The Decline of a Northern Lake Superior Marsh:

A Study of the Cause and Effect

by

Sandra A. Stiles

A thesis submitted in partial fulfilment
of the requirements for the degree of
Master of Science in Biology

Department of Biology
Lakehead University
Thunder Bay, Ontario

Table of Contents

Abstract

This study quantified the loss of vegetation in Mission Marsh located within the city limits of Thunder Bay on the northern shore of Lake Superior, suggested the most likely cause of this vegetation loss, and examined in detail the source of nutrients in the water column along the Thunder Bay waterfront.

In Chapter 1, examination of aerial photographs of the marsh indicated a vegetative decline of 39.8% from 1983 to 2002. Evidence of grazing and the presence of eutrophic indicators in algal blooms suggested that Canada Geese, *Branta canadensis* may be one causative factor.

Wetland degradation was measured using digitized aerial photographs that were subsequently analysed with Erdas Imagine 8.7 imaging software. Cluster analysis of the results isolated distinct plant groups within the wetland area, and yielded 5 broad spectral classes: deep open water (DOW); submerged vegetation (SV); floating/emergent vegetation (FEV); shoreline/emergent vegetation (SEV); and shallow open water (SOW). Emergent and floating plant populations were most severely affected with declines of 77.5% and 55.6% respectively. Submergent declines were measured at 24.8%. In total, 8.8 hectares of vegetation were lost to shallow and deep waters during the study period.

Enclosures placed on the marsh and planted with *Eleocharis smallii* were used to assess whether the sediment may have been toxic to plants and whether grazing by Canada Geese was a problem. Plants within the enclosures were highly productive while the plants outside the enclosure were heavily grazed and exhibited overwinter mortality. Geese were suggested as a likely cause of the loss of plants. It was suggested that the decline in water levels in Lake Superior since the 1980's may have contributed to the decline of the marsh by providing optimum habitat for Canada Geese. Similarly the production of algal mats were thought to have been a factor in macrophyte mortality potentially caused by increased eutrophication due to nutrient release in the excrement of Canada Geese.

In Chapter 2, the levels and sources of N and P in the water column along the Thunder Bay waterfront were determined. There were two point sources of these nutrients – a paper mill located on the Kamanistiquia River and the Thunder Bay Water Pollution Control Plant. The other suspected source of nutrient were Canada Geese. In order to separate out the likely origin of the nutrients, samples were collected below and above the paper mill and along the waterfront including the location of water intake for the city of Thunder Bay at Bare Point. The nutrient levels along the waterfront were often higher than near the point source sites indicating that non-point sites were also contributing to the nutrient levels. Coefficients of variation for the N and P parameters showed that the sites on the water front exhibited much higher levels of variation than did the sites near the point sources. Similarly, non-metric multidimensional scaling for

the data showed that the scatter for sites along the waterfront was much greater than for the point source sites. The likely cause of this non-point eutrophication was assumed to be Canada Geese. Management options to control the populations of Canada Geese and re-establish the vegetation in Mission Marsh were discussed.

Acknowledgements

I would first like to express my sincerest gratitude to Dr. Peter Lee, my thesis supervisor. Dr. Lee provided valuable and much appreciated guidance, support and advice throughout my research. I also thank Dr. Janice Hughes, Dr. Peggy Tripp and Dr. Walter Momot, members of my graduate committee and Dr. Robert Stewart, my external reviewer. A special note of gratitude to Dr. Peggy Tripp for being a mentor and an inspiration to me through the many years I had the privilege of knowing her.

I would also like to thank Johanne Joncas and in particular Suzanne Walford for their help in guiding me through the proper protocols and procedures for sampling and analyzing my water samples at Lakehead University's Environmental Laboratory.

Special thanks to Dr. Ulf Runneson for his knowledge and guidance during my analyses of the aerial photographs of my study site and the generous use of his remote sensing laboratory. Tomislav Sapic provided a great deal of assistance throughout my first journey with remote sensing analysis and has my utmost gratitude!

Finally, I would like to thank my husband, Jeffrey Stiles, for remaining a constant strength for me during this journey. Jeff also served as my field assistant on many occasions and I am forever grateful.

List of Tables

List of Figures

General Introduction

Background

A great diversity of wetlands can be found in the Great Lakes Basin with swamps, fens, bogs and marshes existing in various forms. The coastal marshes are among the most productive wetlands (Maynard and Wilcox 1997; Mitsch and Gosselink 2000) and provide habitat and breeding grounds for waterfowl, fish and invertebrates (Maynard and Wilcox 1997). They also serve as important recreation and aesthetic lands for many communities along the Great Lakes shoreline (Entwistle 1984; McKever and Elder 1981).

Unfortunately, the wetlands of the world have been declining or disappearing at an alarming rate over the past few decades (Maynard and Wilcox 1997; Mitsch and Gosselink 2000). These declines have in some cases been attributed to anthropogenic activities (Maynard and Wilcox 1997) such as the introduction of carp and Canada geese (Badzinski et al. 2006; Giroux and Bedard 1987; Mitchell and Wass 1996). Nutrient enrichment is a primary cause of water quality impairment and the subsequent change in the vegetative structure of marshlands (Environmental Protection Agency 2008). The ecological and aesthetic importance of these wetlands demands their monitoring and preservation.

Wetland monitoring traditionally involves interpretation of low level aerial photographs together with ground-based mapping and plant inventories (Finley 2003). This

technique can be time consuming and subjective. In the past decade, a more objective and cost effective method has arisen, which utilizes remote sensing technology (Finley 2003; Haack 1996; Klemas 2001; Olmanson et al. 2002; Ozesmi and Bauer 2002). Typically, satellite photographs are digitized and then analyzed with specialized computer imaging software. A statistical clustering technique, known as unsupervised classification, is applied to the results (Ozesmi and Bauer 2001).

Although changes in a wetland environment can be detected and quantified by remote sensing analysis, it may provide few clues as to the cause for these changes. In such cases, cause may be better indicated by analysis of the physical parameters in which the wetland plants are growing, and the characteristics of the plants themselves.

Causative Factors for Change:

Water Levels

The impact of changing water levels on the success of aquatic plants has been well documented (Lyon et al. 1986; Wei and Chow-Fraser 2005). Painter et al. (1989) suggest that high water levels are responsible for the loss of emergent plants, while low water levels are viewed as necessary for their reestablishment. Water turbidity is also of concern, as it may interfere with photosynthetic activity and in highly turbid waters, the growth of submerged aquatic populations is severely restricted (Sager 1996).

Invasive Species

The introduction of exotic species is increasing worldwide, particularly in aquatic ecosystems (Cohen and Carlton 1998). Of concern to ecologists is the rapid spread of these exotics and the detrimental effects that their abundance may have on existing flora and fauna (Roth 2007). It is now widely accepted that invasive species are a major threat to aquatic ecosystems and biodiversity (Gunn et al. 2004).

Bronte et al. (2003) recorded the introduction of 39 new species into Lake Superior since 1970. The effect of these introductions and the subsequent degradation of Lake Superior habitats is largely limited to shoreline areas, embayments and tributaries (Bronte 2003). In the Great Lakes watershed, the Rusty crayfish (*Orconectes rusticus*) and Common Carp (*Cyprinus carpio*) have been identified as invasives of concern.

Rusty Crayfish

The rusty crayfish belongs to the Cambaridae family. Although it is indigenous to North America, its range was restricted to the Ohio River Basin until the 1960s (Julien Olden et al. 2006). The subsequent years have seen its spread northward into Wisconsin, Michigan, Iowa, New York, Minnesota, Ontario and all of the New England States (Gunn et al. 2004). The first record of rusty crayfish in the Thunder Bay District occurred in 1985 (Bronte 2003).

The spread of *O. rusticus* into nonnative waters, has been attributed to both accidental and intentional factors. Accidental introductions through the expulsion of ballast water (Bronte 2003), aquaculture, aquarium and pond trades (Olden 2006), and use as live bait (Ludwig and Leitch 1996) have all been proposed. Intentional transport vectors include the release of crayfish by commercial crayfish harvesters (Capelli and Magnuson 1983) and by cottagers for nuisance weed control (Magnuson et al. 1975). This latter recognition of *O. rusticus* as an "aquatic plant manager" hints at its potential for aquatic habitat destruction.

Although the crayfish diet includes submergent macrophytes (Wilson et al. 2005), non consumptive destruction has also been documented. Crayfish are trophic generalists, readily consuming leaf litter, benthic algae, aquatic invertebrates, fish eggs and detritus (Wilson 2005). In foraging for alternate foods, crayfish uproot both seedlings and established plants (Lodge et al. 1994).

The negative effects of crayfish on macrophyte populations are well documented (Lodge and Lorman 1987; Hanson and Chambers 1995). Based on trap catch data, Roth (2007) correlated increased crayfish populations with total macrophyte absence. In his review, Gunn et al (2004) noted the reduction in biodiversity in infested areas, while Wilson (2005) suggested that macrophyte recovery following infestation required prolonged crayfish population control.

The successful establishment of crayfish depends on water and substrate suitability. Crayfish inhabit permanent water bodies that are deep enough not to freeze, and with sufficient oxygen levels to prevent winter kill (Collicut 1998). Crayfish are notably absent from lakes with pH values lower than 5.5 (Berrill et al. 1985) and dissolved calcium concentrations of less than 2.5 mg/l (Capelli and Magnuson 1983). Most commercial trapping efforts are concentrated at water depths of 2 to 3 meters, which seem to harbour the highest concentrations of crayfish (Wilson 2005).

The greatest substrate requirement for crayfish proliferation is the presence of shelter from predators in the form of rocks, logs or thick vegetation (Collicut 1998). Molting crayfish are at particular risk to predation, as are egg and young carrying females (Olden et al. 2006). In controlled studies, the presence of predatory fishes reduced rusty crayfish foraging when inadequate substrate protection was provided (Stein and Magnuson 1976). Roth's Wisconsin study (2007) reports that rusty crayfish and Lepomis abundance were inversely related across a number of study lakes.

Data on within-lake dispersion rates of O. rusticus is provided by Wilson's long term study on Trout Lake in Wisconsin (2005). Crayfish invasion along the littoral zone occurred at an average rate of 0.689 km/year. A sharp rise in site abundance often occurred once trap catches reached 9 crayfish/trap.

Common Carp

Common carp, *Cyprinus carpio*, belong to the Cyprinidae family, and have their origins in temperate regions of Asia (McCrimmon 1968). In the 1880's they were introduced into North America and were stocked for their value as food fish (Royal Botanical Gardens 1998). Their incidental capture in a gillnet near Simpson Island, confirms their presence in Lake Superior in 1954 (Hartviksen and Momot 1989).

Although carp are capable of both surface and bottom feeding (Hartviksen and Momot 1989), the greatest abundance of food occurs among the roots of aquatic plants (Royal Botanical Gardens 1998). Benthic feeding is done by "sucking" or "mumbling" the substrate (Cahn 1929), which can cause the uprooting and dislodging of aquatic vegetation (Lamoureux 1961). The extent of the damage is related to sediment type, the resistance of individual species to uprooting, and the timing of seed production (Royal Botanical Gardens 1998).

The destruction of vegetation by carp is well documented. As early as 1929, Cahn reported the "total destruction of vegetation" following the introduction of carp into an artificial lake. Similarly, "consistent and severe losses in plant biomass" were exhibited in a controlled experiment by Macrae (1979). The relationship of carp density to macrophyte survival was quantified by Robel (1961), who found that a highly significant negative linear relationship existed. His analysis concluded that the adverse affects of

carp on aquatics would be felt at densities of 200 lbs/acre. At densities of 400 lbs/acre, aquatic vegetation would be totally annihilated.

Carp damage to aquatic macrophytes is not limited to "uprooting" but to their contribution to decreased water clarity. Associations between increased tubidity and carp feeding have been noted by numerous researchers (Cahn 1929; Kay 1949; Painter 1989). This turbidity reduces light penetration through the water column, and, in extreme cases, may render the water almost opague (Matsuzaki et al. 2009). Since most submergent plants are restricted to water depths greater than 1 metre, light penetration is of paramount importance to their survival (Painter et al. 1989). In fact, King and Hunt (1967) report a 3000% increase in submergent vegetation following a massive carp cull.

Eutrophication

Eutrophication is defined as the increase in productivity of water bodies caused by the addition of limiting nutrients, generally P but in some cases N (Horne and Goldman 1994). Nutrient loading to a wetland stimulates primary production which may lead to persistent algae blooms and reduction of macrophytic vegetation and water quality (Scherer et al. 1995). A degradation of water quality often includes lower dissolved oxygen or higher pH levels which favour nutrient release from the sediment (Meyer et al. 2005). This autochthonous input of phosphorus to the system further encourages the development of algae blooms (Scherer et al. 1995).

Herbivory by Canada Geese

The Canada Goose, *Branta canadensis*, was extirpated from the Great Lakes during the early years of human settlement (Hughes 2001). In the 1950's, various fish and wildlife agencies began a re-introduction program with alarming success (Gosser et al. 1997). Since their reintroduction into Ontario in 1965, the population has increased exponentially (Ankney 1996; Smith et al. 1999).

Canada Geese feed on the shoots and rhizomes of aquatic vegetation (Zacheis et al. 2001). Research by Prevett et al. (1985) indicates that 83% of their spring diet consists of grass, sedge and horsetail. While the latter two remain important food sources throughout autumn, pondweed rhizomes were added to their fall diet at sites in the Yukon (Coleman and Boag 1987). The same study showed that in the emergent plant zone, preferences included *Eleocharis palustris* which is closely related to *Eleocharis smallii* found at Mission Marsh.

High concentrations of feeding waterfowl can significantly reduce plant biomass (Badzinski et al. 2006; Giroux and Bedard 1987; Mitchell and Wass 1996). Intensive grazing on rhizomes is particularly damaging, as the carbohydrate reserve required for future plant production is destroyed (Giroux and Bedard 1987). Further, foraging (consumption of above ground tissue) and grubbing (consumption of below-ground tissue) by increasing numbers of geese over many years can result in the exposure and erosion of sediments causing severe wetland vegetation losses (Jeffries et al. 2006).

Water levels have dropped in recent years in Hudson Bay. Normally such a decrease in water levels would increase the production of wetland vegetation (Wei and Chow-Fraser 2005) . However, such increased production did not occur in these wetlands because the increasing feeding pressure by geese over more than 20 years reduced the vegetative reproductive potential of the plants (Abraham et al. 2005).

Large numbers of moult migrants often seek out safe areas away from breeding grounds containing sufficient food and accessible water to complete their annual wing moult (Bellrose 1980; Davis et al. 1985; Salmonsen 1968). This moult normally lasts up to 40 days and begins near the end of June (Davis et al. 1985; Hanson 1965). Since the geese are unable to fly during moult they tend to remain in one location and thus consume whatever vegetation may be present. It is during this time that Canada Geese in large numbers were observed at Mission Marsh.

1. Change in vegetation at a Lake Superior marsh over a 19 year time period: an evaluation of the extent of change and its cause.

1.1 Introduction

The coastal wetlands of the Great Lakes are of prime ecological value for fish, waterfowl, nutrient buffering and habitat for a wide variety of mammals, birds, and benthic organisms. These wetlands have been subjected to various environmental stresses that have resulted in either permanent or temporary losses of vegetation (Mitsch and Gosselink 2000). Water levels have been shown to be a prime factor influencing macrophyte production in these wetlands. Lyon et al. (1986) showed that the vegetation in Lake Michigan declined during high water levels. Wei and Chow-Fraser (2005) in the western end of Lake Ontario and Hudon (1997) in the eastern end of Lake Ontario and the St. Lawrence River showed the same relationship of declining vegetation with increasing water levels. Fluctuations in water levels in the Great Lakes are common and thought to be beneficial since they help to maintain diversity within these wetlands (Keddy and Reznicek 1986; Wilcox 2004). Declines in water quality, particularly eutrophication or toxicity and increased turbidity have led to the reduction of vegetation in Lake Ontario (Sager 1996; Eyles et al. 2003; Mayer et al. 2005) and Lake Superior (Sierszen et al. 2006). Invasive species have also impacted these coastal marshes. Likely the best documented example is the introduction of the common carp into Cootes Paradise marsh on Lake Ontario in the late 1880's. In this marsh, vegetation was reduced from 250 ha to 30 ha in a period of approximately 60 years

(Painter et al. 1989) and the marsh only began to re-vegetate after a carp barrier was constructed on the entrance to the marsh in 1999 (Smith et al. 2001). Plant invasions have also been a problem. *Typha angustifolia*, a non-native cattail species has almost completely replaced the once dominant southern wild rice, *Zizania aquatica*, on thousands of hectares of wetlands on the lower great lakes (Finkelstein et al. 2005). Increases in populations of waterfowl which graze on the marsh vegetation have also become a problem. For example, control methods of oiling eggs and planting non preferred habitat species near the edge of Cootes Paradise marsh on Lake Ontario have been in place to reduce numbers of Canada Geese and Mute Swans for several years (Royal Botanical Gardens 1998). Some studies have also tried to integrate a variety of factors into modeling the decline of these coastal wetlands. Wei and Chow-Fraser (2005) successfully isolated the effect of industrialization from water level increases to determine their relative contribution to vegetation loss in a Lake Ontario marsh.

Nearly all studies on the loss of coastal Great Lakes wetlands have been conducted in the lower Great Lakes. However the coastal wetlands of the north shore of Lake Superior are equally important for the ecological integrity of Lake Superior and may be detrimentally affected as they are in the lower Great Lakes. Coastal wetlands on Lake Superior are relatively rare and total only 915 ha (Maynard and Wilcox 1997). Due to their scarcity these wetlands are particularly significant and any declines in their vegetation cover needs to be assessed and causative factors determine.

Historically, wetland losses were quantified using inventory studies, aerial photograph analysis and ground-based mapping (Finley 2003). Although effective, these time-consuming methods require a great deal of resources (Haack 1996; Olmanson et al. 2002).

A more cost-effective and less time-consuming alternative employs remote sensing analysis to inventory and map wetland imagery around the world (Finley 2003; Haack 1996; Klemas 2001; Olmanson et al. 2002; Ozesmi and Bauer 2002). Digital images obtained via remote satellite or low level aircraft photography are subsequently analyzed with highly specialized computer imaging software. This is the approach that is used in this study to quantify the loss of vegetation in Mission Marsh located on Lake Superior at Thunder Bay, Ontario. Once a healthy marsh with diverse vegetation in the early 1980's (Entwistle 1986), by the late 1990's, the marsh was showing an obvious decline in vegetation.

The study is also involved with gaining an initial assessment of the possible cause(s) of this vegetation loss. Although any or a combination of the reasons detailed above and in the General Introduction could result in vegetation loss at Mission Marsh, the approach used was to examine only the most likely candidates defined as those environmental factors or conditions that may have changed since the marsh was productively thriving in the early 1980's. For example, although carp were described as a problem in the eradication of vegetation above, carp were known to be present in

nearby Lake Superior locations as early as 1954 (Hartviksen and Momot 1985) and thus not considered a factor that had changed in Mission Marsh recently. The same was true for waterfowl other than Canada Geese which were present in Mission Marsh in the early 1980's (Entwistle 1986). This left the following factors that were examined:

i. Water depth changes in the marsh. These would correlate with any changes that occurred in the water level of Lake Superior.

ii. Changes in water quality that might cause toxicity or eutrophication. Secondary treatment was added to the paper mill downstream of the marsh in 1995 making it unlikely that nutrient levels would increase, however, any new associated chemical treatments could possibly influence toxicity.

iii. Introduction of Canada Geese and their herbivory effects. Canada Geese were first introduced to the Thunder Bay waterfront in 1982 and continued to 1988 (Dennis et al. 2000). There are no accurate populations of Canada Geese. A winter bird count in 2002 determined that there were 252 overwintering birds (Thunder Bay Field Naturalists 2002). Initial surveys of Mission Marsh prior to the study during their moult period revealed several hundred geese and moult feathers were present in high concentrations. At a minimum, approximately a thousand geese were surveyed at the south end of the city near the study site during each fall period (September – October).

The present study examines the recent decline of Mission Marsh wetland. The objectives of this study were to quantify the loss of wetland vegetation and assess the most likely cause(s) for this decline.

1.2 Methods

1.2.1 Study site

Mission Island Marsh is a coastal wetland located on the northern shores of Lake Superior within the city limits of Thunder Bay, Ontario. Legally known as Lot 8,9 Conc. K Plan 55R-3079 in the city of Thunder Bay it is located at coordinates 48° 22' 1 89° 12' 9. It is partially open to effects of the lake at the north end of the marsh and protected by a sand spit formation at the south end (Figure 1.1). Mission Island Marsh has been recognized as the largest marsh within the city of Thunder Bay with a total wetland area in 1983 of approximately 53 hectares (Entwistle 1984). The wetland has historically been considered the most significant waterfowl migratory stopover and staging area in the Thunder Bay district (Entwistle 1986; McKever and Elder 1981; Tabak 1981). In 1984, it achieved a provincially significant Class 2 wetland designation from the Lakehead Region Conservation Authority.

1.2.2 Aerial photograph analysis

Historical aerial photographs of Mission Island Marsh were obtained from the City of Thunder Bay Planning and Archives Department. Approximately every five years, the City of Thunder Bay has aerial photos taken of the city for planning purposes. Photos

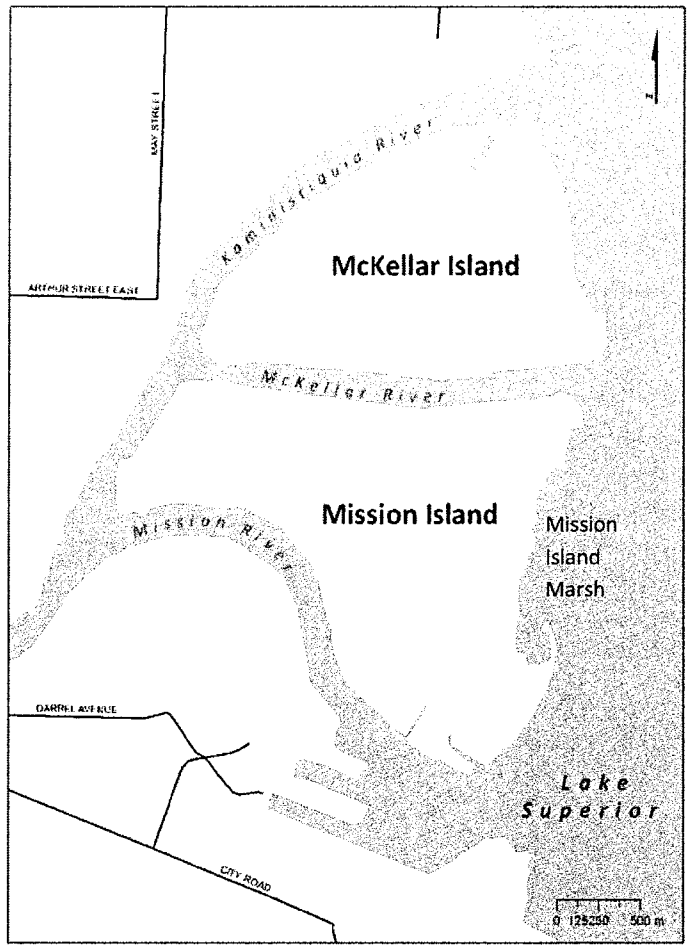

Figure 1.1. Map of Mission Island Marsh and surrounding rivers with the sand spit formation evident at the southern end.

are taken at the end of May during each year they are requested. Photos taken in 1983 and 2002 for the city were available to document the change in the wetland over a 19-year period that precedes the enclosure study. Although images from other years in the time period were available (1987 and 1996), they were insufficient to use for analysis. This was due either to surface glare of the photos or insufficient coverage of the wetland area.

The images were scanned at a resolution of 10, 024 by 8020 pixels as Tiff images. Using imaging software Erdas Imagine 8.7, the 1983 photograph of the wetland area was geometrically corrected to land reference points. The 2002 images were then georeferenced to the 1983 geometrically corrected photo to allow for accurate comparison between the time periods. Residual mean square (RMS) error was maintained at less than one for all geometric referencing of the photos. In 2002 the wetland area was photographed utilizing a different photo line and as a result encompassed two separate photos. The two photographs although taken within seconds of each other were photographed with slightly different exposures causing the photographs to have different brightness values resulting in one of the photographs to appear lighter than the other. A mosaic of the photographs, once geometrically corrected to the 1983 image, was made to form a single image.

For accurate comparison of the two time periods and area of interest (AOI) polygon was created using Erdas Imagine 8.7. Since the 2002 image was rectified to the georeferenced 1983 image, the analysis of pixel data to determine total area for each category was completed on the same precise area for each image. Using Erdas, the 1983 and 2002 images were then classified using an unsupervised classification (clustering) technique. Images were first classified to 250 classes based on similarities in spectral signatures. The classes were narrowed down to 5 broad classes based on similarities between the classes and a comparison with the raw images. The 5 main classes used were Deep Open Water (DOW), Shoreline/Emergent Vegetation (SEV),

Floating/Emergent Vegetation (FEV) , Submerged Vegetation (SV), and Shallow Open Water (SOW). These categories were checked using a ground-survey of the study site and deemed to be suitable. Erdas was used to calculate the total area for each defined class.

1.2.3 Changes in water levels

Monthly mean water levels for Lake Superior from 1983 to 2003 during the summer months were obtained from Fisheries and Oceans water levels database (Fisheries and Oceans 2005). All reported water levels were referred to the International Great Lakes Datum (IGLD) of 1985.

In order to determine if there was any trend for declining water levels, the mean water levels were plotted versus year and a linear regression calculated using Microsoft Excel version 2007.

1.2.4 Plant enclosure experiment

Enclosures were utilized at the study site to examine whether grazing from herbivores was occurring. This method has been successfully utilized to evaluate the long-term destruction of sub-arctic wetland vegetation in northern Manitoba (Kotanen and Jeffries 1996). For all possible causes, the results could be assessed by observing how well the transplanted test species *Eleocharis smalli* survived the season.

Enclosed plots measured an area of one square meter and were set one meter apart with unenclosed plots being designated in this space. Enclosures were constructed from metal t-fence posts that were hammered 0.5 m into the sediment. Snow fencing was wrapped and secured around the posts using plastic tie wraps to complete each enclosure. Ten *Eleocharis smalli* plant clusters containing four to five spikes each were transplanted into each plot (enclosed and non-enclosed).

Twenty test plots of (10 enclosed and 10 non-enclosed) *Eleocharis smalli* were planted at the north end of the marsh in early June of 2003. Five of the enclosed plots were located in 0.5 m of water in soft sediment and five enclosed plots were located in 0.5 m of water in firm sediment 10 meters from the first five enclosures (Figure 1.2). Plants were then observed over the summer months to determine whether or not a physical or biological component was impacting their growth and/or success in the wetland.

