

effects of land use on the concentrations of nitrogen and phosphorus in streams in northwestern
PA

By
Leah Frase Student
Department of Environmental Science
Allegheny College
Meadville, Pennsylvania

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Name: Leah Frase Student

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Thesis Committee: Dr. Rich Bowden, Dr. Rich Bowden, Dr. Claire Griffin

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Excess nitrogen and phosphorus in the stream ecosystem has caused eutrophication leading to hypoxia, especially in Lake Erie. Although there are policies and practices that have been implemented over the years to mitigate the excess nutrients seeping from the land into watersheds surrounding Lake Erie, concentrations are still on the rise; with increased eutrophication as a result. The differing land covers in North Western Pennsylvania have led to different amounts of nitrogen and phosphorus concentration in its surrounding watersheds. The land cover responsible for the most increase in phosphorus and nitrogen concentrations in Pennsylvania is said to be farming. This is due to the use of fertilizers and manure in crop fields however, the results comparing farming land cover percentage to nitrogen and phosphorus concentration showed a decline in both as farming land percentage in the watershed increased. Nitrogen and phosphorus, as well as other pollutants, in Pennsylvania also come from urban areas in septic waste, and stormwater which accumulate on the impermeable surfaces that dominate these urban areas. While the average concentration of nitrogen increased with larger areas of development, the average phosphorus concentration decreased. The phosphorus concentration was expected to increase as well due to the fact that most of the N and P in the developed environment is believed to come from fertilizers. The forested watershed results were also inconclusive; as phosphorus concentrations increased with increased forested area and nitrogen concentrations decreased slightly.

Introduction

Human activities on the earth's surface have now been linked to an acceleration in the rate and extent of eutrophication in water bodies (Chislock et al., 2013). Today, eutrophication is considered to be a result of increased nutrient inputs, specifically nitrogen and phosphorus, from urbanization, industrialization, and modern agriculture (Qin et al., 2012). These higher levels of bioavailable phosphorus found in eutrophic water bodies have been linked to a raised pH and hypoxia (Chislock et al., 2013). Hypoxia is a condition where water has low levels of dissolved oxygen, defined as less than 2-3 milligrams of oxygen per liter (DO/L) (Environmental Protection Agency, 2024). Although hypoxia can occur naturally within aquatic environments, hypoxic conditions have increased since the beginning of the 20th century because of the same human activities that have increased eutrophication (Environmental Protection Agency, 2024). The fact that these two processes are caused by human involvement is not a coincidence; they are linked in causation because hypoxia often becomes a symptom of eutrophication. Once the dense plant matter associated with eutrophication, often algae, dies it sinks to the bottom of the waterbody where it is decomposed by microbes, depleting the supply of dissolved oxygen in the water (Chislock et al., 2013 & Qin et al., 2012). These areas of depleted oxygen supply are called 'dead zones'; areas of a water body that have experienced periodic hypoxia (Chislock et al., 2013 & Environmental Protection Agency, 2024).

One of these 'dead zones' occurs in Lake Erie, the southernmost and shallowest of the Great Lakes. The 'dead zone' of Lake Erie, depending on the year, can be as large as 10,000 square kilometers, and tends to alter the lake's ecosystem from July to October (Almeida, 2015). This 'dead zone', which starts off at the bottom of the central basin of Lake Erie, develops as a result of the lake's annual cyanobacterial algal blooms (Almeida, 2015). These blue-green algal blooms developed as a result of anthropogenic nonpoint runoff of nitrogen (N) and phosphorus (P), which come from both agricultural and urban sources (Almeida, 2015). Historically, Lake Erie's primary production has been influenced by the amount of bioavailable phosphorus (P) (Watson et al., 2016). However, increasing P loads have led to a sharp rise in Lake Erie's phytoplankton biomass, specifically cyanobacteria (Watson et al., 2016). There is also evidence to suggest that together, nitrogen (N) and phosphorus (P) play a role in determining these blooms' composition (Watson et al., 2016). Nitrogen concentrations have been shown to restrict

cyanobacterial biomass which has led many researchers to call for dual management protocols in order to mitigate current eutrophic blooms in Lake Erie (Chaffin et al., 2019).

Analyses done on long term plankton and sediment data have shown that algal blooms are not new to Lake Erie, but over the past 50 years changes in species, composition, and dynamics have occurred to an extraordinarily high degree (Watson et al., 2016). However, data on total phosphorus (TP) loading from watersheds, P concentrations in the lakewater, and algal monitoring data were only taken intermittently prior to the 1970s (Sgro & Reavie, 2018). Regardless, there is evidence to suggest that there were multiple stages of change in the eutrophication of Lake Erie. In fact, the eutrophication of Lake Erie started in the 1700s and 1800s as massive amounts of land were cleared to make room for homes and crops, which resulted in the annual erosion of 6.5 millions tons of sediment into the lake (Reutter, 2019). By the 1900s the lakes eutrophic condition worsened more due rapid population growth and an influx of untreated wastes from sawmills, gristmills, slaughterhouses, steel mills, breweries, and towns which were discharged directly into the lake or its surrounding tributaries (Reutter, 2019). However, there was an observed phytoplankton reduction during the 1970s and 1980s with some areas of lake decreasing their biomass by as much as 89% (Azevedo et al., 2014). This reduction can be linked to passage of the Great Lakes Water Quality Agreement (GLWQA) in 1972 which reduced phosphorus loading from the lakes point sources by 60% by 1981 (Reutter, 2019). However, despite the success in biomass reduction the dissolved oxygen (DO) levels in the lake did not make a recovery during this period, and by the end of the 1980s the lake was once again showing signs of eutrophication (Azevedo et al., 2014). Since the mid-1990s the direct reactive phosphorus (DRP) load has been rising even though the total phosphorus (TP) load of Lake Erie is still around the designated 11,000 MTA target set by the GLWQA (Reutter, 2019). This increase in DRP is the primary driver for the re-eutrophication of the Lake and the current cyanobacterial algal blooms (Reutter, 2019).

Each of the three basins of the lake are demonstrating re-eutrophication in different ways. The western basin has seen a renewal in *Microcystis* algal blooms, while the central basin's hypoxic conditions have increased in their extent and severity (Reutter, 2019). The eastern basin of Lake Erie has seen a renewal of nuisance algal blooms, *Cladophora* (Reutter, 2019). The different conditions of the basins can be attributed to differences in their depths and water chemistry, even though they share a common source. During the first half of the 20th century

pollution from the expanding populations in Lake Erie watersheds was exacerbated by inadequate water treatment facilities, the introduction of phosphate detergents, as well as increasing agriculture and industrialization. Today, a significant majority of the phosphorus runoff is coming from nonpoint agricultural sources, or agricultural runoff, primarily from large storm events (Reutter, 2019; Department of Environmental Protection, 2024). Agricultural runoff is defined as all of the water that drains from an area (field or watershed) including surface and subsurface runoff, leaching, and tile drainage; however in most watersheds P drainage is mostly coming from surface rather than subsurface runoff (Sharpley et al., 1999). Once the P runoff has made it to a waterbody the dissolved P immediately becomes available for biological use while the P in sediment becomes a long term source for aquatic organisms (Sharpley et al., 1999). While the long-term fate of accumulated soil P is unknown, it has become clear that as P in soil increases so does the particulate and dissolved P that is transported during runoff (Bennett et al., 2001). This is particularly worrying as phosphorus accumulations in farm soils are often built up to levels that exceed the crops' needs, increasing the risk of long term eutrophication in water bodies (Bennett et al., 2001).

