Patterns and Concentrations of Phosphorus and Nitrogen in Embayments of Lake Ontario

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INTRODUCTION

Allen (1997) indicated that, the “low surface-to-volume ratio of Lake Ontario provides for ideal oligotrophic characteristics, based upon biological parameters.” He also noted that a strong possibility for eutrophication existed, unless measures were taken to control the nutrient inputs into the lake. Controlling these inputs means protecting the four upper Great Lakes that drain into Lake Ontario, and more importantly the surrounding embayments and wetlands, which buffer the lake from land inhabited and cultivated by humans.

In this project I studied embayments along the southeastern shore of Lake Ontario that vary in depth, hydraulic residence time, and connectivity to Lake Ontario. These factors are critical in determining the extent to which an embayment can assimilate nutrient loads.

NUTRIENTS

For the purpose of this study, two major macronutrients were examined; nitrogen, and phosphorus. Nitrogen is a vital macronutrient to phytoplankton and macrophytes. Nitrogen can exist in many forms throughout soil, air, water, and flora. The element is a major constituent in the structure of proteins and as such, is a “fundamental element in the metabolism of organisms (Allen 1977).” However excess loading of nitrogenous compounds may adversely affect the ambient quality of the water body. Nitrogen exists in water in five major forms, but for the purpose of this analysis only ammonium (NH_4^+) and nitrate (NO_3^-) were considered. Much of the nitrogen draining in the surrounding watersheds can be attributed to the use of fertilizers in nearby agricultural lands.

Ammonium (NH_4^+), and nitrate (NO_3^-) are critical to the energy budget of plants, and are generally in short supply in agricultural soils, which leads to the need to supplement nitrogen through the addition of nitrogen fertilizers (Mihelcic 1999). Heavy fertilization leads to an increase in the loading of inorganic nitrogen to the watersheds and surrounding wetlands and embayments.

Nitrogen chemistry is primarily controlled by biochemical reactions in natural waters, such as lakes and streams (Mihelcic 1999). Ammonium is produced primarily through bacterial decomposition of organic nitrogen, and nitrate is produced by the oxidation of the ammonium ion. Thus, the concentration of the nutrients is dependent upon the residence time of organic nitrogen and the availability of dissolved oxygen in the embayments. A heterotrophic bacterium responsible for the decomposition of organic matter can also generate ammonia, as organic matter is deposited to the hypolimnion; this appears to be a significant source of NH_4^+ within the larger embayments.

There are distinctive seasonal patterns of NH_4^+ in the embayments at consistently low concentrations. Although the concentrations of NH_4^+ are typical of freshwater systems, the residence times of the embayments suggests the availability of the nutrient will have a meaningful impact on the aquatic biogeochemical systems (Allen 1977).

Ammonia also tends to accumulate in the hypolimnion of embayments as the lower waters become more anoxic from deposition of organic matter to the sediments. The sediment-water interface of an anoxic hypolimnion creates a significant release of ammonia during the spring and fall months of a dimictic lake or embayment. Because ammonia oxidation requires a significant supply of oxygen, this process readily occurs in the epilimnion where oxygen concentrations are higher and algae and macrophytes grow in the upper photic zone and utilize the nitrate produced from nitrification. Generally, the distribution of nitrogen in lakes and embayments has a high variability with respect to watershed characteristics, seasonal change, nutrient inputs, and productivity of the embayment.

Although the nitrogen of most natural waters exceeds the concentration of phosphorus by large quantities, the concentration of phosphorus is critical because it is most commonly the limiting nutrient in freshwater ecosystems (Wetzel 1975). The concentration of phosphorus in a lake or embayment is dependent upon the loading rate, the behavior of the nutrient, the depth, and the hydraulic retention time (OWLA 2000). For the purpose of this analysis, total phosphorus, which includes soluble, and particulate as well as, organic, and inorganic forms of the element, was considered.

The major concern with phosphorus concentrations is the direct correlation to low ratios of phosphorus in comparison with other macronutrients, particularly nitrogen and carbon (Wetzel 1975). Through experimentation it has been observed that large algal blooms in aquatic ecosystems are controlled by the input of phosphorus, specifically soluble reactive phosphorus, which is largely inorganic. Soluble reactive phosphorus (SRP), is the form of phosphorus that is most readily available to aquatic plant life, both phytoplankton and macrophytes (OWLA 2000). Thus the threat of eutrophication in natural waters is heavily dependent upon the external phosphorus loadings (Wetzel 1975).

In the embayments surrounding the southern and eastern shore of Lake Ontario, phosphorus loadings, like nitrogen, are attributed to fertilization in agricultural lands within the surrounding watershed (Mihelcic 1999). High loadings of phosphorus to an embayment can lead to eutrophic conditions, and destroy its ability to buffer the ecosystem from further nutrient loadings. Thus, the retention time of phosphorus in the embayments becomes a critical component controlling the ability of the ecosystem to cope with high concentrations of the limiting nutrient.