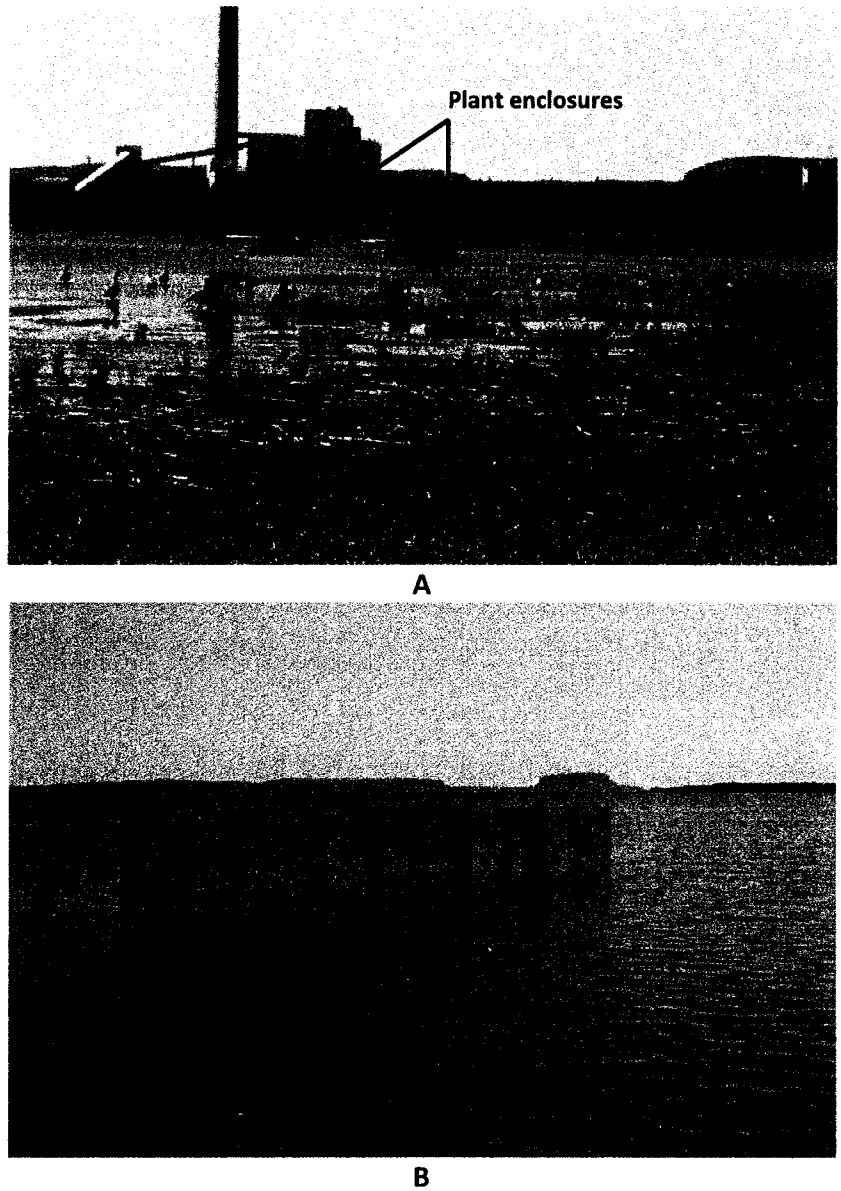

Figure 1.2. **A.** Location of Test plant enclosures at Mission Island Marsh during the summer of 2003 with Canada Geese foraging in the foreground; **B.** Close up of test plant enclosures located at north end of Mission Island Marsh during the summer of 2003.

1.2.5 Phytoplankton Assessment

In order to determine if algal species present could be classified according to their eutrophic level, two algae samples were collected in August of 2006 in 50 ml

polyethelene bottles and preserved with Lugol's solution. One sample was taken in open water near an algal bloom while a second was taken directly from an algal bloom in Mission Marsh. Samples were sent to ALS Laboratories in Winnipeg for species composition analysis. Standard method 10200, 2005 was used for algae identification. Samples were prepared using a sedimentation technique and were then examined using a compound phase contrast inverted microscope (ALS 2006). Final identification of algae by ALS Laboratories provided a general screen of dominant types of algae.

1.3 Results

1.3.1 Aerial photographs

Figure 1.3 shows the original 1983 photo for Mission Marsh and the classified image for the photo. Figure 1.4 shows the original 2002 photo for Mission Marsh and its classified image. The changes in the area for each of the five classes for the marsh are contained in Table 1.1.

From 1983 to 2002, 7.0 ha of vegetation were lost in the Deep Open Water (DOW) and 1.8 ha in the Shallow Open Water (SOW). The combined vegetative loss from the Submerged (S) and Floating/Emergent Vegetation (FEV) categories was 7.1 ha. Shoreline/Emergent Vegetation (SEV) losses totalled 1.7 ha. The greatest actual vegetative loss occurred in the Floating/Emergent Vegetation (FEV) population (3.9 hectares), while the greatest relative loss occurred in the Shoreline/Emergent Vegetation (73.9%). Overall loss of vegetation in Mission Marsh was 8.8 ha or 39.6%.

Figure 1.3. Original photograph of Mission Island Marsh taken in May of 1983 (City of Thunder Bay 1983) and the classified image. (Deep Open Water (blue), Submerged Vegetation (dark green), Floating/Emergent Vegetation (light green), Shoreline/Emergent Vegetation (yellow), and Shallow Open Water (tan)).

Figure 1.4. Original photographs of Mission Island Marsh taken in May of 2002 (City of Thunder Bay 2002a and 2002b) and the classified image. (Deep Open Water (blue), Submerged Vegetation (dark green), Floating/Emergent Vegetation (light green), Shoreline/Emergent Vegetation (yellow), and Shallow Open Water (tan)).

Table 1.1. Vegetation changes in plant communities identified by spectral analysis.

Classification Category	Total Area (ha) in 1983	Total Area (ha) in 2002	Change (ha) +/-	Percent Change %
Water	10.5	17.5	+7.0	+66.6%
Submerged	12.8	9.6	-3.2	-25.0%
Floating/Emergent	7.1	3.1	-3.9	-54.9%
Shoreline/Emergent	2.3	0.6	-1.7	-73.9%
Sand	1.1	3.0	+1.9	+172.7%
Total Vegetation	22.2	13.3	-8.8	-39.6%

1.3.2 Water levels

Table 1.2 lists the monthly mean water levels for Lake Superior during the growing seasons of 1983 through 2002. Only three years record lower average water levels than 2002: 1988, 1990 and 2000. In terms of the two photo years analyzed, 2002 had lower water levels than 1983 for all months. For all preceding years, summer water levels were higher in all months for 12 of the 18 years. This trend in water levels is shown by Figure 1.5. Although there is considerable scatter, there is a significant correlation ($R=-0.57$, $P< 0.05$) of declining water levels versus time.

Table 1.2. Monthly mean water levels for Lake Superior from 1983 to 2003 during the growing season. Lake Superior monthly mean water levels in metres referred to IGLD 1985 (Fisheries and Oceans 2005).

Year	May	June	July	August
1983	183.51	183.59	183.64	183.63
1984	183.49	183.59	183.65	183.66
1985	183.58	183.66	183.74	183.81
1986	183.74	183.76	183.81	183.84
1987	183.42	183.46	183.50	183.55
1988	183.24	183.26	183.27	183.39
1989	183.39	183.50	183.53	183.52
1990	183.18	183.25	183.35	183.36
1991	183.32	183.37	183.46	183.46
1992	183.32	183.36	183.45	183.47
1993	183.38	183.48	183.56	183.62
1994	183.40	183.46	183.53	183.56
1995	183.26	183.31	183.37	183.40
1996	183.46	183.60	183.70	183.78
1997	183.64	183.65	183.72	183.68
1998	183.34	183.39	183.41	183.38
1999	183.20	183.31	183.43	183.47
2000	183.16	183.24	183.33	183.31
2001	183.24	183.32	183.36	183.39
2002	183.26	183.31	183.36	183.40
2003	183.18	183.23	183.26	183.29

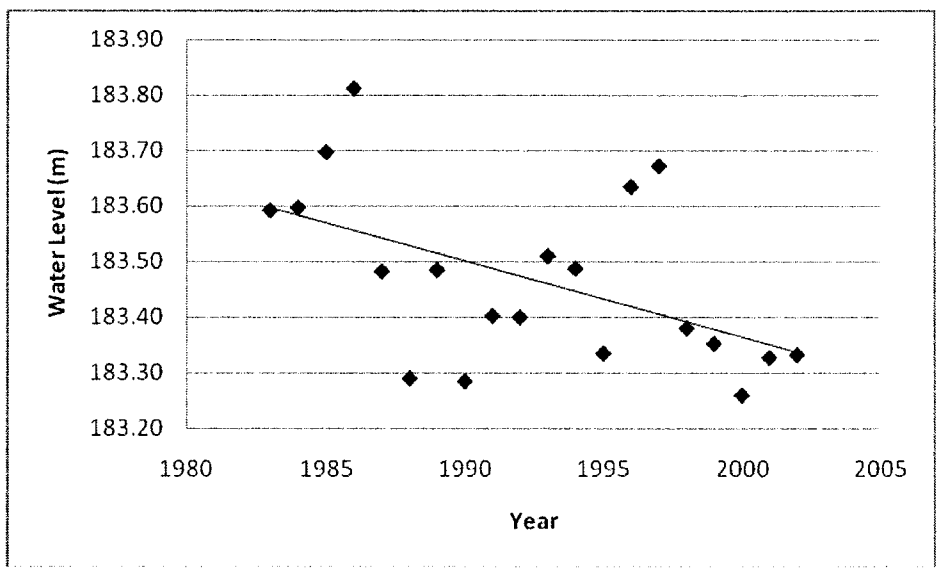

Figure 1.5. Monthly mean May – August water levels for Lake Superior versus year from 1983 to 2002 (Water Level = -0.014 Year + 212.29; r = -0.57).

1.3.3 Plant enclosure experiment

The enclosure experiment was monitored monthly throughout the summer and results are contained in Table 1.3 and visually shown in Figure 1.6. A small reduction in the total number of plants used occurred within both enclosed and open plots due to wave action removing a few transplants. Surviving transplants in both enclosed and open plots grew new spikelets throughout the growing season. The transplants in the open plots, however, were observed heavily foraged to within a few centimeters of the water. By August, 2003, all of the successful transplants within the enclosures survived the season and thrived growing to full height. Enclosures were left intact until the following spring.

Enclosed plants within the enclosures continued to thrive the following growing season while the uneclosed plants were reduced in number or failed to survive.

Table 1.3. Results of enclosure experiment using Eleocharis smalli, summer 2003, spring 2004.

	Enclosed	Unenclosed
Total plots	10	10
Total *Eleocharis smalli* planted	100	100
Transplanted *Eleocharis smalli* surviving to end of August, 2003	97	96
Grazing Damage (%)	0	100
Transplanted *Eleocharis smalli* attaining full size by end of August, 2003	97	0
Survivorship, 2004 (%)	100	16

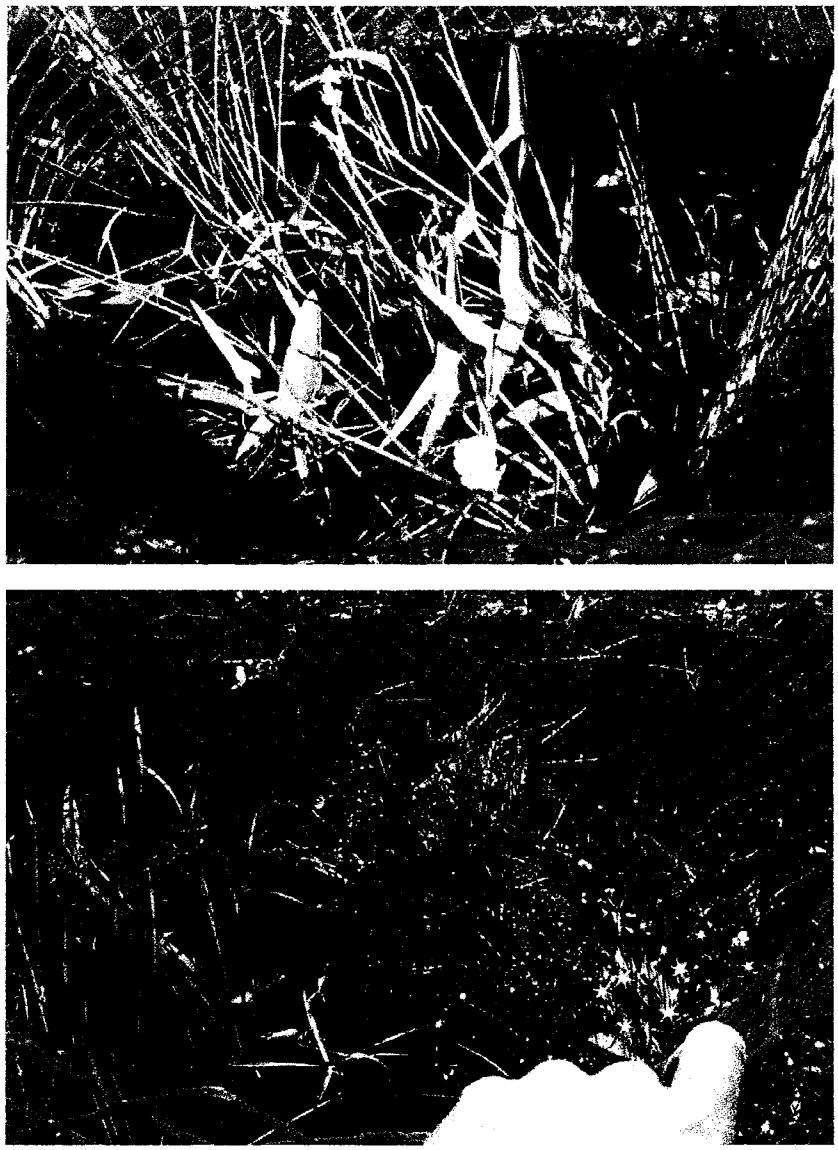

Figure 1.6. Test plants within enclosures thriving along with enclosed resident species of aquatic macrophytes in August, 2003.

1.3.4. Eutrophication - phytoplankton blooms

During observation of the study site algae blooms were observed each summer with the most significant blooms observed during the months of July and August (Figure 1.7). Table 1.4 shows the composition of algal species contained within the open water of the marsh compared to those present within an algal bloom (Table 1.5). In addition to a

reduction of the number of species from 24 to 13 between the open water and the algal bloom, there was also a change in species composition indicative of the trophic status. In the open water, the dominant genera were diatoms (*Bacillariophyceae)* of which *Amphora, Cocconeis, Fragilaria, Navicula, Rhoicosphenia* and *Tabellaria* occurred at moderate or large amounts. Diatoms are often indicators of oligotrophic conditions. A total of fourteen diatomaceous species occurred in the open water. By contrast, only four species of diatoms were present in the algal bloom and only in very small concentrations. The dominant genera in the algal bloom, which formed the algal mat, was *Rhizoclonium* which is a member of the *Cladophoraceae* family and a common indicator of eutrophic conditions. Green algae genera of *Cosmarium, Oedogonium, Pediastrum* and *Scenedesmus* were also present in large or moderate amounts in the algal bloom. These are indicators of nutrient enrichment (Great Lakes Environmental Research Lab 2007).

Figure 1.7. Large matting algal bloom at Mission Island Marsh extending further into Lake Superior on August 30, 2005. Goose moult feathers are evident in the foreground.

Table 1.4. Phytoplankton composition in the north marsh open water sampled in August, 2006 and categorized according to their trophic status.

Trophic Condition	Genera	Quantity
Oligotrophic:	*Amphora*	Moderate amounts
	Cocconeis	Large amounts
	Cyclotella	Small amounts
	Epithemia	Scarcely present
	Melosira	Scarcely present
	Navicula	Large amounts
	Rhodomonas	Scarcely present
	Stephanodiscus	Small amounts
	Tabellaria	Moderate amounts
Mesotrophic:	*Asterionella*	Small amounts
	Fragilaria	Large amounts
	Gomphonema	Small amounts
	Rhoicosphenia	Large amounts
Eutrophic:	*Anabaena*	Small amounts
	Ceratium	Small amounts
	Coelastrum	Scarcely present
	Cosmarium	Scarcely present
	Cryptomonas	Small amounts
	Dinobryon	Small amounts
	Mallomonas	Scarcely present
	Oedogonium	Small amounts
	Pediastrum	Small amounts
	Scenedesmus	Scarcely present
	Synedra	Moderate amounts

Table 1.5. Phytoplankton composition in the algal bloom sampled in August, 2006 and categorized according to their trophic status.

Trophic Condition	Genera	Quantity
Oligotrophic:	*Amphora*	Scarcely present
	Cocconeis	Small amounts
Mesotrophic:	*Fragilaria*	Scarcely present
Eutrophic:	*Closterium*	Scarcely present
	Cosmarium	Large amounts
	Crucigenia	Scarcely present
	Cryptomonas	Scarcely present
	Merismopedia	Scarcely present
	Oedogonium	Moderate amounts
	Pediastrum	Large amounts
	Rhizoclonium	Large amounts
	Scenedesmus	Large amounts
	Synedra	Scarcely present

1.4 Discussion

1.4.1 Loss of vegetation

The results (Figures 1.3, 1.4) showed that there was a 40% reduction in vegetation in Mission Marsh from 1983 to 2002. The greatest loss occurred with the floating or emergent species (Table 1.1) which combined totalled 64% of the total loss in vegetation. The net result was that the marsh now has more deep and shallow unvegetated zones with noticeable changes in vegetation. The dominant species historically were emergents consisting of grasses, sedges, horsetails, pondweeds,

rushes, cattails and arrowheads (McKever and Elder 1981). *Eleocharis smallii* was the most prevalent. Now the emergent vegetation community is reduced to only sporadic populations of mostly pondweeds and arrowheads. Grasses, sedges and horsetails continue to grow near the water's edge and on the mudflat at the north end of the marsh. Submerged vegetation continues to grow throughout the wetland in a similar pattern as documented in 1983. Known historical changes since 1982 should be the cause of this vegetation loss.

1.4.2 Effect of depth

Water levels have shown a decline in Lake Superior since 1982 (Table 1.2, Figure 1.5). This resulted in corresponding lower water depths in Mission Marsh. Although water depths that are too shallow can extirpate annuals like wild rice by dessicating the seeds in the winter (Aiken et al. 1988), generally lowering water levels increases production of emergent macrophytes (Abraham 2005; Keddy et al. 1986). *Eleocharis spp.*, in particular, which were the dominant species in the marsh in 1983, grew well at shallow depths (Newmaster et al. 1997). Furthermore the results of the enclosure experiment (Table 1.3) showed that *Eleocharis spp.* and resident plants within the enclosures (pondweed, rushes, arrowhead) thrived in 2003 and overwintered successfully to 2004. Depth can therefore be dismissed as a direct cause of vegetation decline in Mission Marsh.

1.4.3 Effect of eutrophication

There was clear evidence that the algae community changed from oligotrophic in the open water (Table 1.4) to eutrophic near shore where the algae mates occurred (Table 1.5). Algae genera of *Cosmarium*, *Oedogonium*, *Pediastrum* and *Scenedesmus* dominant in the matting algae bloom sample are all indicators of nutrient enrichment (Environmental Protection Agency 2006). *Cosmarium* are commonly found in large numbers in alkaline eutrophic conditions as is the case with Mission Island Marsh during the peak summer months. *Oedogonium* is a filamentous mat forming algae found in nutrient-rich wetlands (GLER 2007). *Pediastrum* and *Scenedesmus* are especially common throughout North America in nutrient-rich environments (GLER 2007).

More problematic were the algal mats dominated by the *Cladophoracea, Rhizoclonium,* which were common in parts of Mission Marsh in 2005 (Figure 1.7). The dominance of this highly eutrophic species in the algal blooms present in the marsh (Table 1.5) represented a major change from the oligotrophic diatoms dominating the open water (Table 1.4). *Cladophora* species have become a major eutrophication problem in many parts of the Great Lakes (Bootsma et al. 2004; GLER 2007). It is well known that these mat forming algae can cause mortality to aquatic macrophytes and completely eliminate them under certain severe cases of extreme infestation (Lee and Stewart 1981; Wang et al. 2009). The mode of action of *Cladophora spp.* is to effectively smother the macrophytes by coating their leaves and preventing normal gaseous exchange.

Eutrophication and the associated production of mat forming algae can therefore not be dismissed as a factor in the reduction of vegetation in Mission Marsh.

1.4.4 Toxicity effects

Aquatic plants, like aquatic animals, are sensitive to a variety of contaminants that result in reduced growth or mortality (Pfugmacher 2004). Although changes did occur in the treatment of effluent by the paper mill downstream of Mission Marsh, they had no toxic effect on plants since the enclosure experiment demonstrated that luxuriant growth of macrophytes occurred within the protected cages (Figure 1.6).

1.4.5 Grazing effects

The results (Table 1.3, Figure 1.6) showed that grazing was a major factor in the reduction of vegetation in Mission Marsh. Outside the enclosures, the emergent vegetation was chewed to just above the water surface while *Eleocharis spp* and resident plants within the enclosures (pondweed, rushes, arrowhead) thrived. In addition, virtually all emergent vegetation at the north end of the marsh had been foraged. The following spring, the non foraged plants survived while the grazed plants generally did not survive. The major suspect for grazing was Canada Geese. This suspicion was primarily due to the fact that they were not present in the Thunder Bay Harbour area prior to 1982 and they were observed during this study grazing on plants within Mission Marsh. In other studies, Canada Geese have also been shown to drastically impact wetlands where a suitable source of vegetation for grazing exists.

In 1985 a study of the Canada Geese at James Bay, Ontario (Prevett et al. 1985) revealed that grasses, sedges, and horsetails comprised approximately 83% of the Canada Goose diet in the spring months. Coleman and Boag (1987) found that shoots of sedges and horsetails and rhizomes of pondweed were shown to remain an important food source for the geese throughout autumn at one of the most important fall staging grounds for Canada Geese, the Nisutlin River in the southern Yukon. Concentrations of waterfowl in areas with preferred species of macrophytes such as the tidal marshes of the St. Lawrence Estuary in Quebec (Giroux and Bédard 1987) and Long Point on Lake Erie in Ontario (Badzinski et al. 2006) were shown to largely reduce plant biomass. Since the rhizomes of macrophytes serve as a carbohydrate reserve for the plant, their removal by late foraging geese when macrophyte growth decreases becomes particularly damaging to any future plant production (Giroux and Bédard 1987). Certainly the vegetation at Mission Marsh would be considered preferential for Canada Geese.

Historically, according to McKever and Elder (1981), the predominant emergent vegetation growing at the north end of the marsh consisted of grasses, sedges, horsetails, cattails, pondweeds and arrowheads. Research has shown that the shoots and rhizomes of most of these species constitute a major portion (83%) of the Canada Goose diet (Coleman and Boag 1987; Prevett et al.1985). Physical evidence of uprooted, trampled and chewed vegetation was observed throughout the north end of the wetland where the enclosures were located (Figure 1.2).

The habitat at this study site was also ideal for Canada Geese. Canada Geese prefer open areas near water where they have a clear view of predators (Smith et al. 1999). Thus, the north end of Mission Island Marsh where the greatest amount of foraging occurred was ideal for the geese. The landscape is very gently sloped with a large open mud flat area that has historically grown short grasses and sedges (McKever and Elder 1981). The lower water levels and the corresponding exposure of the sediments at the marsh allowed for a suitable grazing habitat for the geese as they completed their annual wing moult and were able to graze on preferred vegetation.

1.4.6 Synergistic effects

Although grazing caused by Canada Geese was likely the reason for major destruction of vegetated areas in Mission Marsh, synergistic effects may have contributed to the extent of this loss. The lower water levels in recent years allowed for a more preferable habitat for the geese to establish and so grazing and trampling of vegetation would increase. This is consistent with Olgilvie's (1978) view that a marsh that has been intensively foraged by geese becomes a mud flat with uprooted plants and broken vegetation. Shallower water levels in Mission Marsh thus enhanced the impact of the geese. The geese likely also caused localized eutrophication. The presence of even small numbers of geese can result in nutrient loading in small wetlands and waterways due to a high density of goose droppings (Allan et al. 1995; Conover and Chasko 1985; Scherer et al. 1995). The formation of algal mats in the marsh likely accelerated the decline of macrophytes. In this instance, the geese would have been acting as non-point nutrient

contributors. The next chapter of the thesis will concentrate on whether eutrophication on the Thunder Bay waterfront could be attributed to this non-point versus point source of nutrient elevation.

1.5 Conclusions

The loss of vegetation in Mission Marsh was able to be accurately quantified using image analysis. Compared to 1983, there was a 40% loss of vegetation in the marsh with most of the loss being due to emergent and floating leaf species. Grazing, likely by Canada Geese, was considered to be the most likely reason for this vegetation loss. Synergistic effects of both lower water levels in the marsh and enhanced eutrophication causing algal mats were suspected as causing added losses of macrophytes.

Future research that quantifies more accurately the loss of vegetation preferred by Canada Geese would be a priority for additional studies. The outline of such a study that was vandalized is contained in Appendix A.

2. Point and non-point sources of eutrophication on the Thunder Bay waterfront

2.1 Introduction

Although oligotrophic and unproductive overall many areas of Lake Superior have regions of higher productivity in the form of coastal wetlands, primarily marshes (Maynard and Wilcox 1997). These wetlands are areas of great ecological importance to the lake as they serve as habitat and migratory staging grounds for a rich biodiversity of birds and breeding grounds and habitat for aquatic organisms (Brazner and Beals 1997; Jude and Pappas 1992). Unfortunately, over the past several decades the coastal wetlands of the Laurentian Great Lakes have been decreasing or disappearing entirely (Mitsch and Bouchard 1998). This is mostly due to human activities (Maynard and Wilcox 1996; Seilheimer et al. 2007).

The direct effects of urbanization have resulted in the complete decline of wetlands in some coastal areas of the Laurentian Great Lakes, in particular, southern Ontario (Seilheimer et al. 2007; Whillans 1982). Similarly, Morrice et al. (2007) found that, while variable, anthropogenic stressors both direct and indirect influenced the water quality of the wetlands along the United States coastline of the Great Lakes.

As reviewed in the General Introduction and Chapter 1, biological stressors, in particular common carp (*Cyprinus carpio*) and Canada Geese (*Branta canadensis*) have negatively

impacted wetland structure and water quality in many wetlands (Badzinski et al. 2006; Giroux and Bedard 1987; Jeffries et al. 2006; Whillans 1996). However, it is not always possible to isolate single sources of degradation. For example, the well-documented decline of Cootes Paradise Marsh on western Lake Ontario is due largely to invasive carp activity compounded by point sources of pollution (Chow-Fraser 1998). Synergistic effects of anthropogenic stressors make it difficult to quantify the relative impact of each type of stressor (Chow-Fraser et al. 1998). Furthermore, the boundaries between point and nonpoint sources of pollution are often indistinct (Mander and Forsberg 2000).

This study examined the potential cause of water quality changes near Mission Island Marsh located on the western shore of Lake Superior within the city limits of Thunder Bay, Ontario, Canada. The main river feeding into Lake Superior near the wetland is the Kaministiquia River which branches into the McKellar and Mission Rivers that isolate Mission Island. Water quality effects in this area are from both point and nonpoint sources. Upstream approximately 9 km from the marsh, a Kraft and newsprint mill intakes its process water from the Kaministiquia River immediately upstream of the mill and following full secondary treatment discharges it downstream of the mill via a submersed diffuser. The second point source is Thunder Bay's Water Pollution Control Plant (WPCP) which discharges secondary treated effluent approximately 2 km from the mouth of the Kaministiquia River. The suspected nonpoint source of water quality effects was Canada Geese which use Mission Island Marsh and the surrounding

tributaries as feeding and staging grounds. Enclosure experiments in Chapter 1 indicated Canada Geese were the likely cause of vegetation decline in the marsh and eutrophication evident in the persistent algal blooms occurring at the marsh caused by fecal input from the geese. It is well known that waterfowl, in particular geese, can accelerate eutrophication of water bodies through their fecal input and foraging activity as numbers increase (Allan et al. 1995; Bazely and Jeffries 1985,1989; Harris et al. 1981; Manny et al. 1994; Pettigrew et al. 1998; Post et al. 1998; Scherer et al. 1995).

