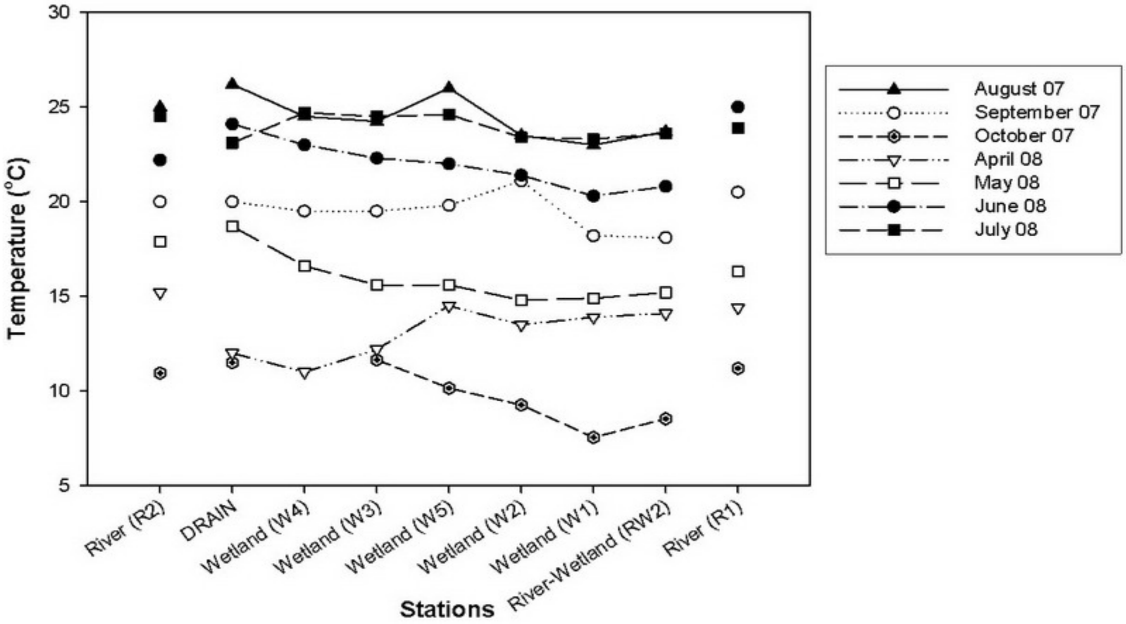

Figure4.14 This figure depict the temperature variations in Dunnville Marsh and the Grand River throughout different months.

4.6 Statistical analysis of different parameters

The statistical analyses were performed on three different treatment groups including river sites group (R), southern wetlands sites group (SW), and northern wetlands sites group (NW).The analysis was applied on three data sets collected at different times (i.e. September 2007, April 2008, and July 2008) (Table 4.2).

The data show there a significant difference in the NW compared to SW and R parts of the Dunnville Marsh: DO and NO3 in September; TN and DOC in September and April; δ^{18}O- water in September and July; and Cl^- in July (Table 4.2).

The NW showed a significant difference from R only while SW did not show a significant difference from both NW and R, in the following parameters: NO_3^-, DOC, and DIC in July; SO_4^{-2} in April; and NH_4^+ in September and April. There were no significant differences for these parameters in the other months (Table 4.2).

Table 4.2 Summary of different parameters measured in the Grand River and Dunnville Marsh. All the parameters were measured in mg/L unit but DO (%),18O-H2O (permil), and Conductivity (µs/cm^2). R represents the Grand River sites (R1 and R2; n=2), SW represents the southern wetland sites (RW2, W1, W2, and W5; n=4), and NW represents the northern wetland sites (W3 and W4; n=2). Means (standard deviations) are shown. For each month, means followed by different letter within columns are significantly different (One Way ANOVA; Turkey's HSD was used for multiple comparison test, *P <0.05* or Dunn's test was performed (April, NH4).

Month	**Location**	**Parameters**				
		DO	**TN**	**NO3**	**NH4**	**DOC**
	R	79.65(10.82)a	2.09(0.16)a	1.21(0.04)a	0.175(0.052)a	6.07(0.45)a
Sept. 2007	**SW**	88.18(10.64)a	1.72(0.30)a	1.08(0.28)a	0.117(0.035)ab	6.17(0.66)a
	NW	123.90(14.28)b	0.72(0.11)b	0.18(0.25)b	0.024(0.004)b	9.52(1.26)b
	R	102.00(10.18)a***	3.17(0.14)a	2.72(0.09)a*	0.096(0.000)a	5.29(0.09)a
Apr. 2008	**SW**	97.39(3.76)a	3.04(0.09)a	2.59(0.08)a	0.026(0.021)ab	5.61(0.45)a
	NW	97.95(9.97)a	1.70(0.47)b	0.98(0.63)a	0.013(0.001)b	11.47(3.09)b
	R	109.20(8.63)a***	2.48(0.08)a***	1.93(0.04)a	0.02(0.002)a*	8.02(0.03)a
Jul. 2008	**SW**	86.58(20.43)a	1.68(0.62)a	1.04(0.46)ab	0.023(0.002)a	9.74(1.10)ab
	NW	75.65(15.20)a	0.83(0.17)a	0.26(0.06)b	0.034(0.019)a	12.34(0.61)b

* Non parametric ANOVA (Kruskal-Wallis, One Way Analysis of Variance on Ranks).

*** Multiple comparisons test was not performed.

Table 4.2 extended

Month	Location	Parameters				
		18O-H2O	SO4	Cl	DIC	Conductivity
	R	9.00(0.21)a	33.30(0.96)a***	87.92(1.41)a***	33.25(0.49)a***	772(5)a***
Sept. 2007	SW	8.63(0.35)a	32.73(1.37)a	88.15(2.35)a	33.48(1.44)a	613(131)a
	NW	6.86(0.69)b	30.29(0.54)a	87.87(0.06)a	32.80(2.69)a	604(199)a
	R	10.33(0.05)a*	32.48(0.59)a	68.35(0.65)a***	44.40(0.57)a	820(11)a*
Apr. 2008	SW	10.20(0.11)a	30.09(2.47)ab	62.18(4.35)a	43.95(0.69)a	811(1)a
	NW	9.38(0.37)a	20.70(6.50)b	52.53(7.65)a	50.35(3.46)a	772(16)a
	R	8.96(0.02)a	19.40(0.28)a***	46.90(0.99)a	42.90(1.27)a	595(2)a*
Jul. 2008	SW	8.72(0.10)a	16.60(3.75)a	51.13(7.18)a	48.93(3.67)ab	615(30)a
	NW	7.56(0.01)b	12.60(2.97)a	89.55(22.98)b	59.10(5.66)b	784(96)a

* Non parametric ANOVA (Kruskal-Wallis, One Way Analysis of Variance on Ranks).

*** Multiple comparisons test was not performed.

Chapter 5
Discussion

Dissolved oxygen concentrations

Little work has been done on spatial and temporal dynamics of DO in temperate wetlands in general, and on wetlands associated with large rivers such as the Dunnville Marsh, specifically. Most of the DO work has been done on closed basin marshes. In one such study, Rose and Crumpton (1996) found low DO content in emergent stands compared to higher values in the open water; in August DO was 0.9 mg/L in a *Typha* spp. stand and as high as 11.4 mg/L 2 m away in open water. They found obvious patterns between vegetation and dissolved oxygen: (1) an emergent macrophyte zone (live emergent plant and dead standing plants and litter in the water column) with low oxygen concentration, (2) a transition zone of sparse emergent macrophytes with slightly higher DO values, and (3) an open water zone with few plant structure and higher DO values. The presence of macrophytes and litter substantially affected the DO (Rose and Crumpton 2006).