Dissolved oxygen is a vital nutrient required for a healthy aquatic ecosystem. Oxygen is produced in the epilimnion of the lake by photosynthesis of macrophytes, and algae, as well as atmospheric aeration (Wetzel 1975). During the daytime aquatic plants convert light energy into chemical energy releasing dissolved oxygen (DO) to the water, and at night the DO in the water is used in the respiration process where the stored chemical energy is released. On a day-to-day basis, these processes tend to compensate each other with little variation in overall concentration. However longer-term changes in ambient DO are generally the result of higher inputs of nutrients and thermal stratification of the embayments (OWLA 2000). As the embayments stratify in the spring, the hypolimnion becomes separated from the warmer waters of the epilimnion and the DO sources by a steep thermocline in the metalimnion causing a limited mass transport between the strata (Cole 1983). Furthermore, as organic matter in the upper, well-lit waters settles to the hypolimnion, it is aerobically decomposed, until the oxygen supply in the hypolimnion is depleted. Since the oxygen cannot be resupplied at a significant rate in relation to the decomposition processes, anaerobic conditions lead to the production of noxious chemicals in the hypolimnion and accelerate the cycling of pollutants from the lake sediments (Mihelcic 1999).

METHODS

The Biocomplexity study, of which my study is a part of, focuses on eight embayments and corresponding watersheds, on the southeastern shore of Lake Ontario (http://ontario.cfe.cornell.edu). The embayments were selected based upon their volume, size, and connectedness to Lake Ontario, watershed area, land use characteristics and hydraulic residence time. Eight embayments were chosen to represent a wide range of varying characteristics to evaluate the effects of such parameters on the structure and function of embayment ecosystems. The physical characteristics of the embayments, used for the nutrient analysis discussed below were determined using information provided by the U.S. Geological Survey (USGS), as well as from aerial photographs, and on-site investigations. This information is available at http://ontario.cfe.cornell.edu, and was used as the source of information for the physical characteristics of the embayments. Maps of the embayments and corresponding watersheds are shown in Appendix A.

Each embayment was sampled at a central location on a weekly basis, and the watershed sampling locations were sampled monthly. Collections at each site involved a 500 mL sample used for chemical analysis, a 250 mL sample taken in a glass container for phosphorus analysis, and a one-gallon sample taken for suspended solids analysis. All of the sample containers were filled completely to eliminate any gaseous losses. The samples were then transported to the laboratory at Syracuse University and stored at 4^{o} C, until chemical analysis. Following analysis, the bottles were acid washed to eliminate any residual solutes, which may have existed in the bottles. Dissolved oxygen concentration, the specific conductivity, and the clarity of the embayments were also measured on a weekly basis. The weekly test results from April 2001 to December 2002 can be found in the data sets section of http://ontario.cfe.cornell.edu.

Once in the laboratory, solutes were analyzed in order based upon their reactivity. Although a whole suite of chemical analyses were performed on each sample, for this study I focused on nitrogenous compounds, specifically NH_4^+, and NO_3^-, as well as total phosphorus concentration. All of these solutes were analyzed using the Standard Methods (Table #1) (SMEWW 1995).

Table #1: Analytical procedures used to determine solute concentrations.

	Methods
NH_4^+	Flow analysis/ colorimetery: Autoanalyzer II
NO_3^-	Ion chromatography: Dionex Ion Chromatograph
TP	Flow analysis/ colorimetery: Bran Luebbe Autoanalyzer 3

RESULTS

For the purpose of this study, I focused on temporal patterns for a subset of the embayments these included Blind Sodus, Sterling, and South Sandy. These sites were selected based on the assumption that each embayment consisted of a single inlet stream. Note some of the physical characteristics of the embayments, were critical to this analyses. Specifically, the hydraulic residence times of the embayments, as provided by Gail Steinhart of the University of Cornell, and the volumes as obtained from U.S. Geological Survey data provided at http://ontario.cfe.cornell.edu/.

Table #2: Physical characteristics of the study embayments.

	Volume (m^3)	Residence Time (days)
Blind Sodus	4,071,000	64
South Sandy	4,031,000	105
Sterling	509,000	1.7

The total phosphorus concentrations within the study embayments are shown below in relation to the inlet concentrations.

Figure 2a: Time series of total phosphorus concentrations of the inlet and embayment of Blind Sodus.

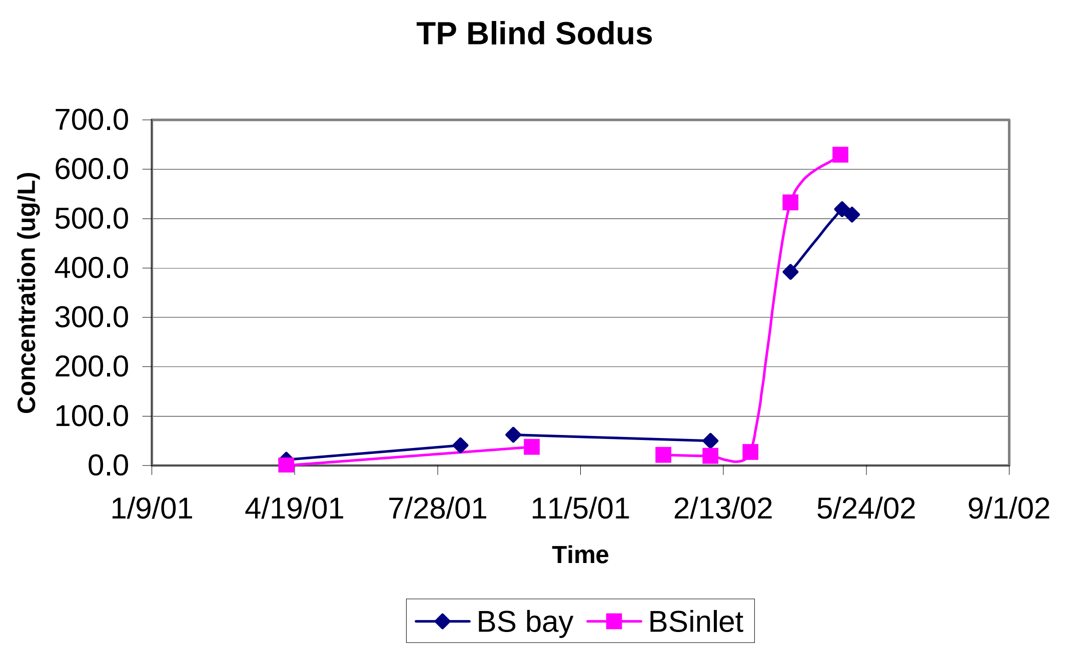


Figure 2b: Time series of total phosphorus concentrations of the inlet and embayment of South Sandy.

