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CASE STUDY

Effect of activities conducted near lakes by comparing contaminant levels, trophic status, and a possible bioremediation method

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ABSTRACT

BACKGROUND AND OBJECTIVES: The lakes in the state of Minnesota (MN) have undergone accelerated changes with the passing of time, where cattle ranching, agriculture, the increase of industrial jobs and urban area development have changed their condition from pristine to critical. To evaluate this problem, secondary data obtained from the public domain of three lakes from a county used for a long period for agriculture and cattle (Carver County) and three lakes from a county where the land has been used more for housing and industrial economy (Hennepin County). The aim of the study was to use the information to evaluate the trophic status, and compare the results of the lakes of rural areas versus lakes in urban areas in order to create a possible mitigation plan to improve the condition of the area.
METHODS: Trophic status was determined to evaluate the water quality of each lake. ANOVA analysis was employed to analyze the data set obtained from the public domain in the official webpage of the Minnesota Pollution Control Agency.
FINDINGS: Data results for total phosphorus, Secchi Disk and Chlorophyll-a, showed that all lakes are under eutrophic-hypereutrophic status with Trophic State Index (TSI) results between 59 to 80. Hennepin County had two of the three lakes evaluated in hypereutrophic states when compared with Carver County lakes. Carver County has only one lake out of the three evaluated under hypereutrophic conditions. Statistical analysis showed that $p < \alpha$. The results demonstrated that lakes near areas used mainly for urban/industrial purposes are more contaminated than lakes near areas used for agriculture/livestock.
CONCLUSION: The restoration of wetlands that are near the lakes is proposed as a possible bioremediation method to improve water quality. Alternatively, an artificial wetland could be implemented in the lakes that do not have this natural system. Placing a Subsurface Flow System (SFS) artificial wetland in parallel trenches, which bypasses the lake and/or into the mouth of the river, would allow the sedimentation process to occur in these spaces. In addition, the use of Phosphor-Accumulator Organisms (PAO) and specialized aquatic plants, such as *Hydrodictyon reticulatum, Elodea canadensis, Eichhornia crasspies, Eleocharis plantaginea, Pistia stratiotes* and *Hydrilla verticillate* will trap contaminants and aid in their removal.

NUMBER OF REFERENCES	NUMBER OF FIGURES	NUMBER OF TABLES
36	9	2

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INTRODUCTION

The state of Minnesota (MN), also known as the "land of 10,000 lakes", has seen accelerated changes to its environment with the passing of time. Changes in cattle ranching and agriculture, along with the increase of industrial jobs and urban areas, have altered the conditions of the bodies of water in this state from pristine to critical. According to the Minnesota Public Radio (MPR) news station, approximately two-thirds of Minnesota's watersheds were tested, and it was determined that 40% of all Minnesota's watersheds, rivers and lakes have been damaged by agricultural runoff, bacteria, mercury, and other pollutants (Gunderson, 2016). The most delicate part of the problem is that this list continues to grow. Minnesota has worked hard to regulate working conditions to take care of not only the bodies of water, but also of the organisms that benefit from them. Regulatory policies that have been implemented in the last 15 years have promoted the reduction of total phosphorus discharged, but not enough to avoid eutrophication of some bodies of water. Creating controls for pollutants, such as nitrogenous compounds, have been on the rise since 2000 (Engelkin and Kovacevic, 2018), although can be extremely costly for the state. Most of the polluted bodies of water lie between central and south-southeast Minnesota, in areas where construction, pharmaceutical, agriculture, and livestock industries are most prominent. Runoff not only damages the quality of water available for consumption, but also directly impacts the species that inhabit these bodies of water. An increase in nutrients will lead to an increase in algae growth in lakes, thereby decreasing the amount of oxygen available to aquatic species and bringing some of these lakes close to eutrophication parameters. Aquatic plants die due to the cycle of freezing and thawing that comes with seasonal temperature changes, creating a sedimentation problem that reduces their water-holding capacity. The state has more than 3,000 lakes, watersheds, streams and other aquatic areas, including parts of the Mississippi River, that appear on the Minnesota Pollution Control Agency (MPCA) 303 (d) list of impaired waters and have been classified as a "category 5" due to their inability to meet various quality standards. A "category 5" classification is used by the United States Environmental Protection Agency (US EPA) where the listed bodies of water do not, or have the future potential to not, meet quality standards, and the Total Maximum Daily Load (TMDL) must be determined and evaluated (United State Environmental Protection Agency (US EPA), 2020). Many of the lakes, basins, streams, and areas of the Mississippi River are on the list as their current condition affects aquatic life, recreation, and consumption. In addition to high levels of nutrients, contaminants such as chloride, deionized ammonium, and chlorpyriphos, and problems with fish such as accumulation of mercury, Polychlorinated Biphenyl (PCB), and Perfluoro Octane Sulfonate (PFOS), have been found in these bodies of water. Furthermore, turbidity problems, Escherichia coli (*E. coli*) and mercury have all been present in the water columns (Minnesota Pollution Control Agency (MPCA), 2021). Sources of organic nutrients include animal pens, sewage treatment plants, and various industries such as construction, pharmaceuticals, and corn plantations, to name a few (Chiras, 2010a). Two of the biggest contributors to water pollution include runoff due to the clearing of vegetation for new construction and snow melting from seasonal temperature changes (Minnesota Pollution Control Agency (MPCA), 2008). Excess of organic material reduces the amount of oxygen in these bodies of water because the living bacteria use it to break down waste, thereby contaminating the water with methane and hydrogen sulfide, which are formed as secondary products in the process, and eventually causing some of the aquatic organisms to perish (Chiras, 2010a). According to Chiras (2010a), "the [water] system can only recover if the source of organic nutrients ceases". In the case of inorganic nutrients, these are produced by a wide variety of sources and generate a large amount of Phosphorus (P) and Nitrogen (N) pollutants. These compounds tend to promote the growth of algae and aquatic plants and function as a limiting factor. An increase in phosphorus is proportional to an increase in algae within the affected water body. Anaerobic bacteria use these inorganic nutrients and degrade them, and the same putrefaction process occurs (Chiras, 2010a). As a result, both aquatic and human lives are impacted. In the past, the Minnesota Department of Health has warned people to avoid blue-green algae in lakes, streams, and ponds because they can cause illness in humans and animals when exposed. "The