As part of a study to understand relationships between DO and phosphorous, McCormick and Laing (2003) studied some sites within the Florida Everglades. More phosphorous enriched sites had much lower DO. The higher the P the lower was the DO; mean DO declined from between 1.81 and 7.52 mg/L at reference stations to between 0.04 and 3.18 mg/L in P-enriched areas.

A survey of 14 wetlands located along 35 km of the southern Grand River between Cayuga and Dunnville were studied and DO concentrations were measured. Mid-summer measurements taken during the day averaged between 5.5-9.5 mg/ L. (Gilbert and Ryan 2007). Two other wetland surveys conducted in August 1998 and July 2001 included the Dunnville Marsh. DO concentrations of around 7.4 mg/L were recorded (Chow-Frazer, 2002). Similar readings were observed in our study during the summer of 2008, except for one reading in site (W1) close to the river which demonstrated low DO. Lowest DO concentrations were recorded in parts of Dunnville Marsh closest to the river. In contrast, Gilbert and Ryan (2007) found that the Highest DO concentrations were recorded in wetlands or parts of the wetlands closest to the Grand River. The lowest DO range observed in the wetlands sites in summer 2008 (5.5- 9.1 mg/L) is close to the DO range (5.5- 9.5 mg/L) of values listed in the Canadian Water quality guidelines for the Protection of Aquatic Life (Canadian Council of Ministers of the Environment, 2003), which are defined as being necessary for the survival of 100% of aquatic species, such as fish. While fish can add oxygen into the water through mechanical aeration, which may create waves and disturbances and so increasing DO concentration, fish can increase the biological oxygen demand by releasing dung in the water and resuspending the dead organic matter on the bottom (Mnaya et al. 2006).

Our study revealed obvious spatial and temporal variability in DO in the river and the wetlands. DO in the Grand River showed undersaturated levels in the fall of 2007 which was in dramatic contrast to supersaturated or just below saturation values in spring and summer of 2008. Slow flowing rivers are more prone to deoxygenation (Kalff 2002) which appears to be the case for the Grand River in the fall 2007 as river levels were quite low at the time. The opposite was the case for much higher water levels and flow rates during the spring and summer of 2008 which would enhance DO concentrations in the river. Moreover, the stable isotope of the oxygen revealed more photosynthetic activities took place in summer of 2008 compared to fall of 2007, and this probably was the reason behind the increase of DO during summer 2008. High rates of community metabolism were associated with higher temperatures levels (McCormic et al. 1997).

The DO saturation at the more upstream river site (R2) was consistently slightly greater than at the downstream river site (R1). Though this difference may not be highly significant, it is possible that the time of field sampling may have contributed, at least in part, to the difference. The upstream river site was always sampled in the afternoon while the downstream site was sampled during the morning. Smith and Able (2003) reported lowest DO concentrations in the early morning and highest concentrations in the afternoon.

Greatest DO variability appears to have occurred during those months that represent the main growing season for the aquatic macrophytes in the wetlands, that is those months with living dense macrophytes (June through September). DO saturations were less variable during the rest of the year when macrophytes were either not growing or growing very little. It is well known that emergent macrophytes contribute to overall marsh primary productivity, but contribute negligible O2 to the water column (McCormick at al. 1997). In contrast, as the Rose and Crumpton (1996) study showed, marsh vegetation can play an important role in DO dynamics, both directly and indirectly. Therefore, the DO variations were most apparent during those months with dense macrophyte growth in the Dunnville Marsh.

Vegetation may have contributed to seasonal differences in Dunnville Marsh. Vegetation influences the supply of oxygen to the water in several ways. Emergent-dominated communities would likely have high rates of O_2 demand because of the tremendous annual contribution of the emergent macrophytes litter and detritus. Litter densities in the emergent vegetation zone can be an order or two greater than in open water communities, and therefore would consume oxygen through decomposition, and contribute to overall low DO concentrations (Rose and Crumpton 1996; Fukuhara et al. 2007). Organic matter from the plants, fallen leaves, dead roots and underground stems, might be supplied to heterotrophic bacteria thereby causing a decrease of oxygen in water and sediment by their respiration. Furthermore, emergent vegetation blocks the wind, and shade out algae, presumably lowering re-aeration (Kadlec 2008). However, vegetation can add oxygen to the water by providing a substratum for periphytic algae which would respire and release oxygen to the water (Rose and Crumpton 1996). Submerged vegetation may supply oxygen through photosynthesis (Kalff 2002). Also, a certain amount of oxygen may leak through the root rhizosphere into the sediments and water column. All these factors might attribute to the seasonal differences in oxygen concentrations throughout the Dunnville Marsh. The observed seasonality differences in DO concentration that was found to be the case in Dunnville marsh, agrees with a similar seasonal patterns found in a wetland in central Florida (Hampson 1998).

We should note that DO concentrations during the spring were supersaturated or just below saturation throughout the wetlands sites. It would seem that the oxygen-rich water from the Grand River would have entered into and inundated large parts of the Dunnville marsh. Thus, the high DO water in the marsh represents river water and inundation which would make sense during the high water period of the spring.

Dunnville Marsh exhibited spatial DO variability, especially during fall 2007 and Summer 2008. The southern part of the Marsh, close to the river, revealed low DO concentrations at site W1 compared to the other sites in the southern part. The specific location of the site in relation to the Grand River and the surrounding vegetation may have played a role in decreasing DO concentrations. Site W1 is located on a bend on the edge of a stream beside Maple Creek as it flows through Dunnville Marsh. It is possible the surrounding *Typha* limited any opportunity to re-aerate the waters (Kadlec 2008). It is more exposed to higher winds which might assist in transporting dead and degraded organic matter to this part of the marsh that might settle in and around the bend that would, in turn, contribute to low DO concentrations.

We should note that the DOC concentrations during the summer of 2008were also high at this site compared to the other sites on the southern side of the Dunnville Marsh. This is further evidence that high DOC also contributes to low DO saturation (Hampson 1989; Hamilton et al. 1997). High organic loads may increase oxygen consumption by increasing the metabolic activities of microbes leading to increasing the oxygen demand (Perna and Burrows 2005). All of these factors could account for the low DO saturation at W1. Some of the low DO saturation values at W1 agreed with oxygen stable isotope data revealing less photosynthetic activities and a tendency towards atmospheric equilibrium, i.e. more enriched in heavy isotopes because of higher respiration activities.

Despite the low DO concentrations at the most of the southern wetland sites, an increase trend of DO was noticed in this part of the wetland, especially during the summer. Relatively low DO at site W1 followed by a slight increase at W2 and an increase in saturation or just below saturation at W5 (320m from the Grand River). This increase might be due to the time of day they were sampled in the field. W5 is situated at the edge of a wide part of Maple Creek with much open area, which helps to aerate the water and increase the DO, while W2 is located on the edge of a narrow channel, and W1 located in a bend of a another stream. The *Typha* stands would act as a physical obstruction to wind decreasing re-aeration of the water. A decreasing trend in DO saturation on the north side of the wetland (W3 and W4) can be due to an influence from the inflow from Maple Creek. In the drainage channel that immediately feed into the inflow point at Maple Creek, dense macrophyte growth could be responsible for blocking the penetration of light and oxygen to the water (Perna and Burrows 2005). Low DO concentrations at the inflow were typical.