Land use, next to and within the watershed, is believed to be one of the major drivers of cyanobacterial blooms (Marion et al., 2017). The eutrophication of waterbodies has also been linked to the rapid growth and intensification of crop and animal farming (Sharpley et al., 1999). This rapid growth and intensification has led to local imbalances in both P inputs and outputs, where on average only 30% of P fertilizer and feed inputs going into the farming system are being taken up by the crops or animals with the rest becoming an output in agricultural runoff (Sharpley et al., 1999). Therefore, according to Sharpley et al (1999) there is an average surplus of P at around 33.6 kg/hectare when compared to total usable agricultural land. Stream nutrient inputs also generally increase with increases in populations as areas of development, deforestation, and land cultivation expand and contribute agricultural runoff and human waste into surface waters (Clune et al., 2020). This is significant because Lake Eries watershed is known for having a large percentage of heavily agricultural and urban land, when compared to the other Great Lakes, with the least amount of forest and wetland areas (Reutter, 2019).

The nutrient sources in the landscape of Pennsylvania include animal manure, synthetic fertilizers, biological nutrient fixation, atmospheric deposition, effluent from septic systems, and point sources from water treatment plants (Boyer et al 2002). However, the most prevalent

source of stream nutrients in Pennsylvania comes from agricultural runoff despite a substantial decline in the area used for agriculture since the 1950s (Clune et al., 2020). In fact, most aquatic ecosystems acquire their phosphorus, one of the main ingredients in fertilizers, from surface flow since phosphates tend to bind to soils and sediments (Correll, 1998). Thus phosphorus is delivered to these aquatic ecosystems as a mixture of dissolved and particulate inputs (Correll, 1998). This application of fertilizers and manure makes agriculture one of the largest nutrient contributors in the state (Clune et al., 2020). However, synthetic fertilizers can also come from urban sources; as fertilizers are the biggest N sources in urban environments. In general, urban catchments are often characterized by impervious surfaces which limit the amount of water able to move into the soil profile (Reisinger et al, 2023). This increases the amount of water available to carry N and P as well as other pollutants into surrounding water bodies.

In Northwestern Pennsylvania land cover is heavily agricultural and urbanized in Erie county, along Lake Erie. Due to this, if Pennsylvania was to initiate or further programs aimed at reducing nutrient inputs into waterways the land use, and its relationship with stream chemistry is necessary for policy makers. To that effect, using GIS the land cover distribution of three specific watersheds in Erie County Pennsylvania, which drain into Lake Erie, were examined to determine the relationship between land cover and nutrient concentration in these streams. Within this framework two different hypotheses were tested: 1) Watersheds that have a higher overall percentage of land cover considered agricultural will have higher P and N concentrations in their streams and 2) Watersheds that have a higher overall percentage of land cover considered urbanized or developed will have higher concentrations of N and P in their streams.

Methods

The Pennsylvania small watersheds and USA streams data set were uploaded from the Eastern Pennsylvania Coalition for Abandoned Mine Reclamation (EPCAMR), Environmental Resources Research Institute, into a GIS map and edited so that each watershed contained only one stream. This was done because several of the small Pennsylvania watersheds had multiple 1st order streams contained in one watershed area. Two of the watersheds were also edited to include areas that were outside of Pennsylvania. This was done because Conneaut Creek had head waters that started in Pennsylvania and a mouth that emptied into Lake Erie in Ohio, and Twenty Mile Creek had headwaters that started in New York and a mouth that emptied in Lake Erie in Pennsylvania. To split and expand the watersheds topographic maps of the area were uploaded

from the online database “topoview” and the delineations were done by hand (Garritty, 2009). NLCD data from the MRLC or Multi-Resolution Land Cover Characteristic website were then uploaded into the GIS file and put into a model to extract individual watershed data.

Over all, the NLCD land cover model was used to extract data for 29 watersheds all of which corresponded to either 1st, 2nd, or 3rd Strahler order streams. This shows the range of land cover across the top of Erie country. The results from the NLCD land cover extraction located in the attribute table were then copied into a spreadsheet where the colored pixel count was converted into land cover percentage. The categories of Open Space Developed, Low Intensity Developed, Medium Intensity Developed, and High Intensity Developed were added together with total development for each watershed. While the categories of Deciduous, Evergreen, and Mixed forests were added to get the total forested area for each watershed, with Pasture/Hay and Cultivated crops being added together to get the total agricultural area for each watershed.

Nutrient data was obtained from the National Water Quality Monitoring Council website from within a 25 mile radius of 42.128728° Latitude and -80.104990° Longitude. This yielded three watersheds that held sufficient nutrient data: Walnut Creek (11/25/2008 - 9/10/2019), Conneaut Creek (10/7/1998 - 8/9/2022), and Twelve Mile Creek (9/10/1998 - 1/11/2005). The data from these streams were then sorted to show only the nutrient measurements of total N and P in mg/L from each creek. The total was chosen due to the fact that it accounts for most types of phosphorus (orthophosphate, condensed phosphate, and organic phosphate) and nitrogen (organic and reduced nitrogen, ammonia, and nitrite-nitrate) in the water column (EPA). Thus it allows for a more comprehensive picture of what is going on in the water column, as both organic and inorganic forms of phosphorus can be dissolved or suspended in the water column. Total nitrogen was used because the measurement of nitrate does not account for other organic forms of nitrogen that may be present in the water column (EPA).

The data points that were too low to be recorded were ones that were stated to be “Present Below Quantification Limit” by the National Water Quality Monitoring Council and were recorded as zero. All of the concentration observation points for each creek (Walnut Creek, Conneaut Creek, and Twelve Mile Creek) were averaged together to get a single concentration of phosphorus and nitrogen for each stream. These single N and P concentrations are the ones used

to look at the relationship between percentage land use (developed/urban, forested, and agricultural) and stream nutrient concentration.

Results

3.1 Land Cover

There are 29 small watersheds along Lake Erie from which the NLCD land cover data were extracted (Fig 1.). There is a heavily urbanized area in the northeastern portion of the watersheds, which corresponds with the city of Erie, along north of Presque Isle (Fig. 1). This is the largest urban area as it stretches east to west over four small watersheds and north to south over 3 (although it is important to note that the NLCD data for small watershed 4381 was not extracted)(Fig. 1). There is also a large section of farm land to the east of the city of Erie which, according to NLCD data legend, is cultivated crops (Fig. 1). The only section of contiguous