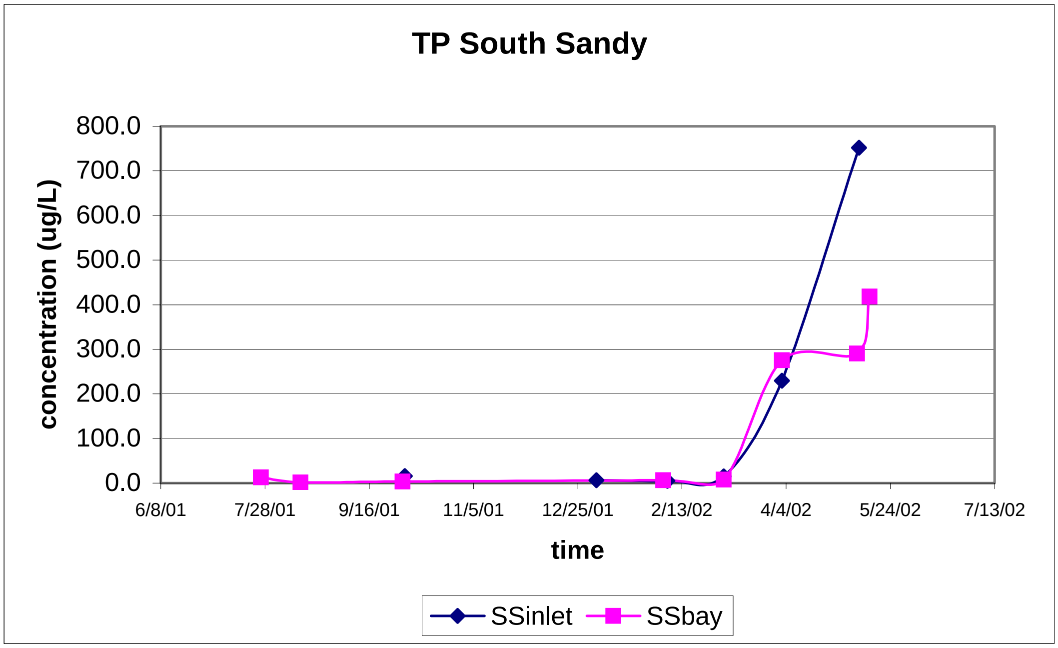
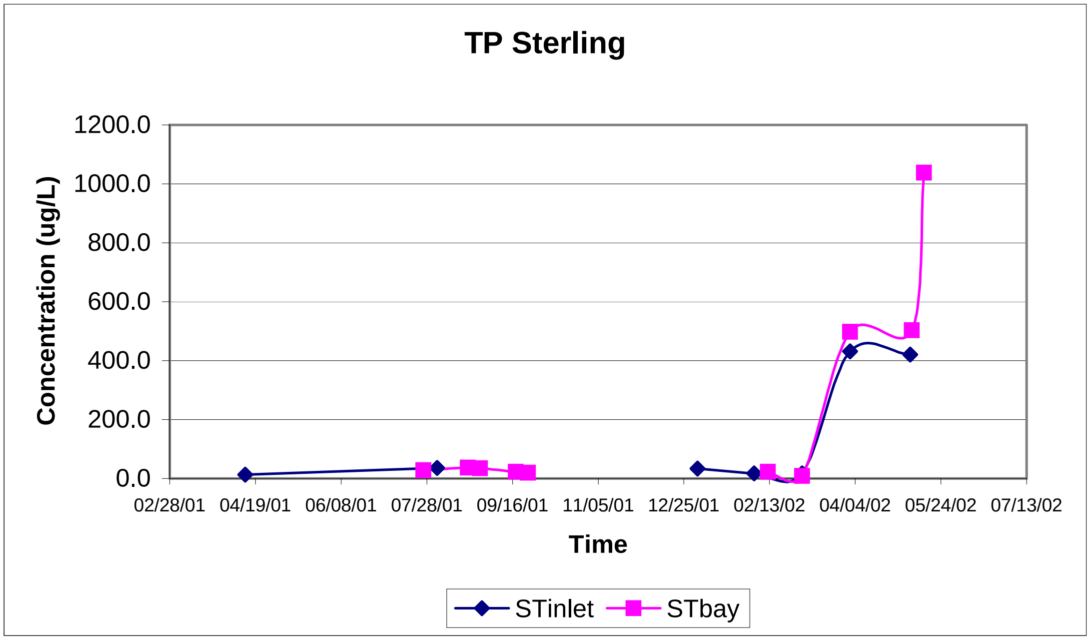
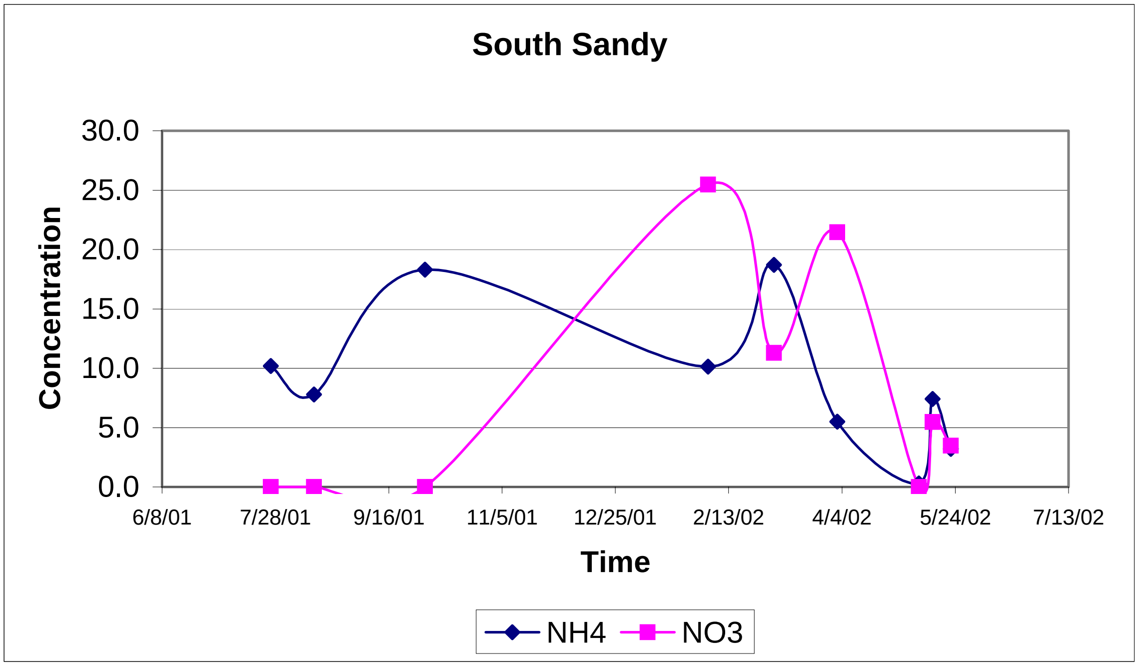