symptom of eutrophication is rapid growth and accumulations of phytoplankton, leading to discoloration of affected waters. These events are termed blooms. Blooms are a prime agent of water quality deterioration, including foul odors and tastes, deoxygenation of bottom waters (hypoxia and anoxia), toxicity, fish kills, and food web alterations. Toxins produced by blooms can adversely affect animal (including human) health in waters used for recreational and drinking purposes" (Dyble, Fulton, Moisander and Paerl, 2001). The biggest contributor to algal blooms is the polluted runoff from farms and agriculture, which is high in phosphate content that is then carried out to surrounding areas (Marohn, 2018). According to MPR in the article from 15th of May 2018, the US EPA has given health advice for two cyanobacterial toxins in drinking water; however, there are currently no legal limits being enforced (Marohn, 2018). There are organizations that demand that more regulations be made in such a way that fertilizer and manure runoff from farms does not continue to reach water bodies. Phosphate pollutants also seem to have a deleterious effect on human health, as well as on bodies of water. According to the EPA, water samples are evaluated against a quality standard of 3 milligrams per liter (mg/L) of phosphate, which is equivalent to one part per million (ppm) of phosphorus (P) (United States Environmental Protection Agency (US EPA), 2012). In waters with low oxygenation, phosphorus can react with water and form what is known as phosphine, an extremely toxic gas, which can bioaccumulate in the body of fish and eventually reach human consumption (Hui Hoon, 2012). On the other hand, an increase in the concentration of phosphorus in water bodies' results in the proliferation of algae, which eventually leads to its eutrophication (United States Environmental Protection Agency (US EPA), 2012). The results conclude that the pollution problem increases further towards the south-southeast region of Minnesota where the predominant industries of these rural areas are agriculture and livestock, the hypothesis of this study expresses that there is a greater probability of eutrophic pollution in lakes near rural areas than in lakes near urban areas. The problem of eutrophication of lakes, streams, and rivers has been increasing along with the increase in population and the activities that sustain human life. The natural eutrophication of water bodies no longer occurs gradually over time, but rather is accelerated by the culture of border ethics (Chiras, 2010b). Sadly, this brings us to the main problem: lakes, streams and rivers suffer from cultural eutrophication. Globalization has forced humans to increase the residential, industrial, harvesting, and livestock areas in order to keep up with the supply and demand requirements of the consumer model of today. The deterioration in the bodies of water has increased so much that it has changed the way in which the system flows, making life around it unsustainable. Cultural eutrophication and the deterioration in the bodies of water directly impacts aquatic plants, fish, and other species that live, feed, or recreate on it. Many of the pollutants can be evaluated provided that the point source is known; however, urban growth, the manipulation of these areas (such as the removal of wetlands, shrubs and other plants that prevent soil erosion), and the inappropriate use of resources have made it so that many of the pollutants found cannot be attributed to a point source. "Non-point sources can come from farms, pastures, crops, forests or urban areas, the source is diffuse, and an owner cannot be assigned" (Chiras, 2010a). These "affects the chemical composition of lake waters by controlling the time available for biogeochemical and photochemical processes to operate, the extent of accumulation, loss of dissolved and particulate materials and the duration of biogeochemical interactions with the lake sediments and littoral zone. In lakes that experience anoxic bottom water conditions and nutrient release from the sediments, a prolonged residence time caused by reduced precipitation and inflows can result in increased phosphorus accumulation (internal phosphorus loading) and eutrophication" (Bhateria and Jain, 2016). Another problem that must be taken into consideration regarding the eutrophication of a water body is sedimentation. This sediment, being suspended in water, reduces the penetration of light, which deteriorates the growth process of aquatic plants, and eventually causes them to die. In turn, this excess of dead material lowers oxygen levels, suffocates fish eggs and disrupts the food chain (Chiras, 2010a) whilst decreasing the capacity of the body of water. According to a 2011 report by Easter and Perry, Minnesota has "about 105,000 miles of streams, distributed among 81 major watersheds, and about 9.3 acres of wetlands. The National

Hydrographic Data Set (NHDS) places the number of lakes at 12,200; of these, 800 are greater than 500 acres, 4,000 are between 100 and 500 acres, and the remainder are between 10 and 100 acres" (Easter and Perry, 2011). The state has 5 main rivers of which three start in the state of Minnesota: the Mississippi River, the Red River, and the Rainy River. In order to properly assess this problem and accept or reject the study hypothesis, the following goals must be carried out:

1) Evaluate and analyze the secondary data obtained at the MPCA public domain for the test concentrations of Secchi Disk, total phosphorus, and Chlorophyll-a in six Minnesota lakes for the period 2008-2016 and determine the potential risk through the degree of eutrophication;

2) Compare the results of the lakes belonging to Carver County with the results of Hennepin County in order to determine if the activities carried out by agriculture and livestock generate more nutrient problems in the lakes than those generated in lakes near urbanized areas (construction activities, industries and other businesses);

3) Recommend bioremediation strategies according to the results obtained for Secchi, total phosphorus and Chlorophyll-a for the six lakes of Minnesota, in order to minimize the trophic problem, taking in consideration findings of studies performed in lakes with similar predicament and adjusting the authors' recommendation to the lakes of MN.

The lakes to be evaluated are supplied by the Mississippi River (Dutch Lake, Wassermann Lake, Turbid Lake and Minnetonka Lake), the South Fork Crow River which also discharges into the Mississippi River (North Whaletail Lake) and the Lower Minnesota River (Lake Hydes). Currently, there are several lakes and parts of the "South Fork Crow" river that do not meet the quality standards for it, thus jeopardizing the use of this body of water for aquatic recreation, drinking and swimming. Longitudinal data collected on June 13, 2013 along the South Fork Crow River shows a general trend of phosphorus values increasing along the South Fork Crow River from upstream to downstream (Minnesota Pollution Control Agency (MPCA), 2017b). This in turn directly affects the Mississippi River as the "South Fork Crow" discharges its polluted waters directly into this river. The same problem was observed with the Minnesota River. "Water quality issues found in this watershed include high suspended sediment lows, high levels of nutrients, and the potential for high DO flux. One reach in the sub watershed had a previous impairment for turbidity that was corroborated with updated TSS information" (Minnesota Pollution Control Agency (MPCA), 2017c), directly affecting the Mississippi River. This excess of nutrients has created a bigger problem since the lakes supplied water from the Mississippi River are also suffering from problems of blue-green algae. It should be noted that most of the land in the area is used for agriculture. Some states have lost up to 90% of their original wetlands, with agriculture being the activity with the greatest impact in these systems (United States Department of Agriculture-Natural Resources Conservation Service/National Resources Inventory (USDA-NRCS/NRI), 2014). Wetlands are transitional areas between aquatic and terrestrial systems (Bigio, 2020). The lack of wetlands prevents water retention in the landscape and leads to increased runoff and discharges related to times when storms occur that can destabilize currents and increase sediments in the water. Similarly, in urban and suburban environments, impervious surfaces send large volumes of water to storm drains and nearby bodies of water (Minnesota Pollution Control Agency (MPCA), 2018), which are non-point sources of pollution. The Mississippi River is the fourth longest river in the world, flowing 2,350 miles from Lake Itasca in Minnesota to the Gulf of Mexico, passing not only through valleys, cliffs, grasslands, and forests (Minnesota Pollution Control Agency (MPCA), 2017a) but also through industrial areas, residential areas, and areas of livestock and agriculture. Since the river is born in Itasca Lake in northern Minnesota, the water has been pristine. As the water continues to descend, the purpose of the land around the river changes to areas for crops, livestock, residential and industrial. The tributaries, as explained previously for "South Fork Crow" River which flows through heavily cultivated areas, bring in pollutants such as sediment, nutrients, and bacteria in addition to those already brought in by the Mississippi River. When these water discharges reach the Minnesota capital, the water no longer meets quality standards, having a cumulative impact that makes it difficult to use the waters of the metropolitan area on several occasions (Minnesota Pollution Control Agency (MPCA), 2017b). This problem of inflows comes from the pollutants dragged by the