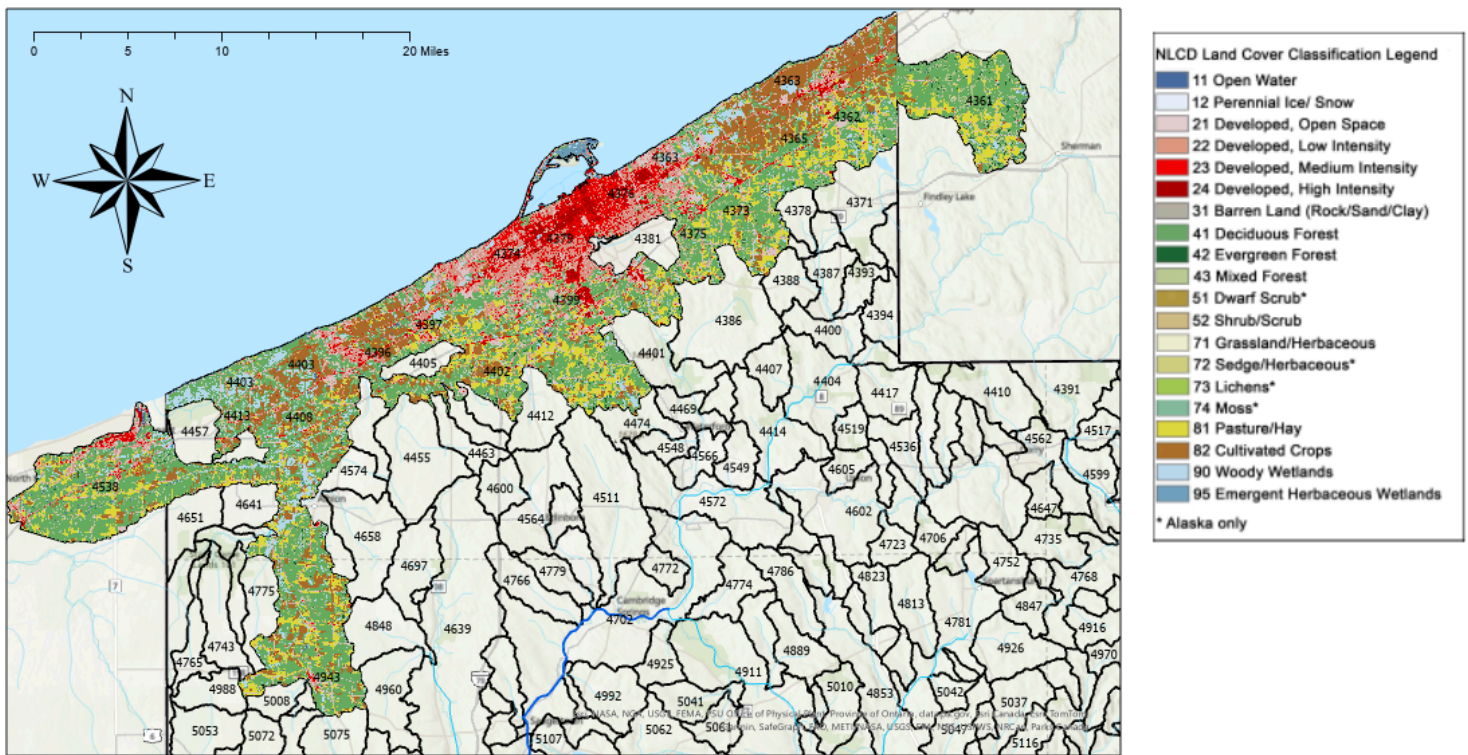


Figure 1: Delineated watersheds with NLCD land use data. Their unique IDs are in the center of the watershed.

cultivated crop land lies to the west of the city of Erie along with thin stretches of pasture/hay land dotted between forested land to the south of the city of Erie and along lakes border (Fig. 1). There are also large sections of woody wetlands on Presque Isle along with tiny areas of

emergent wetlands dotted along the coastline of Lake Erie (Fig. 1). However, NLCD data only give a snapshot of land at a specific point in time, not showing how long farmland has been cultivated for crops or pasture specifically or how long farmland or another land cover has existed in that particular area.

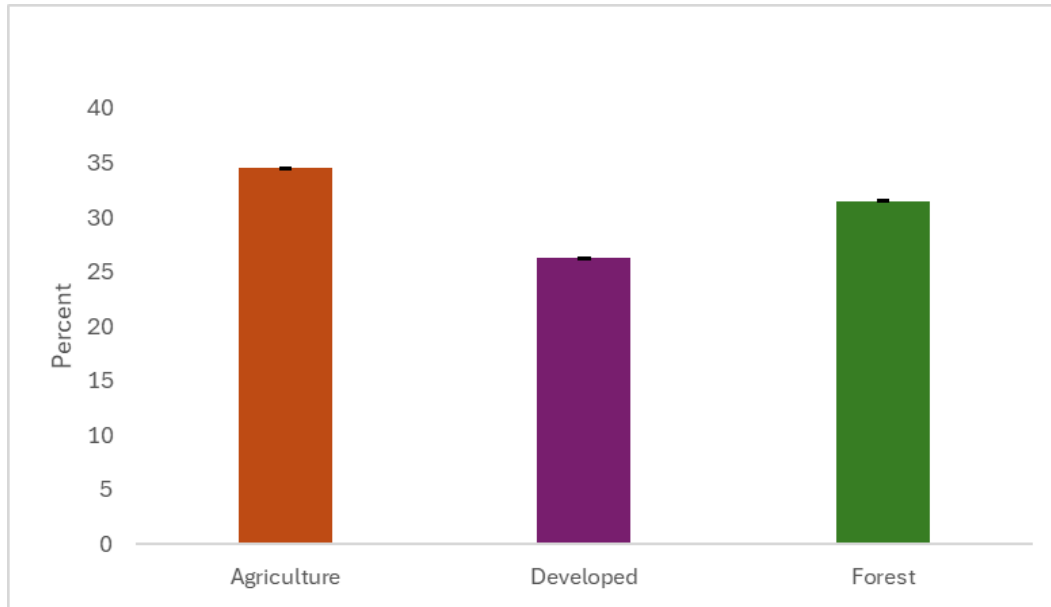


Figure 2: average percentage of agricultural, developed, and forested areas across the 29 watersheds.

The streams without a name are labeled as unnamed while the rest of the streams are labeled with their corresponding stream name next to their unique watershed ID number and percentage of developed, agricultural, and forested land cover in that watershed (Table 1). Thus, the actual land cover distribution along Lake Erie is broken down for each small watershed. On average, agriculture land cover (34.6%) dominates the small watersheds along Lake Erie followed by forested land cover (31.54%), and then developed land cover (26.37%) (Fig 2).

All of the agricultural land cover in the watersheds fall between 70% and .19% (Table 1). The most congruent agricultural land cover, considered cultivated crops by NLCD, are mostly seen along the most northern portions of the watershed while there are only small specks of pasture and hay land in the southern parts of the extracted watersheds (Fig 1.).

The developed/urban land cover, unlike the agricultural land cover, are highly variable with a majority of the watersheds falling between 0 - 40%, and a select few falling somewhere

between 60 - 100% (Table 1). The select few developed watersheds that fell between 60 - 100% were ones that contained the City of Erie (Fig 1).

Similar to the developed land cover, the forest land cover percentages are also highly variable with a majority falling 0 - 60% and one watershed containing forested land cover above 90% (Table 1). The forested land cover exists contiguously in the southern portion of the extracted watersheds and contains mostly small tacks of pasture and hay land cover and a few small tacks of cultivated crop land cover (Fig. 1).

Table 1: developed, forest, and agriculture land use for the watershed.

Stream Name	Watershed ID	Agriculture %	Developed %	Forest %
20 Mile Creek	20 Mile Creek	24.01	4.70	67.56
unnamed	9836	50.13	11.53	35.15
unnamed	9853	68.56	10.93	18.96
unnamed	4359	60.77	15.23	16.10
unnamed	9852	64.20	14.16	10.46
unnamed	4360	55.37	26.65	15.53
16 Mile Creek	4362	35.12	20.08	39.49
unnamed	4363	32.69	39.66	13.78
4 Mile Creek	4375	17.24	31.20	48.20
unnamed	4376	1.07	94.55	2.82
6 Mile Creek	4373	26.22	14.83	52.46
Mill Creek	4377	0.19	1.34	98.45
cascade creek	4379	0.21	97.15	1.45
unnamed	4374	4.39	71.74	8.78
7 Mile Creek	4372	29.24	25.02	36.22
Elliotts Run	4370	46.87	14.03	3.40
8 Mile Creek	4369	42.36	10.17	36.48
Walnut Creek	4392	21.21	44.26	27.92
Trout Run	4397	28.92	32.01	28.74
unnamed	9862	58.15	14.88	21.44
unnamed	4396	39.97	32.98	23.31
unnamed	9864	61.77	61.77	18.08
Elk Creek	4402	36.32	13.94	44.61
unnamed	4403	21.00	5.68	41.52
Crooked Creek	4408	30.75	9.27	46.91
Raccoon Creek	4413	19.07	14.01	48.19
Conneaut Creek	4538	25.89	11.99	53.28
Scott run	4368	56.05	9.19%	17.35
12 Mile Creek	4365	45.53	11.90	38.08

	Average %	34.6	26.4	31.5
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3.2 Land Cover Classifications

The land cover categories of developed, forested, and agricultural are subdivided further by the NLCD. This allows for further extrapolation on the nutrients found under different land cover majorities (Table 2). Only three watersheds are shown with the broken down land cover categories because they were the only watersheds that had corresponding nutrient data (Fig. 4 - Fig. 9).