This study evaluates the water quality at Mission Island Marsh and surrounding tributaries from May to September in 2005 and 2006. The main focus in the water quality analysis in this paper is parameters indicative of eutrophication and the objective was to determine whether the source of these nutrients was from point versus nonpoint sources.

2.2 Methods

2.2.1 Study site and field sampling

The study site is shown by Figure 2.1 and was described in detail in Chapter 1. During late May of 2005, water samples were taken from the north and south end of Mission Island Marsh for analysis (Sites 5 and 6). Also included for analysis at this time was a control sample outside of the marsh at the lakefront near the mouth of the McKellar River (Site 4). By July of 2005 results of the water quality analysis indicated

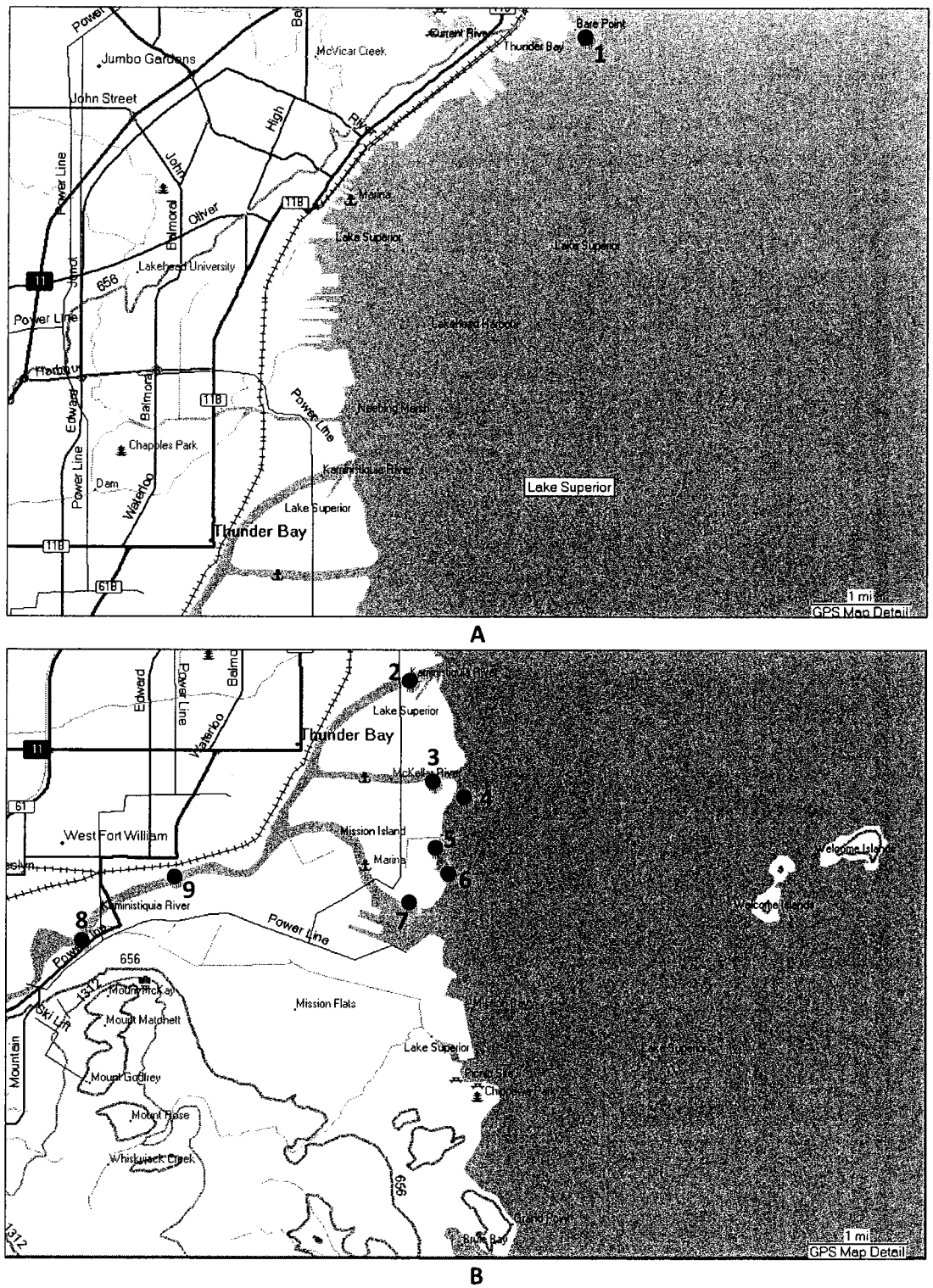

Figure 2.1. Water quality site locations: **A.** 1. Bare Point (control); **B.** 2. Kaministiquia River; 3. McKellar River; 4. Lakefront; 5. North marsh; 6. South Marsh; 7. Mission River; 8. Above Mill; 9. Below Mill.

that the lakefront location was not an appropriate control. The study was then amended to include four additional sites: Mission River (Site 7), McKellar River (Site 3), Kaministiquia River (Site 2) and Bare Point (Site 1) as a control. The point source sites were also added and were located immediately upstream (Site 8) and downstream (Site 9) of the Kraft and newsprint mill on the Kaministiquia River. Site 2 was confounded by both effluent from the Thunder Bay Water Pollution Control Plant (WPCP) as well as suspected nonpoint sources. As such, results of effluent from the WPCP were obtained from the City of Thunder Bay. Sampling continued in 2006, but due to the cost of analyses, the point source sites were not sampled.

Monthly samples at a depth of 0.5 m were collected from May to September and included both field and travel blanks. Samples were collected in 500 mL Nalgene bottles for pH, conductivity, nutrient analysis, alkalinity and metals. Water temperature and dissolved oxygen levels were taken in the field using YSI dissolved oxygen/temperature field meter. Samples were taken from the field and immediately refrigerated until processing the same or following day in the Environmental Analytical Laboratory of Lakehead University's Centre for Analytical Services.

2.2.2 Laboratory procedures

All in-lab analysis adhered to strict Quality Assurance/Quality Control (QA/QC) Protocols. A blank sample was run at the beginning of each tested parameter, followed by a standardized QA/QC sample and a repeat of the succeeding field sample. The

QA/QC and the repeat samples were tested after every ten field samples. Each of the tests followed Lakehead University Environmental Lab (LUEL) Standard Operating Procedures (LUEL 2000) which were modified from Standard Methods for the Examination of Water and Wastewater 18^{th} ed. by Greenberg et al., 1992. Any samples with extreme outliers were retested to confirm their values.

Alkalinity, pH, and conductivity were measured within 24 hours of sampling, after samples reached ambient laboratory temperature. A 50 ml aliquot of the unpreserved water sample was analysed for alkalinity and pH using the automated Mettler DL20 Compact Titrator with Mettler Probe #DG115-SC. Conductivity was measured with a VWR Digital Conductivity Meter with Automated Temperature Compensation calibrated at 200 $uS \cdot cm^{-1}$.

An aliquot of the filtered water sample was used to determine anion NO_2 and NO_3 concentrations using a Dionex DX-120 Ion Chromatograph (IC) in conjunction with an AS40 automated sampler. The two values were then combined to give the value for NO_x.

Total Phosphorus and Total Kjeldahl Nitrogen (TKN) were digested then analysed using a colorimetric determination on the Skalar Autoanalyser system. Before analysis, samples were treated with sulphuric acid and digested stepwise to $400^{\circ}C$ to achieve a three fold preconcentration. The samples were then restored to their original volume. TKN concentrations were determined spectrophotometrically at 660 nm based upon a

modified Berthelot reaction. Total Phosphorus was simultaneously carried out on the same sample aliquot. The digestion converted all forms of phosphorus to orthophosphate which was determined colorimetrically at 880nm based on the ascorbic acid procedure (Greenberg et al. 1992).

An aliquot of the sulfuric acid preserved water was used for the determination of Ammonia-Nitrogen (NH_4-N). The method was also based on the modified Berthelot reaction: ammonia was chlorinated to monochloriamine which reacted with salicylate to 5-aminosalicylate. After oxidation and oxidative coupling a green coloured complex was formed. The absorption of the formed complex was measured spectrophotometrically at 660 nm using the SKALAR.

Total metals analysis was performed after a nitric acid digest at 100°C for 12 -24 hours resulting in a two fold concentration of the sample. Samples were analysed using the Jarrell Ash Inductively Coupled Argon Plasma 9000 Spectrometer (ICP) for Fe, Mn, Zn, Cu, Ni, Al, B, Co, Cr, Sr, Ca, B, S, K, Mg, and Na. Only those elements that were above detection limits were included in the results.

Monthly averaged total phosphorus, pH and ammonia levels in treated effluent were obtained from the City of Thunder Bay's Water Pollution Control Plant reports for 2005 and 2006 (City of Thunder Bay 2005, 2006).

2.2.3 Data analysis

Data analysis proceeded in three steps:

(i) In order to assess whether the degree of variation differed among the nonpoint and point sites, coefficient of variance was calculated for all parameters at all sample locations for each year.

(ii) Non-metric multidimensional scaling (NMS), a nonparameteric ordination technique, was performed on the log transformed nutrient data (NH_3, TKN, NO_x, TOTP) to calculate the amount of variation among and within the sampling sites using PC-ORD v5.10 (Kruskal 1964). This type of analysis allows multi-dimensional, multivariate data to be viewed in a few dimensions. Since ranked distances are used in this method it is a more robust technique to use for data that may not be normally distributed. NMS was performed using the squared Euclidean distance measure.

(iii) Results of the NMS analyses were visualized using the graphing option in the PC-ORD program.

2.3 Results

Although a complete water quality analysis (Appendix B) was performed, only the parameters that show evidence of eutrophication are discussed in detail. The metals analysis (Table 1) indicated parameters within acceptable ranges or below detection limits.

Table 2.1. Metal analysis for 2005 and 2006 at all sample sites. Values reported are in mg/L and are expressed as the seasonal mean value ± standard deviation.

Site #	Aluminum	Iron	Manganese	Calcium	Magnesium	Sodium	Barium	Sulfur
1. 2005	.025 ± .022	.034 ± .027	.003 ± .001	15.662 ± 1.362	3.201 ± .357	2.608 ± .552	.012 ± .001	1.393 ± .091
1. 2006	.070 ± .034	.049 ± .028	.003 ± .001	15.379 ± .653	3.118 ± .121	2.164 ± .369	.011 ± .001	1.396 ± .044
2. 2005	.104 ± .069	.165 ± .105	.026 ± .020	17.289 ± 3.010	3.997 ± 1.064	10.322 ± 6.950	.015 ± .004	3.773 ± 2.074
2. 2006	.085 ± .068	.196 ± .145	.025 ± .019	21.426 ± 10.390	4.822 ± 2.177	14.788 ± 17.589	.015 ± .004	3.798 ± 2.902
3. 2005	.074 ± .022	.140 ± .021	.015 ± .006	15.317 ± 2.169	3.278 ± .422	7.892 ± 2.775	.014 ± .002	3.477 ± .982
3. 2006	.109 ± .034	.219 ± .080	.021 ± .008	15.820 ± 1.176	3.650 ± .489	7.929 ± 1.806	.015 ± .002	3.382 ± .888
4. 2005	.120 ± .084	.317 ± .282	.016 ± .007	14.779 ± .854	3.367 ± .471	6.168 ± 2.720	.014 ± .002	2.880 ± 1.030
4. 2006	.206 ± .195	.440 ± .492	.021 ± .007	15.871 ± 1.265	3.670 ± .591	6.534 ± 3.107	.017 ± .004	3.104 ± 1.219
5. 2005	.096 ± .042	.413 ± .339	.025 ± .022	14.262 ± .914	3.382 ± .490	6.362 ± 2.487	.015 ± .003	2.629 ± .570
5. 2006	.294 ± .286	.877 ± .902	.028 ± .013	15.930 ± .994	3.910 ± .448	7.586 ± 2.347	.020 ± .005	3.530 ± 1.063
6. 2005	.033 ± .021	1.203 ± .292	.052 ± .027	17.041 ± 2.324	4.500 ± .480	7.650 ± 1.604	.025 ± .006	3.747 ± 1.115
6. 2006	.056 ± .054	1.318 ± .353	.077 ± .051	17.537 ± .795	4.368 ± .340	7.756 ± .991	.027 ± .003	3.142 ± 1.293
7. 2005	.084 ± .063	.186 ± .055	.032 ± .003	19.116 ± 1.423	5.416 ± .288	15.494 ± 4.843	.018 ± .002	6.483 ± 2.520
7. 2006	.137 ± .034	.417 ± .390	.034 ± .011	15.265 ± 1.127	3.676 ± .287	11.444 ± 2.931	.017 ± .001	4.996 ± 1.506

The temperature (11° C – 27° C) and dissolved oxygen (4 mg/L – 11 mg/L) levels were acceptable throughout the summer and at times the dissolved oxygen levels exceeded saturation due to the shallow depth of samples taken and the wave action of the lake. Most parameters showed temporal and localized variability during both sampling seasons.

2.3.1 pH and Ammonia

In 2005, pH levels at the nonpoint sites nearest Mission Marsh (Sites 4, 5, and 6) were alkaline throughout most of the sampling season (Figure 2.2). The highest pH values occurred during July at Site 6 (South Mission Marsh) with a pH of 10.13. pH values moderated by the end of August to near neutral or slightly alkaline conditions and by the end of the sampling season in early October all sample sites had slightly acidic pH values ranging from 6.54 at the north marsh site to 6.82 at Bare Point. Overall pH values

during 2006 were higher than those of 2005 with all sites having alkaline values ranging from 7.17 to 9.32. The point source locations upstream and downstream of the paper mill (Sites 8 and 9) exhibited little fluctuation with mean pH values of 7.8 and 7.2 respectively.

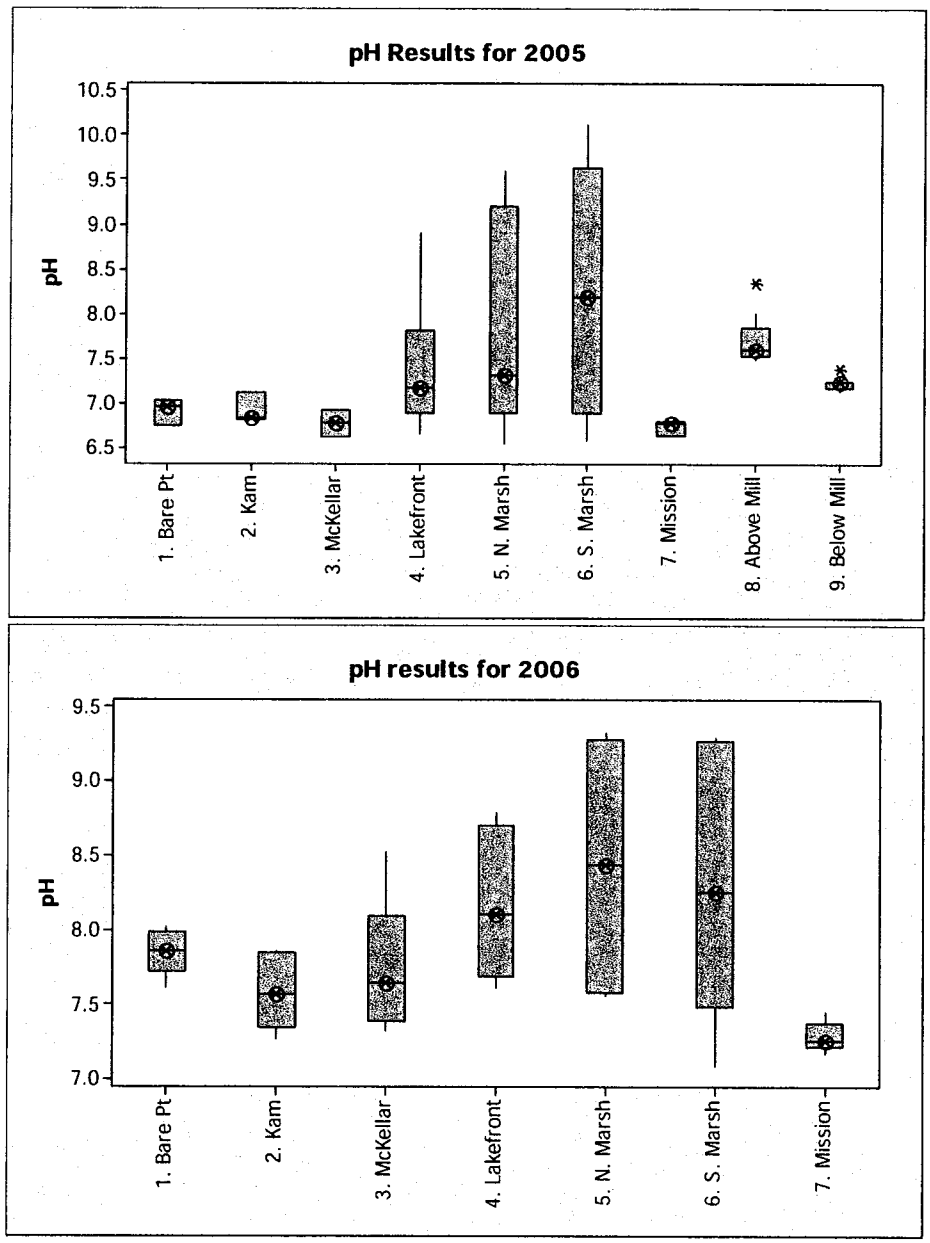

Figure 2.2. Comparison of pH values for all sample sites from May to October, 2005 and May to September, 2006. The solid line across each box represents the median value. The limits of each box represent the 25th and 75th percentiles of the data.

In 2005, ammonia levels at the nonpoint sample sites showed a general trend of increasing as the summer progressed (Figure 2.3). Toxic levels (>0.015 mg/L dependent on species (EPA 1999)) of ammonia occurred at Sites 7 (Mission River) and Site 2 (Kaministiquia River) in early August of 2005 with concentrations of 0.196 mg/L NH_3-N and 0.139 mg/L NH_3-N respectively. All sample locations with the exception of the Site 1 (Bare Point) were at chronic or toxic levels (> 0.015 mg/L) during late August of 2005 and early October of 2005 with values ranging from 0.048 mg/L NH_3-N at Site 4 (Lakefront) to 0.308 mg/L NH_3-N at Site 3 (McKellar River) and 2.072 mg/L NH_3-N at Site 2 (Kaministiquia River).

Chronic levels occurred more often during the 2006 sampling season (Figure 2.3) and included all sample sites with the exception of Site 1 (Bare Point) which remained below detection limits the entire summer. Levels were chronic in May of 2006 ranging from 0.069 mg/L NH_3-N at Site 7 (Mission River) to 0.156 mg/L NH_3-N at Site 3 (McKellar River). The sites nearest the marsh (Sites 4, 5, 6) were at chronic levels during June of 2006 with 0.05 mg/L NH_3-N at both the south marsh and lakefront sites and 0.062 mg/L NH_3-N at the north marsh site. Levels of ammonia rose to chronic values again in August and September of 2006 at most of the sites with the exception of Site 1 (Bare Point).

At the point source sites (Figure 2.3), ammonia levels were low with mean values of 0.03 mg/L +/- 0.17 at Site 8 and 0.03 mg/l +/- 0.22 at Site 9.

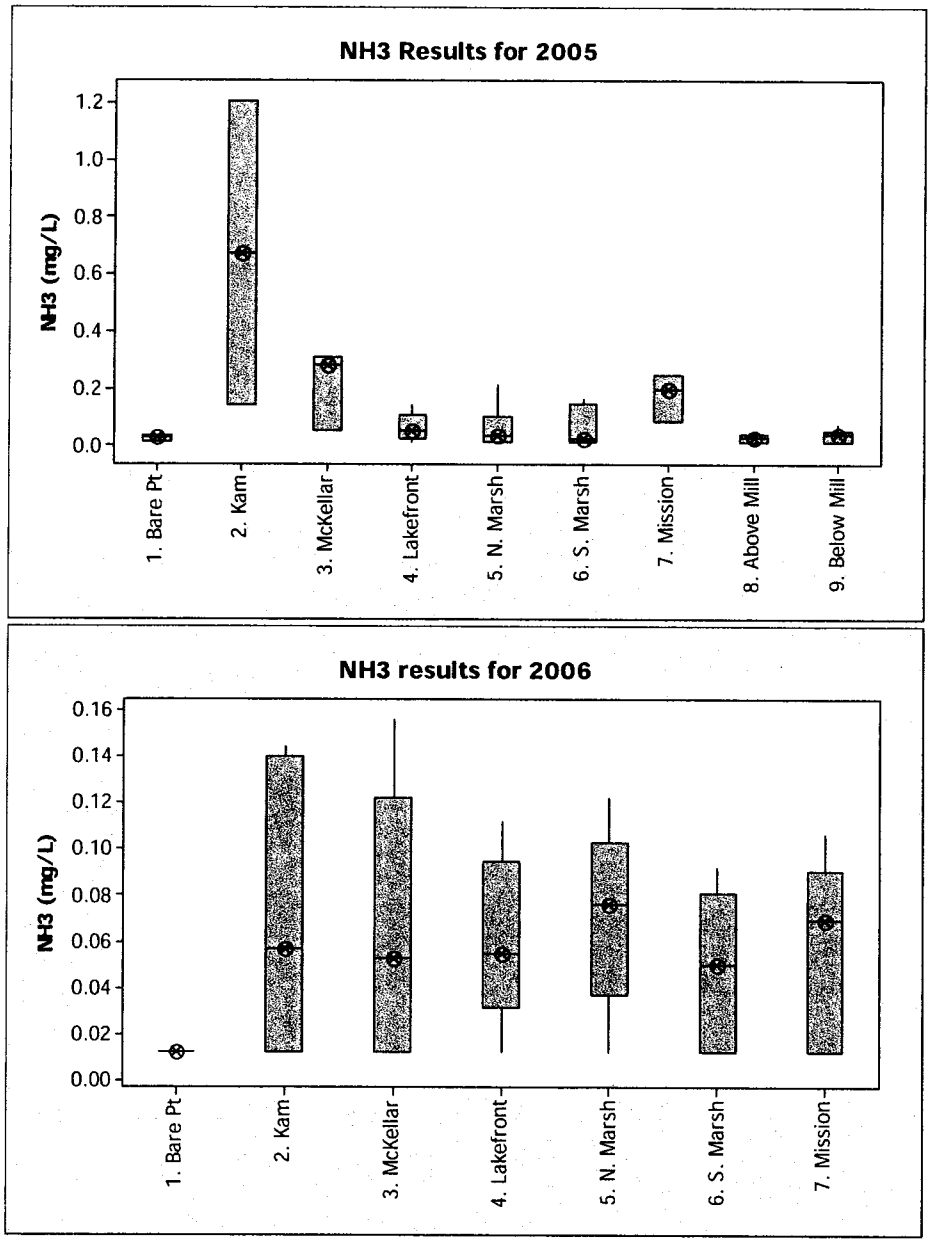

Figure 2.3. Comparison of ammonia values for all sample sites from May to October, 2005 and May to September, 2006. The solid line across each box represents the median value. The limits of each box represent the 25th and 75th percentiles of the data. (MDL = 0.025mg/L; results reported at 0.0125 are below detection limit)

2.3.2 Total Kjeldahl Nitrogen and NO_x

In both 2005 and 2006 total Kjeldahl nitrogen (TKN) (Figure 2.4) increased as the summer progressed. In both years, TKN was highest at Site 2 (Kaminstiquia River) and lowest at Site 1 (Bare Point). Levels of NO_x (Figure 2.5) were more variable than that of total nitrogen but still indicated levels increasing as each summer progressed. The highest levels for total nitrogen and NO_x occurred at the Kaministiquia River site at the end of each sampling season (1.5 mg/l, 2005; 2.6 mg/l, 2006). In both years, Bare Point had the lowest values.

In terms of the point source sites (Figure 2.4), both TKN and NO_x had low, relatively constant values during 2005. Site 8 (Above Mill) had mean TKN and NO_x values of 0.33 mg/l +/- 0.05 and 0.14 mg/l +/- 0.02 respectively while Site 9 (Below Mill) had TKN and NO_x values of 0.39 mg/l +/- 0.08 and 0.14 mg/l +/- 0.02 respectively. These values were very similar to what was found at Site 1 (Bare Point).

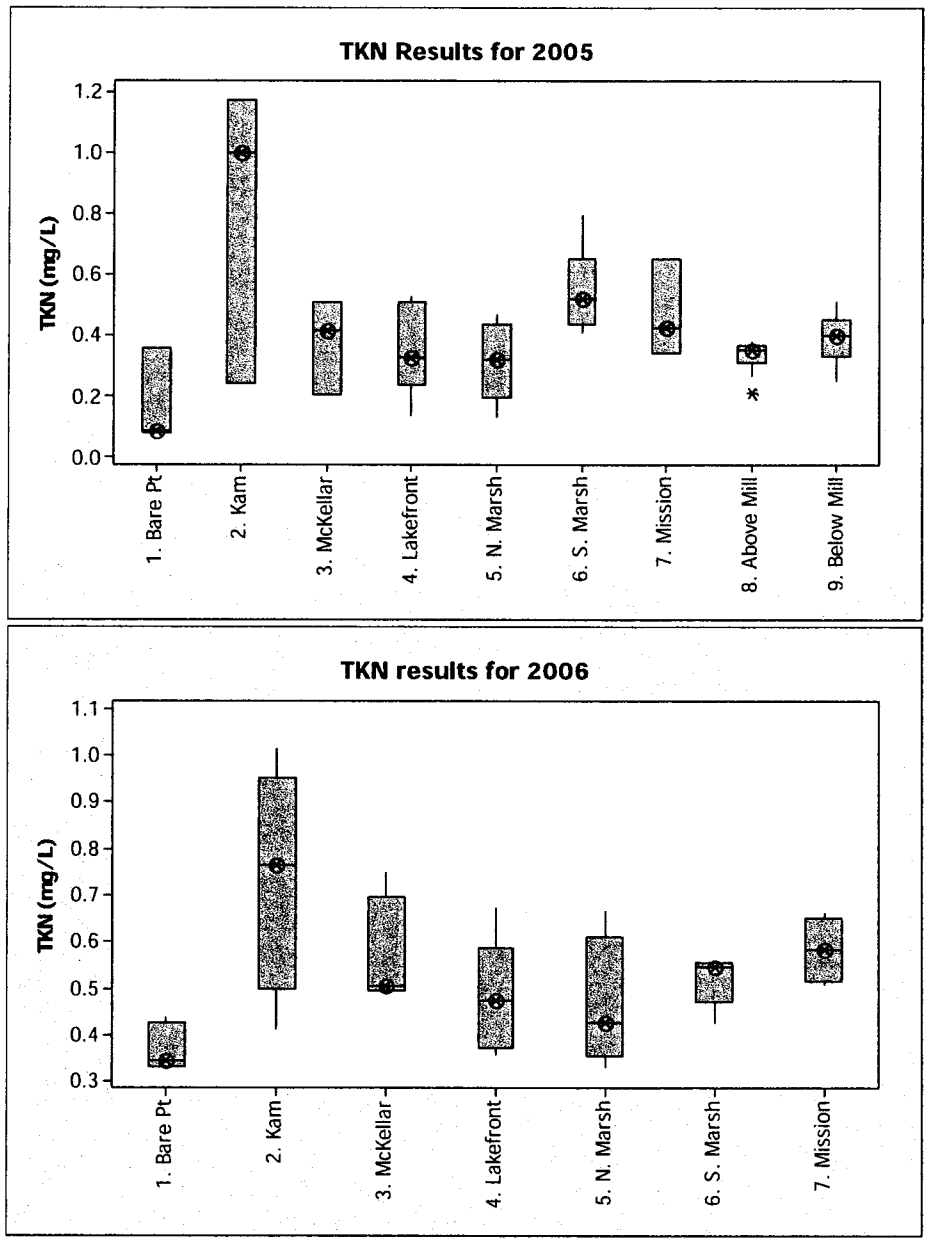

Figure 2.4. Comparison of total Kjeldahl nitrogen values for all sample sites from May to October, 2005 and May to September, 2006. An outlier of 6.24 mg/L in the Kaministiquia River in September of 2006 was not included in the graphic for better representation of the data. The solid line across each box represents the median value. The limits of each box represent the 25th and 75th percentiles of the data. (TKN: MDL = 0.015 mg/L). Outliers are indicated with an asterisk.

