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A Senior Honors Thesis

Submitted in Partial Fulfillment of the Requirements for Graduation in the College Honors Program

By

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#### Abstract

Phosphorus, a key nutrient in many aquatic systems that limits the growth of algae, plays a key role in the occurrence of eutrophication and toxic algal blooms. Past research has shown that land use and lithology are major contributors of phosphorus in a creek. High levels of organic phosphorus occur in agricultural areas of a watershed, and high levels of inorganic phosphorus occur in residential areas, especially near waste water treatment plants. The bedrock of an area also influences the chemical composition of stream sediment. Limestone bedrock results in high levels of calcium associated phosphorus. Northrup Creek, a mixed land use watershed in western Monroe County, New York, was examined to determine the main contributors of phosphorus in the creek. Fluvial sediment samples were collected from eleven sites in the Northrup Creek to determine if phosphorus levels in the creek were correlated to the type of land use occurring in specific sections of the watershed. Phosphorus fractionation was performed to analyze the phosphorus distributions at each site, focusing on organic phosphorus, iron-manganese, aluminum, and calcium associated inorganic phosphorus. Land use land cover data was used to determine the land area percentages and hectares of agricultural and residential land in each stream segment. The phosphorus concentrations and percentages from the total phosphorus level were correlated to land use data using a Kendall Tau correlation coefficient. Linear regressions were also run to test the statistical significance of the relationship between phosphorus concentration and land use. The results were not statistically significant and could not be used to support the hypothesis statement that agricultural areas of the catchment would have high levels of organic phosphorus and residential areas would have high levels of inorganic phosphorus.

#### Summary

Phosphorus can enter a stream through diffuse sources such as the formation of sediment from bedrock and local soils, the application of fertilizers for agricultural, recreational, and residential purposes, and can also be introduced by point sources of input, commonly sewage treatment plants. To better understand the impact of agriculture, residential areas, and geology on the water quality of a stream, Northrup Creek in Monroe County, New York, was examined because it provides a good representation of these three major potential contributors of phosphorus. It is expected that high concentrations of organic phosphorus should be found near the agriculturally influenced headwaters of the stream and will decrease downstream. Inorganic phosphorus in the form of iron-manganese and aluminum associated phosphorus should have the highest values near the site of the former sewage treatment plant input and decrease downstream. Calcium associated phosphorus concentrations should be elevated throughout the stream due to the limestone bedrock found within the catchment. Sediment from the stream was collected and underwent a series of tests including a phosphorus fractionation and particle size distribution analysis to determine if land use practices and local bedrock are influencing phosphorus levels. If phosphorus concentrations follow the pattern of the hypothesis, then agriculture and urbanization can be recognized as major contributors of phosphorus, and geology can be recognized as a major influence on the distribution of phosphorus within Northrup Creek. If concentrations follow the opposite pattern, show no major changes, or reveal a different pattern of concentrations, then it may suggest that sources other than agriculture, residential areas, and geology are responsible for the organic, inorganic, and calcium associated phosphorus levels within Northrup Creek.

#### Introduction

There are numerous implications of excess phosphorus input from non-point and point sources. Non-point sources of phosphorus can include bedrock lithologies, the application of fertilizers and erosion due to agricultural and industrialized practices. Point sources of pollution are commonly the released effluent from waste water treatment plants. Variations in land use practices can influence the concentrations of phosphorus resulting in high levels of phosphorus in the stream sediment corresponding to the land use activities within the surrounding area of the catchment. The purpose of this project is to determine if there is a correlation between land use practices and the concentrations of phosphorus in a mixed land use watershed.

#### Background

Phosphorus is a key nutrient in freshwater aquatic systems and is typically the limiting nutrient for the growth of algae and macrophytes. Excess phosphorus plays a role in the occurrence of eutrophication and toxic algal blooms (House, 2003). Many recent studies have examined the implications of fluvial phosphorus by focusing on point and non-point sources of phosphorus input, the concentrations of phosphorus being released from these sites, and the variations in concentrations that occur with changes in land use (Evans et al., 2004; Owens & Walling, 2002). The local geology and land use practices within a catchment have been shown to be two of the most important characteristics that influence the total phosphorus content in fluvial sediments (Evans & Jones, 2004; Evans et al., 2004). The bedrock and soils of an area reflect the chemical composition of channel sediment. Sediment input from anthropogenic activities, erosion due to agricultural practices and the deposition of waste material, can reflect

the chemical composition of the additional material such as manures and fertilizers (Ballantine et al., 2009).

#### **Hypothesis**

Many studies have examined the effects of land use, point source pollution, and geology on the phosphorus content of fluvial sediment, but few have examined the interactions of all three in one study. The Northrup Creek watershed was examined for how its calcareous bedrock, rural and residential land use areas, and the historical input from waste water treatment plant effluent influence phosphorus concentrations throughout the stream. The hypothesis of this project is that fine grained fluvial sediment will reflect land use and related inputs to Northrup Creek. Sub hypotheses state that 1) agricultural areas of the catchment will have the highest levels of organic phosphorus, 2) the sediment collected directly downstream of the effluent input site from the waste water treatment plant in a residential area will have the highest levels of inorganic phosphorus in the forms of iron-manganese and aluminum associated phosphorus, and 3) high levels of calcium associated phosphorus will be found at all sample sites due to the local lithology.