Table 2: breaks down the developed/urban land cover, forested land cover, and agricultural land cover into three sections

	Walnut	Conneaut	Twelve Mile
Open Space	14.3	5.7	6.3
Low Intensity	1.9	4.3	3.9
Medium Intensity	8.4	1.5	1.3
High Intensity	3.5	0.49	0.37
Total %	27.9	12.0	11.9
Deciduous	37.5	49.9	33.4
Evergreen	0.86	0.44	0.73
Mixed	5.9	2.9	3.9
Total %	44.3	53.3	38.1
Pasture/Hay	15.8	15.8	16.1
Cultivated Crops	5.4	10.1	29.4
Total %	21.2	25.9	45.5

The developed land cover is broken down into four categories: open space development, low intensity development, medium intensity development, and high intensity development. Open space development is defined by the NLCD as an area with impervious surfaces accounting for less than 20% of said area. This type of area is most commonly composed of large to single family housing units, parks, golf courses, and vegetation planted in urban areas for recreation, erosion control or aesthetic purposes (Multi-Resolution Land Characteristics (MRLC) Consortium, 2024). This type of development makes up the largest percentage of developed land in the watersheds sampled (Table 2) and is most prominent around the border of the City of Erie (Fig 1.)

Low intensity development is defined as developed area with impervious surfaces accounting for 20 - 49% of the total coverage, and is mostly composed of single family housing

units (Multi-Resolution Land Characteristics (MRLC) Consortium, 2024). This was the category with the second lowest percentages for all three watersheds (Table 2) and can be seen in the town of Conneaut (Fig. 1).

The medium intensity development is defined as an area with impervious surfaces accounting for 50-79% of the total area and is also most commonly made up of single family housing units (Multi-Resolution Land Characteristics (MRLC) Consortium, 2024). The medium intensity developed areas are located in the center of the City of Erie mixed in with high intensity development (Fig. 1) and is the second largest developed land cover category.

Lastly, high intensity development is defined as an area with impervious surfaces accounting for 80-100% of the total area and includes apartment complexes, row houses, and commercial/industrial areas (Multi-Resolution Land Characteristics (MRLC) Consortium, 2024). This is the lowest category of development and only exists within the watersheds that contain the city of Erie.

The forested land covers are broken down into 3 categories: deciduous, evergreen, and mixed. However, in order to be considered any type of forested area by the NLCD the area has to be dominated by trees that are over 5 meters tall and make up more than 20% of the vegetation cover.

A deciduous forest according to the NLCD, is made up of more than 75% of the trees that shed their foliage simultaneously in response to seasonal change (Multi-Resolution Land Characteristics (MRLC) Consortium, 2024). This is the dominant forest type in all of watersheds because Lake Erie is located in a temperate deciduous region.

An evergreen forest contains 75% or greater of the tree species that maintain their leaves throughout the year (Multi-Resolution Land Characteristics (MRLC) Consortium, 2024). This is the smallest forested category among the watersheds sampled.

To be defined as a mixed forest 75% of the trees within the area cannot be defined as solely as being deciduous or solely as being evergreen (Multi-Resolution Land Characteristics (MRLC) Consortium, 2024). This category of forests is also small but is larger than the forests considered evergreen.

The agricultural land is broken down into two categories: pasture/hay and cultivated crops (Table 2). The category of Pasture/Hay is defined as an area of grass, legumes,

or grass-legume mixtures that is planted for livestock grazing or the production of seed or hay crops. These areas typically operate on a perennial cycle and must account for greater than 20% of the vegetated area (Multi-Resolution Land Characteristics (MRLC) Consortium, 2024). All of the watersheds used for this study have close to the same percent of land cover considered to be pasture/hay (Walnut Creek and Conneaut Creek 15.8%, Twelve Mile Creek 16.1%) (Table 2).

An area of cultivated crop is defined by the NLCD as an area used for the production of annual crops such as corn, soybeans, vegetable, tobacco, and/or cotton. Cultivated crops could also include woody perennials such as orchards or vineyards, and also includes all land that is being tilled. Areas considered to be cultivated crop land may have any of these plant species but they must make up over 20% of the vegetation (Multi-Resolution Land Characteristics (MRLC) Consortium, 2024). This agricultural category increased across the watershed (Table 2). The increase in cultivated crops is tied to the watersheds location along the lake as watersheds closer to the New York border possess more cultivated crop land than areas near the Ohio border (Fig. 1).

3.3 Nutrients

Out of the 29 watersheds with extracted NLCD data three were chosen: Twelve Mile Creek, Conneaut Creek, and Walnut Creek. All three of these watersheds had phosphorus and nitrogen data that was free and accessible (unfortunately no other creeks had available nutrient data). All of the collected P samples from the three streams have a trend line that increase

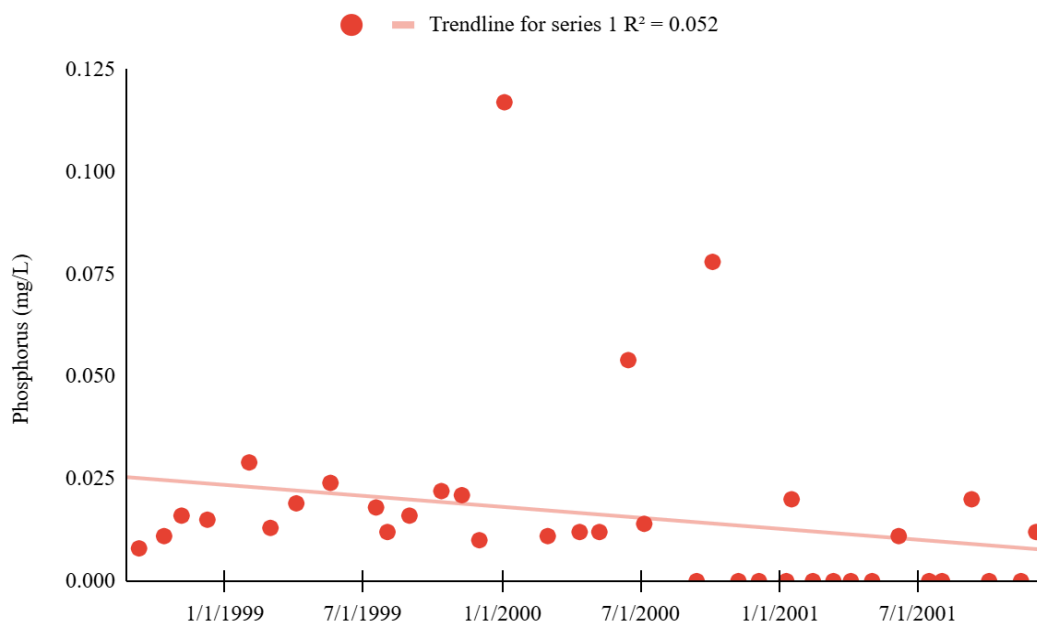
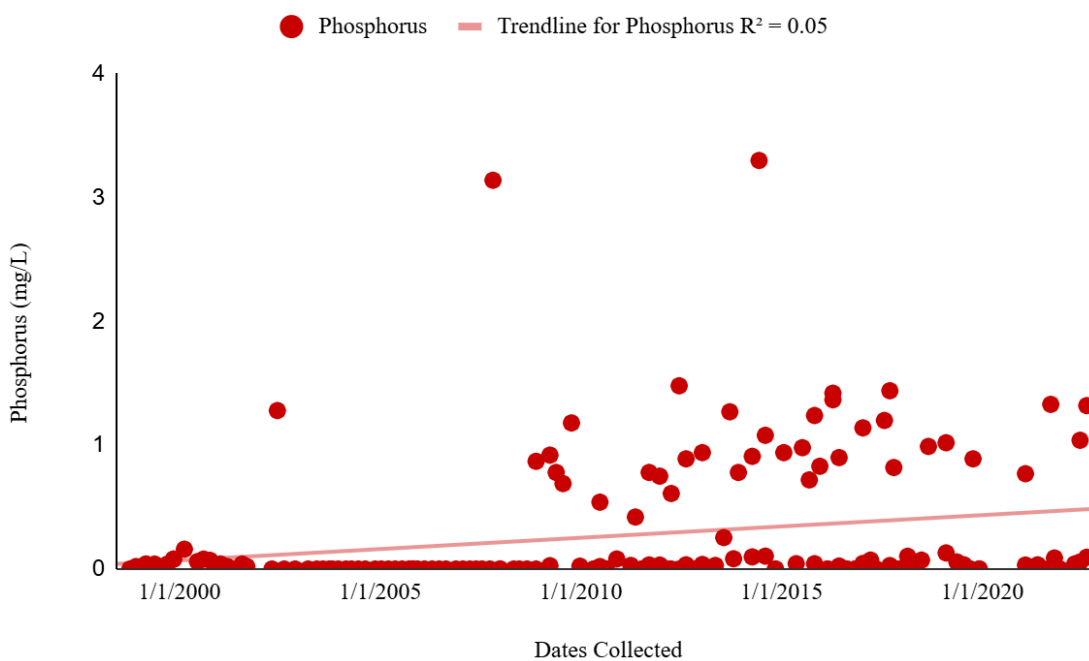