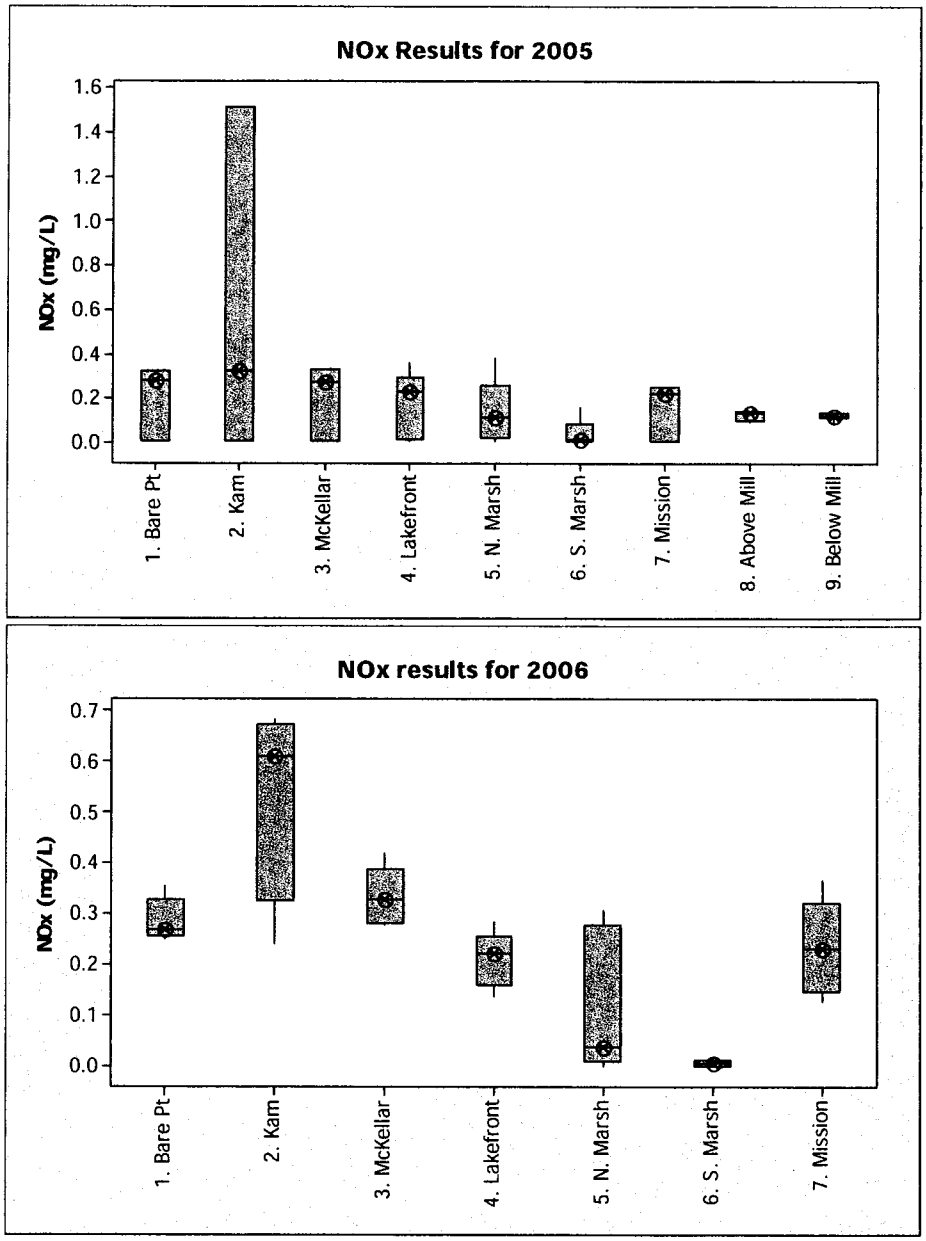

Figure 2.5. Comparison of total nitrates and nitrites values for all sample sites from May to October, 2005 and May to September, 2006. Total nitrates only were recorded for sites 8 and 9. An outlier of 2.583 mg/L in the Kaministiquia River in September of 2006 was not included in the graphic for better representation of the data. The solid line across each box represents the median value. The limits of each box represent the 25th and 75th percentiles of the data. (NOx: MDL = 0.0001 mg/L; results reported at 0.00005 are below detection limit)

2.3.3 Total Phosphorus

Phosphorus levels at all non point sample sites showed an increase in concentration as the summer progressed during both sample seasons in 2005 and 2006 (Figure 2.6). Mesotrophic levels of phosphorus (> 0.01 mg/L) were first evident at Site 6 (South Marsh) in June of 2005 when concentrations reached 0.020 mg/L. Site 1 (Bare Point) remained below detection limits during the 2005 sampling season. By the end of August, 2005 most of the sampling sites remained at mesotrophic to eutrophic levels ranging from 0.016 mg/L at Site 5 (North Marsh) to 0.062 mg/L at Site 7 (Mission River). By early October the levels of phosphorus moderated to some extent but remained at eutrophic levels at both Site 7 (Mission River) and Site 2 (Kaministiquia Rivers) with concentrations of 0.036 mg/L and 0.039 mg/L respectively. The summer of 2006 sampling season began with eutrophic levels of phosphorus at all sample locations with the exception of the control site at Bare Point (Site 1). Levels of total phosphorus (TOTP) in May of 2006 ranged from 0.026 mg/L at Site 5 (North Marsh) to 0.040 mg/L at Site 6 (South Marsh). Levels of phosphorus were highest for most sites during August of 2006 however the peak level recorded for the season was 0.257 mg/L at Site 2 (Kaministiquia River) in September of 2006.

The point source sites (Figure 2.6) showed concentrations of 0.01 mg/l +/- 0.004 at Site 8 (Above Mill) to 0.06 mg/l +/- 0.014 at Site 9 (Below Mill).

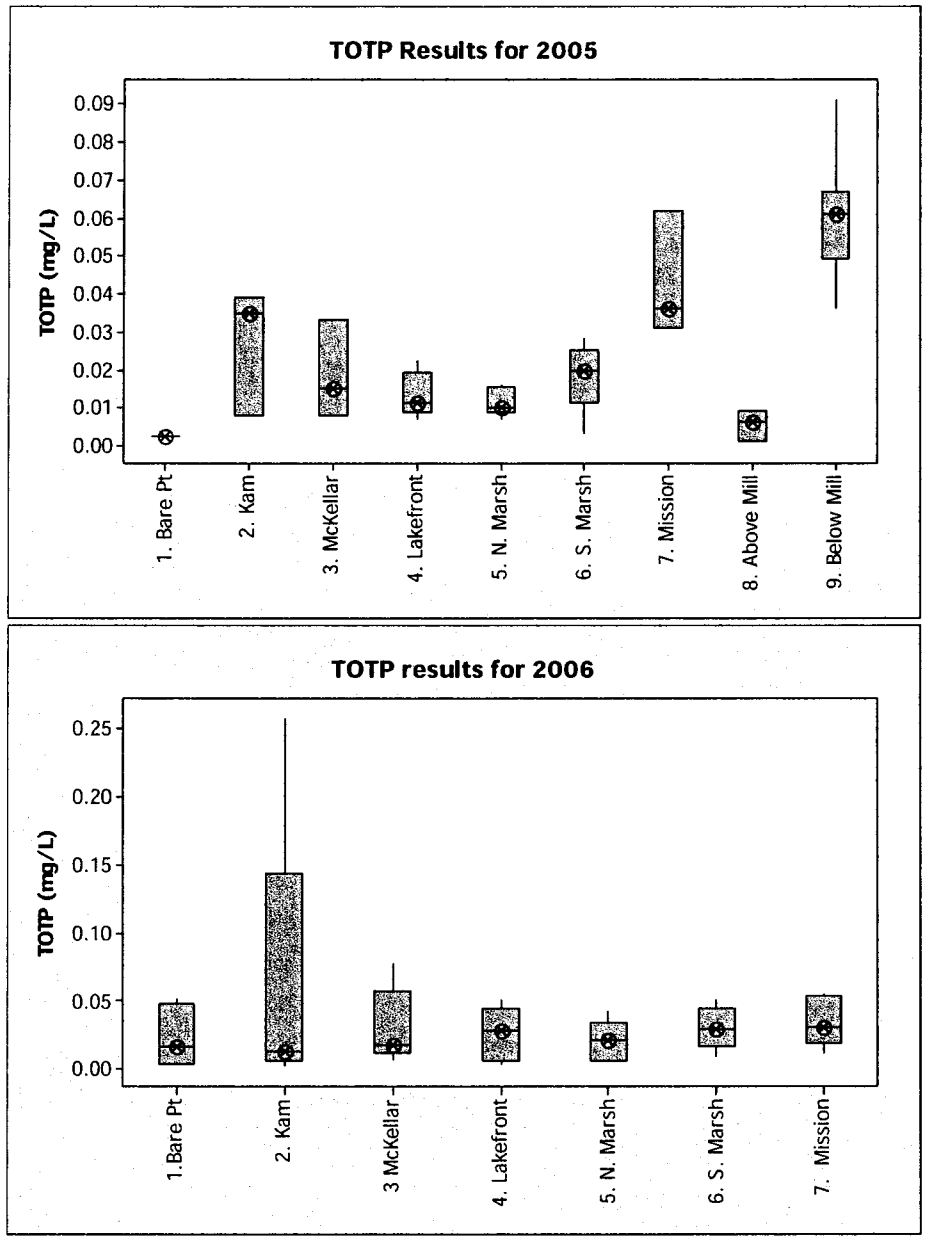

Figure 2.6. Comparison of total phosphorus (TOTP) values for all sample sites from May to October, 2005 and May to September, 2006. The solid line across each box represents the median value. The limits of each box represent the 25th and 75th percentiles of the data. (TOTP: MDL = 0.005 mg/L)

2.3.4 Parameter variability

Table 2.2 compares the coefficient of variation for both nonpoint and point sample sites for 2005 while Table 2.3 shows the coefficients of the nonpoint sites for 2006.

Table 2.2. Coefficient of variation for all sample locations for pH, TKN, NOx, NH3, and TOTP for July to early October during the summer of 2005.

Site	pH	TKN	NOx	NH_3	TOTP
1. Bare point	0.02	0.92	0.08	0.17	0.00
2. Kaministiquia River (mouth)	0.03	0.62	0.93	0.85	0.62
3. McKellar River	0.02	0.42	0.09	0.67	0.70
4. Lakefront	0.05	0.50	0.27	0.66	0.37
5. North Marsh	0.18	0.52	0.67	1.06	0.28
6. South Marsh	0.18	0.21	1.26	0.83	0.53
7. Mission River	0.01	0.34	0.12	0.47	0.39
8. Kaministiquia River (above mill)	n/a	0.15	0.14	0.56	0.40
9. Kaministiquia River (below mill)	n/a	0.19	0.14	0.73	0.23

Table 2.3. Coefficient of variation for all sample locations for pH, TKN, NOx, NH3, and TOTP for the summer of 2006.

Site	pH	TKN	NOx	NH_3	TOTP
1. Bare Point	0.02	0.14	0.14	0.00	0.85
2. Kaministiquia River (mouth)	0.03	1.34	0.99	0.76	1.76
3. McKellar River	0.06	0.20	0.17	0.79	0.90
4. Lakefront	0.06	0.26	0.28	0.51	0.98
5. North Marsh	0.10	0.29	1.20	0.48	0.75
6. South Marsh	0.11	0.11	1.04	0.56	0.51
7. Mission River	0.01	0.12	0.40	0.58	0.50

In 2005, Site 6 (South Marsh) and Site 5 (North Marsh) exhibited the greatest amount of parameter variability during the summer of 2005 (Figure 2.7). Ammonia exhibited the greatest amount of variability at all sites (with the exception of Site 1, Bare Point) ranging from CV of 0.47 to 1.06. A high degree of variation was also evident for nitrates

and nitrites (NO_x) with coefficient of variation values highest for Site 2 (Kaministiquia River) (CV = 0.99), Site 6 (South Marsh) (CV = 1.04) and Site 5 (North Marsh). Although it had the lowest concentrations (Figure 2.4), Site 1 (Bare Point) exhibited the highest amount of variability for Total Kjeldahl nitrogen with CV = 0.92 likely due to one outlier.

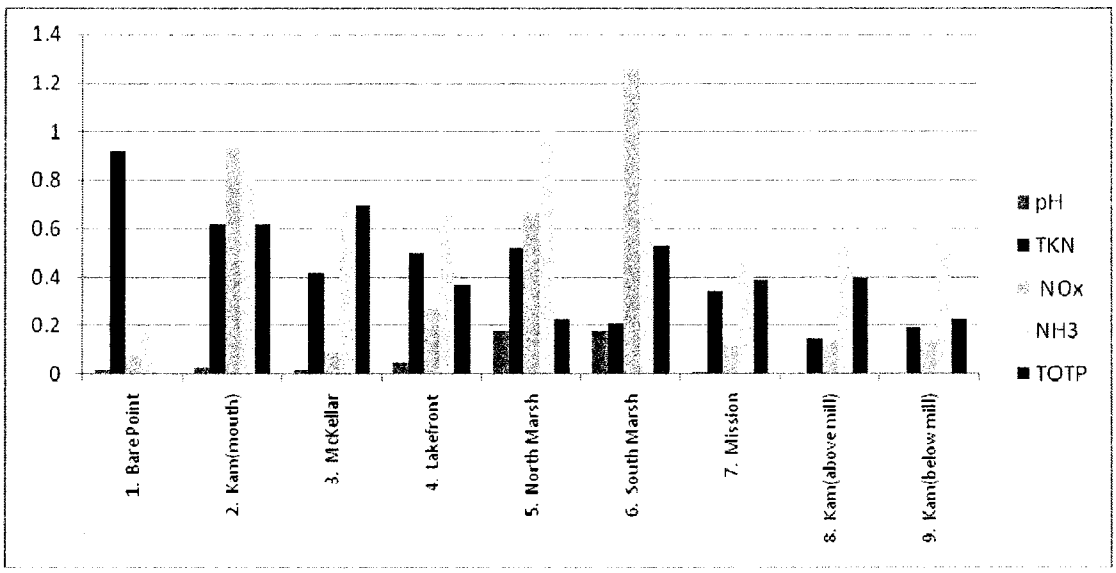

Figure 2.7. Comparison of the coefficient of variation for pH, TKN, NOx, NH3, and TOTP for all sample sites for July to October, 2005.

In 2006, Site 2 (Kaministiquia River) exhibited the greatest amount of parameter variability (Figure 2.8). Coefficient of variation values for this site were high for all nutrient parameters with values of 0.76, 0.99, 1.34 and 1.76 for ammonia, nitrates/nitrites, Total Kjeldahl nitrogen and total phosphorus respectively. A high degree of variation in NO_x was again evident at the South Marsh and North Marsh sites with coefficient of variation values of 1.04 and 1.20 respectively.

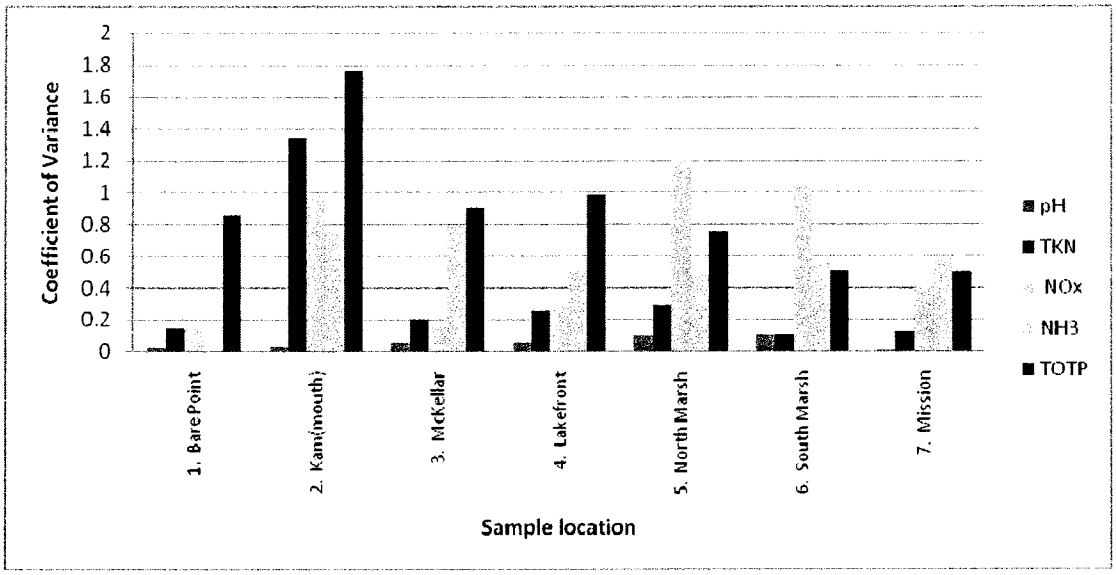

Figure 2.8. Comparison of the coefficient of variation for pH, TKN, NOx, NH3, and TOTP for all sample sites for May to September, 2006.

2.3.5 Effluent from Thunder Bay Water Pollution Control Plant

Table 2.4 documents the monthly average recorded levels of pH and TOTP for the final effluent from the City of Thunder Bay's Water Pollution Control Plant for 2005 and 2006, average monthly flow in the Kaministiquia River for 2005 and 2006, and results for TOTP and NH_3 for Site 2 (Kaministiquia River). Ammonia was recorded from June of 2006. Coefficient of variation for pH and TOTP for both years is included. Both pH and TOTP had low CV's versus the sampling sites (Table 2.4). Only Site 8 (Above Mill) had a lower CV for TOTP in 2005 and the CV's for pH were not exceeded by any of the sampling sites.

The NH_3 and TOTP values in Site 2 should be influenced by both the discharge from the treatment plant as well as any nonpoint influences. In turn, the concentrations of nutrients from the treatment plant will have a greater or lesser influence on the

concentration at Site 2 dependent on the flow in the river. However, concentrations at Site 2 do not appear to be influenced at all times from these two factors. For example, the highest concentrations for NH_3 in the effluent from the treatment plant occurred in June and July of 2006. The flow rates in the Kaministiquia River were low at this time, but the levels of NH_3 at Site 2 were below detection limits.

Table 2.4. Thunder Bay Water Pollution Control Plant monthly average final effluent results for 2005 and 2006. River flow (m^3/s) for both years are included as are NH_3 from site 2 for comparison.

Month	River flow 2005 (m^3/s)	River Flow 2006 (m^3/s)	pH 2005	pH 2006	TOTP 2005 (mg/L)	TOTP 2006 (mg/L)	NH3 2006 (mg/L)	Site 2 NH_3 2005 (mg/L)	Site 2 NH_3 2006 (mg/L)
Jan	-	-	6.73	6.91	1.24	0.56	-	-	-
Feb	-	-	6.71	7.02	1.00	0.94	-	-	-
Mar	-	-	6.59	6.94	1.04	1.11	-	-	-
Apr	-	-	6.74	7.07	0.55	0.82	-	-	-
May	85.51	61.26	6.70	7.00	0.69	0.39	-	-	0.144
Jun	83.66	37.39	6.70	6.96	0.89	0.36	1.49	-	< DL
Jul	81.05	28.93	6.56	6.97	0.93	0.49	2.64	-	< DL
Aug	25.86	24.02	6.58	7.16	0.95	0.39	0.48	1.205	0.057
Sep	25.66	20.55	6.81	7.06	0.85	0.51	0.56	-	0.136
Oct	42.43	19.69	7.38	7.00	0.32	0.65	0.63	2.072	-
Nov	-	-	7.25	7.05	0.37	0.68	0.88	-	-
Dec	-	-	6.98	6.94	0.38	0.85	1.10	-	-
CV (coefficient of variation)	-	-	0.04	0.01	0.39	0.37	-	-	-

2.3.6 Site separation from non-metric multidimensional scaling (NMS)

Figure 2.9 and Figure 2.11 show the separation of the sampling sites using the NMS procedure and are particularly useful for illustrating the closer clustering of the point (2005 only) and control site (Bare Point) versus the nonpoint sites.

In 2005 (Figure 2.9), the NMS solution had two dimensions with an average stress of 8 and a Monte Carlo test result less than 0.004 indicating the results were greater than expected by chance alone. Iterations for the final solution were greater than 100.

Axis 1 was primarily associated with NO_x ($r = -0.98$, $\tau = -0.562$) and NH_3 ($r = -0.328$, $\tau = -0.519$) while Axis 2 was mainly associated with total P ($r = -0.894$, $\tau = -0.710$) and conductivity ($r = -0.786$, $\tau = -0.639$) (Figure 2.10). Site 1 (Bare Point), Site 8 (Above Mill) and Site 9 (Below Mill) exhibited the least amount of separation on the axes indicating less dissimilarity in the data than the other site locations.

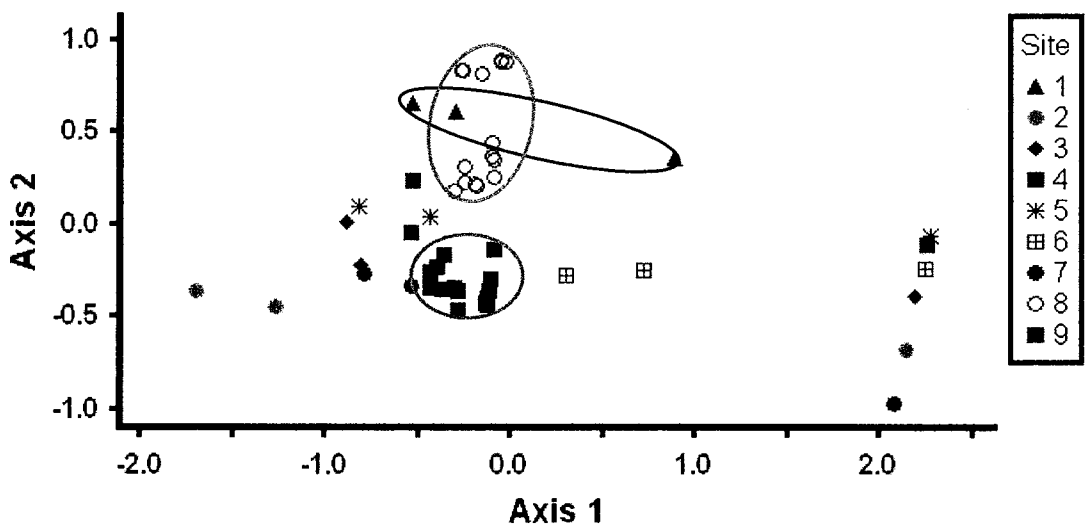

Figure 2.9. Non-metric multidimensional scaling graphical display for 2005 data. Additional water quality stations upstream (site 8: orange ellipse) and downstream (site 9: blue ellipse) the paper mill are included for comparison. Site 1 (Bare Point control) is highlighted with a red ellipse.

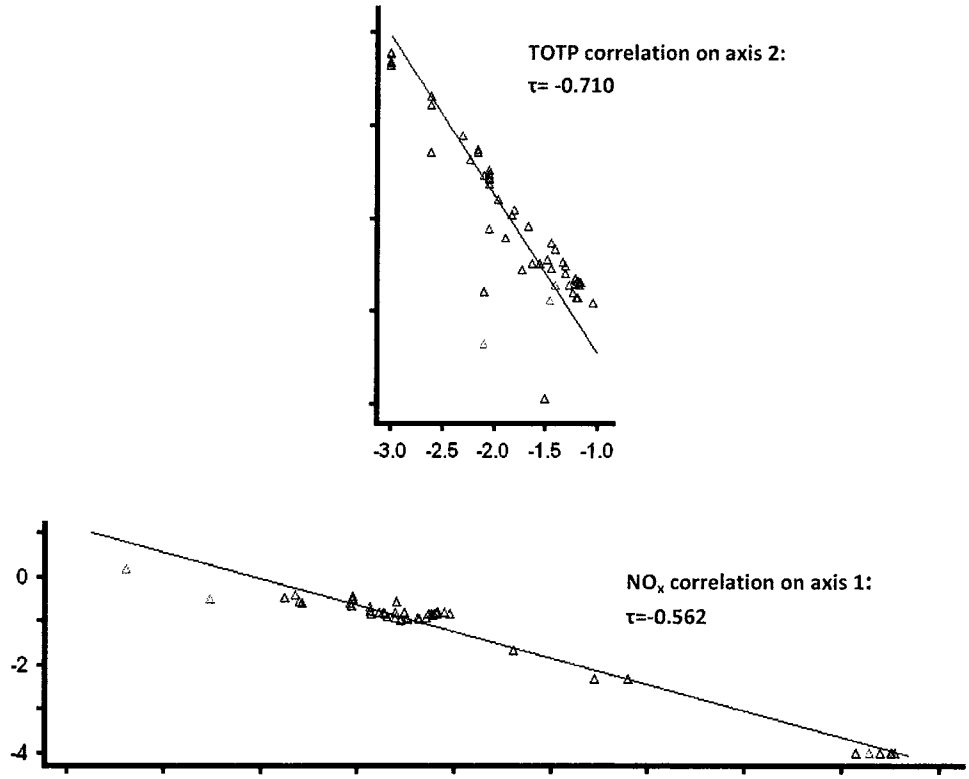

Figure 2.10. Non-metric multidimensional scaling solution to the 2005 data depicting the highest correlation on each axis (axis 1 correlation to NO_x; axis 2 correlation to TOTP).