Figure 2c: Time series of total phosphorus concentrations of the inlet and embayment of Sterling.



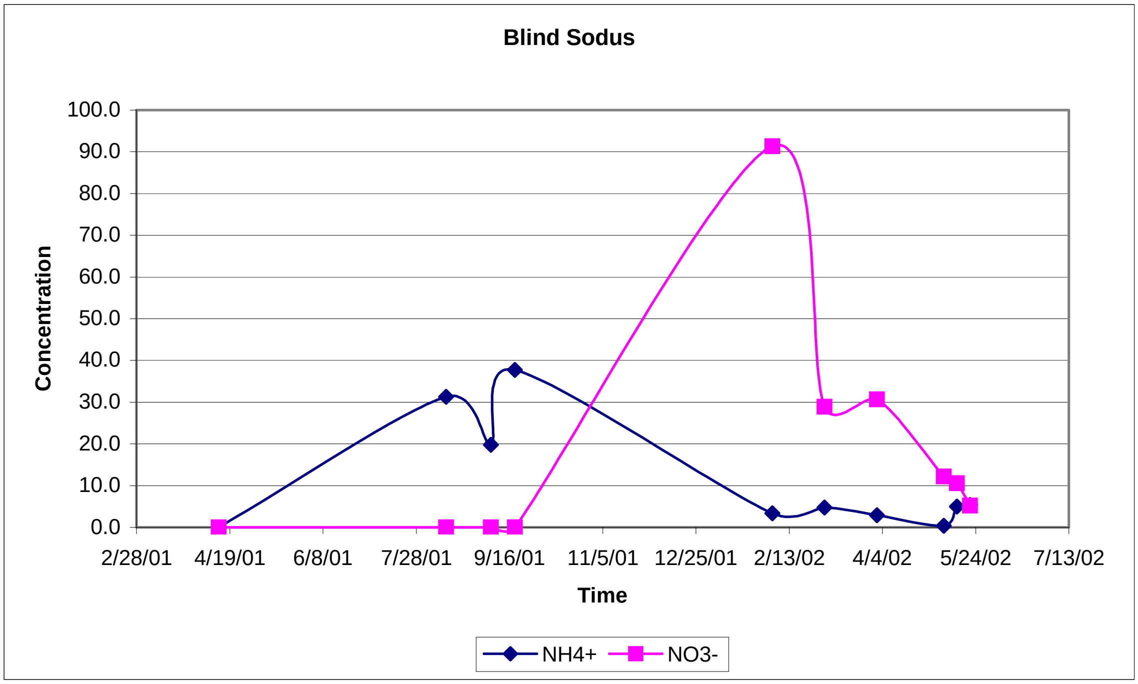
Because the analysis of total phosphorus incorporates all forms of phosphorus a detailed assessment of the dynamics of the element within the embayments is not possible. However seasonal variations and linkages of element concentrations with inlet concentrations can be analyzed within the embayment, as is discussed further in later sections of the report. The analysis of nitrogen is more difficult than that for total phosphorus because of the potential for interconversion between ammonium and nitrate. Thus, it is necessary to explore the fate of the nutrients within the embayments. The direct relation of the ammonium concentration and the nitrate concentration in South Sandy is shown in Figure 3a.