Figure 4: Total phosphorus concentrations from Twelve Mile Creek.



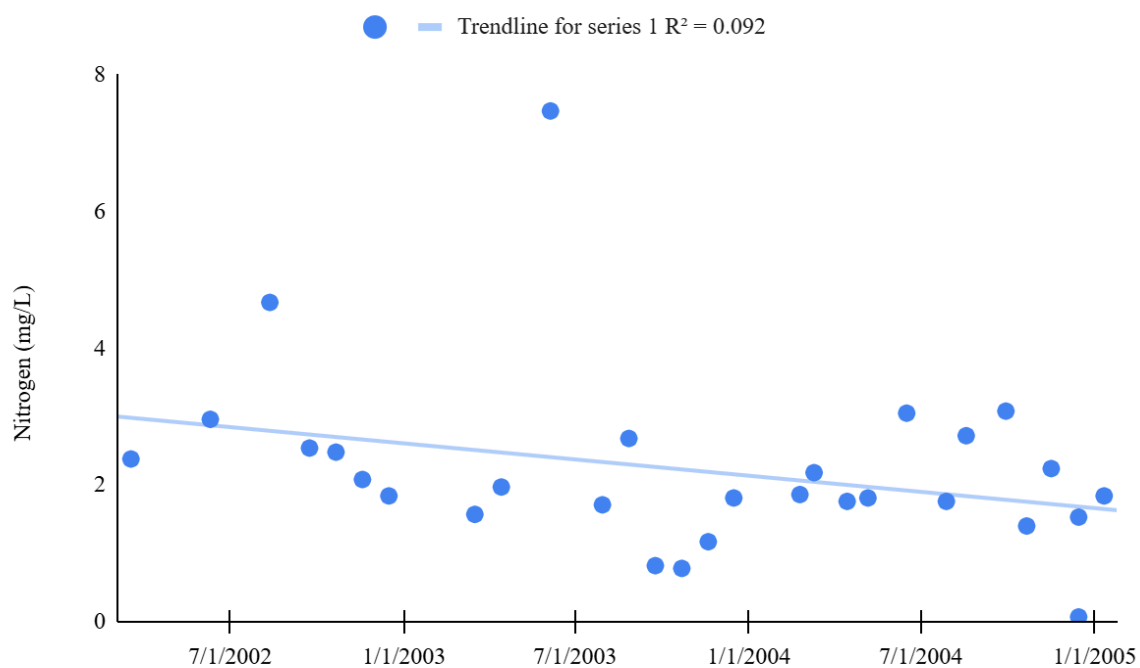


Figure 7: nitrogen concentration in Twelve Mile creek from 3/18/2002 to 1/11/2005.

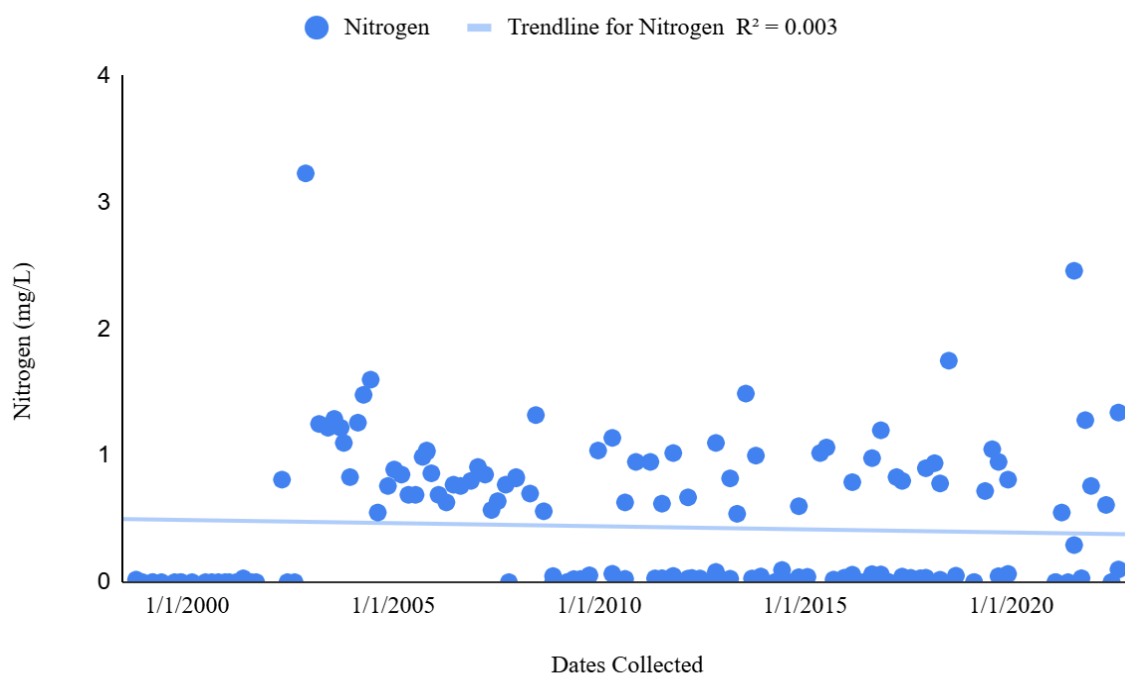


Figure 8: nitrogen concentrations in Conneaut Creek from 10/7/1998 to 8/9/2022.