Diurnal variations in DO

Wetlands exhibit not only seasonal but also a diel pattern. Well-vegetated wetlands show pronounced diurnal changes in DO concentrations (Kalff 2002). Typically, wetland water is near-saturation for oxygen during the photosynthetic period and often approaches values of around 20% saturation during the night (Reddy and DeLaune 2008). Few studies have been conducted on marshes regarding diel DO monitoring. Those that have been done, were on closed basin marshes. Bursey, and Guber (1989) studied the diurnal variation in the physico-chemical conditions within a marsh pond at Wallops in Virginia, US. The lowest concentration of DO occurred at 7:00 h, highest concentration was at 17:00 h. Another diurnal DO study was conducted in a *Spartina alterniflora* marsh in New Jersey by Smith and Able (2003). The DO peaked at approximately 16:00 h, and reached a minimum in early morning around 05:00 h. The greatest variation occurred in mid-July, when DO ranged from over 20 mg/L at midday to 0 mg/L in the early morning. Coastal wetlands at Old Woman Creek Wetland, a coastal marsh on the south shore of Lake Erie in Ohio were studied by Mitch and Reeder (1989) who reported diurnal DO patterns. The July data showed dramatic changes over 24 hrs: readings ranged from 2 mg/L at 6:00 h to peaks of 12-15 mg/L at dusk. Water temperatures were around 24 to 29°C. In contrast, the DO data from October showed less dramatic changes; DO readings ranged from 6 to 10 mg/L with water temperature between 6 to 14°C. Dissolved oxygen during July was clearly under saturated at dawn, while it remained much closer to saturation during the October readings.

Most of these studies showed that the greatest DO range was observed in July. Our diel study was also conducted in July of 2008 at three sites, two in the river (R1 and R2) and one in the wetland (W5). The DO, in the wetland site (W5), peaked (10.8 mg/L), at approximately 15:00 h, and reached a minimum during early morning (6.4 mg/L), at 05:30 h. The water temperatures were around 28 to 29 °C. Our data show a similar pattern to that found in the literature. Furthermore, the diel DO trends in Dunnville Marsh agreed with other studies regarding supersaturation peaks during the day time and subsaturation levels during the night. These other diurnal studies showed that the greatest variations occurred during the mid of the summer while Dunnville Marsh revealed a smaller range of variation in DO at the same time. These differences in the diurnal DO variations in our study compared to others can be attributed to weather, longer summer day, higher trophic status, and type of the marsh (open or closed) . In the case of the Dunnville Marsh, the river influence on site W5 can be a reason for sustaining relative higher minimum DO saturation in the marsh, since the DO values in the river were higher than the marsh. Overall, the favorable comparison of diel patterns of DO concentration between our study site and other studies reported in the literature suggest that oxygen concentrations are influenced more by ecological processes in the marsh rather than factors, such as weather, external to the marsh. Respiration and photosynthesis associated with biota in the marsh are responsible for controlling the observed diurnal patterns in oxygen concentrations (Bursey, and Guber 1989).

The upstream river site (R2) had a large diel in both O2 saturation and $\delta^{18}O_{DO}$. The mean O2 saturation exceeded 100% probably because primary productivity was stronger than respiration but the $\delta^{18}O_{DO}$ was consistently below atmospheric equilibrium. This might be because of the high production rates adding O2.

The downstream river site (R1), on the other hand, revealed smaller magnitude of the diel O2 saturation and $\delta^{18}O_{DO}$ compared to the upstream river site (R2). Hampson (1989) mentioned that the relatively small range of diel variation indicates that photosynthesis generally is not a major controlling factor for DO concentrations. The smaller magnitude of the diel curve at the downstream site (R1) can be attributed to the closer location of the site to Lake Erie (more open area) that to increases in water turbulence; hence, the gas exchange rate (G). The smaller magnitude in the diel O2 saturation and $\delta^{18}O_{DO}$ does not mean necessarily that primary production and respiration at R1 (smaller diel curve) is less than R2 (larger diel curves) because G can act primarily to dampen the magnitude of the diel O2 saturation and $\delta^{18}O_{DO}$ swings driven by primary production and respiration (Venkiteswaran et al. 2008). The relative magnitude of primary production and respiration cannot be immediately assessed by simply comparing diel curves. O2 diel curves (and $\delta^{18}O_{DO}$ curves) exhibit the balance between P, R, and G.

Venkiteswaran et al. (2007) study showed that the South Saskatchewan River has much higher primary production and respiration rates than either the slough wetland or reservoir. The magnitude of the diel range, however, is less than the slough due to the much higher G (Venkiteswaran et al. 2007).

Despite the incomplete diurnal data that we have, we can assume that the river sites showed an autotrophic state, in July 2008, based on the diel curves. If this was the case, then our assumption does not agree the River Continum Concept (RCC) that says the highest order streams has an increased turbidity which reduces primary productivity; hence, the system is heterotrophic (Mitsch and Gosselink 2007). Descy ansd Gosselain's (1994) study on the Muse River in Belgium, showed that in large lowland rivers, primary production (P) may exceed community respiration (R), *i.e.* P:R> 1, whereas they are assumed to be heterotrophic (P:R< 1) in the River Continuum concept. Our interpretation from our study agrees with the latter study.

In the three sites (R1, R2, and W5) the $\delta^{18}O_{DO}$ signature showed that there was an increase in the photosynthetic activities during the day time and a decrease during the night. Following sunrise, the addition of O2 with low $\delta^{18}O_{DO}$ values from photosynthetic activities decreases the $\delta^{18}O_{DO}$ value in the water column. Following noon, photosynthetic activities decrease and respiration causes an increase in the $\delta^{18}O_{DO}$ (Venkiteswaran et al. 2008). This was the case for the two river sites and the wetland site during the day time on the 7th of July and the night of the 8th .July. However, the morning and the noon samples on the 8th showed lower photosynthetic activities; hence, lower DO saturation than the 7th. This might be due to much more hazy and overcast weather on the 8th compared to the clear weather on the 7th that affect the photosynthetic activities. The rate at which aquatic photosynthetic O2 is produced is inherently linked to incident photosynthetically active radiation (PAR). PAR increases and decreases predictably during the day (barring clouds) but in the water column can be affected by other factors (e.g. turbidity change, and variable water velocity and depth). In general, aquatic primary production causes daytime dissolved O2 concentrations to increase from sunrise to shortly after solar noon and decrease thereafter (Venkiteswaran et al. 2007).

Using Oxygen isotopes as a tool for monitoring oxygen dynamics

The oxygen isotope values of DO varied from +20.3 to + 26.5 permil for the Grand River and from + 15.3 to + 25.3 permil for the Dunnville Marsh. Since the gas exchange set the oxygen isotope value of DO at +24.2 permil (Quay et al. 1995). The photosynthesis took place in the Grand River at times of low oxygen isotope values, with a minimum in spring and summer 2008. Respiration took place at times of high oxygen isotope values, with a maximum in fall 2007. Based on our assumption derived from the diel data that the river is autotrophic in the summer and it might be affected by the gas exchange more than the wetland. Therefore, the regular day time sampling of the River showed lower $\delta^{18}O_{DO}$ signature in the summer 2008 compared to the fall 2007. Also, these lower oxygen stable isotopes in the river were more shifted to the atmospheric equilibrium point compared to the wetland. This assumption refer to the less affect of the gas exchange in the wetland because of the vegetation canopy which is in turn reduce the re-aeration; consequently, the $\delta^{18}O_{DO}$ signatures of the wetland showed lower values than the river. Moreover, the biological activities (photosynthesis during the day time) in the wetland might contribute to these lower values compared to the river.

Dunnville Marsh showed more variable $\delta^{18}O_{DO}$ values during the fall of 2007. This variability can be attributed to higher photosynthetic activities in September 2007 (low oxygen isotope values) compared to the higher $\delta^{18}O_{DO}$ values in October 2007. The high photosynthetic activities of some of the wetlands sites in September 2007 can be attributed to sampling about one meter from the vegetation stand. The low water levels prevented sampling in the vegetation itself; hence, the negative impact of the vegetation will be reduced such as less light exposure. If the surface wetland sediments receive light at low intensities, photosynthesis of epipelic algal communities growing on the sediments and particulate organic detritus can quickly produce high, often markedly supersaturated water (Reddy and Delaune 2008) which is reflected in low oxygen isotope values of September 2007. On the other hand, October $\delta^{18}O_{DO}$ readings in the wetland revealed values around the atmospheric equilibrium. This can be explained due to the senescence of the emergent plant population (*Typha* spp.) that may result in more organic matter for aquatic decomposition (more respiration; higher $\delta^{18}O_{DO}$ values) and it might increases the rate of air-water gas exchange by the reduction of their dense canopies ($\delta^{18}O_{DO}$ values near the atmospheric equilibrium).