Figure 3a: Time series of nitrogen species within South Sandy.



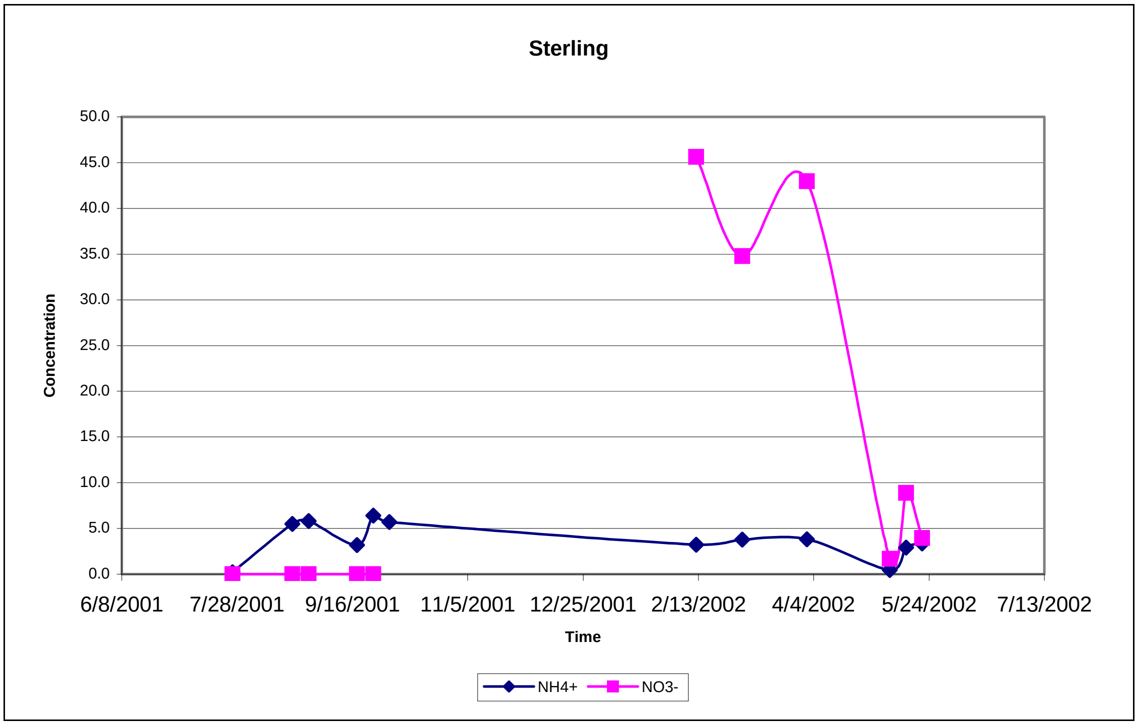
The relation between ammonium and nitrate within Blind Sodus is shown in Figure 3b. Note the weak correlation in comparison to that exhibited in South Sandy.

Figure 3b: Time series of nitrogen species within Blind Sodus.



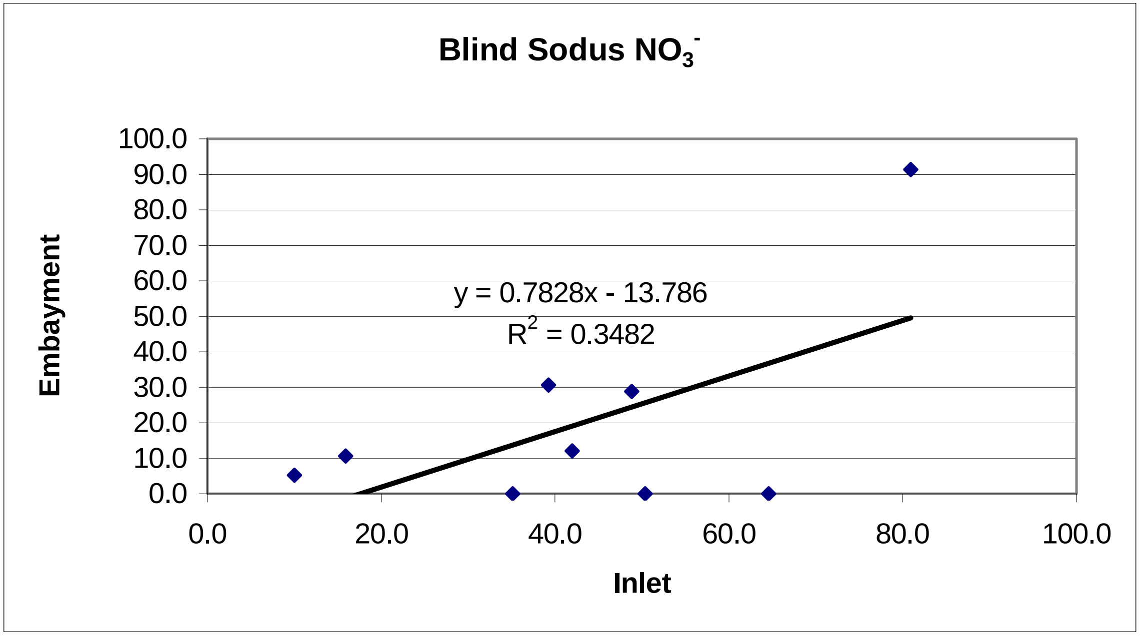
Finally, the correlation present in Sterling, as shown in Figure 3c, below.