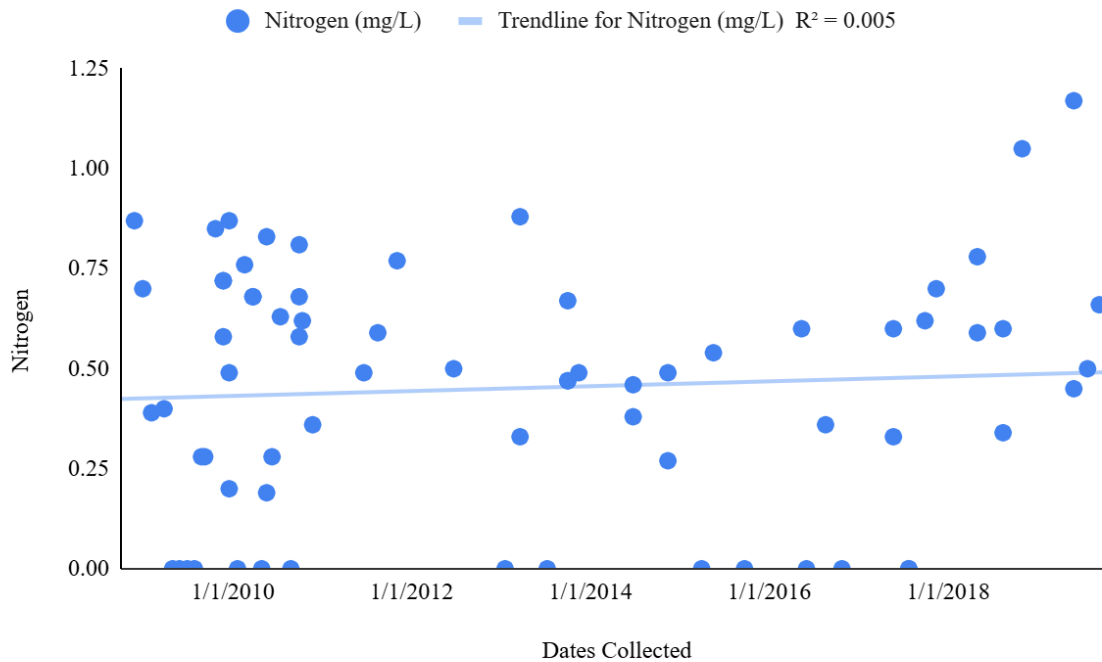


Figure 9: Nitrogen concentrations in Walnut creek from 11/25/2008 to 9/10/2019.

Two out of three N concentration trend lines decrease over time (Twelve Mile Creek and Conneaut Creek) with only one trend line increasing slightly over time (Walnut Creek). Similarly to P concentration, time does not explain the variation in N nutrient concentrations in the data set ($R^2 = 0.092$, $R^2 = 0.003$, and $R^2 = 0.005$). These data sets also varied in the number of data points available. Of all three concentration data sets only one stream (Walnut Creek) has N concentrations present in the range that the EPA considers acceptable (0.12mg/L - 2.2mg/L). The other two streams (Conneaut Creek and Twelve Mile Creek) contain outlier data points that are much higher than what the EPA considers to be the acceptable limit (Conneaut Creek with 3.23mg/L and 2.46mg/L; Twelve Mile Creek with 2.38mg/L, 2.96mg/L, 4.67mg/L, 2.54mg/L, 2.48mg/L, 7.47mg/L, and 2.68mg/L) (2008). Twelve Mile Creek, which has the most data points considered higher than acceptable, also has the highest agricultural land cover percentage (Table 2).

3.4 Land Cover and Nutrients

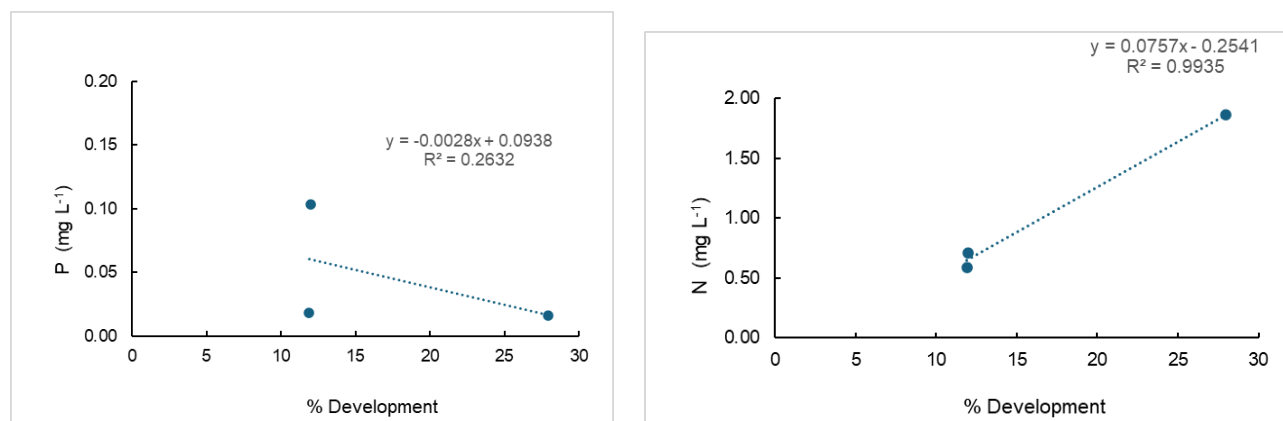


Figure 10 & Figure 11: relationship between the percent land cover of the watersheds and the average phosphorus and nitrogen levels recorded in those streams.

The P concentration decreases as the area of development increases (Fig. 10). This decrease in P concentration is not explained by the percentage of area in the watershed that is considered urban; there is no correlation between the area of a watershed considered urban and P concentration in streams ($R^2 = 0.26$).

The N concentration increases as the area of development increases (Fig. 11). This relationship is explained by the percentage of developed area in the watershed; as the area of a watershed that is considered urban goes up so does the N concentration ($R^2 = 0.99$).

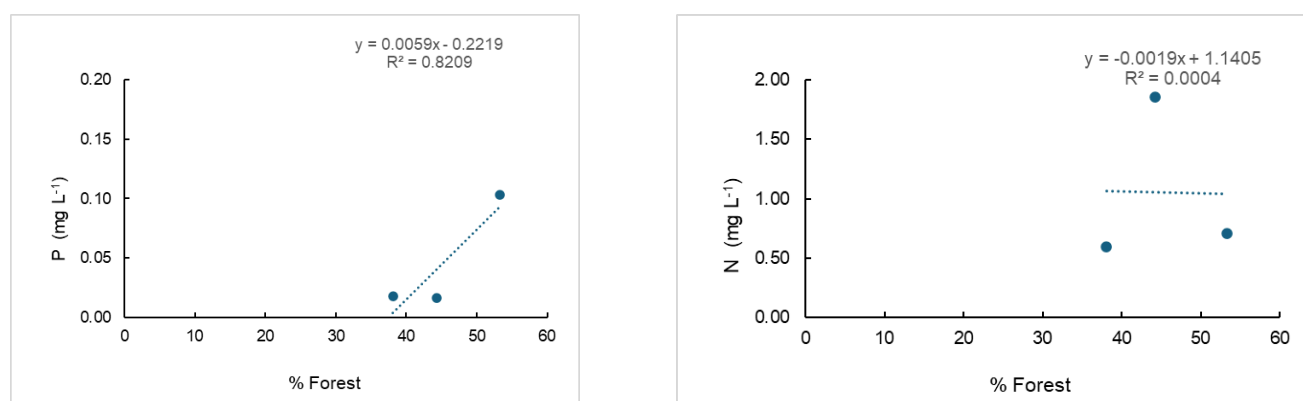


Figure 12 & Figure 13: the relationship between the percentages of forested land cover in relation to their average phosphorus and nitrogen concentrations.

The increased P stream concentrations as the percentage of area considered forested increases is strongly correlated ($R^2 = 0.82$). However, the slight decrease in N concentrations as forested area increases in the watershed is very weakly correlated ($R^2 = 0.0004$). Thus, while P

concentration in streams increases as forested area of a watershed increases, N concentration does not.