The wetlands sites, especially those on the north side, revealed a decreasing trend of $\delta^{18}O_{DO}$ signature (more photosynthetic activities) which suppose to reflect an increase in DO levels. Although, a decrease of DO levels were noticed in our study while low $\delta^{18}O_{DO}$ signatures were recorded.

Different water samples had similar oxygen levels but significantly different oxygen stable isotope values. Quay et al. (1995) found that this may be due to other factors such as tributary input, upriver conditions, depth integrated respiration, O2 gas exchange, and photosynthesis. Any one or combination of these factors could explain the disagreement between DO and oxygen stable isotopes data observed at some of our wetlands sites.

There is a relative importance of sediment versus water column respiration (Ostrum et al. 2005). Brandes and Devol (1997) found that isotopic changes in overlying water of $\delta^{18}O_{DO}$ were small, with an average apparent sediment respiration fractionation-factor of 3. This fractionation-factor is much smaller than that measured in either the open ocean or in the laboratory. The respiration in sediment has unusual isotopic characteristics that no fractionation is involved. This is because sediments contain high numbers of bacteria that easily consume all oxygen from the bottom waters. These bacteria use any and all oxygen that arrives to the sediments, regardless of isotope content (Fry 2006). This can be one of the factors contributed to the disagreement between DO and oxygen stable isotopes data because of the relative importance between the sediment and the water column respiration, since the sampled water was collected from a shallow marsh near the sediment, or the ground water influence might play a role in this case.

Nitrogen influences on the oxygen dynamics

Wetlands serve as sinks for nitrogen, especially when human activities such as from agriculture and sewage, can be the primary sources. Significant amounts of nitrogen are transported, usually as nitrate, in rivers and streams, leading to eutrophication and episodic and persistent hypoxia (Mitsch and Gosselink 2007). Wetlands along the riparian fringes and edges of rivers have been shown to be effective for the removal of nonpoint-sources of nitrogen and other organic contaminants (Fukuhara at al. 2007; Gilliam 1994; Mitsch and Gosselink 2007). Ecological impacts associated with eutrophication result directly from reductions in the concentrations of water-column DO, which is caused by excessive biomass production and decomposition (McCormic and Laing 2003). Non photosynthetic organisms use nutrients as a source of energy for their metabolism, and during the process consume oxygen (Reddy and Delaune 2008). In this study, the nitrogen input from the agricultural areas was relatively low and so probably had little influence on the DO in and around the Dunnville Marsh.

There are two points at which nitrogen can enter Dunnville Marsh. One is along the northern side immediately adjacent to agricultural fields and pastureland. The other source is along the southern edge adjacent to the Grand River which may also contain nitrogen from sources farther upstream. Most of the wetlands study sites in my study, varying with the season, showed influences from nitrogen from these two sources and subsequent decreases, presumably due to uptake.

The nitrogen concentrations immediately at the inflow at the drain into the wetland from Maple Creek were used to determine any nitrogen inputs so as to track it in the Dunnville marsh. If present, it would be possible to track the attenuation through the wetland through site W4 (1000m from the drain), W3 (1400m), and W5 (1800m). There was low nitrogen concentration during the dry year of 2007 (August, September, and October 2007). TN and NO_3^- concentrations records were zero or below detection. Tile drainage systems flow into the drainage channels at Maple Creek which can result in an increased loading of mobile agrichemicals such as NO_3^- (Randall and Iragavarapu 1995). The north-east side of Dunnville Marsh showed low nitrogen concentrations of different nitrogen loads during the dry year of 2007 at a time when water flow was slow. This probably increased the residence time of NO_3^- in the water where denitrification may have occurred (Kellman 2005). The drainage channel was overgrown with macrophytes, likely took up any nitrogen by plant assimilation before reaching the inflow point at Maple Creek and Dunnville marsh. Additionally, macrophytes can decrease DO levels by preventing the light and the air to enter the water column in the drain channel (Perna and Burrows 2005). The assumed low DO in the drain channel will enhance the denitrification process which converts NO_3^- to nitrogen gas.

There are many potential effects of vegetation on nitrogen processing and removal in wetlands. Submersed litter and stems provide surface on which microbes reside. These include nitrifiers and denitrifiers. Furthermore, the carbon content of plant litter supplies the energy needed for heterotrophic denitrifies (Kadlec 2008). These factors might account for some of the low nitrogen during the summer months in most of the wetlands sites compared to slightly higher values at the inflow. In general, the inflow site and this side of the Dunnville marsh had high DOC concentrations which might contribute to NO_3^- removal by adding a carbon source to fuel the conventional heterotrophic denitrification (Fukuhara et al. 2007; Kadlec 2008; Tomaszek et al. 1997).

The presence of DO in the surface water at the inflow from Maple Creek and the wetlands sites immediately beside it might not necessarily affect the denitrification processes. Rysgaard et al. (1994) studied oxygen regulation of nitrification and denitrification and found that increasing O2 concentration will decrease denitrification derived from NO_3^-, and stimulate denitrification of NO_3^- produced endogenously by nitrification. Denitrification activities have been observed in wetland systems that have measurable dissolved oxygen concentrations in their surface waters. In such a situation it has been hypothesized that denitrification occurred in the microscopic anoxic zone of bacterial biofilm (Sirivedhin and Gray 2006). This might explain the reason behind lower NO_3^- concentrations while DO increase in some of the sites in the Dunnville marsh. Furthermore, plant uptake can play an important role in the wetlands in decreasing nitrogen input (Gilliam 1994). Thus, the abundance of wetland plants (i.e. the *Typha*) would have immediately taken up any nitrogen that might be available. Moreover, nitrate removal can be conducted by dilution (Cey et al. 1999)

The dry summer month (August 2007) revealed low NO_3^-concentrations compared to the other wetter summer months of 2008. This can be attributed to the greater removal of NO_3^- recorded in the shallow water wetlands (Sirivedhim and Gray 2006).

The relatively poor nitrate removal performance in April 2008 was partially caused by higher discharge rate that resulted in less time for the water to be retained in the wetland. In addition, seasonal temperature effects on denitrification rates as well as nitrate immobilization by marsh vegetation and soil microorganisms also contributed to the observed difference in nitrate removal rates (Yu et al. 2006). This might explain the differences between April (non growing vegetation month) and May 2008 (growing vegetation month) in Dunnville Marsh regarding NO_3^- availability. The high nitrogen concentration in April agree with a study by Lopes and Silva (2006) who showed that there was an increase of the NO3 and NH_4^+ concentrations in spring which is not unusual in spring.

The wetland sites W4 and W3, 1000m and 1400m respectively far from the inflow at Maple Creek revealed a decrease in nitrogen forms through all the sampling dates except for October 2007 that showed an increase of nitrogen. The cold weather might have affected nitrogen removal in October 2007. The denitrifying bacteria in wetland sediment tends to be more abundant in the spring/summer compared to the fall/ winter (Sirivedhim and Gray 2006) and this will lead to decreased NO_3^- removal. NO_3^- decreased in these wetland sites for the rest of the year. Most researchers agree that the primary mechanisms of NO_3^- removal in wetlands are denitrification and plant uptake (Gilliam 1994). Observations made at Dunnville marsh agree with this.

Site W5 (1800m from the inflow) showed a small increase in the NO_3^- and TN concentration compared to the sites on the north side (W3 and W4). The nature of W5 site was similar to W3 but W5 showed higher nitrogen concentrations. The assumption is that the relative short distance between the Grand River and the W5 site (ie. 320 m) and the influence by the main river led to an increase in the nitrogen concentrations at site W5 since the Grand River had higher nitrogen concentrations compared to Dunnville Marsh.