river, plus the contaminants in the runoff, cause the lakes in question to be in, or close to, a state of eutrophication. To address the areas more effectively, the environmental protection agency (EPA) has zoned resources according to similar characteristics, and the agency has a Roman numeral classification scheme for different hierarchical levels of ecoregions, ranging from general regions to more detailed ones. An ecoregion is an ecological region that is intended to provide a spatial framework for ecosystem assessment, research, inventory, monitoring, and management (Easter and Perry, 2011). The state of Minnesota is classified at a level III. This level contains 105 ecoregions on the continent and the border of the United States has 84 ecoregions (Omernik and Griffith, 2014). Of these, the state of Minnesota has 7 ecoregions: Northern Minnesota Wetlands, Red Lake Valley, Northern Lakes and Forests, Northern Glacial Plains, Western Plains Corn Belt, Driftless Areas, and the North Central Hardwood Forest area. The lakes to be assessed are contained within region 5 and division 51. That means they belong to the north central hardwood forest area. This ecoregion contains many lakes, and the water clarity and nutrient levels they are presumed to be within moderate parameters. The land surrounding many of these lakes has been developed for housing and recreation, and the metropolitan area is densely populated and dominates the eastern part of this region. The water quality problems faced by many of the water bodies in this area are associated with contaminated runoff from paved surfaces and treated lawns (United States Environmental Protection Agency (US EPA), 2003). Urban stormwater and snowmelt pollution contribute significantly to the deterioration of surface waters quality (Müller, *et al.,* 2020). In the case like Carver County, the contamination problem also comes from the crops and livestock in the area. The state has a duty to assess the lakes initially to find out what type of pollutants and calculate the trophic level. For this, they take samples and evaluate the data for the summer season (June 1 to September 30) in the lakes for total phosphorus, Secchi disk and Chlorophyll-a, although in some cases different periods of sampling and other types of tests are generated that are also indicative of if the body of water is in good condition or that it is detrimental. Regulation §7050.0222 sub-part 4a-B, the state has multiple rules to prevent a body of water from reaching eutrophic levels for point source

pollutants. For the lakes in question, the pollution is presumed to be mostly from a non-point source. The state has classified them as 2B, and according to Minnesota statute, they are suitable for aquatic recreation of all kinds, including bathing, for which the waters can be usable, these are not protected as drinking water, but they are as a reserve, which allows the state to create specific standards to ensure the integrity of the body. For deep lakes belonging to the "North Central Hardwood" ecoregion, the water quality is measure with the following parameters:

- Total Phosphorus (TP): <40 µg/L
- Chlorophyll-a (Chl-a): <14 µg/L
- Transparency per-Secchi disc: Not less than (≥) 1.4 m

In some cases, they evaluate the values of nitrates/nitrogen, dissolved oxygen, and suspended solids to calculate the survival ratio of the fish and their food source (MPCA *et al*., 2018). In the event that the lake is in the eutrophication process and has excessive algae growth, according to sub-part 5aB, the magnitude, duration and frequency are evaluated (Minnesota Administrative Rules (MAR), 2017a) to work on a method that decreases the nutrients of which these are fed. In statute §114D.26, the state provides strategies to restore and protect the state's watersheds. The state expects that for the year 2020, the evaluation of 80% of the lakes of Minnesota is completed, where this evaluation includes a physical, chemical, and biological evaluation; and describes which basins, streams, rivers and lakes are at delicate levels of quality. In this evaluation, it is decided whether the body of water should be within the TMDL study, and which are the stressors identified as a contaminant. With this information, the organization begins to work on an improvement plan and strategy (Minnesota Administrative Rules (MAR), 2019). On November 2020, the state reported that for the assessment performed on the ecoregions of Northern Forests, Eastern Temperate Forest, and the Great Plains, 44% and 24 % of the lakes were in eutrophic and hypereutrophic condition, respectively (Minnesota Pollution Control Agency (MPCA), 2017). The current study has been carried out in Minnesota in the year 2020 and updated during the year 2021.

MATERIALS AND METHODS
Investigation design and data collection

The most polluted area of lakes is in the central

south-southeast area of the state. Therefore, two counties were chosen within the area of interest: Carver and Hennepin. The lakes that were evaluated had as characteristic that they are known as deep lakes since they are more than 15 feet deep. Hennepin County was selected as a county that is more urbanized, it is close to the metropolis, there are different industries (pharmaceuticals, medical device company, grocery industries, among others), and there are many new constructions. The runoff was mainly from the removal of land from the construction of new developments, from the particulate of the streets in general and/or businesses in the area. Carver County borders the southwest area of Hennepin County and was chosen as a county governed mostly by agriculture and the livestock industry. Runoff comes mostly from washing areas where there are livestock and from chemicals added to plantations. Some of these pollutants percolate through the ground and others reach the lakes when during the rainy season, or throughout the snowmelt season.

Study timeframe

In Minnesota, the water analysis for the lakes had not been constant and/or they were governed by specific rules for each place, so finding lakes that were evaluated under the same parameters in the area of interest, during the same period and classified as a deep lake in the state, was challenging. The Minnesota Pollution Control Agency (MPCA) tested water samples for lakes throughout the year, but most samples were taken during the June through September period. As explained above, the state measured the eutrophication level through tests for total phosphorus, Secchi Disk, and Chlorophyll-a. The analysis of all these parameters has not been constant. Therefore, the period evaluated spanned approximately seven (7) years (years 2008, 2010 to 2011 and 2013 to 2016) during the summer season (June to September, with the exception of 2010 that is from July to September) and averaging the values per month to have the same amount of data. This data was in the public domain on the official website of the Minnesota Pollution Control Agency and was used as secondary data for this study.

Sample Description

The lakes assessed are deep lakes, within the

"North Central Hardwood" forest ecoregion, and mostly within a large-scale surface area (over 100 acres, except for Turbid Lake). The sampling areas have been classified by the state with a numerical code so that data can be collected in the same area later, and the results were reported on the information webpage for each lake. This secondary data, taken from the official webpage by February-March of 2020, were used in this study and evaluated to verify the status of the lake. According to the law §7050.0222 of the state of Minnesota, a lake was in good condition, if the following parameters were met (Minnesota Administrative Rules (MAR), 2017a):

• Total Phosphorus (TP) : <40 µg/L
• Chlorophyll-a (Chl-a) : <14 µg/L
• Transparency per Secchi disc: Not less than (≥) 1.4 m

The information station used for each lake was the following:

a. Dutch Lake: 27-0181-00-201 for Hennepin County
b. North Whaletail Lake: 27-0184-01-203 for Hennepin County
c. Minnetonka-Halstead Bay Lake: 27-0133-09-201 for Hennepin County
d. Wassermann Lake: 10-0048-00-201 for Carver County
e. Hydes Lake: 10-0088-00-201 for Carver County
f. Turbid Lake: 10-0051-00-201 for Carver County

The lakes in Carver County, even though urban areas are developing in this area, were mostly used for agriculture and livestock in the past; the lakes belonging to Hennepin County are in a more urbanized and industrial area.

Experimental design

No testing was performed to the lakes for this study. The data used was from analytical tests performed by analysts hired by the Minnesota Pollution Control Agency (MPCA) and results were documented in the public domain (Secondary data). Therefore, these results were used to calculate the trophic state of each lake and to perform the comparison between counties using statistical analysis.