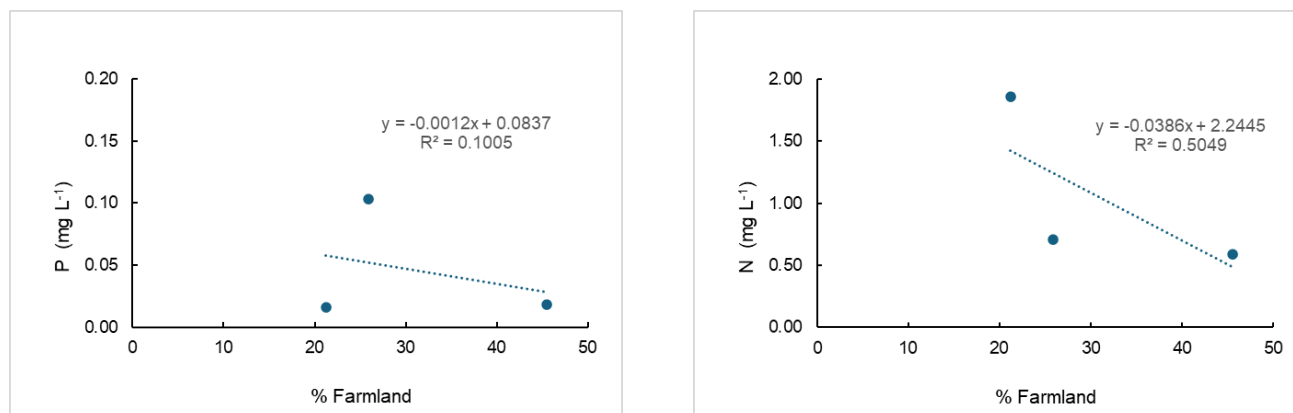


Figure 14 & Figure 15: are graphs that show the relationship between the watersheds percentage of agricultural land cover and the average percentage of phosphorus and nitrogen recorded in the streams

Both N and P concentrations decrease as the agricultural area in a watershed increases (Fig. 14 and Fig. 15). Neither the decrease in N concentration or P concentration is correlated with increase in agricultural area in watersheds ($R^2 = 0.10$ and $R^2 = 0.50$). Thus the decrease in N and P concentrations in streams is not explained by the increase in agricultural area in watersheds.

Discussion

While time does not offer any explanation for the variation seen in the nutrient concentrations in any of the three creeks these variations could potentially be explained by seasonal variation. The water levels of Lake Erie can vary in the short term seasonally, annually, as well as over longer periods with changes in the net basin water supplies (Watson et al., 2016). While annual water level cycles typically peak in June, longer term changes are driven by factors of climate (Watson et al., 2016). These seasonal changes in water supply to Lake Erie are due to changes in discharge patterns of the surrounding creeks which are also influenced by precipitation and climate. Stream flow or discharge is the amount of water moving off the watershed and into the stream channel (EPA, 2012). What's more, discharge is affected by precipitation, as it generally increases with large storm events, and seasonality, as it generally decreases in the summer months due to high evaporation rates (EPA, 2012). This could explain large piques in N and P concentrations in agricultural and urban areas as both experience higher N and P concentrations during large storm events (Reutter, 2019). These changes in

concentration could also account for the changes in discharge due to a dilution effect. This is because fast or swiftly moving streams, that are larger, are better positioned to be less affected by watershed pollution than smaller streams, which have a diminished capacity to dilute nutrients (EPA, 2012). Overall, increases in stream discharge could dilute nutrients within said stream, as flow is a function of volume, making their concentration, or the amount of N and P present in the stream's water, lower than if the was at its base flow or lower.

Over all, time does not explain the variation of nitrogen or phosphorus concentrations seen in any of the three streams. The variations of concentrations in figures 4-9 allow for general trends to be established but the low R^2 values for all of the graphs means that time is not the explanatory variable. While figure 4, figure 5, figure 7 and figure 8 all have linear trend lines with an R^2 value that, while low, is not the lowest it could be, the other graphs were more inconclusive. Figure 6 has the lowest number of data points of all the concentration figures, however, it also has the highest R^2 value. However, figure 9 data exists in a cloud making it equally useful in drawing conclusions. Overall, the variable number concentrations in the data sets coupled with the low R^2 values creates a handicap when using the graphs (Fig. 4 - Fig. 9) to draw conclusions, as we can not say for certain if there is a trend.

4.1 Development/Urban Land cover effects on nutrient concentrations

The results from this study only half support hypothesis two as across all three streams N concentration increased as urban areas increased, and P concentrations decreased as urban areas increased. Developed/urban areas alter both the physical and hydrologic features of a watershed, and add anthropogenic nutrient sources through lawn fertilizers, pet waste, septic tank effluent and accelerated erosion and thus are important causes of lake and stream quality degradation (Brett et al., 2005). The large amount of impervious surfaces present in urban areas limit the amount of water that is able to move into and through a soil profile, thus increasing the amount of water that is available to carry nutrients from available surfaces (Reisinger et al., 2023). This is why hypothesis two predicted that both P and N concentrations would increase as the areas of urbanization increased across watersheds. However, Manning et al. (2020) does note that increases in N concentrations were weaker in urban watersheds when compared to agricultural watersheds, while P concentrations tended to be higher in highly urbanized watersheds. The results of this study are the opposite, suggesting that either something else was at play or that there was not enough data. Something that could cause a different N:P ratio in urban streams is

the sources of natural organic debris, like grass clippings and leaf litter in storm water. While both grass clippings and leaves are natural stream sources of N and P when collected at higher than normal rates in stormwater runoff, like in urban neighborhoods, they can become a major source of nitrogen enrichment (Reisinger et al., 2023). However, different combinations of leaf types as well as fertilized and unfertilized could change the concentration of N and P and the ratio they exist at in said stream.

A few other important urban anthropogenic nutrients sources are fertilizers, pet waste, and even compost (Reisinger et al., 2023). However, the application of synthetic fertilizers is one of the main direct sources of nutrients in Pennsylvania (Clune et al. 2020) and typically dominates N input in urban areas (Reisinger et al., 2023). Since the largest percentage of the urban area in this study was classified by the NLCD as open space development it stands to reason that a majority of the N and P being supplied into these watersheds comes from fertilizers. Open space development is defined as large to single family housing units, parks, golf courses, and vegetation planted in urban areas for recreation, erosion control or aesthetic purposes (NLCD). Areas such as these are often treated with N - fertilizers in order to create and promote healthy and aesthetically pleasing landscapes (Reisinger et al., 2023). In addition, these areas of single and large family housing could also include construction which, in urban and suburban areas, expedite erosion of P-enriched soils into aquatic ecosystems (Brett et al., 2005). Family housing units also mean pet feces is likely to be in the mix of N and P sources. In fact an estimated 40% of pet waste is believed to end up somewhere in the landscape making it another major contributor of N and P in differing amounts (Reisinger et al., 2023).

Differences in N:P ratio could also be due to the different timelines for the data sets as these different time periods have different total stream discharge and thus different concentrations based on the possible dilution of nutrients. This dilution of nutrients is due to the fact that urbanized streams flow through rougher environments with low surface permeability causing quicker piques in discharge (Reisinger et al., 2023). Urban streams also typically have larger peak flows during precipitation events along with lower base flows during dry periods, both of which can impact the transport of nutrients, like N and P (Brett et al., 2005). This difference in flow regime along with the different timelines for data collection indicates that the discrepancies in the data could be due to differences in precipitation and flow. However, Manning et al. (2020) states that in highly urban areas the relationship between dissolved ratios

of N:P appeared weak indicating that sources and transport of these nutrients, N and P, were relatively consistent across flow conditions in urbanized watersheds. Thus the results of that particular study would indicate a lack of data.