NH_4^+ concentrations in wetland sites revealed low concentrations which are related to the low ammonium input from the agriculture, except for a slight increase of the NH_4^+ input in October of 2007 and June 2008. Ammonification might be the reason behind the increase of the NH_4^+ input. Ammonification of organic nitrogen results in the release of ammonium into the soil solution (Reddy and DeLaune 2008) that refers to the conversion of organically bound nitrogen to ammonium nitrogen as the organic matter being decomposed and degraded (Mitsch and Gosselink 2007). There was a clear difference in the way the wetland affected NH_4^+ consumption. June data showed an obvious decrease of NH_4^+ through the wetlands sites while the NH_4^+ concentrations in October exhibited a relative high concentration in the wetlands sites. This can be explained by the lack of the living macrophytes in October 2007 where NH_4^+ would have been taken up.

The Grand River and the Dunnville Marsh interaction

The Grand River showed an effect on Dunnville Marsh. Isotope data of $\delta^{18}O$-water showed how far waters from the Grand River can inundate Dunnville Marsh along its edges. The water along some of the northern part of Dunnville Marsh had distinct $\delta^{18}O$- water signatures compared to the southern part and the Grand River. The $\delta^{18}O$-water signature ranged from -8.85 to -10.37 ‰ for the river, from –6.37 to -10.32 ‰ for the wetlands, and from -5.51 to -9.48 ‰ for water at the inflow into Maple Creek . The higher values from the wetlands and the Drain site compared to the river is probably due to the significant amount of evaporation compared to the water being evaporated, which lead to a measurable isotopic enrichment in the wetland water (Clark and Aravena 2005).

Sufficient change in the $\delta^{18}O$-water of water bodies such as streams, rivers, and lakes needs large precipitation, reservoir discharge events, or evaporation over a few days (long dry season for example); otherwise, it will be insufficient to have a change in the isotopic signature (Clark and Fritz 1997). A strong enrichment of the $\delta^{18}O$- water in September took place after the long dry summer and fall in 2007 that enhanced evaporation in the northern sites of the Dunnville Marsh along Maple Creek towards the Drain site. The shallow stagnant water, especially near the inflow site might enhanced the evaporation processes; thus, the enrichment of $\delta^{18}O$- water. Evaporation is a kinetic fractionation process that favors the light isotopes. The heavy isotopes become concentrated in the water. If the amount of evaporation is significant compared to the volume of water being evaporated, an isotopic enrichment can be measured in the water (Clark and Aravena 2005). The less evaporation in the northern sites during July 2008 compared to September 2007 is reflected in less enrichment. Bouchard (2007) conducted a study on a coastal freshwater wetland on Lake Erie and found that areas farther away from the outlet had water with heavier isotopic signatures, indicating that they were affected by evaporative loss and were poorly replenished by lake water.

Locally, the $\delta^{18}O$- water value of a water body may be temporally altered by evaporation, storm events, and snowmelt runoff (Venkiteswarn et al. 2008). Snowmelt runoff can be one reason for depleted $\delta^{18}O$- water values in the spring. This agrees with the study of Wang and Veizer (2000) that revealed significantly depleted $\delta^{18}O$- water values in the spring, coincident with the snowmelt season.

The Grand River water may have intruded into the Dunnville Marsh up to site W5 (about less than one third of the marsh) during September 2007, the very dry fall, and July 2008. The $\delta^{18}O$- water values during these two months, revealed no significant differences between the river sites and the southern wetlands sites (RW2, W1, W2, and W5), but a significant difference was recorded in northern wetlands sites compared to the southern sites and those in the river. At the end of the flood season, April 2008, no significant differences were observed between the river sites, the southern wetlands sites, and the northern wetlands sites (W3; 700m far from the river and W4; 1100m). However, the $\delta^{18}O$-water signature at site W3 showed a slight enrichment in the values and more enrichment at site W4. Therefore, river water may have extended up to two-thirds of the main stream within Dunnville Marsh on the 29th of April of 2008. We have to mention that the water flow in the Grand River at York station, during the first 10 days of April, was more than 10 folds higher than the last 10 days of April when we conducted the spring sampling (said by John Bartlett, GRCA). Therefore, it is highly probable that when the river flood reaches the peak, the river water could extend even further throughout significant part of the Dunnville Marsh towards the agricultural drainage in the north.

Lake Erie water can also intrude Dunnville Marsh, all the way to the agricultural drainage, when seiche events occur. In 2008, major seiche took place on the 30th of January. The water level was very high at the inflow site (northern Dunnville Marsh) which flooded the adjacent road (personal communication, Archie Merigold; local landowner). Seiche events happen in Lake Erie and affect the Grand River and the adjacent marshes including Dunnville Marsh (Gilbert and Ryan 2007) especially when there is a south west wind (Bedford 1992). Unfortunately, I was not able to collect samples from Dunnville Marsh during a seiche event to confirm the influence, or not, of Lake Erie water.

The hydrologic characteristics of the river wetland system, as well as the productivity of the wetland vegetation, are important factors affecting nutrient concentrations and chemistry (Elder 1985). Therefore, many measured elements might not give a clear idea regarding the river water interaction with the marsh.

Dissolved oxygen concentrations showed variability throughout the marsh. The vegetation canopy in the wetland was one of the major factors responsible for changing DO concentrations within the wetland. DO concentrations in the marsh, during April did not demonstrate the same variability as in the other seasons because of the lack of vegetation. When the river water inundated the marsh in April, the major factor influencing the DO (vegetation) was absent because it was too early in the growing season. Therefore, river water might influence the DO in the wetlands sites and brought it to around saturation which is similar to the DO in the river. This agreed with the δ^{18}O-water data which showed no significant differences between the river and most of the wetland during April 2008. Hamilton et al. (1997) indicate that in densely vegetated floodplains, net O2 consumption by the aquatic plants potentially results in deoxygenation of the river water. Nevertheless, Dunnville Marsh influences on the Grand regarding DO and many elements was not apparent or weak. The slight DO decrease recorded in the downstream site (R1) is probably more a function of sampling time than any real difference in hydrological or ecological differences between river and wetland. Therefore, this decrease might not be considered due to the Dunnville Marsh effect. Nitrogen input from the upland; however, was attenuated through the Dunnville Marsh which can be considered as a positive affect on the river even if it is a small amount compared to the already relative higher nitrogen in the river that come form upper part of the river.

The high total nitrogen concentrations in the river were reflected in some of the southern wetlands sites. This indicates that despite the biogeochemical reactions in the wetland, the river water intrusion, which was loaded with nitrogen, was apparent through the lower part of the marsh.

It would be of interest to see if other chemical species (such as Cl^- and SO_4^{-2}) might also prove useful for detecting mixing zones, beside oxygen stable isotope tool (Hardegree et al.1995). In geochemical studies, chloride has always been considered to be a conservative element (Clark and Fritz 1997). In spite of the non reactive behavior of Cl^-, no clear difference was shown measuring this element between the river and the wetland. The only obvious difference was recorded in July 2008 that revealed a difference in the northern wetlands sites from the southern wetland sites and the river sites. This probably due to the influence of the agricultural drainage input on the northern wetlands sites (W4, W3) that separate these sites form the southern wetlands sites (RW2, W1, W2, and W5) which are apparently more influenced by the river.

It is difficult to use SO_4^{-2} as an element for detecting mixing zones. Biogeochemical reactions can change the sulfate concentrations in the wetlands. Sulfate reduction and oxidation can take place in the wetlands depending on the oxygen availability (Mitsch and Gosselink 2007).

DOC concentrations in Dunnville Marsh were high. There was a noticeable decreasing trend in DOC in the wetland sites closest to the river. This can be because of the dilution effect that happened due to the river water intrusion into the southern wetland part.