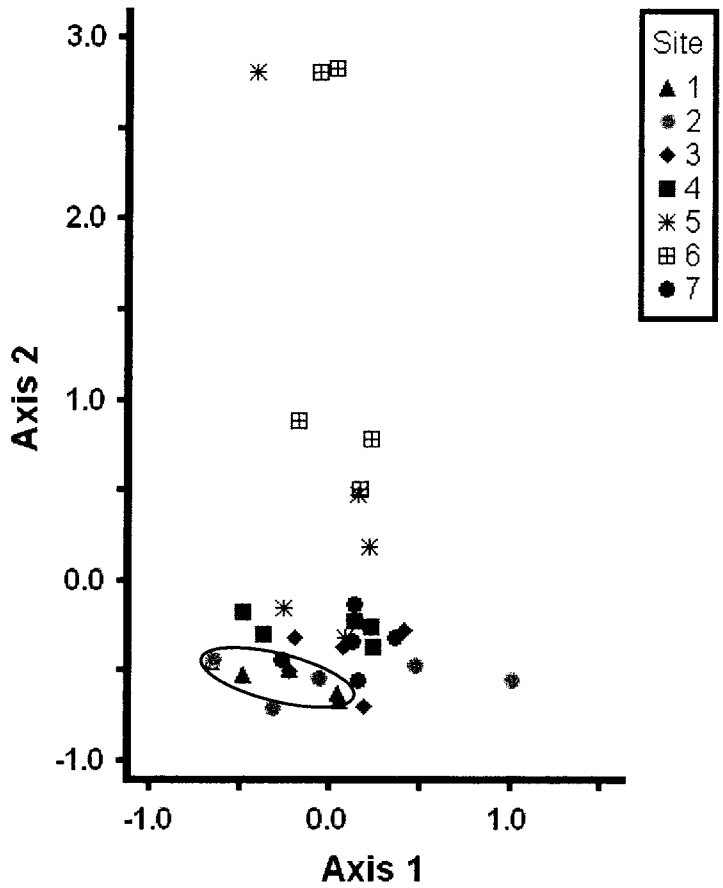

Figure 2.11. Non-metric multidimensional scaling graphical display for 2006 data. Site 1 (Bare Point control) is highlighted with a red ellipse.

In 2006 (Figure 2.11), the NMS solution had two dimensions with an average stress of 8 after 65 iterations. The 2006 data showed a similar trend with species of nitrogen (NH_3 and NO_x) and phosphorus responsible for most of the relationships on the axes. Axis 1 was primarily associated with total P ($r=0.910$, $\tau=0.675$) and conductivity ($r=0.710$, $\tau = 0.483$) while Axis 2 was mainly associated with NO_x ($r=-0.999$, $\tau = -0.632$) (Figure 2.12). Site 1 (Bare Point) showed the most amount of clustering indicating the other nonpoint sources had greater variation in terms of their nutrient concentrations.

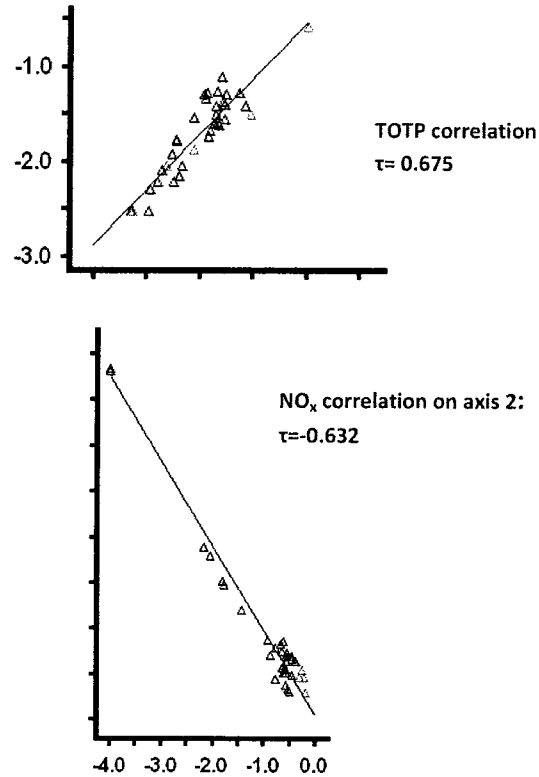

Figure 2.12. Non-metric multidimensional scaling solution to the 2006 data depicting the highest correlation on each axis (axis 1 correlation to TOTP; axis 2 correlation to NO_x).

2.4 Discussion

2.4.1 Eutrophication stimulus

Eutrophication is normally stimulated by elevated levels of phosphorus. However, as a lake becomes more productive a shift from P to N limitation occurs and thus requires the addition of this nutrient to cause eutrophic conditions. Sterner (2008) found that lakes are co-limited by both nutrients when total phosphorus was in the range of 0.01 mg/L to 1 mg/L requiring both P and N for enhanced primary production. Wold and Hershig (1999) found that the co-limitation of N and P for periphyton growth was predominant in rivers entering Lake Superior. Similar results seemed to occur in this study.

At Site 8 (Above Mill), P levels were less than 0.01 mg/l and increased to 0.06 mg/l at Site 9 (Below Mill) (Figure 2.6). According to Vollenwieder's (1976) definition for critical P concentrations, Site 8 would be considered mesotrophic (concentrations of > 0.01 mg/l) while Site 9 would be eutrophic (concentrations > 0.03 mg/l). However, N levels did not increase above the mill at Site 9 (Figures 2. 3, 2.4, 2.5) and, as reported in Chapter 1, visual eutrophication effects consisting of phytoplankton blooms at Site 5 (North Marsh) and Site 6 (South Marsh) were not evident until N was also elevated at these sites. Although some of the other nonpoint sites also contained high concentrations of both P and N, the shallow protected water in the marsh provided ideal conditions for algal production. Results from July of 1983 for nearshore water quality at Thunder Bay on Lake Superior (Anderson 1986) show a mean TOTP of 0.015 ± 0.018 mg/L indicating mesotrophic to eutrophic conditions along the waterfront during summer, similar to the results seen in this study. Mean TKN at this time was recorded at 0.26 ± 0.12 mg/L which were considerably lower than the values found in this study (Figure 2.4). According to Anderson (1983) nuisance algae growth did not occur during the water quality study in 1983.

Phytoplankton blooms at Sites 5 and 6 were extensive and the demand placed on CO_2 would cause pH to increase (Lee and Stewart 1981) as shown by Figure 2.2. Although the concentrations would be tempered by uptake from the algae, the pH levels at Sites 5 and 6 (consistently over 9 in June and July of both years and reaching over 10 in the summer of 2005) and high water temperatures in the shallow water would promote the

production of unionized ammonia (NH_3) from the ionized form (NH_4^+) (Boardman et al. 2004; Cameron and Heisler 1983). Even low levels of NH_3 ranging from 0.001 to 0.006 mg/l can adversely affect aquatic life (EPA 1999) and levels at Sites 5 and 6 were an order of 10 higher than these values (Figure 2.3). Unionized ammonia is toxic to aquatic life because of its ability to readily pass through gills of invertebrate and vertebrate species (Evans and Cameron 1986). Chronic effects of ammonia to aquatic organisms include reductions in survival, growth, reproductive success, behavioural responses, tissue damage and/or physiological and biochemical changes which can affect the community structure of the aquatic environment (Miranda-Filho et al. 2009; Spenser et al. 2008). Eutrophication effects at these two sites from the production of NH_3 could therefore be considered significant. Furthermore, although none were identified, the development of cyanobacteria under the alkaline and high P conditions observed could occur (Unkless and Markarewicz 2007) with resultant further degradation to the water quality at the marsh.

2.4.2 Cause of eutrophication at Thunder Bay waterfront: point versus nonpoint

It is possible that a case could be made for the source of nutrients causing eutrophication at the Thunder Bay Waterfront (in particular at Sites 5 and 6 (North and South Marsh)) to be from the point sources consisting of the paper mill adding P and the TBWPCP adding N. However, the interpretation of the observed data suggest that this is unlikely.

As discussed above in 2.4.1, P is discharged from the paper mill in concentrations that are considered eutrophic but increased primary production does not occur until N is added. If the source of this N is the TBWPCP, then the highest concentrations in Site 2 (Kaministiquia River, downstream of the plant), once flow within the river is considered, should correspond to the peak discharge concentrations from the treatment plant. However, Table 2.3 showed that during June and July of 2006, when the greatest influx of ammonia from the WPCP effluent occurred and flows within the river were at a minimum, the levels of ammonia at Site 2 were below detection. Additionally, levels of nutrients discharged to the Kaministiquia River were also higher historically. Secondary treatment was installed at the paper mill in 1995 greatly reducing the amount of suspended solids and the problem of low oxygen levels below the mill that previously characterized the water quality of the lower Kaministiquia River (Cullis et al. 1987). Secondary treatment was not installed at the TBWPCP until September, 2005. These previously higher nutrient levels were not known to cause localized eutrophication in Mission Marsh and aquatic macrophytes completely occupied the habitat within the marsh (Entwistle 1984).

A final consideration suggesting nonpoint sources of nutrients as the cause of eutrophication is that other studies have shown that such sources tend to have greater variation in the observed concentrations of contaminants than do point sources (Gunes 2008). According to Dowd et al. (2008) nonpoint source contamination is diffuse and

prone to discharge in pulses resulting in greater variation than point sources. Similarly higher variation for nonpoint sources occurred in this study.

Table 2.1 showed that the nonpoint sources in 2005 generally had higher coefficients of variation (CV) for most parameters relative to the point source Site 8 (Above Mill), Site 9 (Below Mill) or the control site (Site 1, Bare Point). The Mission Marsh sites in particular (Sites 5 and 6) had the highest CVs for NO_x versus any of the other sites in both 2005 and 2006. The NMS results for 2005 (Figure 2.9) gave similar results to that shown by the CV's in Table 2.1 and showed that the point source sites (Sites 8, 9) as well as Site 1 (Bare Point) were tightly clustered while the nonpoint sites had scattered points indicating widespread variation in their seasonal values. This high variation indicated that the source of nutrients was temporary, and indicative of sources that changed in their impact throughout the growing season.

2.4.3 Canada Geese as a nonpoint nutrient source

Canada Geese could be considered as a nonpoint nutrient source causing eutrophication on the Thunder Bay waterfront. The reasons for their inclusion as a suspect candidate were outlined in Chapter 1: (1) they were not present on the Thunder Bay waterfront until after their re-introduction in 1982 (Dennis et al. 2000), (2) they were shown to graze on aquatic vegetation in Mission Marsh, and (3) their numbers had grown to a population of at least a thousand by 2005.

Certainly, ammonia addition to the sites along the waterfront and surrounding rivers may be occurring as a result of fecal input by the geese. According to Bazely and Jeffries (1985) most of the soluble nitrogen in goose feces occurs as soluble ammonia and trampling of vegetation as they forage serves to compound the problem as mineralization rates of organic matter increase and result in high levels ammonification. Deposition rates for Canada Geese has been documented to be as high as 175 g/bird/day dry weight and although only approximately 1.6% of the droppings is nitrogen the high level of fecal output can sufficiently influence the trophic status of a water body (Allan et al. 1995). Associated with this input are generally reduced water quality, degradation of habitat and accelerated algal blooms (Manny et al. 1994; Scherer et al. 1995). The populations observed on the Thunder Bay Waterfront of at least a thousand birds would certainly be sufficient to cause local changes in water quality. The presence of even small numbers of geese have been shown to result in nutrient loading in small wetlands and waterways due to a high density of goose droppings (Allan et al. 1995; Conover and Chasko 1985; Scherer et al. 1995). The behaviour of the geese could also account for some of the observed results. Often, geese complete their moult in one location and later congregate in nearby locations with carbohydrate rich food options (Hanson 1965). Other studies have shown that as aquatic food becomes less available by late fall Canada Geese will use areas away from their regular feeding grounds (Badzinski et al. 2006). Large migratory herbivorous geese are known to exploit spilled grain, a rich food source, in autumn resulting in a habitat shift (Fox et al. 2005). This could account for the high levels of NH_3 at the marsh sites in the summer followed by elevated levels

at Site 3 (Mckellar River) and Site 4 (Kaministiquia River) in the fall (Figure 2.3) as these locations are nearby the rail network that transports grain through the city.

2.4.4 Management of nonpoint nutrient Input and availability

It seems essential that attempts be made to reduce the amount of nonpoint nutrient input along the Thunder Bay Waterfront. Assuming Canada geese are the major source of nonpoint nutrients, a variety of methods are available to possibly reduce the population that have been tried elsewhere within urban areas. The main techniques to reduce the populations have included repellents (methiocarb), hazing (sonic deterrents, dogs), frightening devices (lasers, flags), egg destruction and hunting (Conover 1985; Cummings et al. 1992; Gosser et al. 1997; Heinrich et al. 1990). Although effective, these techniques for deterring Canada Geese have been developed mainly for agricultural fields, golf courses and parks and have had varying success. For example, Aguilera et al. (1991) found that two hazing techniques suitable for use in urban environments (screamer shells and geese distress calls) had mixed results. Goose distress calls were ineffective in displacing the geese from the study area while the screamer shells showed promise with all the geese leaving the area when the shells were fired twice daily. Another less intrusive strategy has been to reduce the amount of optimum habitat available to the geese. Canada geese prefer open, cultivated lawn areas near water that offer them the chance to observe any predators and take appropriate actions to avoid them (Smith et al. 1999). If the habitat is changed to discourage their presence, the geese will move elsewhere. The planting of long grasses

has been shown to be an effective bird deterrent (Brough and Bridgman 1980; Smith et al. 1999). This strategy has been successfully used by the Royal Botanical Gardens at Cootes Paradise marsh in Hamilton, Ontario (Houston 2008). In this case, grassed areas along the marsh were permitted to grow and cattails were planted along the shore. The net result was a dramatic reduction in geese numbers and the marsh was able to be re-vegetated without the previously intense grazing caused by the geese.

In addition to the reduction of the likely source of the nonpoint nutrients, areas along the Thunder Bay Waterfront could be vegetated to help absorb the influx of nitrogen into the water column. This would seem a particularly appropriate approach at Mission Marsh where the vegetation was shown in Chapter 1 to be reduced by 39.8% since 1982. Wetlands have been created to absorb nutrients and contaminants from such diverse sources as municipal wastewater and mining effluent (Kadlec and Knight 1996) and have been particularly useful in reducing N and P from eutrophic waters (Mitsch et al. 2000).

2.5 Conclusions

The results of this study showed that nutrients continue to be added to water discharged into Lake Superior from both point and nonpoint sources. Localized eutrophication caused by elevated N levels was present at several sampling stations including the Mission Marsh and was attributed mostly to nonpoint sources.

Further efforts should be extended at quantifying the extent of eutrophication caused by Canada Geese and creating and re-establishing wetlands along the waterfront which could absorb excess nutrients.

General Conclusions and Future Work

This thesis documented the vegetative loss at Mission Island Marsh using image analysis.

Compared to 1983, there was a 40% loss of vegetation in the marsh with most of the loss being due to emergent and floating leaf species. Grazing, likely by Canada Geese, was considered to be the most likely reason for this vegetation loss. Synergistic effects of both lower water levels in the marsh and enhanced eutrophication causing algal mats were suspected as causing added losses of macrophytes.

Marshes so heavily affected by goose foraging can take years to recover naturally (Olgilvie 1978) with the effects of nutrient loading lasting long after the absence of further input (Scherer et al. 1995; Unkless and Makarewicz 2007). Other related detrimental effects can also occur. As the macrophytic vegetation declines sediment transport and further biomass loss due to wave action and ice scour increases due to less rooting structure available to maintain the sediment. These factors have been shown to be a contributing factor to biomass reduction in many macrophyte communities (Crowder and Painter 1991; Jeffries et al. 2006).

Monthly water samples from the Thunder Bay waterfront taken during the growing seasons of 2005 and 2006 were analyzed for their contribution to eutrophication. Coefficient of variation and NMS analysis supported the hypothesis that the locations suspect of being goose grazing and staging grounds (North Marsh, South Marsh and Kaministiquia River) exhibited greater dissimilarity in the data than the Bare Point control and the paper mill point source locations (upstream and downstream of the paper mill). Results from Thunder Bay's Water Pollution Control Plant indicated that its influence as a point source was also not responsible for the highly variable results at the Kaministiquia River (mouth) sample location. These data indicate that a nonpoint source of nutrient enrichment, possibly the direct and indirect effects of grazing by Canada geese, is occurring at Mission Island Marsh and the Kaministiquia River mouth location.

Because of its importance ecologically, Mission Island Marsh should be continually monitored and assessed for further decline. Regular sampling and analysis of the water quality at Mission Island Marsh and its surrounding tributaries is also recommended. Further research into the planting of non-palatable vegetation to dissuade the Canada Geese from feeding in the area may prove to alleviate the loss of vegetation and help return the marsh structure. A detailed population study of the number of geese present on the Thunder Waterfront is certainly neded.

Finally outright remediation of Mission Island Marsh by planting native plant species within protected enclosures is highly recommended to restore the marsh to its former prominence on the Thunder Bay waterfront.

References

Abraham, K.F., R.L. Jeffries, and R.F. Rockwell. 2005. Goose-induced changes in vegetation and land cover between 1976 and 1997 in an Arctic coastal marsh. Arctic, Antarctic and Alpine Research 37(3): 269-275.

Aguilera, E., R.L. Knight, and J.L. Cummings. 1991. An evaluation of two hazing methods for urban Canada Geese. Wildlife Society Bulletin 19(1): 33-35.

Aiken, S.G., P.F. Lee, D. Punter, and J.M. Stewart. 1988. Wild rice in Canada. NC Press Ltd., Toronto, 176 pp.

Allan, J.R., J.S. Kirkby, and C.J. Feare. 1995. Biology of Canada Geese (*Branta canadensis*) in relation to management of feral populations. Wildlife Biology 1: 129-143.

ALS Laboratory Group. 2006. ALS Laboratory Group analytical report on algae Identification, 3 pp.

Anderson, J. 1986. Nearshore Water Quality at Thunder Bay, Lake Superior, 1983. Ontario Ministry of the Environment Great Lakes Section Water Resources Branch. Queen's Printer for Ontario, 55 pp.

Ankney, C. D. 1996. An embarrassment of riches: too many geese. Journal of Wildlife Management 60: 217-233.

Badzinski, S.S., C.D. Ankney, and S.A. Petrie. 2006. Influence of migrant tundra swans (*Cygnus columbianus*) and Canada Geese (*Branta canadensis*) on aquatic vegetation at Long Point, Lake Erie, Ontario. Hydrobiologia 567: 195-211.

Bazely, D.R., and R.L. Jeffries. 1985. Goose faeces: a source of nitrogen for plant growth in a grazed salt marsh. Journal of Applied Ecology 22: 693-703.

Bazely, D.R., and R.L. Jeffries. 1989. Lesser snow geese and the nitrogen economy of a grazed salt marsh. Journal of Ecology 77: 24-34.

Bellrose, F.C. 1980. Canada Goose *Branta canadensis* 3rd Ed. Stackpole Books. Wildlife Management Institute, Harrisburg, Pa.

Berrill, M., L. Hollett, A. Margosian, and J. Hudson. 1985. Variation in tolerance to low environmental pH by the crayfish *Orconectes rusticus*, *O. propinquus*, and *Cambarus robustus*. Canadian Journal of Zoology 63: 2586-2589.

Boardman, G.D., S. M. Starbuck, D.B. Hudgins, X. Li, and D.D. Kuhn. 2004. Toxicity of ammonia to three marine fish and three marine invertebrates. Environmental Toxicology 19: 134-142.

Bootsma, H.A., E.B. Young, and J.A. Berges. 2004. Temporal and spatial patterns of *Cladophora* bioamass and nutrient stoichiometry. *Cladophora* Research and Management in the Great Lakes Workshop proceedings at the Great Lakes Water Institute University of Wisconsin-Milwaukee, pp. 81-88.

Brazner, J.C., and E.W. Beals. 1997. Patterns in fish assemblage from coastal wetlands and beach habitats in Green Bay, Michigan: a multivariate analysis of abiotic and biotic forcing factors. Canadian Journal of Fish and Aquatic Science 54: 1743-1761

Bronte, C.R., M.P. Ebener, D.R. Schreiner, D.S. DeVault, M.M. Petzold, D.A. Jensen, C. Richards and S.J. Lozano. 2003. Fish community change in Lake Superior, 1970 – 2000. Canadian Journal of Aquatic Science 60: 1552-1574.

Brough, T., and C.J. Bridgman. 1980. An evaluation of long grass as a bird deterrent on British airfields. Journal of Applied Ecology 17: 243-253.

Buchsbaum, R.N., I. Valiela, and T. Swain. 1984. The effect of phenolic compounds and other plant constituents on feeding by Canada Geese in a coastal marsh. Oecologia 63: 343-349.

Cahn, A.R. 1929. The effect of carp on a small lake: the carp as a dominant. Ecology 10: 271-275.

Cameron, J.N., and N. Heisler. 1983. Studies of ammonia in the rainbow trout: physic-chemical parameters, acid-base behavior and respiratory clearance. Journal of Experimental Biology 105: 107-125.

Chow-Fraser, P. 1998. A conceptual ecological model to aid restoration of Cootes Paradise Marsh, a degraded coastal wetland of Lake Ontario, Canada. Wetlands, Ecology and Management 6: 43-57.

Chow-Fraser, P., V. Loughheed, V. Le Thiec, B. Crosbie, L. Simser, and J. Lord. 1998. Long-term response of the biotic community to fluctuating water levels and changes in water quality in Cootes Paradise Marsh, a degraded coastal wetland of Lake Ontario. Wetlands Ecology and Management 6: 19-42.

City of Thunder Bay. 1983. Aerial Photograph 1983-L6-200. City of Thunder Bay Planning and Archives Department.

City of Thunder Bay. 2002a. Aerial Photograph 2002-L8-184. City of Thunder Bay Planning and Archives Department.

City of Thunder Bay. 2002b. Aerial Photograph 2002-L9-208. City of Thunder Bay Planning and Archives Department.

City of Thunder Bay. 2005. Water Pollution Control Plant Annual Report 2005. City of Thunder Bay Transportation and Works Sewage Treatment Section, 33 pp.

City of Thunder Bay. 2006. Water Pollution Control Plant Report 2005. City of Thunder Bay Transportation and Works Sewage Treatment Section, 33 pp.

Cohen, A.N., and J.T. Carlton. 1998. Accelerating invasion rate in a highly invaded estuary. Science 279: 555-558.

Coleman, T. S., and D.A. Boag. 1987. Canada Goose foods: their significance to weight gain. Wildfowl 17: 243-253.

Conover, M.R. 1985. Alleviating nuisance Canada Goose problems through methiocarb-induced aversive conditioning. Journal of Wildlife Management 49: 631-636.

Conover, M.R., and G.G. Chasko. 1985. Nuisance Canada Goose problems in the Eastern United States. Wildlife Society Bulletin 13: 228-233.

Conover, M.R., and G.S. Kania. 1991. Characteristics of feeding sites used by urban-suburban flocks of Canada Geese in Conneticut. Wildlife Society Bulletin 19: 36-38.

Crowder, A., and D.S. Painter. 1991. Submerged macrophytes in Lake Ontario: current knowledge, importance, threats to stability, and needed studies. Canadian Journalof Fisheries and Aquatic Science 48: 1539-1545.

Cullis, K., W.T. Momot, and R. Sein. 1987. Kaminististiquia River Study 1987: Fish Community and Aquatic Habitat of the Kaministiquia River. North of Lake Superior Remedial Action Plans Technical Report Series, 148 pp.

Cummings, J.L., D.L. Otis, and J.E. Davis Jr. 1992. Dimethyl and methyl anthranicate and methiocarb deter feeding in captive Canada Geese and mallards. Journal of Wildlife Management 56: 349-355.

Dennis, D.G., N.R. North, and H.G. Lumsden. 2000. Range expansion and population growth of giant Canada Geese in southern Ontario: benefits, drawbacks and management techniques. Canadian Wildlife Service Occasional Paper No. 103: 159-164.

Dowd, B.M., D. Press, and M. Los Huertos. 2008. Agricultural nonpoint source water pollution policy: the case of California's central coast. Agriculture, Ecosystems and Environment 128: 151-161.

Entwistle, J. 1984. Thunder Bay Harbour Marshes Study 1982/1983. Lakehead Region Conservation Authority. Thunder Bay, Ontario, 69 pp.

Environmental Protection Agency. 1999. Update of ambient water quality criteria for ammonia. EPA Office of Water: Office of Science and Technology. Washington, D.C. EPA-822-R-00-014.

Environmental Protection Agency. 2006. Impacts on quality of inland wetlands of the United States: a survey of indicators, techniques and applications of community level biomonitoring data: wetland algae. Available from http://www.epa.gov/OWOW/wetlands/wqual/algae.html [Accessed October 10, 2008]

Evans, DH., and J.N. Cameron. 1986. Gill ammonia transport. The Journal of Experimental Zoology 239: 17-23.

Eyles, N., M. Doughty, J.I. Boyce, M. Meriano, and P. Chow-Fraser. 2003. Geophysical and sedimentological assessment of urban impacts in a Lake Ontario watershed and lagoon: Frenchman's Bay, Pickering, Ontario. Geoscience Canada 30: 114-128.

Finkelstein, S.A., M.C. Peros, and A.M. Davis. 2005. Late holocene paleoenvironmental change in a Great Lakes coastal wetland: integrating pollen and diatom datasets. Journal of Paleolimnology 33: 1-12.

Finley, S.R. 2003. Using satellite remote sensing to map aquatic vegetation. Remote Sensing and Geospatial Analysis Laboratory Fact Sheet 7. Department of Forest Resources, University of Minnesota, 4 pp. Available from http://rsl.gis.umn.edu [Accessed August 20, 2007]

Fisheries and Oceans Canada. 2005. The Canadian Hydrographic Service Central and Arctic Region: historical water level data for Lake Superior. Available from http://www.waterlevels.gc.ca/C&A/tidal_e.html [Accessed August 20, 2008]

Fox, A.D., J. Madsen, H. Boyd, E. Kuijkens, D.W. Norriss, I.M. Tombre, and D.A. Stroud. 2005. Effects of agricultural change on abundance, fitness components and distribution of two artic-nesting goose populations. Global Change Biology 11: 881-893.

Great Lakes Environmental Research Lab (GLER), Sea Grant Lakes Network. 2007. Great Lakes water life photo gallery: dominant phytoplankton of the Great Lakes. Available from:http://www.glerl.noaa.gov/seagrant/GLWL/Algae/DominantAlgae.html[Accessed October 10, 2008]

Giroux, J.F., and J. Bédard. 1987. The effects of grazing by greater snow geese on the vegetation of tidal marshes in the St. Lawrence estuary. Journal of Applied Ecology 24: 773-788.

Gosser, A.L., M.R. Conover, and T.A. Messmer. 1997. Managing problems caused by urban Canada Geese. Berryman Institute Publication 13, Utah State University, Logan, 8 pp.

Greenberg, A.E., L.S. Clesceri, and A.D. Eaton (eds). 1992. Standard methods for the Examination of water and wastewater, 18th ed. American Public Health Association, Washington, D.C., 1000 pp.

Gunes, K. 2008. Point and nonpoint sources of nutrients to lakes – ecotechnological Measures and mitigation methodologies – case study. Ecological Engineering 34: 116-126.

Gunn, J.M., R.J. Steedman, and R.A. Ryder. 2004. Boreal Shield Watersheds: Lake Trout Ecosystems in a Changing Environment. CRC Press, Boca Raton, Florida.

Haack, B. 1996. Environmental auditing: monitoring wetland changes with remote sensing: an East Africa example. Environmental Management 20(3): 411-419.