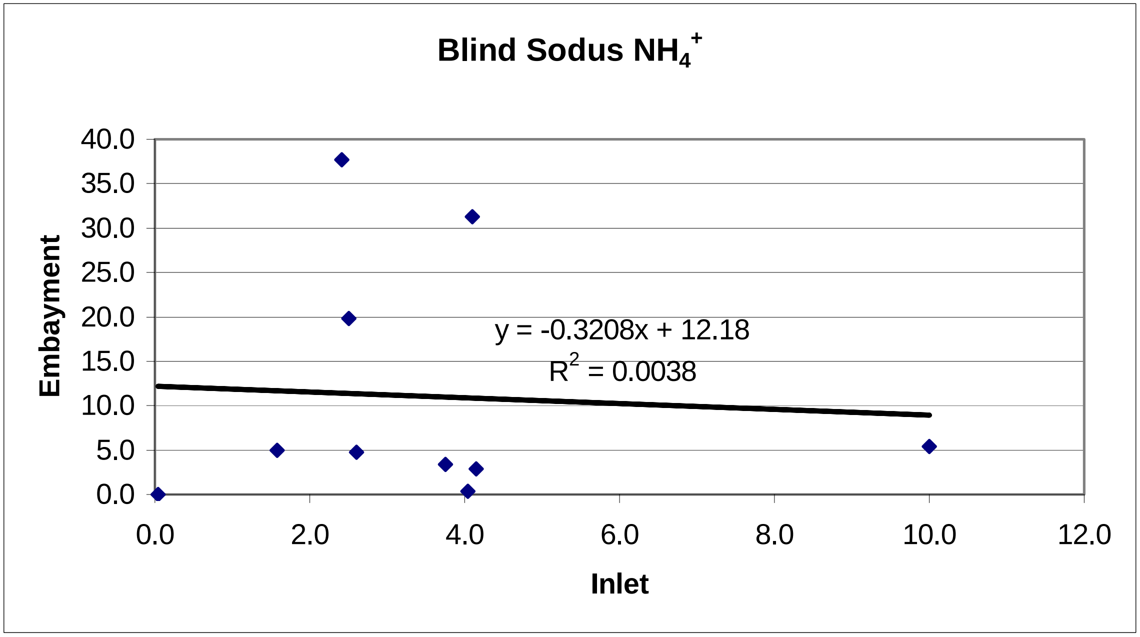
Figure 3c: Time series of nitrogen species within Sterling.



To determine the source of nutrients to the embayments an analysis was performed on the embayment concentrations and the inlets to the bays (Figure 1).

Figure 1: Relationship between embayment concentration and inlet concentration of nitrate(a) and ammonium(b) for Blind Sodus.





Note that there were low values of correlation coefficients for both nitrate and the ammonium concentrations, between the inlet and embayment. Also note that for three study sites the correlation coefficients were stronger for nitrate than for ammonium. And finally, note the correlation coefficients were stronger for Sterling, the embayment with a very short hydraulic residence time.

Table #3: Inlet and embayment nitrogen correlation coefficients.

R^2	**NO_3^-**	**NH_4^+**
Blind Sodus	0.35	0.004
South Sandy	0.57	0.21
Sterling	0.92	0.76

As was shown in Table 3, the correlation coefficients of Blind Sodus and South Sandy were very low for both ammonium and nitrate.

DISCUSSION

In the embayments surrounding the southern and eastern shore of Lake Ontario, the major source of phosphorus appears to be from external loadings. Phosphorus loadings, like potassium and nitrogen (Murphy 2002), are attributed to fertilization in agricultural lands within the surrounding watershed. The presence of the solutes was determined to be a result of runoff during storm events and during heavy snowmelt, from areas heavily fertilized, or agricultural land zones. The concentrations of the total phosphorus from the embayments inlets increased markedly during early March and

June. This increase occurred during a time period of heavy discharge from precipitation and snowmelt. The runoff generated and transported into the embayment also caused the total phosphorus concentrations within the embayment to increase. Thus, total phosphorus concentrations, which were extremely low throughout the year in the study embayments, increased and decreased in accordance to inputs of agricultural runoff through the inlet stream.

Internal sources of phosphorus within the embayment stemming from decomposition of organic matter are not as prevalent as was hypothesized with nitrogen. Internal sources located within the embayment such as, nutrient release from hypolimnetic sediments and the dye-off of aquatic macrophytes occurs in the fall (OWLA 2000), which may release phosphorus to the water but does not appear to influence the concentrations in the study embayments. Instead total phosphorus concentrations remained consistently below 0.1 P mg/L throughout the year with little seasonal or site-to-site variations, except during the spring. A large increase in the concentrations of phosphorus within the embayments during the spring corresponds to a large increase in the external loading of total phosphorus from the watersheds.

Another major solute, which is shown to be transported from direct runoff within the watersheds, is nitrate. In fact, both nitrate and ammonium are common constituents in fertilizers and are readily transported into the three studied embayments. As was previously mentioned, nitrate is formed by the oxidation of ammonium, thus the form may increase as the latter decreases. There was an inverse pattern between the concentrations nitrate and ammonium within the South Sandy embayment (Figure 3a). As the concentration of the ammonium ion increased, the nitrate concentration, decreased, and vice-a-versa. However, this inverse correlation between the ammonium and nitrate concentrations was less noticeable in Blind Sodus, and almost nonexistent in Sterling (Figure 3b:c). The correlation between the two solutes is dependent upon physical characteristics of the embayments, particularly, residence time, and volume.