Statistical analysis

To verify the trophic status of each lake, and to

be able to compare whether lakes in rural areas are more prone to contamination than lakes belonging to urbanized areas, the data evaluated was from the Minnesota Pollution Control Agency. The data from June to September was used within the period from 2008 to 2016 and the experimental method was a quantitative. Since the number of samples were not the same for all lakes analyzed, the values were averaged per month. Trophic status was calculated per year and evaluated how the activities carried out near the areas of interest had affected the lakes.

After evaluating the trophic level, the data was evaluated using the bilateral hypothesis, where:

H_0: Pollution in Lakes of Rural Area = Pollution in Lakes of Urbanized Area (when p>0.05)

H_1: Pollution in Lakes of Rural Area ≠ Pollution in Lakes of Urbanized Area (when p≤0.05)

Using the data from the three lakes per county, the data was processed using the ANOVA test and the results were evaluated to see if the null hypothesis was correct or if, on the contrary, the alternate hypothesis was correct. The usage of Histograms and Pareto's method was also used for the evaluation.

RESULTS AND DISCUSSION

General Evaluation

For total phosphorous results (Fig. 1), three of the six lakes showed a pattern of increasing in nutrients parameters through the years: Minnetonka Halstead Bay Lake, Wassermann Lake and Dutch Lake, which had the highest amount in total phosphorus during the 2015 year. After an evaluation of the Secchi Disk data (Fig. 2), it showed that the visibility in Minnetonka Halstead-Bay Lake had decrease, indicating the lowest result by the year of 2010. A similar pattern was observed for Dutch Lake and Wassermann Lake. For Chlorophyll-a (Fig. 3), the results were decreasing by year 2010 and then started to increase with the
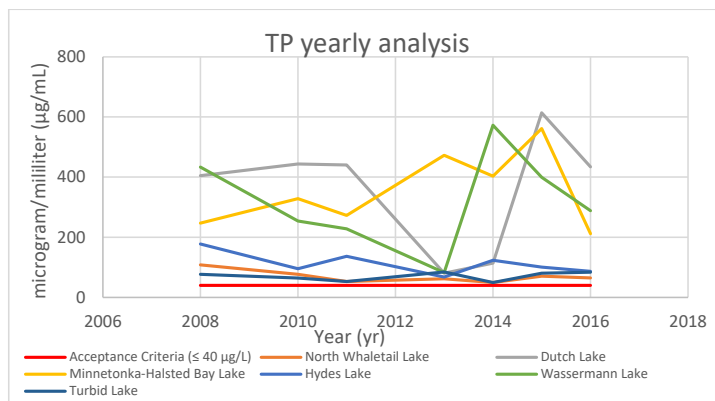

Fig. 1: Total Phosphorus Evaluation for all lakes through the study period: 2008-2016
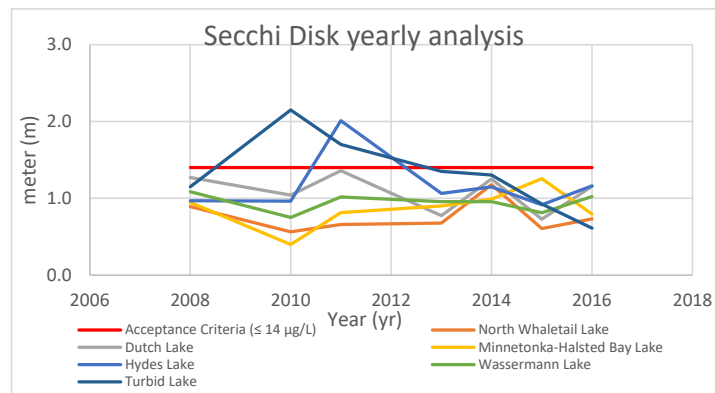

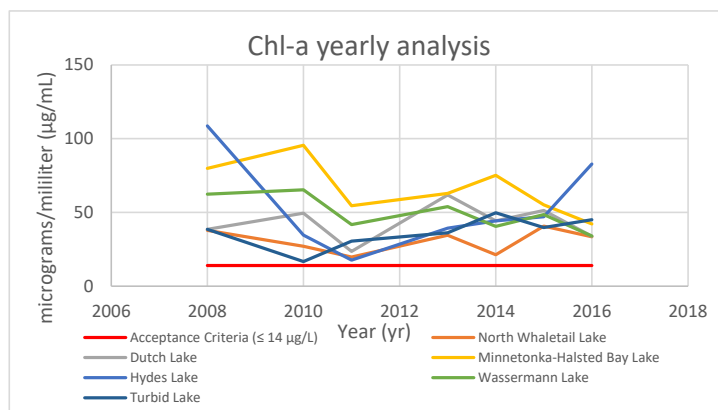Fig. 2: Secchi Disk Evaluation for all lakes through the study period: 2008-2016

Fig. 3: Chlorophyll-a Evaluation for all lakes through the study period: 2008-2016

highest results during the 2016 year for Hydes Lake. The remaining lakes showed a similar pattern; Dutch Lake and Wassermann Lake had an increase by 2013 and Minnetonka Halstead-Bay Lake had an increase by the year of 2014.

Trophic status evaluation

Results were evaluated for trophic status and are discussed in Table 1. The results obtained showed that for Hennepin County, North Whaletail Lake had a 65 result of trophic level, Dutch Lake showed a 72 result of trophic level, and Minnetonka-Halstead Bay Lake a 74 result of trophic level. For Carver County, Hydes Lake showed a 66 result of trophic level, Wassermann Lake showed a 72 trophic level, and Turbid Lake showed a 63 trophic level. A comparison of the results against the trophic status parameter (Carlson and Simpson, 1996) was performed and the results showed that two of the three lakes evaluated for Hennepin County was under hypereutrophic conditions. Conversely for Carver County, two of the three lakes evaluated were under eutrophic condition. These results are the initial indication that the null hypothesis should not be accepted, and confirms that for the data analyzed, the activities performed in urban areas affect more of the lake's water quality than the activities carried out in rural areas. A possible root cause is that the state has identified the agriculture and livestock as a punctual source and has a program with guidelines to maintain the integrity of water near the areas. Since 2015, the state governor Mark Dayton had a proposal to improve water quality by implementing a buffer initiative, where he wanted to "establish 50-foot-wide buffer strips between nearly every state waterway and farmland, from which fertilizer and other agricultural runoff had become one of the leading causes of the state's deteriorating water quality" (Bierschbach, 2015). This buffer seems to work better for rural areas than for urban areas. Conversely, regarding the controls the state has for construction sites and other industries, the buffer initiative is not enough to control the contamination, and for the time period analyzed, these activities had a deteriorating effect in the water quality for urban areas. Literature cases for bodies of water in quasi-similar to similar conditions (less cold than the study area or depth) had lakes with similar trophic conditions as they found in this study for both counties. Lakes such as Carey Lake in MN and Caohai Lake in China, evaluated different aquatic plants and sediment modifications to eliminate these contaminants. Both studies are a good proposal to improve the conditions of the lakes.

A statistical analysis was performed by using ANOVA two factor with replica, to compare properly both counties' data. Results obtained (Table 2), showed a $p < 0.05$ and values obtained for F are higher than F critical, demonstrating that there is a difference between the two counties that had been compared and therefore, the second indication that the null hypothesis should be rejected.