Lambs (2000) found a correlation between conductivity and oxygen stable isotope. However, in our study, conductivity measurements demonstrated no significant differences between the river and wetland sites. $\delta^{18}O$-water data, on the other hand, showed a significant difference in the northern wetland sites form the southern wetland sites and the river.

In brief, oxygen isotopes are probably the best tool in detecting mixing zones, because the $^{18}O/^{16}O$ value of a water mass, being part of the water molecule itself, behaves as a truly conservative tracer. In contrast, many chemical constituents and the suspended load can be affected by many factors such as precipitation, sedimentation, and a variety of biological activities — all processes that may not be directly related to mixing between two water masses (Hardegree et al.1995).

Conclusions

The following conclusions can be drawn from this project:

1- Dunnville Marsh has little influence on the oxygen regime of the Grand River except to "protect" the river from nutrients coming from the upland, which would consume oxygen in the river.

2- DO saturation in the wetland was similar to river in the spring because river water floods the wetland during the spring melt thereby producing similar oxygen characteristics in both river and wetland water. Also, the vegetation, which can be considered as the main factor affecting the DO in the wetland, was absent at that time.

3- Nitrogen input from the agricultural areas or other possible human sources was not high enough to affect the DO in the wetland. The low nitrogen input may be attributed to the growth of macrophytes in and adjacent to the channel that could assimilate any nitrogen coming from agricultural sources.

4- Dunnville Marsh was able to attenuate some of the nitrogen that entered it, which suggests that wetlands along the Grand River can be useful for managing nitrogen and other nutrients from human activities.

5- River water intrusion into the marsh could reach around one-third of the marsh during the fall and the summer, and might reach two-thirds of it just after the flood season. We do assume that the river water intrusion can inundate significant part of the marsh towards the agricultural drainage when the flood reaches the peak.

6- It seems emergent macrophytes in the wetland play an important role in decreasing the dissolved oxygen saturation. Therefore, affecting the overall oxygen dynamics of the wetland as a whole.

7- There was high respiration in the river during the fall which suggests minimal photosynthetic activities derived from autotrophs, presumably because of less phytoplankton biomass

8- The wetland showed higher photosynthetic activities than the river throughout most of the year; the wetland; however, had lower dissolved oxygen saturation occasionally in spring and mostly in summer compared to the river

9- Diel data exhibited constant high levels of DO saturations and constant low levels of oxygen stable isotopes throughout the course of the 24 hrs that can refer to the autotrophic status in the river.

10- Gas exchange (more water turbulence lead to re-aeration) was more prevalent in the river.

11- δ^{18}O-water is an effective tool for detecting and monitoring the interplay of river and wetland waters .

Recommendations for Further Work

1. Seiches and their effects on the Dunnville Marsh and other wetlands in the southern reaches of the Grand River are needed to be studied. Seiches are a common occurrence along Lake Erie, although the contributions of these events to the oxygen regime, nutrient budgets, and biotic communities of wetlands are not well known (Mitsch and Reeder 1992).
2. Despite the low nitrogen input from agricultural areas, Dunnville Marsh exhibited positive attenuation ability. Therefore, preservation of existing marshes and restoring or creating more wetlands throughout the southern Grand River watershed would be an effective way to control nitrogen contamination in the Grand River. More wetlands would be especially useful near the four water pollution control plants near Brantford, Caladonia, Cayuga, and Dunnville (Gilbert and Ryan 2007), which could significantly reduce current nitrogen loading to this section of the river.
3. The influence of the dam on the river and the surrounding marshes needs some attention. In order to understand the role of the dam, an improved understanding of the interaction between river flows and floodplain ecology, and investigations into ecological impacts of management practices, is essential. Furthermore, a comparison study between two representative wetlands, one on the north side and another on the south side of the dam, might be one approach. .
4. Our oxygen diel study was conducted once in July 2008. To gain a better understanding on the seasonality, additional diel samplings of dissolved oxygen and oxygen stable isotopes in fall and spring is needed.

5. The limited data that we derived form the diel study showed us the necessity of applying a non steady state model, such as photosynthesis-respiration-gas exchange; PoRGy (Venkiteswaran et al. 2007), that might be a useful approach to better understand aquatic metabolism in Dunnville Marsh and other marshes located in the southern Grand River.
6. It is important to have a monitoring device installed to measure the water quality in the Grand River south of the dam. This device will enable us to monitor the water quality changes in this part of the river and to observe any lake-water intrusion during seiche events. Consequently, monitoring some of the factors affecting the wetlands below the dam. The Grand River Conservation authority might be interested in achieving this idea.
7. To verify our assumption regarding the river water intrusion more than 2 km in Dunnville Marsh during the peak of a flood season, $\delta^{18}O$- water measurement will be required during that period of time. The flood peak in 2008 took place during early April while our sampling was conducted in late April of 2008.

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Appendix 1: Field and laboratory measurements collected during this study.

Table 1: Spatial and temporal variations of dissolved oxygen saturation (%) in the Dunnville Marsh and the Grand River.

DO Saturation	**Month**					
Station	**September 07**	**October 07**	**April 08**	**May 08**	**June 08**	**July 08**
River (R1)	72	90	95	95	107	103
River (R2)	87	99	109	106	106	115
River-Wetland (RW2)	84	89	97	97	83	97
Wetland (W1)	75	77	97	97	37	68
Wetland (W2)	98	85	93	104	61	71
Wetland (W5)	96	99	103	107	88	110
Wetland (W3)	134	92	105	99	83	86
Wetland (W4)	114	…..	91	93	89	65
DRAIN	101	79	86	80	63	65

…..Not measured

Table 2: Spatial and temporal variations of dissolved oxygen (mg/L) in the Dunnville Marsh and the Grand River.

Dissolved Oxygen mg/L	**Month**					
Station	**Sept 07**	**Oct 07**	**April 08**	**May 08**	**June 08**	**July 08**
River (R1)	6.47	9.83	9.66	9.33	8.90	8.66
River (R2)	7.91	10.90	10.92	10.00	9.30	9.61
River-Wetland (RW2)	7.90	10.40	9.90	9.74	7.55	8.18
Wetland (W1)	7.09	9.16	10.10	9.72	3.40	5.76
Wetland (W2)	8.74	9.71	9.70	10.42	5.45	6.10
Wetland (W5)	9.05	11.13	10.45	10.58	7.80	9.15
Wetland (W3)	12.30	9.94	11.20	9.75	7.33	7.19
Wetland (W4)	10.43	…..	10.00	9.02	7.70	5.39
DRAIN	9.14	8.57	9.27	7.42	5.35	5.53

…..Not Measured

Table 3: Spatial and temporal variations of temperature in the Dunnville Marsh and the Grand River.