Ammonification is the chemical reaction responsible for transforming NH_4^+ into NO_3^-, and the rate of this reaction will depend upon the amount of oxygen present and the amount of time the constituents are available for reaction. It has been observed through this study that the concentration of dissolved oxygen within the embayments has no effect on the reaction, which suggests the DO concentration within the epilimnion of the embayments are consistently high enough to allow for nitrification to proceed.

The time for reaction however has a very strong effect on the solute concentrations within the embayments. This phenomenon was evident in North and South Sandy embayments. The South Sandy embayment, which drains from its northwest corner through a narrow channel into the southern end of North Sandy bay, exhibited identical fluctuations in the concentration of nitrogenous species but at higher concentrations for most of the year. The lower concentrations seen in North Sandy bay may be attributed to the longer residence of elements within the limited embayment ecosystems. The time available for the reaction to occur is considered to be the residence time of the embayment, as this is presumably the amount of time the solutes will take to travel through the embayments. And in fact, South Sandy, the embayment with the highest solute correlation has a hydraulic residence time of 105 days, Sterling, which has virtually no correlation between the nitrate concentration and the ammonium concentration has a residence time of 1.7 days, and Blind Sodus, which exhibits a mild correlation has a residence time of 64 days. Thus, the availability of nutrients can have a meaningful impact on the biogeochemical system (Allen 1977).

Apart from the hydraulic residence time of the embayments, another characteristic responsible for controlling the fate of solutes through the embayments is their volume. For example, in Sterling Bay, there is no correlation between the concentrations of NH_4^+ and NO_3^-, so what controls the concentration and seasonal variability within this particular embayment? All of the embayments receive nutrient loadings from their inlet as a result of runoff (Table 3). The nitrate correlation and ammonium correlation between inlet and embayment water were high in Sterling, due to the low volume and residence time of the embayment. Thus, the concentrations of the solutes showed little variation in magnitude once they entered Sterling.   But as the volume of the study embayments increased, the solute concentrations become more dilute as the inlet concentrations enter the embayments. Thus, Blind Sodus which has the largest volume of the study sites had R^2 values of 0.35 for nitrate and 0.004 for ammonium between inlet and embayment waters, South Sandy had R^2 values of 0.57 and 0.21 respectively, and Sterling, the smallest embayment with respect to volume had R^2 values of 0.92 for NO_3^- and 0.76 for NH_4^+. Thus direct runoff, which enters via an inlet stream will impact the embayment, however, the larger the embayment, the greater the attenuation of nutrient inputs.

So Sterling Bay, the smallest embayment studied has a strong signal of the inlet water. As a result of the short residence time there is little effect of internal embayment processes on solute concentrations. The South Sandy and Blind Sodus embayments do not reflect a strong signal of inlet water. Instead the temporal variations in solute concentrations in these bays are impacted by processes occurring in the embayments. In the hypolimnion of the embayments organic nitrogen is broken down by heterotrophic bacteria producing ammonium ions. And as the embayments turn over during the spring and fall the ammonium is supplied from the lower waters creating increases in the surface concentrations of the embayment. These large increases in NH_4^+ concentrations can be seen in Figure 3a during March and October. Thus, the larger embayments have greater capacities for retaining nutrients from Lake Ontario through physical and chemical processes.

CONCLUSIONS

The purpose of this study was to analyze patterns of nitrogen species and phosphorus concentrations within the embayments. In order to qualitatively characterize the behavior of such elements, it was important to determine the source of the nutrients, the reactions that may take place within the embayments, the hydrodynamics of the embayments, and finally, to analyze the impact of such nutrient loadings on the structure and function of the embayments. Through experimental observations it has been concluded that:

- Phosphorus and nitrogen are largely transported into the embayments via runoff from agricultural lands during periods of high discharge.
- Total phosphorus concentrations were extremely low except during the spring.

- Ammonium and nitrate concentrations in the epilimnion of the embayments varied temporally according to the volume, depth, and residence time.
- The effect of the loading of nitrogenous compounds via an inlet stream depended on the volume of the embayment. The smaller the embayment, the stronger the signal of the inlet water on the embayment chemistry. Similarly, the larger the embayment, the weaker the signal of the inlet water due to mixing and attenuation within the embayments.
- The annual fluctuations of ammonium and nitrate were dependent upon the depth of the embayment. Deeper embayments, which stratify, exhibited nitrogen variations in the epilimnion according to the turnover periods. Shallower embayments, which do not turnover, exhibit nitrogen variations in a higher accordance to the day-to-day variations with the inflow concentrations.
- The biochemical relation between ammonium NH_4^+ and nitrate NO_3^- was dependent upon the hydraulic residence time of the embayment. The longer the residence time, the stronger the correlation between ammonium reduction and nitrate production.
- Overall, the concentrations of phosphorus and nitrogen were generally low in comparison to health standards and pose no immediate threat to Lake Ontario.