There are differences between the conditions of the lakes between the areas of study, but the original statement presumed that rural areas are more polluted than urbanized areas. For Hennepin County, Minnetonka Halstead-Bay and Dutch lakes are under hypereutrophic conditions, and North Whaletail Lake

Table 1: Average results for Total Phosphorus, Secchi Disk and Chlorophyll-a and trophic state for Hennepin and Carver Counties Lakes

County	Lake	Month	TP	Secchi	Chl-a	TP	Secchi	Chl-a	Mean	Lake status
			AVERAGE Results			Trophic status				
Hennepin	North Whaletail Lake	Jun	65	0.9	24	64	61	62	63	eutrophic
		Jul	77	0.8	33	67	64	65	65	
		Aug	68	0.7	36	65	66	66	65	
		Sep	64	0.7	30	64	65	64	64	
		Grand AVG	69	0.8	31	65	64	64	64	
	Dutch Lake	Jun	235	1.6	28	83	53	63	66	hypereutrophic
		Jul	322	0.8	51	87	64	69	73	
		Aug	378	0.7	53	90	65	70	75	
		Sep	482	1.3	38	93	56	66	72	
		Grand AVG	354	1.1	42	89	59	67	72	
	Minnetonka-Halstead Bay Lake	Jun	189	2.2	19	80	49	60	63	hypereutrophic
		Jul	367	0.7	57	89	66	70	75	
		Aug	573	0.5	83	96	70	74	80	
		Sep	278	0.4	95	85	72	75	78	
		Grand AVG	352	0.9	64	89	61	71	74	
	Hydes Lake	Jun	67	2.1	27	65	49	63	59	eutrophic
		Jul	126	1	73	74	61	73	69	
		Aug	136	0.8	82	75	63	74	71	
		Sep	117	1	30	73	60	64	66	
		Grand AVG	112	1.2	53	72	57	70	66	
Carver	Wassermann Lake	Jun	153	2	23	77	50	61	63	hypereutrophic
		Jul	301	0.8	50	86	63	69	73	
		Aug	401	0.6	67	91	68	72	77	
		Sep	422	0.6	52	91	67	69	76	
		Grand AVG	319	1	48	87	60	69	72	
	Turbid Lake	Jun	65	1.9	27	64	51	63	59	eutrophic
		Jul	79	1.1	52	67	58	69	65	
		Aug	64	1	33	64	60	65	63	
		Sep	74	1.2	36	66	58	66	63	
		Grand AVG	70	1.3	37	65	56	66	63	

Table 2: ANOVA: Two factor with Replica comparison results for Hennepin and Carver counties

SUMMARY	Hennepin County			Carver County			Total
Chl-a	North Whaletail	Dutch Lake	Minnetonka-Halsted Bay	Hydes Lake	Wassermann Lake	Lake Turbid	
Count	27	27	27	27	27	27	162
Sum	830.7083	1161.187	1764.983	1462.15	1320.45	1007.3	7546.778
Average	30.76698	43.00691	65.36975	54.1537	48.90555556	37.30741	46.58505
Variance	117.3097	478.561	1165.12	3979.845	381.2701496	507.8676	1198.908
Secchi							
Count	27	27	27	27	27	27	162
Sum	20.65833	29.29167	23.98833	31.95417	25.6419755	34.61	166.1445
Average	0.765123	1.084877	0.888457	1.183488	0.949702796	1.281852	1.025583
Variance	0.062634	0.375264	0.570721	0.409198	0.349839154	0.597814	0.413282
TP							
Count	27	27	27	27	27	27	162
Sum	1861.417	9680.117	9659.817	3055.833	8778.633333	1906	34941.82
Average	68.94136	358.5228	357.771	113.179	325.1345679	70.59259	215.6902
Variance	490.8636	48007.79	56371.2	2432.812	43937.99987	735.7892	42262.71
Total							
Count	81	81	81	81	81	81	
Sum	2712.783	10870.6	11448.79	4549.938	10124.72531	2947.91	
Average	33.49115	134.2049	141.3431	56.17207	124.9966088	36.39395	
Variance	985.7835	41528.52	43114.4	4202.94	35069.90796	1215.477	
ANOVA							
Source of Variation	SS	df	MS	F	P-value	F crit	
Sample	4144669	2	2072335	235.1826	2.00684E-71	3.01499	
Columns	1052693	5	210538.6	23.89335	2.00588E-21	2.233275	
Interaction	1820865	10	182086.5	20.66441	8.14019E-32	1.850937	
Within	4123829	468	8811.599				
Total	11142056	485					

Therefore, if F > F crit and p values is < α, then H_0 is rejected (α=0.05).

is under eutrophic conditions. The difference between the trophic status results progresses from 49 to 96 result, and for all the lakes the trophic values start increasing from June to August and begins to decrease in September. For Carver County, Wassermann Lake is in hypereutrophic condition and Hydes and Turbid lakes are under eutrophic conditions. The difference between the trophic status results progresses from 49 to 91, and for all the lakes the trophic values start increasing from June to August and begin to decrease in September. Histogram and Pareto analysis was performed for each parameter and county. Relating to Chlorophyll-a results at Hennepin County (Fig. 4), second-class interval (23, 39] contains most of the