Hanson, J.M., and P.A. Chambers. 1995. Review of effects of variation in crayfish abundance on macrophyte and macroinvertebrate communities of lakes. ICES Mar. Sci. Symp. 199: 175-182.

Hanson, H.C. 1965. The Giant Canada Goose. Southern Illinois University Press.

Heinrich, J.W., and S.R. Craven. 1990. Evaluation of three damage abatement Techniques for Canada Geese. Wildlife Society Bulletin 18: 405-410.

Harris, H.J. Jr., J.A. Ladowski, and D.J. Worden. 1981. Water-quality problems and management of an urban waterfowl sanctuary. Journal of Wildlife Management 45(2): 501-507.

Hartviksen, C., and W. Momot, 1989. Fishes of the Thunder Bay area of Ontario. Wildwood Publications, Thunder Bay, Ontario. 282 pp.

Holenstein, J. 1994. Mission Island Marsh Conservation Area Master Plan. Lakehead Region Conservation Authority, Thunder Bay, 40 pp.

Horne, A.J., and C.R. Goldman. 1994. Limnology. McGraw-Hill, New York.

Houston, S. 2008. What's good for the geese. Now @ the Gardens. Vol. 5 Number 2. Royal Botanical Gardens.

Hudon, C. 1997. Impact of water level fluctuations on St. Lawrence River aquatic vegetation. Canadian Journal of Fish andAquatic Science 54: 2853-2865.

Hughes, J.M. 2001. Royal Ontario Field Guide to the Birds of Ontario. Special Bulletin, Royal Ontario Museum and McClelland and Stewart, Toronto, Ontario.

Jeffries, R.L., A.P. Jano, and K.F. Abraham. 2006. A biotic agent promotes large-scale catastrophic changes in coastal marshes of Hudson Bay. Journal of Ecology 94: 234-242.

Jeffries, R.L., D.R. Klein, and G.R. Shaver. 1994. Vertebrate herbivores and northern plant communities: reciprocal influences and responses. Oikos 71: 193-206.

Jude, D.J., and J. Pappas. 1992. Fish utilization of Great Lakes coastal wetlands. Journal of Great Lakes Research 18: 651-672.

Kadlec, R.H., and R.L. Knight. 1996. Treatment Wetlands. CRC Press/Lewis Publishers, Boca Raton, Florida, 893 pp.

Capelli, G.M., and J.J. Magnuson. 1983. Morphoedaphic and biogeographical analysis of crayfish distribution in northern Wisconsin. Journal of Crustacean Biology 3: 548-564.

Kay, E.R.M. 1948. Limnological studies of the Dundas Marsh region. M.A. thesis, McMaster University.

Keddy, P. and A.A. Reznicek. 1986. Great Lakes vegetation dynamics: the role of fluctuating water levels and buried seeds. Journal of Great Lakes Research 12: 25-36.

Khan, T.A., M.E. Wilson, and M.T. Khan. 2003. Evidence for invasive carp mediation trophic cascade in shallow lakes of western Victoria, Australia. Hydrobiologia 506(1-3): 465-472.

King, D.R., and G.S. Hunt. 1967. Effect of carp on vegetation in a Lake Erie marsh. Journal of Wildlife Management 31: 181-188.

Klemas, V.V. 2001. Remote sensing of landscape-level coastal environmental indicators. Environmental Management 27(1): 47-57.

Kotanen, P.M., and R.L. Jefferies. 1997. Long-term destruction of sub-arctic wetland vegetation by lesser snow geese. Ecoscience 4(2): 179-182.

Kruskal, J.B. 1964. Nonmetric multidimensional scaling: a numerical method. Phychometrika 29(2): 115-129.

Lakehead Region Conservation Authority. 1984. Wetland evaluation of the Thunder Bay harbour marshes. Lakehead Region Conservation Authority, Thunder Bay, Ontario, 50 pp.

Lamoureux, W.J. 1961. A strange project – for a botanical garden. Royal Botanical Gardens Bulletin 15: 13-18.

Lee, P.F., and J.M. Stewart. 1981. Ecological relationships of wild rice, *Zizania aquatica* L.1. A model for among-site growth. Canadian Journal of Botany 59: 2140-2151.

Lodge, D.M., M.W. Kershner, J.E. Aloi, and A.P. Covich. 1994. Effects of an omnivorous crayfish (*Orconectes rusticus*) on a freshwater food web. Ecology. 75: 1265-1281.

Lodge, D.M., and J.G. Lorman. 1987. Reductions in submersed macrophyte biomass and species richness by the crayfish Oronectes rusticus. Canadian Journal of Fish and Aquatic Science 44: 591-597.

LUEL, 2000. Lakehead University Laboratory Operating Procedures.

Lyon, J.G., R.D. Drobney, and C.E. Olson. 1986. Effects of Lake Michigan water levels on wetland soil chemistry and distribution of plants in the straits of Mackinac. Journal of Great Lakes Research 12: 175-183.

Macrae, D.A. 1979. The impact of carp on the summer production of aquatic vegetation as indicated by an enclosure experiment and food habits study. M.Sc. thesis, Trent University, Peterborough, Ontario, 110 pp.

Magnuson, J.J., G.M. Capelli, J.G. Lorman and R.A. Stein. 1975. Consideration of crayfish for macrophyte control. In The Proceedings of a Symposium on Water Quality Management. Edited by P.L. Brezonik and J.L. Fox. University of Florida. Gainsville, Florida. p. 66-74.

Mander, V., and C. Forsberg. 2000. Nonpoint pollution in agricultural watersheds of endangered coastal seas. Ecological Engineering 14: 317-324.

Manny, B. A., W.C. Johnson, and R.G. Wetzel. 1994. Nutrient additions by waterfowl to lakes and reservoirs: predicting their effects on productivity and water quality. Hydrobiologia 279/280: 121-132.

Matsuzaki, S.S., N. Usio, N. Takamura, and I. Washitani. 2008. Contrasting impacts of invasive engineers on freshwater ecosystems: an experiment and meta-analysis. Oecologia 158(4): 673-686.

Mayer, T., F. Rosa, and M. Charlton. 2005. Effect of sediment geochemistry on the nutrient release rates in Cootes Paradise Marsh, Ontario, Canada. Aquatic Ecosystem Health and Management 8: 133-145.

Maynard, L., and D. Wilcox. 1997. State of the Lakes Ecosystem Conference 1996 Background Paper: Coastal Wetlands. Canadian Wildlife Service, 80 pp.

McCrimmon, H.R. 1968. Carp in Canadian Fisheries Research Board of Canada, Ottawa. Bulletin No. 165.

McKever, J., and J. Elder. 1981. Thunder Bay harbour marsh study: Mission Island Marsh. Lakehead Region Conservation Authority, Thunder Bay, Ontario, 147 pp.

Miranda-Filho, K.C., G.L. Pinho, W. Wasielesky Jr., and A. Branchini. 2009. Long-term ammonia toxicity to the pink-shrimp *Farfantepenaeus paulensis*. Comparative Biochemistry and Physiology, Part C 150: 377-382.

Mitchell, S.F., and R.T. Wass. 1996. Grazing by black swans (*Cygnus atratus Latham*), physical factors, and the growth and loss of aquatic vegetation in a shallow lake. Aquatic Botany 55: 205-215.

Mitsch, W.J., and V. Bouchard. 1998. Enhancing the roles of coastal wetlands of the North American Great Lakes. Wetlands Ecology and Management 6:1-3.

Mitsch, W.J., and J.G. Gosselink. 2000. Wetlands. 3rd ed. John Wiley and Sons, Inc., 920 pp.

Mitsch, W.J., A. Horne, and R.W. Nairn, eds. 2000. Nitrogen and phosphorus retention in wetlands. Special issue of Ecological Engineering 14: 1-206.

Morrice, J.A., N.P. Danz, R.R. Regal, J.R. Kelly, G.L. Niemi, E.D. Reavie, T. Hollenhorst, R.R. Axler, A.S. Trebitz, A.M. Coller, and G.S. Peterson. 2007. Human influences on water quality in the Great Lakes coastal wetlands. Environmental Management 41(3): 347-357.

Newmaster, S.G., A.G. Harris, and L.J. Kershaw. 1997. Wetland Plants of Ontario. Lone Pine Publishing and Queen's Printer for Ontario, 240 pp.

Olden, J.D., J.M. McCarthy, J.H.T. Maxted, W.W. Fetzer, and M.J. Vander Zanden. 2006. The rapid spread of rusty crayfish (*Orconectes rusticus*) with observations on native crayfish declines in Wisconsin (USA) over the past 130 years. Biological Invasions 8: 1621-1628.

Olgilvie, M. A. 1978. Wild Geese. Buteo Books, Vermillion, South Dakota, 350 pp.

Olmanson, L.G., M.E. Bauer, and P.L. Brezonik. 2002. Aquatic vegetation surveys using high-resolution IKONOS imagery. Pecora15/Land Satellite Information IV/ISPRS Commission/FIEOS 2002 Conference Proceedings, 5 pp.

O.P.C., P.M. Kotanen, and K. F. Abraham, 2006. Geese and gazing lawns: responses of the grass *Festuca rubra* to defoliation in a subarctic coastal marsh. Canadian Journal of Botany 84: 1732-1739.

Ozesmi, S.L., and M.E. Bauer. 2002. Satellite remote sensing of wetlands. Wetlands Ecology and Management 10: 381-402.

Painter, D.S., K.J.McCabe, and W.L. Simser. 1989. Past and present limnological conditions in Cootes Paradise affecting aquatic vegetation. Technical Bulletin No. 13. Royal Botanical Gardens.

Pettigrew, C.T., B.J. Hann, and L.G. Goldsborough. 1997. Waterfowl feces as a source of nutrients to a prairie wetland: responses of microinvertebrates to experimental additions. Hydrobiologia 362: 55-66.

Pfugmacher, S. 2004. Promotion of oxidative stress in the aquatic macrophyte *Ceratophyllum demersum* during biotransformation of the cyanobacterial Toxin Microcystin-LR. Aquatic Toxicology 70(3): 169-178.

Post, D.M., J.P. Taylor, J.F. Kitchell, M.H. Olson, D.E. Schindler, and B.R. Herwig. 1998. The role of migratory waterfowl as nutrient vectors in a managed wetland. Conservation Biology 12(2): 911-920.

Prevett,. J.P., I.F. Marshall, and V.G. Thomas. 1985. Spring foods of Snow and Canada Geese of James Bay. Journal of Wildlife Management 49: 558-563.

Robel, R.J. 1961. The effects of carp populations on the production of waterfowl food plants on a western waterfowl marsh. 26th North American Wildlife Natural Resources Conference 26: 147-159.

Roth, B.M., J.C. Tetzlaff, M.L. Alexander, and J.F. Kitchnell. 2007. Reciprocal relationships between exotic rusty crayfish, macrophytes, and *Lepomis* species in Northern Wisconsin Lakes. Ecosystems 10: 74-85.

Royal Botanical Gardens. 1998. The Cootes Paradise Fishway, carp control techniques. Royal Botanical Gardens, Hamilton, Ontario.

Royal Botanical Gardens. 1998. Waterbirds of Cootes Paradise. Royal Botanical Gardens Fact Sheet.

Sager, E.P.S. 1996. Factors influencing the light environment in Cootes Paradise, Hamilton Harbour, and other coastal marshes of Lake Ontario. Water Qualit Research Journal of Canada: 31: 553-575.

Salmonsen, F. 1968. The moult migration. Wildfowl 19: 5-24.

Scherer, N.M., H.L. Gibbons, K.B. Stoops, and M. Muller. 1995. Phosphorus loading of an urban lake by bird droppings. Lake and Reservoir Management 11(4): 317-327.

Seilherimer, T.S., A. Wei, P. Chow-Fraser, and N. Eyles. 2007. Impact of urbanization on the water quality, fish habitat, and fish community of a Lake Ontario marsh, Frenchman's Bay. Urban Ecosystems 10: 299-319. Online publication by Springer Science & Business Media.

Sierszen, M.E., G.S. Peterson, A.S. Trebitz, J.C. Brazner, and C.W. West. 2006. Hydrology and nutrient effects on food-web structure in ten Lake Superior coastal wetlands. Wetlands 26: 951-964.

Smith, A.E., S.R. Craven, and P.P. Curtis. 1999. Managing Canada Geese in urban environments. Jack Berryman Institute Publication 16 and Cornell University Cooperative Extension, Ithaca, New York, 44 pp.

Smith, T., J. Lundholm, and L. Simser. 2001. Wetland vegetation monitoring in Cootes Paradise: measuring the response to a fishway/carp barrier. Ecolological Restoration 19: 145-154.

Spenser, P., R. Pollock, and M. Dubé. 2008. Effects of un-ionized ammonia on histological, endocrine, and whole organism endpoints in slimy skulpin (*Cottus cognatus*). Aquatic toxicology 90: 300-309.

Stein, R.A., and J.J. Magnuson. 1976. Behavioural response of crayfish to a fish predator. Ecology 57: 751-761.

Sterner, R.W. 2008. On the phosphorus limitation paradigm for lakes. International Review Hydrobiologia 93(4-5): 433-445.

Tabak. J. 1981. The vegetation of Mission Island Marsh Thunder Bay. Honours Thesis. Lakehead University, Thunder Bay, Ontario, 54 pp.

Thunder Bay Field Naturalists. 2002. Christmas bird count. Thunder Bay Field Naturalists Birding Page. Available from: http://www.tbfn.net/xmas.htm [Accessed: August 20, 2009]

Topographical Map Thunder Bay 52/A6 Ed. 4 1:50,000.

Unckless, R.L., and J.C. Makarewicz. 2007. The impact of nutrient loading from Canada Geese (*Branta canadensis*) on water quality, a mesocosm approach. Hydrobiologia. 586: 393-401.

Vollenweider, R.A. 1976. Advances in defining critical loading levels for phosphorus in lake eutrophication. Memorie dell'Istituto di Idrobiologia 33: 53-83.

Wang, L.X., L.M. Zhang, H. Chua, X.D. Li, M.F. Xia, and P.M. Pu. 2009. A mosaic community of macrophytes for the ecological remediation of eutrophic shallow lakes. Ecological Engineering 35: 582-590.

Wei, A., and P. Chow-Fraser. 2005. Untangling the confounding effects of urbanization and high water level on the cover of emergent vegetation in Cootes Paradise Marsh, a degraded coastal wetland of Lake Ontario. Hydrobiolgia 544: 1-9.

Whillans, T.H. 1982. Changes in marsh area along the Canadian shore of Lake Ontario. Journal of Great Lakes Research 8: 570-577.

Wilcox, D.A. 2004. Implications of hydrologic variability on the succession of plants in Great Lakes wetlands. Aquatic Ecosystem Health: 7: 223-231.

Wilson, K.A., J.J. Magnuson, D.M. Lodge, A.M. Hill, T.K. Kratz, W.L. Perry and T.V. Willis. 2004. A long-term rusty crayfish invasion: dispersal patterns and community change in a north temperate lake. Canadian Journal of Aquatic Science 61: 2255-2266.

Wold, A.P., and A.E. Hershey. 1999. Spatial and temporal variability of nutrient limitation in 6 north shore tributaries to Lake Superior. Journal of North American Benthological Society 18(1): 2-14.

Zacheis, A., J.W. Hupp, and R.W. Ruess. 2001. Effect of migratory geese on plant communities of an Alaskan salt marsh. Journal of Ecology 89: 57-71.

Appendix A. Using species of non-palatable emergent vegetation as a natural deterrent to foraging by Canada Geese

Abstract

The effectiveness of planting of non-palatable vegetation to deter Canada Geese from Mission Island Marsh was assessed in this study. Three wetland species, *Typha angustifolia, Phragmites communis* and *Calla palustris* were transplanted during the summer of 2004 into unenclosed plots in the wetland. A total of 15 plots for the test species were set up along with 15 plots of the control species *Eleocharis smalli*. The test plots performed poorly during this time partially due to transportation problems with two of the test species that subsequently did not survive transplant. Hence data could not be obtained for any of the test plants. Since physical evidence obtained during the growing season of 2004 confirmed the failure of the test species, the research plan for the following growing season was amended. The same test and control species were utilized during the summer of 2005. Plots for the test species were to remain enclosed until the following growing season at which time the enclosure was to be removed. Then the amount of foraging on the test species was to be compared to that of the control.

Unfortunately, by early August of 2005 the entire enclosure, including plants, had been vandalized and no virtually no evidence of the study site remained. Due to time constraints this second season attempt had to be abandoned.

Since much time had been spent on researching this study, some observational evidence obtained during this time is worth noting. This report documents the design and physical evidence obtained during the study period. The emergent species considered during this experiment are likely effective natural deterrents to foraging by Canada Geese although the data obtained are strictly circumstantial. Further study utilizing these species and other similar species as deterrents to foraging by Canada Geese is recommended.

Introduction

There are many techniques for deterring Canada Geese that have been established as being quite effective such as repellents (methiocarb), hazing (sonic deterrents, dogs), frightening devices (lasers, flags), landscape modification (tall trees, fences), egg destruction and hunting (Gosser et al. 1997; Heinrich et al. 1990; Conover 1985; Cummings et al. 1992). Although effective, these techniques for deterring Canada Geese have been developed for agricultural fields, golf courses and parks. In order to maintain the integrity of the wetland these techniques are not considered to be feasible for Mission Island Marsh. Repellents, hazing and frightening devices cannot be utilized at the marsh because of their nonspecific nature. These methods would disturb the entire bird population at the wetland. Destruction of goose eggs is labour intensive and will limit the growth of the Canada Goose population in Thunder Bay, however, this will not stop existing birds from further damaging the wetland nor will it affect the impact of late spring moult migrants arriving at the wetland. Hunting can reduce the population

to manageable levels but may be difficult to implement within the boundaries of an urban center. Approvals from each level of government are required for a bird cull. Although hunting may ultimately be the only solution to reduce the Canada Goose population in the Thunder Bay area it will be opposed by animal rights groups. Habitat modification and planting of non-palatable vegetation as suggested by Conover and Kania 1991 and Smith et al. 1999 might prove to be an effective deterrent in this case.

Methods

Summer 2004

Three species of wetland plants (*Phragmites communis*, *Typha angustifolia* and *Calla palustris*) were planted into unenclosed plots in three different locations. These locations were negatively affected by observed goose foraging activity in mudflat, shoreline and offshore locations. *Eleocharis smalli* was also planted into unenclosed plots at each location as a control. It was chosen because of its successful transplantation and survival in the wetland the previous summer. Also, it was heavily foraged by the geese outside of enclosures and therefore should be an effective control species to compare to suspected non-palatable species.

Five plots for each test species were set up in the marsh during early July of 2004. Five plots of *Eleocharis smalli* were planted near each test species location for a total of 15 control plots. *Phragmites communis* was planted into designated plots in the mudflat

area of the wetland in a couple of inches of water. *Calla palustris* were planted into plots designated along the shoreline in approximately one foot of water. Also, *Typha angustifolia* were planted into offshore plots in approximately one foot of water. Each plot measured one square meter and was set two to three feet apart from each other for each species.

A square frame measuring one square meter delineated each plot area with bamboo garden stakes placed into the corners of each plot serving as markers (Figure 1). Ten plants for each species were planted into each plot. This gave a total of 50 plants for each test species and 150 plants in total for the control.

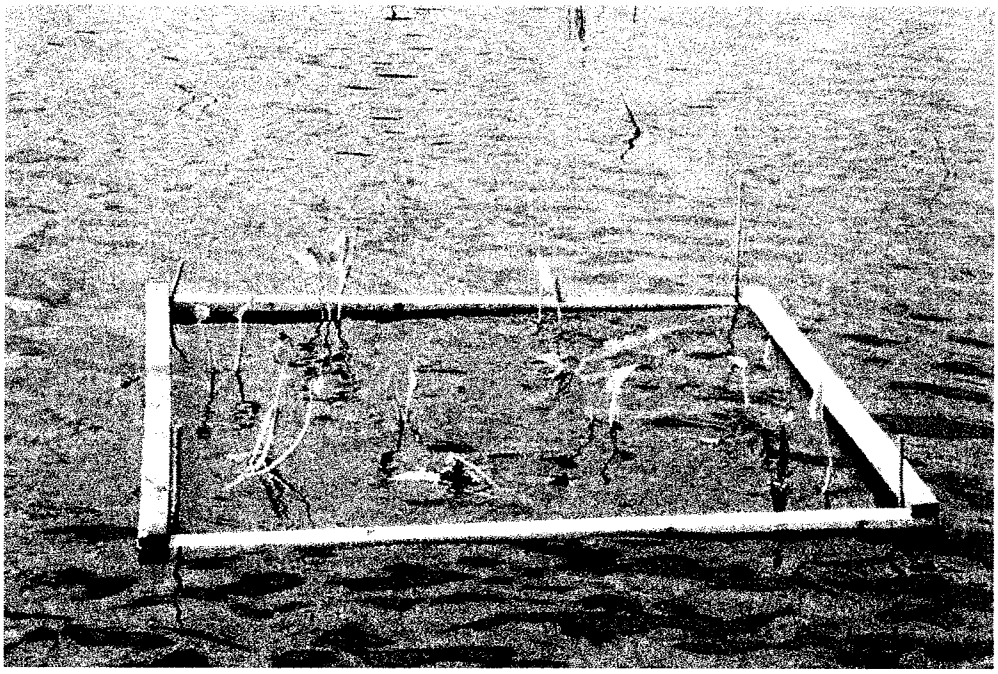

Figure 1. Test plot design used during the summer of 2004 with Calla palustris planted within.

Summer 2005

The sample design incorporating unenclosed plots of test and control species of emergent vegetation at three separate areas at the north end of Mission Island Marsh was revised for summer, 2005. Twenty trial plots of test and control species were planted within approximately one foot of water in the north end of Mission Island Marsh at one location. The three test species, *Calla pallustris*, *Typha angustifolia*, *Phragmites australis*, along with the control species *Eleocharis smalli* were planted in five 1 m^2 plots each. Fifteen plants of each species were transplanted per plot resulting in 75 plants total per species being used in this experiment.

The entire exclosure encompassed a total area of 75 m^2 with dimensions of 5 m by 15 m. The exclosure was constructed of the same materials that had been used the previous two seasons. Metal t-fence posts were hammered two feet into the sediment. Snow fencing was wrapped and secured around the posts using plastic tie wraps to complete the exclosure (Figure 2). Several additional metal t-fence posts were located within the exclosure to mark the boundary of the different species' plots and also to discourage the geese from flying into the exclosure to feed.

Figure 2. Plant exclosure containing twenty plots of test and control species at Mission Island Marsh in July, 2005.

Results and Discussion

Summer 2004

Several wetland plant species common to northwestern Ontario were planted in several plots within the marsh. Since common reed, *Phragmites spp*, is not considered to be an important food to waterfowl and grows to several meters in height (Newmaster et al. 1997) it was planted within several plots in the mud flat area. The planting of long grasses has been shown to be an effective bird deterrent (Brough and Bridgman, 1980; Smith et al. 1999). Although Canada Geese often use *Phragmites spp.* for nest material this reed grass should form an effective barrier once established.

Aquatic emergents in the shallow water have also been greatly disturbed by the geese foraging in this area. Species such as pondweed and arrowhead have been chewed, broken and uprooted as the geese forage the plants' roots and tender shoots (Figure 3). Water arum, *Calla palustris*, which contains poisonous calcium oxalate (Newmaster et al. 1997) was also considered as a test species for this experiment since geese avoid plants with poisonous secondary metabolites (Bushsbaum et al. 1984).

Figure 3. Evidence of chewed, broken and uprooted vegetation at Mission Island Marsh due to foraging by Canada Geese (picture taken August, 2004).

Typha angustifolia was the third test species used in this study. The resident cattail species *Typha latifolia* grows primarily along the shore's edge and inland along the mudflat. The geese often avoid cattails as a primary food source even though the tubers often constitute part of their diet (Newmaster et al). The density of cattails within the marsh was not affected by the foraging geese. Since *Typha angustifolia*

grows at greater depths it was chosen as the third emergent test species used for this study.

Eleocharis smalli was the control for this study because of its successful use during the preliminary study in 2003 and its acceptance by the geese as a food source.

Plots were set up during early July of 2004. The plots were closely observed throughout the summer. During summer it is important to deter geese from the wetland since this normally is the time when geese moult. This happens over a period of approximately 40 days (Hanson, 1965). At this time they cannot fly well and so tend to remain in an area where: they feel safe, have adequate food supply and are located near open water. The north end of the marsh provides all the characteristics that a moulting flock of geese prefer. By planting unpalatable vegetation and tall perennial wetland plants geese would be forced to spend most of their moult elsewhere.

Data were to be collected from the plots by the end of August. At this time the plants would have become established enabling the geese time to consider the new species as potential food sources. Data collected were to be measured as percent of total test or control species within each plot showing extensive damage. Extensive damage to the plants was to be measured as plants uprooted by foraging geese whenever 50% or more plant tissue above the water was eaten. Total number of plants within each plot that

exhibit extensive damage was to be converted to a percentage value for each plot. A two-by-three way ANOVA on these data at p=.01 significance was to be used to determine whether the test species were significantly effective at deterring foraging Canada. The 99% confidence interval was chosen because of variation introduced by utilizing 3 separate locations within the marsh and 3 different species of vegetation.

Plots of the control and test species were set out in early July of 2004. *Eleocharis smalli* was collected from Chippewa Marsh and transplanted into the 15 control plots. *Calla palustris*, also collected from Chippewa Marsh were transplanted into the 5 plots designated for the shoreline emergent zone on July 7. The remaining 2 test species, *Typha angustifolia* and *Phragmites communis* were ordered as rootstock from Kester's W.G.F. Nurseries Inc. in Wisconsin, U.S.A. The shipment of plants during the last week of June would be preferable there was concern as to whether shipments would have made it to Thunder Bay in reasonable time due the Canada Day and Independence Day holidays during that week. If plants were held up over a weekend due to shipment or customs problems they would not remain viable. Although the plants were shipped on July 5th after the holidays there was still a delay in receiving them. The plants arriving in Thunder Bay on July 8 were promptly transplanted into the remaining plots. *Phragmites communis* were transplanted into plots designated for the mud flats while *Typha angustifolia* were transplanted slightly offshore in the emergent zone plots.

During the planting of *Phragmites communis* and *Typha angustifolia* it became obvious that geese had already grazed the area in which *Calla pallustris* and *Eleocharis smallii* were transplanted. *Eleocharis smallii* had been grazed primarily over the mud flat area. Several of the *Calla pallustris* in one of the plots had been sampled by the geese. The geese refrained from eating in the remaining 4 plots while grazing around the *Calla pallustris* (Figure 4). This early evidence indicated that this species was not a very palatable choice for the geese.