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APPENDIX A

BLIND SODUS (Western site)

WATERSHED CHARACTERISTICS

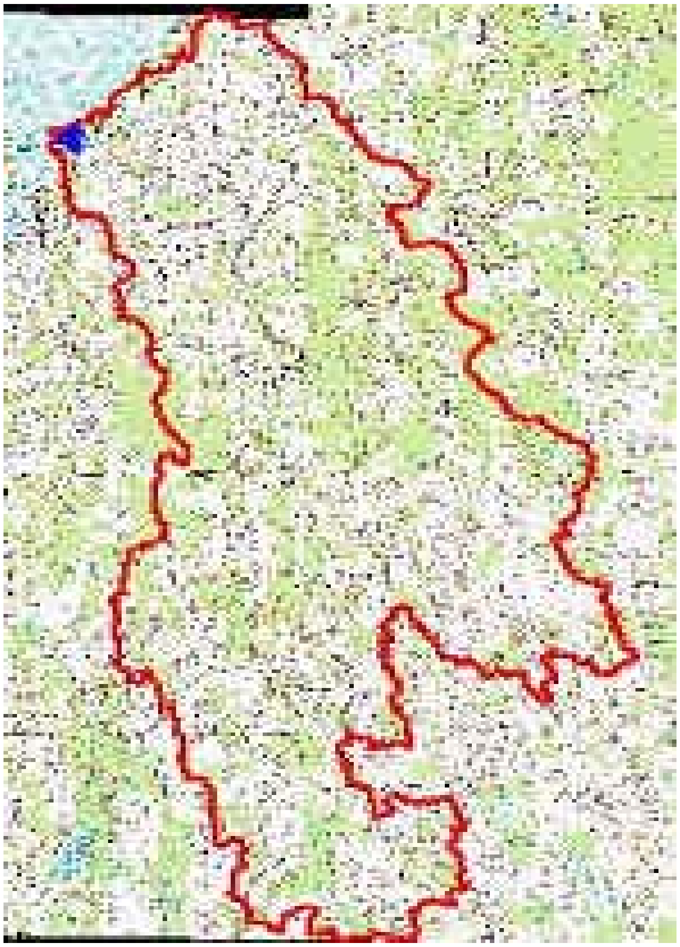
AREA *	km^2	Acres
WATERSHED W/BAY	36	8924
WATERSHED W/OUT BAY	35	8684
BAY ONLY	0.97	240

*watersheds and bays delineated on
USGS 1:24,000 scale DRG (digital raster graphics)
topographic maps: metadata

BATHYMETRY **Deepest point* :** 24 feet

* when lake level at ~245 feet, or 74.67 meters based on the IGLD-1985 datum: metadata

STERLING (Western Site)



WATERSHED CHARACTERISTICS

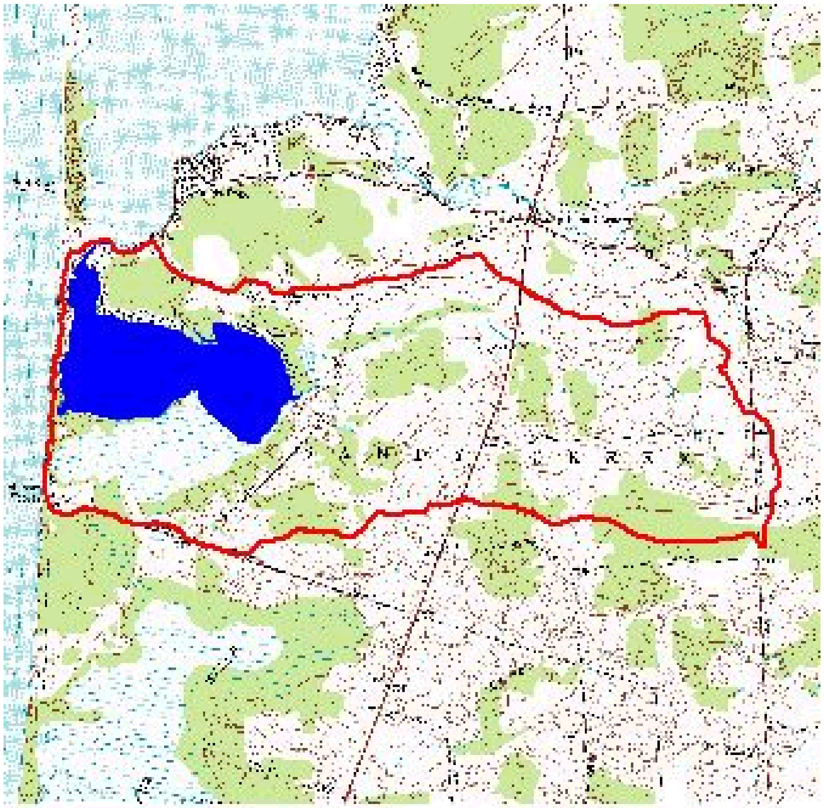
AREA*	**km^2**	**Acres**
WATERSHED W/POND	203	50200
WATERSHED W/OUT POND	202	50130
POND ONLY	0.38	94

*watersheds and bays delineated on
USGS 1:24,000 scale DRG (digital raster graphics)
topographic maps: metadata

BATHYMETRY **Deepest Point* :** 10 feet

* when lake level at ~245 feet, or 74.67 meters
based on the IGLD-1985 datum: metadata

SOUTH SANDY (Eastern site)



WATERSHED CHARACTERISTICS

AREA*	**km^2**	**Acres**
WATERSHED W/POND	9.5	2,346
WATERSHED W/OUT POND	8.3	2,043
POND ONLY	1.23	303

*watersheds and bays delineated on
USGS 1:24,000 scale DRG (digital raster graphics)
topographic maps: metadata

BATHYMETRY **Deepest Point *** : 21 feet

* when lake level at ~245 feet, or 74.67 meters based on the IGLD-1985 datum: metadata

LOCATION MAP OF STUDY SITES