results with an approximate of 28% of the values, and a cumulative percent of about 51%. Results conforming to the specification (≤14 µg/L) are contained in the first-class interval and are less than 22%, since this interval also contains results above acceptance value. Therefore, approximately 78% of the results in the period of study are in eutrophic-hypereutrophic status. For Carver County, (Fig. 5) shows the same pattern as Hennepin County but the class interval values contain results higher than the results from Hennepin County. The interval goes from (35, 69] and contain 43% of the results with a cumulative of 85%. Less than 42% of the results conform to specification, and about 58% does not
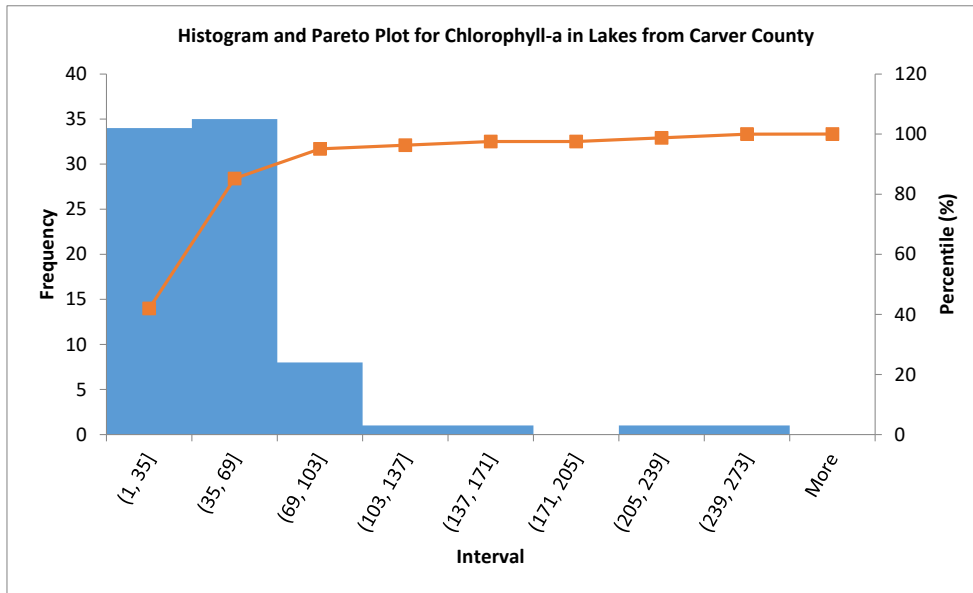
Fig. 4: Histogram and Pareto Plot for Chlorophyll-a in Lakes from Carver County (n=81)
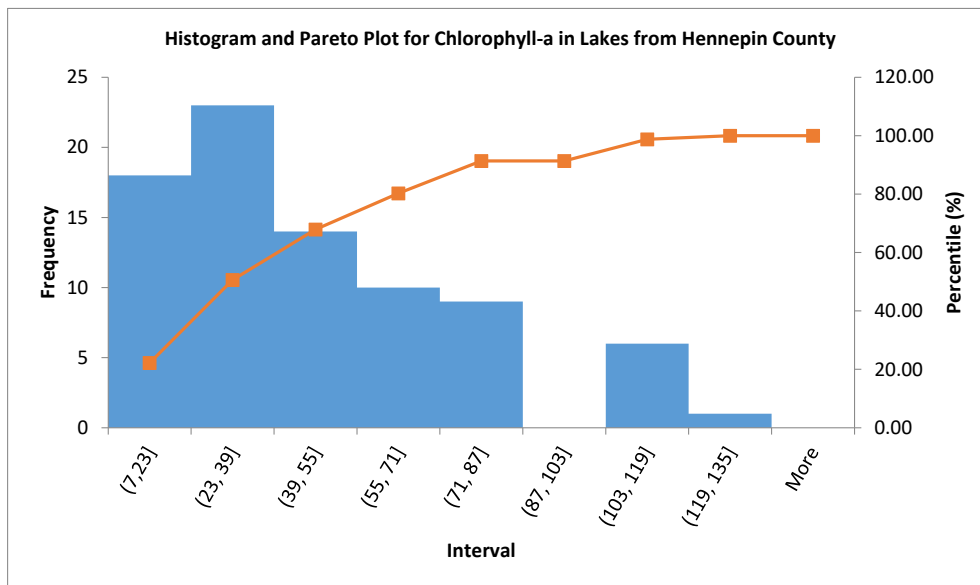

Fig. 5: Histogram and Pareto Plot for Chlorophyll-a in Lakes from Hennepin County (n=81)

conform to the specification and are in eutrophic-hypereutrophic status. Regarding Secchi Disk results at Hennepin County (Fig. 6), first-class interval (0.4, 0.8] contains most of the results with an approximate of 54%, and all the results contained in the interval do not conform to the specification (≥1.4 m). In fact, 78% of the cumulative results do not conform to the

specification and are in eutrophic-hypereutrophic status. For this county, only 15% of the results for SD conform to the specification. Carver County shows the same pattern as Hennepin County, but the number of results is less (Fig. 7). The first-class interval goes from (0.4, 0.8] and contain 40% of the results. Less than 12% of the results conform to specification and
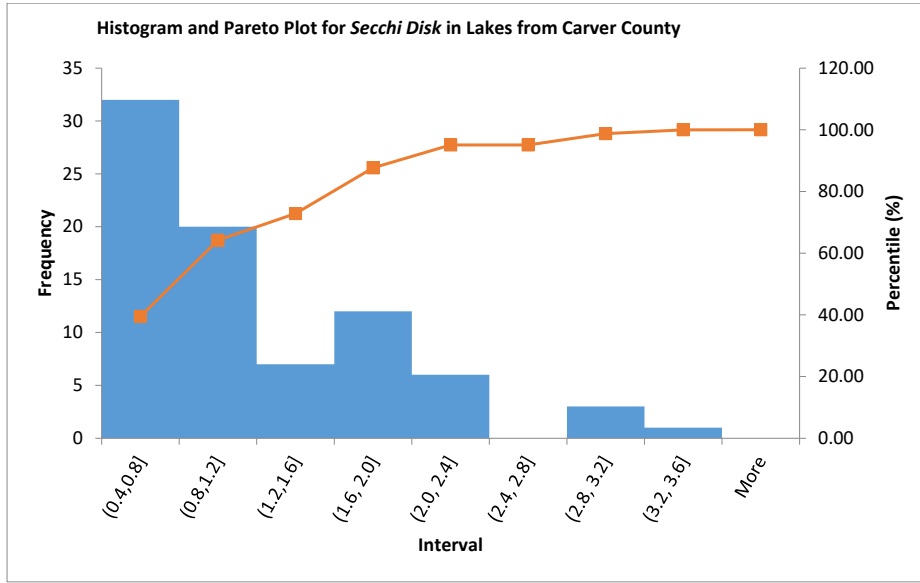
Fig. 6: Histogram and Pareto Plot for Secchi Disk in Lakes from Carver County (n=81)
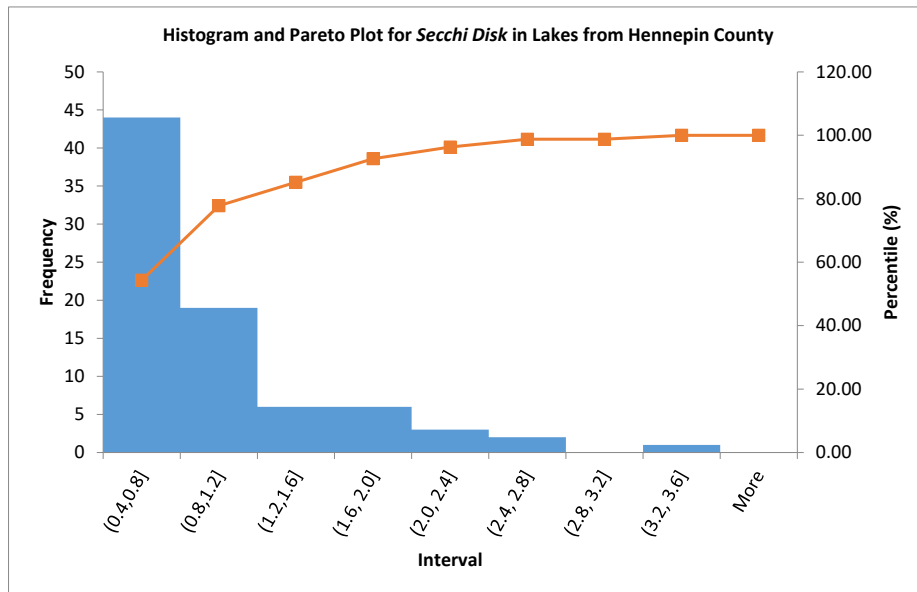