Temperature (^{0}C)	**Month**						
Station	**August 07**	**September 07**	**October 07**	**April 08**	**May 08**	**June 08**	**July 08**
River (R1)	…..	20.5	11.2	14.4	16.3	25.0	23.9
River (R2)	25.0	20.0	11.0	15.2	17.9	22.2	24.5
River-Wetland (RW2)	23.7	18.1	8.5	14.1	15.2	20.8	23.6
Wetland (W1)	23.0	18.2	7.6	13.9	14.9	20.3	23.3
Wetland (W2)	23.5	21.1	9.3	13.5	14.8	21.4	23.4
Wetland (W5)	26.0	19.8	10.2	14.5	15.6	22.0	24.6
Wetland (W3)	24.2	19.5	11.7	12.2	15.6	22.3	24.5
Wetland (W4)	24.5	19.5	…..	11.0	16.6	23.0	24.7
DRAIN	26.2	20.0	11.5	12.0	18.7	24.1	23.1

…..Not Measured

Table 4: Spatial and temporal variations of conductivity (µs/cm^2) in the Dunnville Marsh and the Grand River

Conductivity (µs/cm^2)	**Month**						
Station	**August 07**	**September 07**	**October 07**	**April 08**	**May 08**	**June 08**	**July 08**
River (R1)	…..	775	938	812	857	655	593
River (R2)	875	768	984	827	855	712	596
River-Wetland (RW2)	825	592	969	813	860	713	588
Wetland (W1)	833	494	985	811	859	768	605
Wetland (W2)	862	…..	1006	810	865	744	607
Wetland (W5)	876	754	954	811	856	747	658
Wetland (W3)	880	744	955	783	844	774	716
Wetland (W4)	363	463	…..	760	844	791	852
DRAIN	960	654	664	853	824	818	932

…..Not Measured

Table 5: Spatial and temporal variations of oxygen stable isotopes (‰) in the Dunnville Marsh and the Grand River

δ^{18}O-DO (‰)	Month					
Station	**September 07**	**October 07**	**April 08**	**May 08**	**June 08**	**July 08**
River (R1)	26.5	24.5	21.9	22.2	21.3	22.2
River (R2)	24.4	23.6	20.3	20.8	20.5	21.3
River- wetland (RW2)	25.1	24.2	21.1	20.8	22.3	20.8
Wetland (W1)	23.9	25.3	20.4	19.5	23.1	19.5
Wetland (W2)	19.7	22.9	19.4	18.6	19.9	18.9
Wetland (W5)	19.4	22.8	19.6	16.3	19.9	16.9
Wetland (W3)	17.2	24.0	19.2	16.4	19.2	17.0
Wetland (W4)	17.2	…..	16.9	15.3	17.8	17.1
DRAIN	17.2	18.5	18.9	13.8	17.6	16.9

…..Not Measured

Table 6: Spatial and temporal variations of stable isotopes of water (‰) in the Dunnville Marsh and the Grand River for the months September 2007, April and July 2008. One sample was collected from Lake Erie in July 2008.

δ^{18}O-water (‰)	Month		
Station	**September 2007**	**April 2008**	**July 2008**
River (R1)	-8.85	-10.29	-8.97
River (R2)	-9.15	-10.37	-8.94
River-Wetland (RW2)	-9.04	-10.32	-8.79
Wetland (W1)	-8.60	-10.21	-8.57
Wetland (W2)	-8.70	-10.05	-8.78
Wetland (W5)	-8.19	-10.24	-8.73
Wetland (W3)	-7.34	-9.64	-7.55
Wetland (W4)	-6.37	-9.12	-7.56
DRAIN	-5.51	-9.48	-8.05
Lake Erie	…..	…..	-6.79

…..Not Measured

Table 7: Diel measurements of dissolved oxygen saturations (%) in two river sites (R1 and R2) and one wetland site (W5) on the 7th and 8th of July 2008

(Diel Data) DO Saturation	Stations		
Time	**R1**	**R2**	**W5**
12:00	165.0	156.3	108.5
15:00	170.8	172.0	141.1
16:30	178.3	186.2	123.2
18:00	179.0	200.9	98.4
20:40	168.2	196.8	…..
0:00	164.6	179.0	104.9
3:00	162.0	162.4	85.5
5:15	155.1	130.8	80.2
9:00	146.7	121.3	99.8
12:00	149.2	126.8	96.0

…..Not Measured

Table 8: Diel measurements of oxygen stable isotopes (‰) in two river sites (R1 and R2) and one wetland site (W5) on the 7th and 8th of July 2008.

(Diel Data) δ^{18}O-DO (‰)	Stations		
Time	**R1**	**R2**	**W5**
12:00	15.9	18.3	15.1
15:00	16.1	14.4	15.8
16:30	14.8	13.9	14.0
18:00	14.9	12.8	14.7
20:40	14.6	13.0	16.8
0:00	14.5	13.3	18.5
3:00	15.3	17.3	19.8
5:15	17.0	20.0	19.7
9:00	17.9	22.1	19.0
12:00	17.7	20.6	19.0

Table 9: Diel measurements of different parameters were conducted on the 7th and the 8th of July 2008 using the multi-meter probe to measure: temperature, conductivity, pH, dissolved oxygen saturations and dissolved oxygen concentrations in two river sites (R1 and R2) and one wetland site (W5). Winkler method was applied on some of the samples to measure dissolved oxygen concentrations.

Station	Date	Time	Temp °C	Conductivity µs/cm^2	pH	DO%	DO mg/L	DO mg/L(winkler)
R1	7, July, 08	11:57	26.3	654	8.23	165.0	13.30	…..
R2	7, July, 08	12:21	25.9	663	8.39	156.3	12.69	…..
W5	7, July, 08	12:44	28.0	691	8.07	108.5	8.42	…..
R1	7, July, 08	15:04	27.5	649	7.88	170.8	13.49	…..
R2	7, July, 08	15:20	27.4	659	8.11	172.0	13.57	…..
W5	7, July, 08	15:35	29.4	674	7.94	141.1	10.77	…..
R1	7, July, 08	16:30	27.3	645	7.96	178.3	14.11	…..
R2	7, July, 08	16:47	27.3	645	8.26	186.2	14.72	…..
W5	7, July, 08	17:10	29.8	686	7.92	123.2	9.32	…..
R1	7, July, 08	18:00	27.4	647	7.98	179.0	14.18	…..
R2	7, July, 08	18:18	27.9	641	8.19	200.9	15.72	…..
W5	7, July, 08	18:35	29.6	687	7.87	98.4	7.50	…..
R1	7, July, 08	20:40	27.0	653	8.15	168.2	13.41	…..
R2	7, July, 08	21:16	27.8	636	8.21	196.8	15.47	…..
W5	7, July, 08	21:37	28.4	686	7.84			…..
R1	8, July, 08	0:00	26.7	648	8.23	164.6	13.20	…..
R2	8, July, 08	0:32	27.1	647	7.99	179.0	14.25	…..
W5	8, July, 08	1:26	27.7	680	7.99	104.9	8.22	…..
R1	8, July, 08	3.09	26.5	646	8.23	162.0	13.01	12.6
R2	8, July, 08	3.37	26.7	653	8.19	162.4	12.99	12.5
W5	8, July, 08	4:00	27.0	676	7.82	85.5	6.81	7.1
R1	8, July, 08	5:20	26.3	648	7.99	155.1	12.49	11.7
R2	8, July, 08	5:45	26.1	670	8.08	130.8	10.51	10.2
W5	8, July, 08	6:05	26.5	671	7.71	80.2	6.40	7.2
R1	8, July, 08	9:00	26.2	650	8.00	146.7	11.84	10.9
R2	8, July, 08	9:25	25.9	676	7.83	121.3	9.84	9.3
W5	8, July, 08	9:50	26.6	663	7.80	99.8	8.01	7.6
R1	8, July, 08	12:00	26.9	650	7.84	149.2	11.90	11.1
R2	8, July, 08	12:25	26.3	680		126.8	10.22	9.5
W5	8, July, 08	12:50	27.7	679		96.0	7.63	7.8

….. Not Measured

Table 10: Spatial and temporal variations of total nitrogen (mg/L) in the Dunnville Marsh and the Grand River

TN (mg/L)	Month						
Station	**August 07**	**September 07**	**October 07**	**April 08**	**May 08**	**June 08**	**July 08**
River(R1)	…..	2.20	…..	3.07	3.24	2.60	2.54
River(R2)	1.56	1.98	2.56	3.27	3.24	2.53	2.42
River-Wetland(RW2)	1.52	1.98	2.27	3.13	3.17	2.36	2.44
Wetland (W1)	0.92	1.78	1.78	3.08	2.77	1.42	1.41
Wetland(W2)	0.64	1.85	2.17	2.92	1.23	1.70	1.88
Wetland(W5)	1.10	1.29	1.35	3.02	1.92	1.72	1.00
Wetland(W3)	0.76	0.80	1.31	2.03	0.73	1.21	0.71
Wetland(W4)	0.66	0.64	…..	1.36	0.74	1.15	0.95
DRAIN	0.85	0.83	0.77	2.01	1.18	2.08	1.32