4.2 Forested Land cover effects on nutrient concentrations

Unlike developed or agricultural areas, forested area nutrients are more likely to come from natural sources instead of anthropogenic sources. In fact the nutrient concentration levels found in forested streams are usually less than 15 % of the levels found in agricultural or urban streams (Binkley et al. 2007). In figure 12 the trend line for phosphorus is seen to increase across the watershed with the increase in forested area. This upward sloping trend line indicates that the relationship between forested areas in a watershed explains the increase in phosphorus seen in the watersheds ($R^2 = 0.82$). The increase in phosphorus within the forested watersheds could be linked to natural variations in the stream's ecosystems. According to Sohrt et al. (2019) the biota in low order streams can act as both sources and sinks of phosphorus, functionally changing the phosphorus levels in these streams. The vast majority of the streams in all of the watersheds are classified as first and second strahler order streams with only one third order stream. The classification of stream using the strahler stream order system allows for the correlation of the order to basin parameters like drainage area or channel length (Federal Interagency Stream Restoration Work Group, 1995). This is because on average smaller order streams receive less input from other areas, meaning they carry smaller volumes of waters (NSW Government Water, 2024). Thus they have less of a capacity to dilute nutrients.

The majority of these streams were also surrounded by forests classified as deciduous, by the NLCD, making leaves a major nutrient source for the aquatic ecosystem (NLCD). This means that when the leaves fall into the stream there is a short period of time with higher P concentrations while these leaves are decomposed by biota in the stream (Sohrt et al. 2019). This is the most likely explanation for the results in the study as the phosphorus concentrations seem to have both a high range and a low range (fig. 4 and fig. 5). These fluctuations could also be influenced by seasonal variations as once autumn leaf supplies have been depleted during the summer, in-stream biomass can become a P source rather than sink (Sohrt et al., 2019). Juxtapositionally, nitrogen concentrations within a specific stream will generally remain relatively constant as approximately one-third of all nitrogen inputs are exported from the catchment area (Jarvie et al. 2010). Furthermore, no single region or forest type can represent

the full spectrum of US forest streams and nitrogen concentrations are known to typically vary by geographic region and tree composition (Ellison and Brett, 2006). This might be why the study revealed no relationship between Nitrogen and forested land cover.

4.3 Agricultural Land Cover effects on nutrient concentrations

Despite substantial declines in the land being used for agriculture since the 1950s, agricultural pollutants continue to be a main source of pollution in Pennsylvania, with fertilizers, manure, and other agricultural inputs being the largest sources of N and P runoff (Clune et al. 2020). Streams surrounded by agricultural land tend to suffer from channel instability and erosion due to tillage, lack of riparian buffer zone, and being stripped of their forest layer that originally would have provided water storage (Clune et al. 2020). However, the results of the study indicate that P and N concentrations found in streams are not explained by the percentage of agricultural land cover ($R^2 = 0.10$, $R^2 = 0.50$). In fact the watershed with the lowest percentage of agricultural land cover (Walnut Creek) had the highest concentrations of N, while the watershed with the second lowest percentage of agricultural land cover (Conneaut Creek) had the highest concentration of P (Fig. 15). Thus, these studies results do not align with the theme of the overall literature on the topic agricultural land runoff, which predicted an upward sloping trend line (Watson et al., 2016, Marion et al., 2017, & Chislock et al., 2013).

It is possible that the lack of correlation stems from the difference in watershed size and make-up. Of the three watersheds only two are a similar size (Twelve mile creek and Walnut creek), with one (Conneaut creek) being significantly larger (Fig. 1). However, the main reason for the difference in nutrient concentrations in two of the watersheds (Walnut Creek and Conneaut Creek) could be the percentage of cultivated crop land within them (10.1% and 5.4% respectively) (Table 4). In agricultural watersheds excess nutrient inputs come from traditional agricultural practices such as tillage, tile drains, and ditches (Clune et al. 2020). Tillage itself, which is most commonly used in cultivated crop land, has been linked to soil erosion and fertilizer runoff (Wallander, 2005). What's more, according to the USDA report most prevalent agricultural practice used in Erie county is intensive tillage which makes up 19% of farm practices (USDA, 2022). The differences in cultivated cropland area does not explain the overall lack of correlation as the watershed with the highest percentage of agricultural land (Twelve mile creek) has the lowest concentrations P and N (Table 2) and the highest number of individual concentrations higher than recommended by the EPA (Fig. 4 & Fig. 7).

The discrepancies in the data could also be due to differences in the dates that the nutrient concentrations were taken; Walnut Creek (11/25/2008 - 9/10/2019), Conneaut Creek (10/7/1998 - 8/9/2022), and Twelve Mile Creek (9/10/1998 - 1/11/2005). There does seem to be some sort of yearly pattern with each graph showing crests and valleys that span approximately over a year, and could be attributed to changes in stream discharge and precipitation patterns (Fig. 4 - 9). In agricultural catchments excess nitrogen and phosphorus can be washed in from farm fields during rain events, snow melts, and can also leach in through the soil and into groundwater over time (EPA, 2008). For these reasons nitrate concentrations and export rates tend to be high in fall, medium in the winter, and low in the spring (Jarvie et al. 2010). Agricultural catchments also tend to build up and store N in the soil from significant summer application of manure and green bean waste (Jarvie et al. 2010). However, these N stores are often depleted by the end of the summer season, having either gone into the plant or eroded into the watershed (Jarvie et al. 2010). However, the seasonal patterns are difficult to see due to the number of years the graphs show, and each year or two year cycle would need to be zoomed in on in order for the pattern to become more clear (Fig. 4 - 9).

Conclusion

Nutrient inputs into streams have, in general, increased with the human population, as development, deforestation, and land cultivation have allowed for the contribution of both human and agricultural runoff to move into surface waters (Clune et al. 2020). However, the results of this study were inconclusive. While I did find increasing concentrations of nitrogen as the percentage of areas considered developed increased, the figures also showed a decrease in phosphorus. The abundance of impervious surfaces in urban areas allows for less water to enter soil profile which increases water runoff with pollution and excess nutrients. The high amount of impervious surfaces also makes urban streams flashier and have quicker pique discharges. The sources of nitrogen and phosphorus within urban areas are the same, both coming from synthetic fertilizers, pet waste, and organic matter; however N and P exist as different ratios within an urbanized stream. The N:P ratio found was different then the one found in a previous study which is most likely due to lack of data points.

The results for the agricultural land cover also revealed discrepancies, as both nitrogen and phosphorus trend lines decreased as the agricultural land cover percentage increased. These results conflict with the literature on the subject as both were expected to increase with

agricultural area. This also conflicts with the fact that there were data points above what is considered the optimum rate for the EPA. In looking at the overall pattern there seems to be some sort of seasonal change in the earlier figures. However, we would still expect to see more of an increase in N and P due to the fact that tillage is still the most widely used farming practice in Erie county, and is associated with increases in agricultural runoff due to loss of topsoil.

In contrast the results for the forested area does seem to exert strong controls over stream chemistry. However, the overall relationship is unclear due to outside factors. According to the literature, it is not unusual for N concentrations in forest streams to vary depending on region, tree type, precipitation, and soil type. Thus, it is impossible to state what the “normal” N concentrations are for these streams without more extensive research into these influencing factors. The P results may follow some sort of seasonal pattern when the figures showing the timeline of P concentrations were used. These seasonal patterns could be due to the fact that the autumn leaves are depleted in the summer months allowing for in-stream biomass to become a P source.

Overall, this study is very limited in the conclusions it is able to draw due to a lack of nutrient data. While there were ten total data stations along Lake Erie that corresponded with the mouths of streams only three had available nutrient data. This lack of data could most likely be attributed to the fact that, in Erie county, most of the streams along lake's border are first and second Strahler order streams and will not be monitored as closely as other large order streams who are seen as having more of an impact on eutrophication. The lack of available nutrient data is most likely the cause for the differences between the results and the literature. Additionally, the NLCD data categories were specific but at the same time broad as we were able to categorically see the impact of deciduous forest or agriculture but were unable to see the specific types of trees and agricultural practices which influenced the results. However these streams should not be discounted due to their size as multiple first order streams when put together have the possibility to have a large impact.

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