Fig. 7: Histogram and Pareto Plot for Secchi Disk in Lakes from Hennepin County (n=81)

about 88% do not conform to the specification and are in eutrophic-hypereutrophic status. For Total Phosphorus results in Hennepin County (Fig. 8), first-class interval (43,159] contains most of the results with an approximate of 51% and no results contained in the interval conform to the specification (≤40 µg/L). In fact, 100% of the results do not conform to

the specification and are in eutrophic-hypereutrophic status. For Carver County (Fig. 9), the results show the same pattern as Hennepin County, but the class interval values contain results lower than the results from Hennepin County. The interval goes from (21, 134] and contain 67% of the results. Less than 67% of the results conform to specification and about
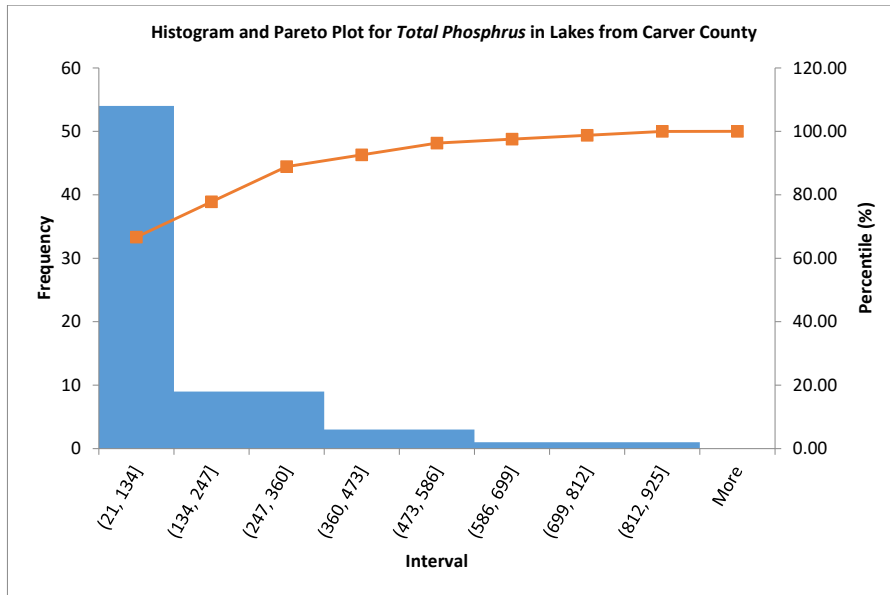
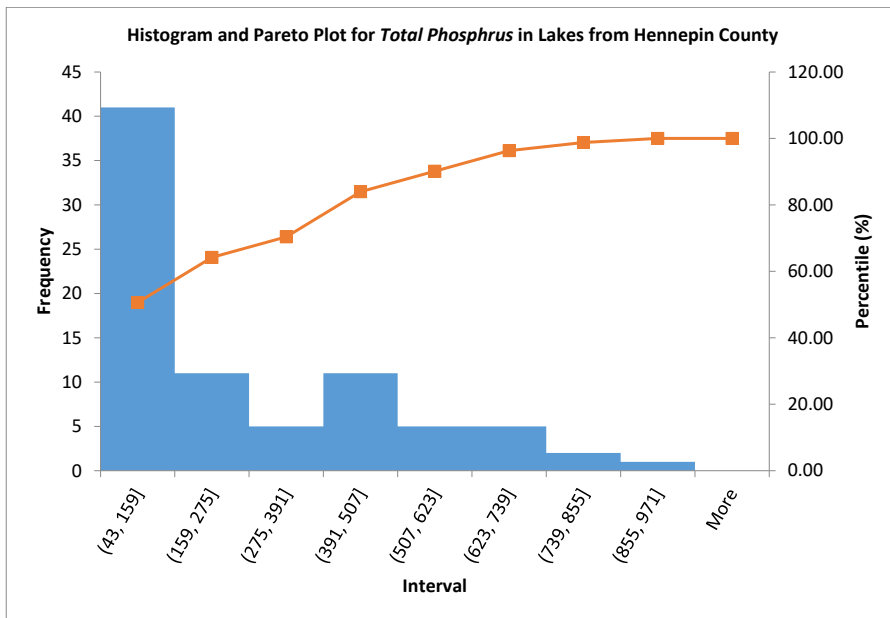Fig. 8: Histogram and Pareto Plot for Total Phosphorus in Lakes from Carver County (n=81)

Fig. 9: Histogram and Pareto Plot for Total Phosphorus in Lakes from Hennepin County (n=81)

33% do not conform to the specification and are in eutrophic-hypereutrophic status.

Literature Comparison

Similar cases were evaluated in lakes that are close to or at a similar temperature to the lakes of Minnesota or in lakes with similar eutrophication problems. Bioremediation plans have been started, where the work consists of the creation of artificial wetlands that promote denitrification and

phosphorus removal using different sedimentation and plants, which effectively removes them from the body of water. A similar case in Taihu Lake Bay in China has soil erosion problems, causing high increase in nutrients and turbidity, and is severely in eutrophic status. These problems are due to a "significant urbanization over the last 20 years, deforestation, soil erosion and poorly regulated horticultural and agricultural activities resulted in a heavy inflow of nutrients into the lake from catchment areas" (He, Lin and Ma, 2016). Other authors suggest the usage of integrated systems where ecological modifications are performed using "locally available natural resources in ecologically balanced systems" (Shutes, 2001). Literature cases for water bodies in quasi-similar to similar conditions (less cold than the study area or depth), had lakes with similar trophic conditions as the found in this study for both counties. As explained previously, lakes in eutrophic conditions such as Carey Lake in MN and Caohai Lake in China, evaluated different aquatic plants such as Eichhornia crassipes removing almost a 100% of TP (Zhang et al, 2019), and sediment modifications such as the zinc modification performed by Huang group (Huang et al, 2019), to eliminate these contaminants, and should be considered as a possible bioremediation method to improve the water quality of the studied lakes by restoring the wetlands near these lakes, or implementing these changes by creating an artificial wetland in these areas.

CONCLUSION

According to the results obtained during this study, the following conclusions were made:

1. There was enough evidence to reject the null hypothesis since the F-statistical value obtained is higher than F-critical, and the p-value obtained is lower than alpha (α=0.05). There was a difference in the water quality between the counties, but not as expected. The original statement specified that the lakes near areas mostly used for agriculture or livestock should have worse water quality that urbanized areas. The results obtained showed that for the lakes studied, the urban areas have more contamination than the lakes in rural areas, but still both areas have eutrophic-hypereutrophic conditions. During the past decade, the state resulted data that indicated an increase in nutrients and are

shown in the annual graphs for total phosphorus, Secchi Disk and Chlorophyll-a, Figs. 5 to 10. It is also observed that the state's resulted data had a decrease in the contaminant early in the decade and suddenly the contaminants started an increasing during the following years. This evidence that anthropogenic activities from a non-point source are the most probable cause for the rise in contaminants. The state adopted a buffer project to lessen the effect of the contaminants inserted in the lakes, rivers, watershed, and streams by runoffs. As explained previously, the urban growth and the manipulation of the areas (such as the removal of wetlands, shrubs and other plants that prevent soil erosion) and the inappropriate use of the resource, have shown that many of the pollutants found cannot be attributed to a point source, making this a huge problem. This is the case for Hennepin County. Carver County, even though is developing in urban and commercial areas, still has most of the lands used for agriculture or livestock. Therefore, the state already identified these as a point-source and has created different strategies to mitigate the impact of these activities in the lakes (such as a program with guidelines to maintain the integrity of water near the areas);

2) Trophic status objective was completed, and the results showed that the lakes under the study are in eutrophic-hypereutrophic conditions. In fact, lakes evaluated under this study, demonstrated that Hennepin County had worse conditions for the lakes than Carver County. The possible root cause redounds to anthropogenic activities affecting the lakes at different levels. Phosphorus (in its variation) in the lake water, limits Chlorophyll-a and therefore in excess (usually also in the presence of nitrogen and its variations), proliferate growth of aquatic plants, algae and cyanobacteria in the lakes that eventually, with the changes in temperatures due the seasons, will affect the transparency of the lakes;

3) After evaluating the results, it can be concluded that the buffer parameters implemented by the state are either not sufficient or need more time to be evaluated for the significance of implementing this method into the water quality. Therefore, the restoration or the implementation of a variation of an artificial wetland is recommended. Also, an evaluation of the soil and plants used in the buffer zones should be re-evaluated.