….. Not Measured

Table 11: Spatial and temporal variations of nitrate (mg/L) in the Dunnville Marsh and the Grand River

NO3 (mg/L)	Month						
Station	**August 07**	**September 07**	**October 07**	**April 08**	**May 08**	**June 08**	**July 08**
River (R1)	…..	1.24	1.63	2.66	2.55	1.98	1.95
River (R2)	0.98	1.19	2.67	2.79	2.61	1.98	1.90
River-Wetland (RW2)	0.89	1.33	1.74	2.68	2.20	1.68	1.62
Wetland (W1)	0.31	1.08	1.20	2.63	1.94	0.75	0.74
Wetland (W2)	0.28	1.21	1.26	2.52	0.59	1.06	1.19
Wetland (W5)	0.53	0.69	0.60	2.52	1.26	1.08	0.61
Wetland (W3)	0.00	0.35	0.55	1.43	0.00	0.46	0.22
Wetland (W4)	0.00	0.00	…..	0.54	0.00	0.37	0.30
DRAIN	0.00	0.00	0.00	1.22	0.29	1.06	0.69

….. Not Measured

Table 12: Spatial and temporal variations of ammonium (mg/L) in the Dunnville Marsh and the Grand River

NH4+ (mg/L)	**Month**						
Station	**August 07**	**September 07**	**October 07**	**April 08**	**May 08**	**June 08**	**July 08**
River(R1)	…..	0.212	0.070	0.096	0.032	0.051	0.024
River(R2)	0.015	0.138	0.043	0.096	0.017	0.026	0.021
River-Wetland(RW2)	0.052	0.130	0.059	0.057	0.023	0.036	0.026
Wetland(W1)	0.050	0.154	0.097	0.016	0.020	0.051	0.020
Wetland(W2)	0.046	0.115	0.084	0.016	0.016	0.033	0.022
Wetland(W5)	0.032	0.070	0.124	0.016	0.014	0.026	0.025
Wetland(W3)	0.028	0.021	0.213	0.014	0.010	0.025	0.021
Wetland(W4)	0.027	0.027	…..	0.013	0.011	0.038	0.048
DRAIN	0.023	0.031	0.230	0.096	0.055	0.173	0.070

….. Not Measured

Table 13: Spatial and temporal variations of dissolved organic carbon (mg/L) in the Dunnville Marsh and the Grand River.

DOC (mg/L)	**Month**						
Stations	**August 07**	**September 07**	**October 07**	**April 08**	**May 08**	**June 08**	**July 08**
River (R1)	……	6.38	4.79	5.35	4.71	5.17	8.00
River (R2)	5.65	5.75	5.11	5.22	4.96	5.07	8.04
River-Wetland (RW2)	6.70	5.71	4.98	5.22	5.31	5.61	8.42
Wetland (W1)	7.61	6.39	6.73	5.47	6.15	9.62	10.47
Wetland (W2)	8.62	5.58	5.78	6.25	9.10	7.56	9.25
Wetland (W5)	6.88	6.99	7.70	5.49	8.14	8.71	10.80
Wetland (W3)	9.93	8.63	8.70	9.28	12.04	10.01	11.91
Wetland (W4)	9.95	10.41	…..	13.65	12.28	12.19	12.77
DRAIN	12.39	13.71	9.70	10.89	11.59	10.92	11.67

….. Not Measured

Table 14: Spatial and temporal variations of sulfate (mg/L) in the Dunnville Marsh and the Grand River

SO4 (mg/L)	**Month**						
Station	**August 07**	**September 07**	**October 07**	**April 08**	**May 08**	**June 08**	**July 08**
River (R1)	…..	32.62	38.96	32.07	32.60	24.29	19.20
River (R2)	35.31	33.98	37.51	32.90	32.88	22.94	19.60
River-Wetland (RW2)	35.95	32.14	32.89	32.06	41.06	22.04	18.10
Wetland (W1)	33.96	32.26	33.78	26.52	30.20	22.12	13.90
Wetland (W2)	33.84	34.76	32.64	31.37	29.39	21.57	21.20
Wetland (W5)	35.17	31.76	26.33	30.41	31.81	23.11	13.20
Wetland (W3)	33.24	30.67	32.61	25.30	23.51	19.63	10.50
Wetland (W4)	34.01	29.91	…..	16.10	22.11	18.10	14.70
DRAIN	29.13	18.38	13.46	19.63	21.05	16.38	17.30

….. Not Measured

Table 15: Spatial and temporal variations of chloride (mg/L) in the Dunnville Marsh and the Grand River

Cl (mg/L)	**Month**						
Station	**August 07**	**September 07**	**October 07**	**April 08**	**May 08**	**June 08**	**July 08**
River (R1)	…..	88.92	88.47	67.89	82.24	68.95	46.20
River (R2)	92.18	86.93	95.67	68.81	74.42	67.54	47.60
River-Wetland (RW2)	89.58	86.68	89.62	65.17	80.59	68.28	46.50
Wetland (W1)	85.18	86.90	95.04	55.72	82.31	67.52	45.20
Wetland (W2)	92.13	91.64	91.92	63.89	76.76	70.03	51.80
Wetland (W5)	88.17	87.37	82.75	63.94	79.47	69.78	61.00
Wetland (W3)	91.28	87.83	79.78	57.94	76.62	70.72	73.30
Wetland (W4)	93.86	87.92	…..	47.12	76.67	73.40	105.80
DRAIN	95.21	64.53	58.51	73.30	77.28	83.08	129.90

….. Not Measured

Table 16: Spatial and temporal variations of dissolved inorganic carbon (mg/L) in the Dunnville Marsh and the Grand River.

DIC (mg/L)	**Month**						
Station	**August 07**	**September 07**	**October 07**	**April 08**	**May 08**	**June 08**	**July 08**
River(R1)	…..	33.60	37.40	44.80	49.00	43.00	43.80
River(R2)	33.26	32.90	37.70	44.00	47.90	41.80	42.00
River-Wetland(RW2)	31.70	33.60	39.40	44.00	49.90	44.80	44.60
Wetland(W1)	37.30	35.40	46.40	43.50	50.50	55.90	52.40
Wetland(W2)	42.40	32.90	44.40	44.90	56.90	49.50	47.20
Wetland(W5)	32.60	32.00	45.50	43.40	53.30	50.70	51.50
Wetland(W3)	39.50	30.90	47.40	47.90	61.40	56.80	55.10
Wetland(W4)	41.80	34.70	…..	52.80	62.20	60.20	63.10
DRAIN	45.30	39.60	40.30	54.10	60.90	63.30	69.20

….. Not Measured

Table 17: Spatial and temporal variations of pH in the Dunnville Marsh and the Grand River.

pH	**Month**						
Station	**August 07**	**September 07**	**October 07**	**April 08**	**May 08**	**June 08**	**July 08**
River (R1)	…..	8.10	7.59	7.95	7.46	8.47	8.19
River (R2)	8.48	8.00	8.11	8.70	8.28	8.51	8.20
River-Wetland (RW2)	8.15	7.80	7.69	7.95	7.77	8.34	8.05
Wetland (W1)	7.77	8.20	7.60	8.13	7.83	7.74	7.67
Wetland (W2)	8.18	8.70	7.70	8.50	7.81	7.89	…..
Wetland (W5)	8.58	8.20	7.87	8.10	7.94	8.10	8.16
Wetland (W3)	8.27	8.40	7.83	8.65	7.83	7.96	7.91
Wetland (W4)	8.23	8.00	…..	8.00	7.91	7.82	7.58
DRAIN	8.35	8.10	7.64	7.30	7.87	7.77	7.50

….. Not Measured