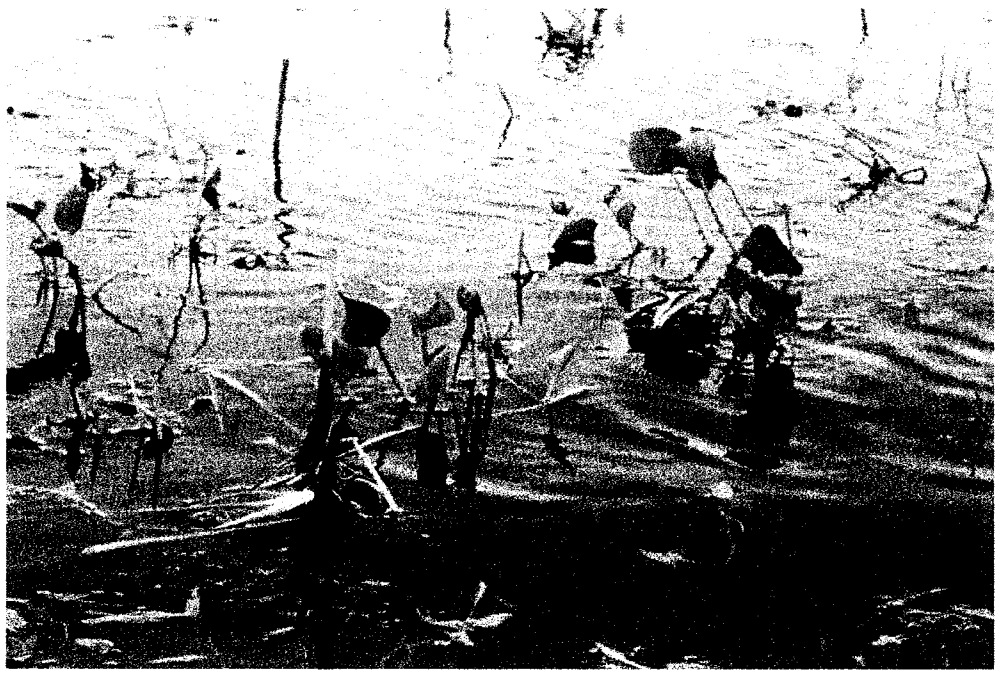

Figure 4. Plot of Calla pallustris with some minor foraging along with resident plants nearby uprooted and foraged by the geese.

The corners of the plots were marked with bamboo stakes in order to be able to recognize the plots throughout the growing season. During the first visit to the wetland

after the initial transplanting, 10 of the plot markers in the mudflat area had been removed by some individual(s) that had walked one of the various trails from the conservation area that lead to this portion of the wetland. The remaining plots, further in the wetland, remained untouched. A single marker was returned into each plot. It was hoped that fewer markers would be less obvious and therefore, less tempting to passersby. The markers then remained untouched the remainder of the season. The spring of 2004 was cooler and wetter than previous years. Due to the wet spring the wetland landscape had changed. The large mudflat area at the north end of the marsh remained flooded throughout the summer. This area had been grazed to the ground the previous year but appeared to be recovering due to the higher water levels. Plants in this area are primarily sedges and grasses. The geese prefer the graze on both types of plants but only the shoot portion. The roots remained viable and were able to recover when water levels rose (Figure 5). Although the geese continued to graze, the species of plants typical for this area can handle a fair amount of grazing stress.

Figure 5. Grasses and sedges on the mudflat area of Mission Island Marsh recovering from grazing pressure because of higher water levels in July, 2004.

Plants adapted to grazing pressure have been shown to recovery rapidly when protected from further foraging (O.P.C. et al 2006).

The mudflat test species *Phragmites communis* survived the transplant process but failed to grow sufficiently to be able to ascertain whether or not the geese considered this species as a food source. The resident sedges and grasses recovered throughout the season in this area due to the wet conditions and filled the test plots. The geese, during the previous dry summer, were observed spending a great deal of time on the mud flat. With the wet conditions, however, there was less evidence of the geese staying on the mudflat area to rest. Feathers from the goose moult and goose droppings were still abundant throughout the area indicating that although they may

not spend much rest time in this area it was still a primary feeding ground. The flooding of the mudflat area had, however, allowed this portion of the wetland to greatly improve.

Although data from the experiment utilizing a test species in this area could not be used, the recovery of the resident species indicates that planting of new species in this area is not necessary.

The shoreline test plots of *Calla palustris* proved resilient throughout the growing season. These plants survived the transplant process and remained untouched by the geese. The exception happened the day after transplant when evidence of foraging was observed in one of the plots. Upon tasting some of the plants the geese determined they were not palatable and they refrained from eating this species. During late August, however, the resident pondweed species still existing in this plot area began to grow. During late summer and fall the geese will forage on the roots of emergents such as pondweed (Coleman and Boag 1987) and uproot pondweed in the test area. Since the density of test plants per plot (10 plants/1m^2) was low presence of *Calla palustris* did not discourage the geese from continuous foraging on roots of other species in the same area. The result was that much of the *Calla pallustris* were uprooted along with the pondweeds (Figure 6). I could not determine whether or not the geese were actually foraging the roots of the test species or by foraging for other preferred species incidentally uprooted the *Calla*.

Figure 6. Transplanted Calla pallustris uprooted by Canada Geese as they forage the pondweeds and arrowheads in the area in August, 2004.

Offshore test plots of *Typha angustifolia* did not perform at all during the season. During the planting of these species Common Carp were observed spawning in the area. Concern at the time centered on whether or not these test plants would be uprooted by the carp. The carp appear to only use the wetland as a spawning ground but not a major feeding area. This was the only evidence of carp activity observed during the two seasons. Carp numbers in the future could threaten the emergent species in the wetland but do not appear to be a problem at this time. The plants remained undisturbed by the carp but still did not survive. The rootstock may have been affected by the delay in shipping to Thunder Bay. As a result data could not be obtained from test areas.

Summer 2005

Utilization of suspected non-palatable vegetation encompassed only the emergent zone during the revised experiment during summer 2005. This was because the mudflat area was recovering. *Calla palustris* was again utilized since geese did not appear to prefer this plant as a food source. *Phragmites communis* and the control species *Eleocharis smalli* were also utilized but were not planted in the form of nursery rootstock. They were collected from nearby wetlands. The exception was *Typha angustifolia* which was ordered from an Ontario wetland nursery and arrived within 24 hours from harvest. The plants were quickly transplanted into the test areas. This ensured more control over the quality of plants. Less handling of test and control species and rapid transplantation increased transplant success. The density of these plants in the test plots during the past sampling season may not have been sufficient to deter the geese. Since transplants must compete with native species planting a greater density would increase survival. Therefore a higher density of 15 plants per $1m^2$ was planted. Also since unprotected test plants were being foraged immediately after transplant the test plants were to remain enclosed after transplant (late May - early June, 2005) until the following spring. This would have allowed the test species a greater chance of surviving the transplant process without the added stress of foraging.

This new experimental design utilized a single large exclosure thus excluding the geese from the test plots. Once the transplants were established the exclosure was to be removed. The removal of the exclosure was to occur during the spring of 2006.

However, by early August of 2005 the entire exclosure and its contents of test and control species of emergent vegetation had been vandalized by unknown individual(s). Further attempt at this experiment was not possible at this late stage in the researcher's sampling season.

Conclusions

From the physical evidence obtained during the summer of 2004 a number of conclusions can be drawn. The recovery of the resident species in the mudflat area indicates that testing in this area is unnecessary at this time. The previous year's low water levels contributed to the decline of species in this area. The dry conditions allowed for a more preferable landscape for the geese to occupy. With the wet cool conditions during the summer of 2004 this area has recovered despite the fact that the geese still moderately forage in this area. The plants appear chewed but to a lesser extent than the previous year, again due to the higher water level.

The greatest threat that the geese pose to the wetland continues to be towards emergent and floating species. Since the geese prefer the roots of many emergent species, their foraging activity drastically reduces the numbers of these plants. Since very little has been documented on the use of non-palatable and/or tall emergent wetland species as a deterrent to foraging by Canada Geese in a wetland environment, more study is recommended. The plant species documented within this paper are

supported by the literature as plants having good potential plants to utilize in studies such as this one. As Mission Island Marsh continues to experience foraging stress by Canada Geese the dynamics of the wetland environment are constantly changing. With the constant removal of macrophyes from the wetland there will come a time when the seed and root bank located at Mission Island Marsh will be depleted. As the marsh becomes devoid of macrophytic vegetation, more sediment transport will occur due to the absence of root structure within the sediment. At some time, perhaps in the very near future, the marsh portion of this ecologically valuable wetland will be reduced to limited shoreline emergents. If successful establishment of non-palatable and tall emergents could occur at this site the marsh structure could be maintained.

Appendix B. Complete water quality analysis results for summers of 2005 and 2006

Lakehead University Centre for Analytical Services Environmental Laboratory

Client : PLEE Research **Date:07/28/05**
Jobnum: EL050118 **Sample Date: 05/26/05**

LABID:				004	005	006	007
CUSTID:				North Marsh	North Marsh Replicate	South Marsh	Lake Front
Par Code	Description	MDL	UNITS				
WALK	Total Alkalinity as CaCO3	1.0	mg/L	50.1	50.4	51.3	46.3
WCOND	Conductivity	0.2	uS/cm	141.5	141.6	137.3	135.3
WICP1AL	Aluminum, HNO3 digest	0.0050	mg/L	0.1394	0.1303	0.0702	0.2562
WICP1AS	Arsenic, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL
WICP1BA	Barium, HNO3 digest	0.0030	mg/L	0.0188	0.0187	0.0235	0.0183
WICP1BE	Be, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL
WICP1CA	Calcium, HNO3 digest	0.0050	mg/L	14.4341	14.6567	15.2699	16.0122
WICP1CD	Cd, HNO3 digest	0.0010	mg/L	<DL	<DL	<DL	<DL
WICP1CO	Cobalt, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL
WICP1CR	Chromium, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL
WICP1CU	Copper, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	0.0022
WICP1FE	Iron, HNO3 digest	0.0020	mg/L	0.8497	0.8388	1.0058	0.6648
WICP1K	Potassium, HNO3 digest	0.0200	mg/L	1.0243	1.0316	0.9764	1.2616
WICP1MG	Magnesium, HNO3 digest	0.0050	mg/L	4.0736	4.1267	4.1683	4.2706
WICP1MN	Manganese, HNO3 digest	0.0002	mg/L	0.0252	0.0251	0.1063	0.0249
WICP1NA	Sodium, HNO3 digest	0.0050	mg/L	10.2080	10.3157	8.2487	7.8408
WICP1NI	Nickel, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL
WICP1P	Phosphorus, HNO3 digest	0.080	mg/L	<DL	<DL	<DL	<DL
WICP1PB	Lead, HNO3 digest	0.0050	mg/L	<DL	<DL	<DL	<DL
WICP1S	Sulfur, HNO3 digest	0.05	mg/L	2.91	2.96	3.15	4.07
WICP1SI	Silicon, HNO3 digest	0.1000	mg/L	1.3317	1.3301	0.5356	2.4058
WICP1SR	Strontium, HNO3 digest	0.050	mg/L	<DL	<DL	<DL	<DL
WICP1TI	Titaniuim, HNO3 digest	0.010	mg/L	<DL	<DL	<DL	<DL
WICP1V	Vanadium, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL
WICP1ZN	Zinc, HNO3 digest	0.0010	mg/L	0.0040	0.0070	0.0038	0.0046
WNH3	NH3-N (IC)	0.025	mg/L	<DL	<DL	<DL	0.026
WNOX	NO3 + NO2 as N Colorimetry	0.000	mg/L	0.131	0.114	0.155	0.274
WPH	pH	n/a	n/a	6.97	7.01	6.98	6.98
WTNUV	Total Nitrogen UV digestable	0.015	mg/L	0.571	0.527	0.566	0.605
WTOTN	Total K. Nitrogen	0.015	mg/L	0.440	0.413	0.411	0.331
WTOTP	Total Phosphorous	0.005	mg/L	0.009	0.009	0.014	0.009

Lakehead University Centre for Analytical Services Environmental Laboratory

Client : PLEE Research **Date:07/28/05**
Jobnum: EL050165 **Sample Date: 06/27/05**

LABID:				004	005	006	007
CUSTID:				North Marsh	South Marsh	South Marsh Replicate	Lake Front
Par Code	Description	MDL	UNITS				
WALK	Total Alkalinity as CaCO3	1.0	mg/L	48.1	54.3	54.6	46.1
WCOND	Conductivity	0.2	uS/cm	127.8	137.7	135.5	120.1
WICP1AL	Aluminum, HNO3 digest	0.0050	mg/L	0.1193	0.0380	0.0399	0.1881
WICP1AS	Arsenic, HNO3 digest	0.0100	mg/L	0.0135	0.0126	0.0117	0.0140
WICP1BA	Barium, HNO3 digest	0.0030	mg/L	0.0148	0.0265	0.0265	0.0112
WICP1BE	Be, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL
WICP1CA	Calcium, HNO3 digest	0.0050	mg/L	14.1798	15.3710	15.6891	13.5534
WICP1CD	Cd, HNO3 digest	0.0010	mg/L	<DL	<DL	<DL	<DL
WICP1CO	Cobalt, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL
WICP1CR	Chromium, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL
WICP1CU	Copper, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	0.0020
WICP1FE	Iron, HNO3 digest	0.0020	mg/L	0.7892	1.1962	1.2422	0.5802
WICP1K	Potassium, HNO3 digest	0.0200	mg/L	0.6032	0.2748	0.2801	0.7377
WICP1MG	Magnesium, HNO3 digest	0.0050	mg/L	3.6276	4.0780	4.1467	3.3653
WICP1MN	Manganese, HNO3 digest	0.0002	mg/L	0.0381	0.0376	0.0406	0.0273
WICP1NA	Sodium, HNO3 digest	0.0050	mg/L	7.2264	7.0370	6.9804	6.2807
WICP1NI	Nickel, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL
WICP1P	Phosphorus, HNO3 digest	0.080	mg/L	<DL	<DL	<DL	<DL
WICP1PB	Lead, HNO3 digest	0.0050	mg/L	<DL	<DL	<DL	<DL
WICP1S	Sulfur, HNO3 digest	0.05	mg/L	2.46	2.82	2.90	2.59
WICP1SI	Silicon, HNO3 digest	0.1000	mg/L	0.2124	0.3294	0.3574	0.2862
WICP1SR	Strontium, HNO3 digest	0.050	mg/L	<DL	<DL	<DL	<DL
WICP1TI	Titaniuim, HNO3 digest	0.010	mg/L	<DL	<DL	<DL	<DL
WICP1V	Vanadium, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL
WICP1ZN	Zinc, HNO3 digest	0.0010	mg/L	0.0017	0.0015	0.0014	0.0023
WNH3	NH3-N (IC)	0.025	mg/L	0.035	0.028	0.033	0.048
WNOX	NO3 + NO2 as N Colorimetry	0.000	mg/L	0.096	0.003	0.004	0.010
WPH	pH	n/a	n/a	9.08	9.52	9.43	8.91
WTNUV	Total Nitrogen UV digestable	0.015	mg/L	0.3660	0.4530	0.4440	0.5370
WTOTN	Total K. Nitrogen	0.015	mg/L	0.271	0.450	0.441	0.527
WTOTP	Total Phosphorous	0.005	mg/L	0.007	0.020	0.020	0.007

Lakehead University Centre for Analytical Services Environmental Laboratory

Client : PLEE Research **Date:08/17/05**
Jobnum: EL050206 **Sample Date: 07/27/05**

LABID:				004	005	006	007
CUSTID:				Lake Front	Lake Front Repeat	North Marsh	South Marsh
Par Code	**Description**	**MDL**	**UNITS**				
WALK	Total Alkalinity as CaCO3	1.0	mg/L	42.6	42.8	46.5	59.6
WCOND	Conductivity	0.2	uS/cm	130.5	130.1	138.5	163.0
WICP1AL	Aluminum, HNO3 digest	0.0050	mg/L	0.0976	0.0971	0.0718	0.0207
WICP1AS	Arsenic, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL
WICP1BA	Barium, HNO3 digest	0.0030	mg/L	0.0135	0.0134	0.0131	0.0166
WICP1BE	Be, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL
WICP1CA	Calcium, HNO3 digest	0.0050	mg/L	14.3977	14.5222	15.1088	18.3844
WICP1CD	Cd, HNO3 digest	0.0010	mg/L	<DL	<DL	<DL	<DL
WICP1CO	Cobalt, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL
WICP1CR	Chromium, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL
WICP1CU	Copper, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL
WICP1FE	Iron, HNO3 digest	0.0020	mg/L	0.1967	0.1964	0.2036	0.9201
WICP1K	Potassium, HNO3 digest	0.0200	mg/L	0.9664	0.9844	0.7762	0.3798
WICP1MG	Magnesium, HNO3 digest	0.0050	mg/L	3.0512	3.0801	3.3690	4.5912
WICP1MN	Manganese, HNO3 digest	0.0002	mg/L	0.0179	0.0177	0.0072	0.0410
WICP1NA	Sodium, HNO3 digest	0.0050	mg/L	7.1069	7.2025	7.0114	7.2558
WICP1NI	Nickel, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL
WICP1P	Phosphorus, HNO3 digest	0.080	mg/L	<DL	<DL	<DL	<DL
WICP1PB	Lead, HNO3 digest	0.0050	mg/L	<DL	<DL	<DL	<DL
WICP1S	Sulfur, HNO3 digest	0.05	mg/L	3.14	3.16	3.11	2.08
WICP1SI	Silicon, HNO3 digest	0.1000	mg/L	1.9716	1.9869	0.8707	1.0391
WICP1SR	Strontium, HNO3 digest	0.050	mg/L	<DL	<DL	<DL	<DL
WICP1TI	Titaniuim, HNO3 digest	0.010	mg/L	<DL	<DL	<DL	<DL
WICP1V	Vanadium, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL
WICP1ZN	Zinc, HNO3 digest	0.0010	mg/L	0.0027	0.0026	0.0015	<DL
WNH3	NH3-N (IC)	0.025	mg/L	0.139	0.139	0.032	0.139
WNOX	NO3 + NO2 as N Colorimetry	0.000	mg/L	0.187	0.191	0.025	0.060
WPH	pH	n/a	n/a	7.39	7.49	9.61	10.13
WTNUV	Total Nitrogen UV digestable	0.015	mg/L	0.6790	0.7040	0.3960	0.8530
WTOTN	Total K. Nitrogen	0.015	mg/L	0.492	0.513	0.371	0.793
WTOTP	Total Phosphorous	0.005	mg/L	0.0169	0.0197	0.015	<DL

Lakehead University Centre for Analytical Services Environmental Laboratory

Client : PLEE Research
Jobnum: EL050234
1
Date:09/27/05
Sample Date: 08/17/05

				004	005	006	007	008	009	010	011
LABID:											
CUSTID:				Bare Point	Bare Pt RPT	Mission River	Lake Front	Kam River	McKellar River	North Marsh	South Marsh
Par Code	Description	MDL	UNITS								
WALK	Total Alkalinity as CaCO3	1.0	mg/L	44.5	44.6	46.0	42.8	43.3	43.4	42.8	57.6
WCOND	Conductivity	0.2	uS/cm	113.3	113.1	163.6	110.3	114.7	129.3	115.5	150.4
WICP1AL	Aluminum, HNO3 digest	0.0050	mg/L	0.0322	0.0319	0.1152	0.0383	0.0592	0.0782	0.0624	0.0254
WICP1AS	Arsenic, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1BA	Barium, HNO3 digest	0.0030	mg/L	0.0106	0.0108	0.0160	0.0123	0.0101	0.0123	0.0134	0.0192
WICP1BE	Be, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CA	Calcium, HNO3 digest	0.0050	mg/L	14.2402	14.6735	14.4869	14.6535	14.5513	14.2046	13.2091	16.8469
WICP1CD	Cd, HNO3 digest	0.0010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CO	Cobalt, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CR	Chromium, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CU	Copper, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1FE	Iron, HNO3 digest	0.0020	mg/L	0.0198	0.0201	0.1463	0.0468	0.0462	0.1163	0.1186	1.4382
WICP1K	Potassium, HNO3 digest	0.0200	mg/L	0.5473	0.5629	1.0967	0.6029	0.7107	0.7880	0.6187	0.2587
WICP1MG	Magnesium, HNO3 digest	0.0050	mg/L	2.8507	2.9262	3.1884	2.9507	2.9329	2.9551	2.7507	4.6529
WICP1MN	Manganese, HNO3 digest	0.0002	mg/L	0.0017	0.0017	0.0304	0.0072	0.0039	0.0128	0.0087	0.0563
WICP1NA	Sodium, HNO3 digest	0.0050	mg/L	1.9916	2.0294	11.5379	2.1479	2.3268	5.6868	2.8156	7.0801
WICP1NI	Nickel, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1P	Phosphorus, HNO3 digest	0.080	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1PB	Lead, HNO3 digest	0.0050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1S	Sulfur, HNO3 digest	0.05	mg/L	1.29	1.33	4.54	1.45	1.48	2.70	1.65	1.84
WICP1SI	Silicon, HNO3 digest	0.1000	mg/L	0.8442	0.8700	2.2400	0.8882	0.8864	1.4149	0.9084	0.4327
WICP1SR	Strontium, HNO3 digest	0.050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1TI	Titaniuim, HNO3 digest	0.010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1V	Vanadium, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1ZN	Zinc, HNO3 digest	0.0010	mg/L	<DL	<DL	0.0044	<DL	<DL	0.0020	<DL	<DL
WNH3	NH3-N (IC)	0.025	mg/L	0.028	<DL	0.196	<DL	0.139	0.050	<DL	<DL
WNOX	NO3 + NO2 as N Colorimetry	0.000	mg/L	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
WPH	pH	n/a	n/a	7.01	7.02	6.79	6.96	7.11	6.92	7.00	8.65
WTNUV	Total Nitrogen UV digestable	0.015	mg/L	0.3911	0.3803	0.6836	0.4582	0.5726	0.4988	0.4474	0.5427
WTOTN	Total K. Nitrogen	0.015	mg/L	0.099	0.058	0.424	0.135	0.241	0.203	0.130	0.558
WTOTP	Total Phosphorous	0.005	mg/L	<DL	<DL	0.031	0.013	0.008	0.008	0.009	0.024

Lakehead University Centre for Analytical Services Environmental Laboratory

Client : PLEE Research
Jobnum: EL050257
1
Date:09/27/05
Sample Date: 08/30/05

LABID:				004	005	006	007	008	009	010	011
CUSTID:				Bare Point	North Marsh	Kam River	Lake Front	McKellar River	Mission River	South Marsh	Kam River Repeat
Par Code	Description	MDL	UNITS								
WALK	Total Alkalinity as CaCO3	1.0	mg/L	49.2	44.8	53.8	45.3	46.5	47.3	55.6	54.1
WCOND	Conductivity	0.2	uS/cm	123.1	131.2	201.7	145.2	160.5	204.2	144.2	201.9
WICP1AL	Aluminum, HNO3 digest	0.0050	mg/L	0.0150	0.0426	0.1815	0.0708	0.0941	0.1246	0.0099	0.1836
WICP1AS	Arsenic, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1BA	Barium, HNO3 digest	0.0030	mg/L	0.0119	0.0120	0.0171	0.0136	0.0146	0.0193	0.0212	0.0173
WICP1BE	Be, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CA	Calcium, HNO3 digest	0.0050	mg/L	15.3885	13.6574	16.6796	14.5396	13.9285	14.1174	15.1529	16.9307
WICP1CD	Cd, HNO3 digest	0.0010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CO	Cobalt, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CR	Chromium, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CU	Copper, HNO3 digest	0.0020	mg/L	<DL	<DL	0.0021	<DL	<DL	<DL	<DL	0.0024
WICP1FE	Iron, HNO3 digest	0.0020	mg/L	0.0174	0.0741	0.2422	0.1198	0.1461	0.1630	1.4669	0.2478
WICP1K	Potassium, HNO3 digest	0.0200	mg/L	0.5924	0.7884	1.8538	1.0118	1.0876	1.3264	0.3889	1.8924
WICP1MG	Magnesium, HNO3 digest	0.0050	mg/L	3.1239	2.9262	3.9528	3.1995	3.1239	3.3195	4.1284	4.0106
WICP1MN	Manganese, HNO3 digest	0.0002	mg/L	0.0040	0.0101	0.0318	0.0139	0.0223	0.0350	0.0343	0.0323
WICP1NA	Sodium, HNO3 digest	0.0050	mg/L	2.7128	5.7661	13.6350	9.6417	11.0083	20.8950	5.7972	13.8306
WICP1NI	Nickel, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1P	Phosphorus, HNO3 digest	0.080	mg/L	<DL	<DL	0.083	<DL	<DL	<DL	<DL	0.085
WICP1PB	Lead, HNO3 digest	0.0050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1S	Sulfur, HNO3 digest	0.05	mg/L	1.38	2.44	5.31	3.92	4.58	9.33	1.99	5.37
WICP1SI	Silicon, HNO3 digest	0.1000	mg/L	0.9329	0.8389	1.8978	1.5129	1.8384	2.8156	0.2060	1.9231
WICP1SR	Strontium, HNO3 digest	0.050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1TI	Titaniuim, HNO3 digest	0.010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1V	Vanadium, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1ZN	Zinc, HNO3 digest	0.0010	mg/L	<DL	0.0010	0.0032	0.0021	0.0022	0.0035	<DL	0.0034
WNH3	NH3-N (IC)	0.025	mg/L	0.035	0.064	1.205	0.092	0.278	0.084	<DL	1.205
WNOX	NO3 + NO2 as N Colorimetry	0.000	mg/L	0.319	0.211	0.319	0.259	0.273	0.217	0.005	0.328
WPH	pH	n/a	n/a	6.96	7.62	6.80	7.36	6.77	6.78	7.73	6.78
WTNUV	Total Nitrogen UV digestable	0.015	mg/L	0.4010	0.4250	1.4860	0.5310	0.6910	0.5590	0.4910	1.5040
WTOTN	Total K. Nitrogen	0.015	mg/L	0.082	0.214	1.167	0.272	0.418	0.342	0.486	1.176
WTOTP	Total Phosphorous	0.005	mg/L	<DL	0.016	0.036	0.022	0.033	0.062	0.028	0.034

Lakehead University Centre for Analytical Services Environmental Laboratory

Client : PLEE Research **Date:11/21/05**
Jobnum: EL050298 **Sample Date: 10/04/05**