Recommendations and limitations

Because of the limitations of this study, creating a complete environmental treatment program is not an appropriate method for this study, but general recommendations for the future to improve water quality are discussed. As a first recommendation, the original buffer zones should be evaluated. The timeframe studied is closed to the implementation of this system but still, the lakes are in eutrophic-hypereutrophic conditions. Therefore, an evaluation of specialized types of plants, soils, and/or bacteria needs to be performed to control the contaminants impacting the water bodies. As an option to improve the water quality of the lakes in Minnesota, a restoration of lakes with wetlands or an artificial wetland project can be implemented and paired with the original buffer plan the state has already implemented. Since the study demonstrated that urban areas suffer from more non-point source contamination than the rural areas, the plan can be focused on the improvement of water quality in this type of area. After evaluating the results obtained, the implementation of an integrated method using a Subsurface Flow System (SFS) is highly recommended because this method can have an effectiveness of 80% the removal of organic material and suspended solids, but nutrient removal efficiency is normally below 60% (Shutes, 2001). The SFS system uses a "layer of soil or gravel as a substrate for plant growth. The water flows go through the substrate and the roots of the plants by gravity and horizontally. During the passage of wastewater through the root system of plants, organic matter decomposes biologically, nitrogen can be denitrified, and phosphorus and heavy metals are fixed in the soil" (Fernández-González, n.d.). Since Minnesota lakes have higher results for PO contaminants, the addition of "Phospho-accumulating organisms" (PAO's) will be useful to help in the conversion of these contaminants in the Phosphorous (P) form, and then be trapped in the plants from the artificial wetland, such as the proposed below (Minnesota Pollution Control Agency (MPCA), 2011). Shutes (2011) has an example of an artificial wetland specifically created for urban surface runoff treatment where the following procedure was followed. The following modifications can be incorporated in the subsurface flow system (SFS) artificial wetland:

1) An area with modified soil can be used to remove properly P and N. Soils like $ZnSO_4$ were used by other authors obtaining good results removing orthophosphates and controlling algal blooms (Huang et al, 2019);

2) Studies suggested the usage of *Eichhornia crassipes* and *Pistia stratiotes* due to its effectiveness removing between 93% to 96% of TP (Irfan, Sayantan, Shardendu and Sharma, 2012 and Bartodziej, Blood and Pilgrim, 2017);

3) Other phosphorus remover plants that can be used such as *Hydrilla verticillate, Hydrodictyon reticulatum Eleocharis plantaginea,* and *Elodea canadensis* (Bartodziej, Blood and Pilgrim, 2017; Irfan, Sayantan, Shardendu and Sharma, 2012 and Zhang, 2019);

4) Additional plant that can be used as nitrogen removers are *Myriophyllum spicatum, Zostera marina, Egeria densa, Lemna obscura, Phragmites australis,* and *Typha* (Irfan, Sayantan, Shardendu and Sharma, 2012).

According to Huang *et al*. (2012), the construction of an artificial wetland that has optimal anaerobic and anoxic conditions for denitrification and nutrient removal, when focusing on Minnesota cases, can be used as an option to bioremediate the problem. As explained by Guadalupe and Llagas, the creation of an SFS has three crucial parts: the physical, biological, and chemical removal process (Guadalupe and Llagas, 2006):

1) The physical process is one in which the flow of water is slow for an effective removal of solids since they are trapped in the plants and the bioturbation and gas evolution process begins.

2) In the biological process, nutrients are absorbed by plants, algae, and shrubs. When plants go to the dying process, the leachate process occurs where water soluble contaminants are suspended in the soil. The material that the microorganisms do not absorb and decompose, eventually turns into peat, storing these contaminants.

3) The chemical process occurs through absorption, where an exchange of cations occurs in the soil: either clay or organic material. Other processes that occur are precipitation by metal sulfides and volatilization of compounds.

Limitations

The monitoring program was not constant and limited the data available for the study. Therefore,

the span of seven years was evaluated: 2008, 2010 to 2011 and 2013 to 2016 through the period of June to September (except for 2010 that June was removed due to missing data for one lake under evaluation). Since multiple lakes have site specific parameters, it was difficult to find bodies of water evaluated under the same parameters. This fact limited the quantity of lakes to be analyzed per county. Therefore, the results obtained under this study are specifically for the lakes analyzed and during the specified timeframe. To have more accurate information of the status of each county, the timeframe needs to be extended to conclude if the efforts made by the state are helping the water quality of the lakes, and if additional remediation plan needs to be implemented.

AUTHOR CONTRIBUTIONS

N. Guerrero Del Castillo performed the literature review, experimental design, analyzed and interpreted the data, prepared the thesis document, and the thesis committee of Ana G. Méndez University: J. Musa, K. Malavé and C. Morales mentored, gave recommendations and review the final thesis report.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest regarding the publication of this work. In addition, the ethical issues including plagiarism, informed consent, misconduct, data fabrication and, or falsification, double publication and, or submission, and redundancy have been completely witnessed by the authors.

ABBREVIATIONS (NOMENCLATURE)

Chl-a	Chlorophyll-a
CWA	Clean Water Act
DW	Dry weight
ENRD	Environmental and Natural Resources Department
FFS	Free Flow system (artificial wetland system)
H_0	Null hypothesis
H_1	Alternate hypothesis
µg/L	Microgram Per Liter
MAR	Minnesota Administrative Rules
MDNR	Minnesota Department of Natural Resources
mg x g^{-1}	Milligrams Per Gram
mg/L	Milligrams Per Liter
MPR	Minnesota Public Radio
MPCA	Minnesota Pollution Control Agency
MN	Minnesota
N	Nitrogen
NHDS	The National Hydrographic Data Set
NOx	Nitrate pollutants
USDA-NRCS/NRI	United States Department of Agriculture-Natural Resources Conservation Service/National Resources Inventory
OS	Oxidized Sediment
PAO	Phospho-accumulating organisms
P	Phosphorus
PCB	Polychlorinated biphenyl
PFOS	Perfluoro octane sulfonate
P/m^2/day	Phosphorus in a square meter per day
ppm	Part per million
PO	Phosphate pollutants
RS	Raw Sediment
S-CTAB	Centrimonium bromide Sediment
SD	Secchi Disk
SFS	Subsurface flow system (artificial wetland system)
S-Zn	Zinc Sulfate Sediment
TMDL	Total maximum daily load
TP	Total phosphorous
TSI	Trophic State Index
US EPA	United States Environmental Protection Agency
WQA	Water Quality Association

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