LABID:				004	005	006	007	008	009	010	011
CUSTID:				McKellar	McKellar Repeat	North Marsh	South Marsh	Mission River	Bare Point	Lake Front	Kam River
Par Code	Description	MDL	UNITS								
WALK	Total Alkalinity as CaCO3	1.0	mg/L	50.6	49.7	45.5	63.3	51.2	47.7	44.8	65.8
WCOND	Conductivity	0.2	uS/cm	146.3	146.3	129.8	189.5	182.0	118.8	119.8	237.6
WICP1AL	Aluminum, HNO3 digest	0.0050	mg/L	0.047	0.055	0.144	0.035	0.111	0.053	0.134	0.070
WICP1AS	Arsenic, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	0.006	<DL
WICP1BA	Barium, HNO3 digest	0.0030	mg/L	0.015	0.016	0.019	0.040	0.019	0.013	0.015	0.017
WICP1BE	Be, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CA	Calcium, HNO3 digest	0.0050	mg/L	17.250	18.383	15.872	21.063	16.745	17.139	15.452	20.512
WICP1CD	Cd, HNO3 digest	0.0010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CO	Cobalt, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CR	Chromium, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CU	Copper, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1FE	Iron, HNO3 digest	0.0020	mg/L	0.147	0.166	0.462	1.165	0.248	0.066	0.292	0.205
WICP1K	Potassium, HNO3 digest	0.0200	mg/L	1.14	1.21	1.15	1.47	1.54	0.64	0.87	3.44
WICP1MG	Magnesium, HNO3 digest	0.0050	mg/L	3.63	3.88	3.52	5.35	3.74	3.59	3.32	5.06
WICP1MN	Manganese, HNO3 digest	0.0002	mg/L	0.0104	0.0121	0.0628	0.0372	0.0311	0.0037	0.0194	0.0423
WICP1NA	Sodium, HNO3 digest	0.0050	mg/L	6.74	7.22	5.09	10.51	14.05	3.10	3.94	14.91
WICP1NI	Nickel, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1P	Phosphorus, HNO3 digest	0.080	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1PB	Lead, HNO3 digest	0.0050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1S	Sulfur, HNO3 digest	0.05	mg/L	3.03	3.26	2.72	4.80	5.58	1.49	2.10	4.53
WICP1SI	Silicon, HNO3 digest	0.1000	mg/L	1.50	1.62	1.43	0.37	2.79	1.08	1.32	2.13
WICP1SR	Strontium, HNO3 digest	0.050	mg/L	<DL	<DL	<DL	0.054	<DL	<DL	<DL	<DL
WICP1TI	Titaniuim, HNO3 digest	0.010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1V	Vanadium, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1ZN	Zinc, HNO3 digest	0.0010	mg/L	<DL	<DL	<DL	<DL	0.004	<DL	<DL	0.002
WNH3	NH3-N (IC)	0.025	mg/L	0.307	0.309	0.214	0.163	0.244	<DL	0.048	2.072
WNOX	NO3 + NO2 as N Colorimetry	0.000	mg/L	0.339	0.314	0.382	0.021	0.251	0.281	0.356	1.518
WPH	pH	n/a	n/a	6.60	6.64	6.54	6.57	6.63	6.73	6.65	6.82
WTNUV	Total Nitrogen UV digestable	0.015	mg/L	0.8250	0.8510	0.8510	0.6280	0.9020	0.6360	0.6740	2.5190
WTOTN	Total K. Nitrogen	0.015	mg/L	0.487	0.537	0.469	0.607	0.651	0.355	0.318	1.003
WTOTP	Total Phosphorous	0.005	mg/L	0.017	0.012	0.011	0.019	0.036	<DL	0.009	0.039

Lakehead University Centre for Analytical Services Environmental Laboratory

Client : PLEE Research **Date:06/14/06**
Jobnum: EL060116 **Sample Date: 05/30/06**

LABID:				004	005	006	007	008	009	010	011
CUSTID:				Bare Point	Bare Point Repeat	Kam River	McKellar River	Lake front	North Marsh	South Marsh	Mission River
Par Code	Description	MDL	UNITS								
WALK	Total Alkalinity as CaCO3	1.0	mg/L	43.1	42.7	49.7	48.3	49.2	52.3	59.7	44.3
WCOND	Conductivity	0.2	uS/cm	105.5	105.1	176.7	158.6	155.5	162.4	163.4	139.1
WICP1AL	Aluminum, HNO3 digest	0.0050	mg/L	0.039	0.039	0.153	0.158	0.117	0.135	0.042	0.184
WICP1AS	Arsenic, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1BA	Barium, HNO3 digest	0.0030	mg/L	0.012	0.012	0.018	0.017	0.017	0.015	0.028	0.018
WICP1BE	Be, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CA	Calcium, HNO3 digest	0.0050	mg/L	15.483	16.061	18.110	17.030	17.390	17.357	18.792	15.490
WICP1CD	Cd, HNO3 digest	0.0010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CO	Cobalt, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CR	Chromium, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CU	Copper, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1FE	Iron, HNO3 digest	0.0020	mg/L	0.041	0.040	0.336	0.345	0.306	0.500	1.253	1.113
WICP1K	Potassium, HNO3 digest	0.0200	mg/L	0.62	0.65	1.75	1.40	1.43	1.37	1.09	1.29
WICP1MG	Magnesium, HNO3 digest	0.0050	mg/L	3.15	3.25	4.84	4.46	4.57	4.69	4.94	4.11
WICP1MN	Manganese, HNO3 digest	0.0002	mg/L	0.0021	0.0019	0.0439	0.0330	0.0257	0.0203	0.0734	0.0516
WICP1NA	Sodium, HNO3 digest	0.0050	mg/L	2.12	2.20	12.85	10.41	9.77	10.32	9.37	10.04
WICP1NI	Nickel, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1P	Phosphorus, HNO3 digest	0.080	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1PB	Lead, HNO3 digest	0.0050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1S	Sulfur, HNO3 digest	0.05	mg/L	1.40	1.46	4.29	4.04	4.37	4.81	3.48	3.94
WICP1SI	Silicon, HNO3 digest	0.1000	mg/L	1.09	1.13	3.40	3.20	2.56	0.35	0.50	3.32
WICP1SR	Strontium, HNO3 digest	0.050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1TI	Titaniuim, HNO3 digest	0.010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1V	Vanadium, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1ZN	Zinc, HNO3 digest	0.0010	mg/L	<DL	<DL	0.003	0.003	0.002	0.002	<DL	0.003
WNH3	NH3-N (IC)	0.025	mg/L	<DL	<DL	0.144	0.156	0.112	0.076	0.070	0.069
WNOX	NO3 + NO2 as N Colorimetry	0.000	mg/L	0.353	0.353	0.577	0.283	0.230	0.017	0.009	0.127
WPH	pH	n/a	n/a	7.79	7.87	7.42	7.45	8.10	8.43	7.89	7.26
WTKN	Total Nitrogen UV digestable	0.015	mg/L	0.085	0.084	0.439	0.467	0.444	0.540	0.549	0.516
WTNUV	Total K. Nitrogen	0.015	mg/L	0.438	0.438	1.016	0.749	0.674	0.557	0.557	0.643
WTOTP	Total Phosphorous	0.005	mg/L	<DL	0.008	0.031	0.038	0.028	0.026	0.040	0.031

Lakehead University Centre for Analytical Services Environmental Laboratory

Client : PLEE Research **Date:07/12/06**
Jobnum: EL060149 **Sample Date: 06/28/06**

LABID:				004	005	006	007	008	009	010	011
CUSTID:				Lakefront	Kam River	Kam River Repeat	McKellar River	Bare Point	North Marsh	South Marsh	Mission River
Par Code	Description	MDL	UNITS								
WALK	Total Alkalinity as CaCO3	1.0	mg/L	46.0	48.0	46.1	45.1	44.0	46.5	54.1	46.5
WCOND	Conductivity	0.2	uS/cm	146.4	153.6	130.0	132.8	111.5	147.2	138.4	154.0
WICP1AL	Aluminum, HNO3 digest	0.0050	mg/L	0.116	0.035	0.033	0.120	0.031	0.079	0.020	0.156
WICP1AS	Arsenic, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1BA	Barium, HNO3 digest	0.0030	mg/L	0.021	0.012	0.012	0.014	0.011	0.019	0.026	0.017
WICP1BE	Be, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CA	Calcium, HNO3 digest	0.0050	mg/L	15.207	17.058	16.765	15.978	15.254	15.047	16.805	14.943
WICP1CD	Cd, HNO3 digest	0.0010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CO	Cobalt, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CR	Chromium, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CU	Copper, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1FE	Iron, HNO3 digest	0.0020	mg/L	0.196	0.080	0.074	0.175	0.024	0.168	1.408	0.258
WICP1K	Potassium, HNO3 digest	0.0200	mg/L	1.28	1.29	0.98	1.06	0.64	1.20	0.40	1.32
WICP1MG	Magnesium, HNO3 digest	0.0050	mg/L	3.58	3.93	3.70	3.61	3.13	3.63	4.13	3.56
WICP1MN	Manganese, HNO3 digest	0.0002	mg/L	0.0237	0.0116	0.0095	0.0164	0.0029	0.0195	0.0339	0.0368
WICP1NA	Sodium, HNO3 digest	0.0050	mg/L	10.01	7.21	5.05	7.25	2.76	9.86	7.08	12.35
WICP1NI	Nickel, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1P	Phosphorus, HNO3 digest	0.080	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1PB	Lead, HNO3 digest	0.0050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1S	Sulfur, HNO3 digest	0.05	mg/L	4.43	2.13	1.85	3.14	1.40	4.53	2.48	5.22
WICP1SI	Silicon, HNO3 digest	0.1000	mg/L	1.96	1.52	1.40	2.00	0.98	1.80	1.00	2.85
WICP1SR	Strontium, HNO3 digest	0.050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1TI	Titaniuim, HNO3 digest	0.010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1V	Vanadium, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1ZN	Zinc, HNO3 digest	0.0010	mg/L	0.003	0.001	<DL	0.002	<DL	0.002	<DL	0.004
WNH3	NH3-N (IC)	0.025	mg/L	0.050	<DL	<DL	<DL	<DL	0.062	0.050	<DL
WNOX	NO3 + NO2 as N Colorimetry	0.000	mg/L	0.178	0.847	0.517	0.327	0.268	0.033	0.007	0.232
WPH	pH	n/a	n/a	8.60	7.78	7.90	7.64	8.01	9.23	9.29	7.26
WTKN	Total Nitrogen UV digestable	0.015	mg/L	0.295	0.093	0.080	0.160	0.063	0.298	0.512	0.277
WTNUV	Total K. Nitrogen	0.015	mg/L	0.473	0.940	0.596	0.487	0.331	0.331	0.519	0.508
WTOTP	Total Phosphorous	0.005	mg/L	0.038	0.005	<DL	0.077	0.045	0.042	0.009	0.012

Lakehead University Centre for Analytical Services Environmental Laboratory

Client : PLEE Research **Date:08/30/06**
Jobnum: EL060174 **Sample Date: 07/26/06**
1

LABID:				004	005	006	007	008	009	010	011
CUSTID:				Mission River	South Marsh	North Marsh	Lakefront	McKellar River	McKellar River Repeat	Kam River	Bare Point
Par Code	Description	MDL	UNITS								
WALK	Total Alkalinity as CaCO3	1.0	mg/L	41.1	59.1	48.1	43.6	44.1	43.6	45.5	42.8
WCOND	Conductivity	0.2	uS/cm	140.4	147.4	134.1	113.0	123.8	124.9	117.5	103.9
WICP1AL	Aluminum, HNO3 digest	0.0050	mg/L	0.107	0.033	0.060	0.056	0.063	0.077	0.019	0.076
WICP1AS	Arsenic, HNO3 digest	0.0100	mg/L	0.008	0.009	0.009	0.008	0.006	0.006	0.005	0.008
WICP1BA	Barium, HNO3 digest	0.0030	mg/L	0.017	0.029	0.016	0.012	0.013	0.013	0.011	0.011
WICP1BE	Be, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CA	Calcium, HNO3 digest	0.0050	mg/L	13.613	17.106	14.928	14.126	14.086	14.284	15.115	14.346
WICP1CD	Cd, HNO3 digest	0.0010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CO	Cobalt, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CR	Chromium, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CU	Copper, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1FE	Iron, HNO3 digest	0.0020	mg/L	0.209	1.879	0.233	0.110	0.122	0.141	0.068	0.030
WICP1K	Potassium, HNO3 digest	0.0200	mg/L	1.14	0.93	0.90	0.79	0.95	0.97	0.65	0.59
WICP1MG	Magnesium, HNO3 digest	0.0050	mg/L	3.32	4.33	3.70	3.02	3.15	3.19	3.23	2.92
WICP1MN	Manganese, HNO3 digest	0.0002	mg/L	0.0264	0.1637	0.0161	0.0103	0.0131	0.0140	0.0095	0.0021
WICP1NA	Sodium, HNO3 digest	0.0050	mg/L	9.94	6.98	6.42	3.68	5.85	5.94	2.97	1.82
WICP1NI	Nickel, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1P	Phosphorus, HNO3 digest	0.080	mg/L	<DL	0.089	<DL	<DL	<DL	<DL	<DL	<DL
WICP1PB	Lead, HNO3 digest	0.0050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1S	Sulfur, HNO3 digest	0.05	mg/L	4.51	1.40	2.49	1.81	2.25	2.28	1.42	1.32
WICP1SI	Silicon, HNO3 digest	0.1000	mg/L	3.08	1.60	0.58	0.92	1.56	1.60	1.06	0.86
WICP1SR	Strontium, HNO3 digest	0.050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1TI	Titaniuim, HNO3 digest	0.010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1V	Vanadium, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1ZN	Zinc, HNO3 digest	0.0010	mg/L	0.004	0.002	0.002	0.002	0.003	0.003	0.001	0.004
WNH3	NH3-N (IC)	0.025	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WNOX	NO3 + NO2 as N Colorimetry	0.000	mg/L	0.170	<DL	<DL	0.138	0.278	0.277	0.240	0.250
WPH	pH	n/a	n/a	7.17	7.08	9.32	8.79	8.53	8.50	7.85	7.96
WTKN	Total Nitrogen UV digestable	0.015	mg/L	0.352	0.542	0.376	0.244	0.216	0.238	0.172	0.164
WTNUV	Total K. Nitrogen	0.015	mg/L	0.522	0.545	0.379	0.383	0.493	0.515	0.412	0.414
WTOTP	Total Phosphorous	0.005	mg/L	0.055	0.029	0.006	0.008	0.021	0.011	<DL	0.017

Lakehead University Centre for Analytical Services Environmental Laboratory

Client : PLEE Research **Date:09/13/06**
Jobnum: EL060216 **Sample Date: 08/29/06**

LABID:				004	005	006	007	008	009	010	011
CUSTID:				Mission River	South Marsh	North Marsh	Lake Front	Lake Front Repeat	McKella River	Kam River	Bare Point
Par Code	Description	MDL	UNITS								
WALK	Total Alkalinity as CaCO3	1.0	mg/L	47.6	50.9	44.0	44.1	43.8	45.6	46.1	44.7
WCOND	Conductivity	0.2	uS/cm	180.4	140.6	120.7	117.2	114.6	142.2	134.6	106.6
WICP1AL	Aluminum, HNO3 digest	0.0050	mg/L	0.136	0.035	0.516	0.138	0.132	0.115	0.054	0.095
WICP1AS	Arsenic, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1BA	Barium, HNO3 digest	0.0030	mg/L	0.019	0.023	0.022	0.014	0.014	0.016	0.014	0.012
WICP1BE	Be, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CA	Calcium, HNO3 digest	0.0050	mg/L	16.718	17.153	16.273	16.169	15.804	16.769	17.080	16.060
WICP1CD	Cd, HNO3 digest	0.0010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CO	Cobalt, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CR	Chromium, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CU	Copper, HNO3 digest	0.0020	mg/L	<DL	<DL	0.002	<DL	<DL	<DL	<DL	<DL
WICP1FE	Iron, HNO3 digest	0.0020	mg/L	0.239	0.996	1.153	0.285	0.270	0.214	0.129	0.094
WICP1K	Potassium, HNO3 digest	0.0200	mg/L	1.34	0.22	1.00	0.78	0.76	1.17	1.24	0.65
WICP1MG	Magnesium, HNO3 digest	0.0050	mg/L	3.69	4.35	3.64	3.36	3.28	3.62	3.65	3.23
WICP1MN	Manganese, HNO3 digest	0.0002	mg/L	0.0302	0.0469	0.0370	0.0176	0.0169	0.0170	0.0116	0.0038
WICP1NA	Sodium, HNO3 digest	0.0050	mg/L	16.14	7.32	5.10	4.16	4.07	9.11	6.40	2.18
WICP1NI	Nickel, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1P	Phosphorus, HNO3 digest	0.080	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1PB	Lead, HNO3 digest	0.0050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1S	Sulfur, HNO3 digest	0.05	mg/L	7.50	3.48	2.78	2.31	2.25	4.50	2.67	1.42
WICP1SI	Silicon, HNO3 digest	0.1000	mg/L	3.15	0.51	2.14	1.31	1.29	1.93	1.43	0.90
WICP1SR	Strontium, HNO3 digest	0.050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1TI	Titaniuim, HNO3 digest	0.010	mg/L	<DL	<DL	0.015	<DL	<DL	<DL	<DL	<DL
WICP1V	Vanadium, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1ZN	Zinc, HNO3 digest	0.0010	mg/L	0.005	<DL	0.003	<DL	0.001	0.003	0.002	0.001
WNH3	NH3-N (IC)	0.025	mg/L	0.106	<DL	0.084	0.053	0.057	0.053	0.057	<DL
WNOX	NO3 + NO2 as N Colorimetry	0.000	mg/L	0.280	<DL	0.306	0.295	0.280	0.357	0.642	0.306
WPH	pH	n/a	n/a	7.29	9.24	7.56	7.76	7.76	7.66	7.57	7.86
WTKN	Total Nitrogen UV digestable	0.015	mg/L	0.303	0.426	0.122	0.064	0.079	0.145	0.121	0.025
WTNUV	Total K. Nitrogen	0.015	mg/L	0.583	0.426	0.428	0.359	0.359	0.502	0.763	0.331
WTOTP	Total Phosphorous	0.005	mg/L	0.053	0.050	0.021	0.084	0.016	0.007	0.013	0.052

Lakehead University Centre for Analytical Services Environmental Laboratory

Client : PLEE Research **Date:10/30/06**
Jobnum: EL060255 **Sample Date: 09/29/06**

LABID:				004	005	006	007	008	009	010	011
CUSTID:				Bare Point	Kam River	McKellar River	Lakefront	North Marsh	South Marsh	Mission River	Mission River Repeat
Par Code	Description	MDL	UNITS								
WALK	Total Alkalinity as CaCO3	1.0	mg/L	43.1	69.8	44.8	46.3	45.8	52.4	43.7	43.7
WCOND	Conductivity	0.2	uS/cm	111.0	509.5	140.6	132.3	137.5	169.1	146.5	144.4
WICP1AL	Aluminum, HNO3 digest	0.0050	mg/L	0.107	0.163	0.084	0.546	0.682	0.151	0.104	0.100
WICP1AS	Arsenic, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1BA	Barium, HNO3 digest	0.0030	mg/L	0.011	0.020	0.014	0.021	0.027	0.030	0.016	0.016
WICP1BE	Be, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CA	Calcium, HNO3 digest	0.0050	mg/L	15.462	30.911	15.138	16.644	16.047	17.827	15.644	15.476
WICP1CD	Cd, HNO3 digest	0.0010	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CO	Cobalt, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CR	Chromium, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1CU	Copper, HNO3 digest	0.0020	mg/L	<DL	0.006	<DL	0.002	0.002	<DL	0.002	<DL
WICP1FE	Iron, HNO3 digest	0.0020	mg/L	0.057	0.368	0.230	1.310	2.332	1.055	0.271	0.262
WICP1K	Potassium, HNO3 digest	0.0200	mg/L	0.61	13.15	1.16	1.18	1.39	1.92	1.27	1.25
WICP1MG	Magnesium, HNO3 digest	0.0050	mg/L	3.11	8.57	3.39	3.86	3.89	4.09	3.71	3.67
WICP1MN	Manganese, HNO3 digest	0.0002	mg/L	0.0029	0.0478	0.0228	0.0258	0.0460	0.0673	0.0261	0.0254
WICP1NA	Sodium, HNO3 digest	0.0050	mg/L	1.90	45.59	6.98	5.09	6.23	8.03	8.79	8.70
WICP1NI	Nickel, HNO3 digest	0.0020	mg/L	<DL	<DL	<DL	<DL	0.002	<DL	<DL	<DL
WICP1P	Phosphorus, HNO3 digest	0.080	mg/L	<DL	0.429	<DL	<DL	<DL	<DL	<DL	<DL
WICP1PB	Lead, HNO3 digest	0.0050	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1S	Sulfur, HNO3 digest	0.05	mg/L	1.41	8.62	2.96	2.63	3.04	4.87	3.84	3.78
WICP1SI	Silicon, HNO3 digest	0.1000	mg/L	0.89	4.67	1.89	1.68	2.25	0.51	2.56	2.54
WICP1SR	Strontium, HNO3 digest	0.050	mg/L	<DL	0.064	<DL	<DL	<DL	<DL	<DL	<DL
WICP1TI	Titaniuim, HNO3 digest	0.010	mg/L	<DL	<DL	<DL	0.015	0.020	<DL	<DL	<DL
WICP1V	Vanadium, HNO3 digest	0.0100	mg/L	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
WICP1ZN	Zinc, HNO3 digest	0.0010	mg/L	<DL	0.009	<DL	0.002	0.005	<DL	0.003	0.002
WNH3	NH3-N (IC)	0.025	mg/L	<DL	0.136	0.088	0.077	0.122	0.092	0.076	0.073
WNOX	NO3 + NO2 as N Colorimetry	0.000	mg/L	0.265	2.583	0.419	0.222	0.248	0.016	0.382	0.352
WPH	pH	n/a	n/a	7.61	7.27	7.32	7.61	7.60	8.25	7.47	7.42
WTKN	Total Nitrogen UV digestable	0.015	mg/L	0.079	3.654	0.229	0.277	0.417	0.538	0.281	0.280
WTNUV	Total K. Nitrogen	0.015	mg/L	0.344	6.240	0.647	0.499	0.665	0.554	0.662	0.661
WTOTP	Total Phosphorous	0.005	mg/L	<DL	0.257	0.018	<DL	0.006	0.024	0.029	0.020

ALS Laboratory Group
ANALYTICAL CHEMISTRY & TESTING SERVICES

Environmental Division

ANALYTICAL REPORT

ATTN: SANDRA STILES

461 E. BROCK STREET

THUNDER BAY ONT P7E4H8

Reported On: 19-OCT-06 11:02 AM

Lab Work Order #: L442222 **Date Received:** 11-OCT-06

Project P.O. #: PAID BY MASTER CARD
Job Reference: SANDRA STILES~TB
Legal Site Desc:
CofC Numbers:

Other Information:

Comments:

APPROVED BY: _____
JIM VUKMANICH
Project Manager

ETL Chemspec Analytical Ltd.
Part of the **ALS Laboratory Group**
1081 Barton Street, Thunder Bay, ON P7B 5N3
Phone: +1 807 623 6463 Fax: +1 807 623 7598 www.alsglobal.com
A Campbell Brothers Limited Company

ALS LABORATORY GROUP ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	By	Batch
L442222-1 NORTH MARSH WATER								
Sampled By: S.S. on 29-AUG-06								
Matrix: WATER								
Algae Identification								
Amphora (Bacillariophyceae)	moderate amounts		1			19-OCT-06	GMK	R455139
Asterionella (Bacillariophyceae)	small amounts		1			19-OCT-06	GMK	R455139
Cocconeis (Bacillariophyceae)	large amounts		1			19-OCT-06	GMK	R455139
Cyclotella (Bacillariophyceae)	small amounts		1			19-OCT-06	GMK	R455139
Cymbella (Bacillariophyceae)	moderate amounts		1			19-OCT-06	GMK	R455139
Epithemia (Bacillariophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Fragilaria (Bacillariophyceae)	large amounts		1			19-OCT-06	GMK	R455139
Gomphonema (Bacillariophyceae)	small amounts		1			19-OCT-06	GMK	R455139
Melosira (Bacillariophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Navicula (Bacillariophyceae)	large amounts		1			19-OCT-06	GMK	R455139
Rhoicosphenia (Bacillariophyceae)	large amounts		1			19-OCT-06	GMK	R455139
Stephanodiscus (Bacillariophyceae)	small amounts		1			19-OCT-06	GMK	R455139
Synedra (Bacillariophyceae)	moderate amounts		1			19-OCT-06	GMK	R455139
Tabellaria (Bacillariophyceae)	moderate amounts		1			19-OCT-06	GMK	R455139
Coelastrum (Chlorophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Cosmarium (Chlorophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Oedogonium (Chlorophyceae)	small amounts		1			19-OCT-06	GMK	R455139
Pediastrum (Chlorophyceae)	small amounts		1			19-OCT-06	GMK	R455139
Scenedesmus (Chlorophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Cryptomonas (Cryptophyceae)	small amounts		1			19-OCT-06	GMK	R455139
Dinobryon (Chrysophyceae)	small amounts		1			19-OCT-06	GMK	R455139
Mallomonas (Chrysophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Rhodomonas (Cryptophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Anabaena (Myxophyceae)	small amounts		1			19-OCT-06	GMK	R455139
Ceratium (Peridineae)	small amounts		1			19-OCT-06	GMK	R455139
Note: Baccillariophyceae dominate sample, including large amounts of empty diatom frustules.								
L442222-2 NORTH MARSH BLOOM								
Sampled By: S.S. on 29-AUG-06								
Matrix: WATER								
Algae Identification								
Amphora (Bacillariophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Cocconeis (Bacillariophyceae)	small amounts		1			19-OCT-06	GMK	R455139
Fragilaria (Bacillariophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Synedra (Bacillariophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Closterium (Chlorophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Cosmarium (Chlorophyceae)	large amounts		1			19-OCT-06	GMK	R455139
Crucigenia (Chlorophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Oedogonium (Chlorophyceae)	moderate amounts		1			19-OCT-06	GMK	R455139
Pediastrum (Chlorophyceae)	large amounts		1			19-OCT-06	GMK	R455139
Scenedesmus (Chlorophyceae)	large amounts		1			19-OCT-06	GMK	R455139
Cryptomonas (Cryptophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Merismopedia (Myxophyceae)	scarcely present		1			19-OCT-06	GMK	R455139
Note: Empty diatom frustules present in bloom amounts. Algal mat made of filamentous algae Rhizoclonium.								

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

Reference Information

Methods Listed (if applicable):

ALS Test Code	Matrix	Test Description	Preparation Method Reference(Based On)	Analytical Method Reference(Based On)
ALGAE-ID-WP	Water	Algae Identification		Microscopic Examination

Standard Methods 10200, 2005

This procedure is applicable to the general identification of algae occurring in samples of fresh water. Samples are prepared using a sedimentation technique, and are then examined using a compound phase contrast inverted microscope. This test is a general screen of dominant types of algae. Dominant genera of algae are reported.

** Laboratory Methods employed follow in-house procedures, which are generally based on nationally or internationally accepted methodologies.

Chain of Custody numbers:

The last two letters of the above test code(s) indicate the laboratory that performed analytical analysis for that test. Refer to the list below:

Laboratory Definition Code	Laboratory Location	Laboratory Definition Code	Laboratory Location
WP	ALS LABORATORY GROUP - WINNIPEG, MANITOBA, CANADA		

GLOSSARY OF REPORT TERMS
Surr - A surrogate is an organic compound that is similar to the target analyte(s) in chemical composition and behavior but not normally detected in environmental samples. Prior to sample processing, samples are fortified with one or more surrogate compounds. The reported surrogate recovery value provides a measure of method efficiency. The Laboratory control limits are determined under column heading D.L.
mg/kg (units) - unit of concentration based on mass, parts per million.
mg/L (units) - unit of concentration based on volume, parts per million.
< - Less than.
D.L. - The reporting limit.
N/A - Result not available. Refer to qualifier code and definition for explanation.

Test results reported relate only to the samples as received by the laboratory.
UNLESS OTHERWISE STATED, ALL SAMPLES WERE RECEIVED IN ACCEPTABLE CONDITION.
UNLESS OTHERWISE STATED, SAMPLES ARE NOT CORRECTED FOR CLIENT FIELD BLANKS.
Although test results are generated under strict QA/QC protocols, any unsigned test reports, faxes, or emails are considered preliminary.

ALS Laboratory Group has an extensive QA/QC program where all analytical data reported is analyzed using approved referenced procedures followed by checks and reviews by senior managers and quality assurance personnel. However, since the results are obtained from chemical measurements and thus cannot be guaranteed, ALS Laboratory Group assumes no liability for the use or interpretation of the results.