Support for the hypothesis statement comes from numerous sources of past research in catchments with similar characteristics. The results of Ballantine et al. (2009) and Noll et al. (2009) showed that the highest organic phosphorus concentrations were found in agricultural areas of a catchment that had a historical application of manure to fields. This same practice has also been observed in the Northrup Creek watershed. Owens & Walling (2002) found an increase in inorganic phosphorus in urbanized areas containing point source inputs of treated human waste from sewage treatment plants, such as the one that was located along the Northrup

Creek in Spencerport, New York. High levels of calcium concentrations are expected due to phosphorus co-precipitation with calcite caused by the limestone bedrock at the headwaters of the creek, this same result was found by Evans & Jones (2004) and Noll et al. (2009) who examined catchments with a chalk and limestone bedrock respectively, and showed that the local geology correlated to high calcium associated phosphorus concentrations within the fine grained bed sediment.

#### Data and Methodology

#### Site Description

Northrup Creek is a 64km<sup>2</sup> watershed that drains into Long Pond, a hypereutrophic pond that enters into Lake Ontario, in Monroe County, New York. The headwaters of Northrup Creek are located in Ogden, New York, and the creek flows northward through the towns of Spencerport, Parma and Greece, where it drains into Long Pond. The Northrup Creek watershed is bordered by the Larkin Creek watershed to the east, the Buttonwood Creek watershed to the west, the Little and Black Creek watersheds to the south, and Lake Ontario to the north. At its widest the watershed is approximately 6.5km wide, and is about 16km long (Figure 1) (Schulz, 2012).

#### Field Methods

Fluvial sediment samples were collected from eleven previously designated sites along the Northrup Creek (Figure 1). Beginning at the headwaters and working downstream, the sites are located where roads or public paths intersect the creek. These locations include Vroom Road, Nichols Road West, Nichols Road East, Bartons Cove, Dean Road, Latta Road, North Greece Road, Burret Road, Parma Center Road, the Parma Park, and Route 104. Once the stream flow had receded from the winter snow melt and flow rates were low enough for a person to stand in the stream, sampling began. Sediment was collected and stored in acid washed 125mL nalgene bottles. Samples were obtained by using the open mouth of the bottle to scrape sediment from the base of the channel. Sampling occurred across the channel in the attempt to collect a uniform representation of the stream sediment at the location. Once the samples were collected from across the stream they were placed in a metal pan and homogenized with a metal trowel, then the mixture was placed in the bottle and represented the sample from the site.

At two locations on Northrup Creek, Bartons Cove, site D, and North Greece Road, site G, a different sampling approach was used to test the validity of the homogenized sampling approach. These two locations had eight samples collected across the stream channel by using the open mouth of the bottle to scrape sediment from the base of the channel; a separate acid washed 125 ml nalgene bottle was used for each individual sample. The samples were not homogenized and each one represents sediment as it is found across the channel. The sediment samples from these two sites were individually analyzed, and the data from the separate samples was averaged to represent one sampling from each site.

#### Sample Preparation

After collection, all of the samples remained closed and refrigerated until they were analyzed in the lab. The first procedure was to sieve the samples with a 2.0mm sieve as sediment with a larger particle size is not typically found to hold significant amounts of phosphorus. Walling et al. (2001) discussed the correlation between large grain size and the decrease in its ability to hold phosphorus. A 2.0mm sieve, basin, scoopula, and acid washed collection tube were thoroughly rinsed in DI water. The sample was run through the sieve and sediment that entered the basin was transferred to the collection tube using the scoopula. The tube was then labeled and placed in the refrigerator. These steps were used to process all of the sediment samples.

Percent moisture and organic matter content of the samples was calculated for future uses. Crucibles were cleaned with a dry cloth, numbered, and their masses were measured and recorded. About five grams of sample were placed into each crucible, the mass of the crucible and sediment was measured and recorded, and the mass of the sample added to the crucible was calculated. The uncovered filled crucibles were then placed in a drying oven set at 102°C for two days. After two days the crucibles were removed, cooled, and their mass was measured and recorded. From the mass of the dry sample, the percent moisture was calculated along with the mass of wet sample that is equal to one gram of dry sample. To determine the organic matter content by loss on ignition, the crucibles with the dried samples were placed back in the oven at 350°C for 16 hours. Crucibles were weighed after cooling to determine the mass of organic material lost.

#### **Phosphorus Fractionation**

Phosphorus levels were analyzed using the Olsen P extraction method discussed in the Methods of Phosphorus Analysis to determine how much phosphorus was available for macrophytes intake within the stream (Pierzynski, 2000). The process of a phosphorus fractionation was conducted using the Psenner method sequential extraction to determine the concentrations of exchangeable phosphorus, organic phosphorus, iron-manganese associated phosphorus, calcium associated phosphorus, and aluminum associated phosphorus (Psenner et al., 1988). Both extraction methods were conducted using a Beckman model DU640 spectrophotometer. The absorbance of light based on the correlation to the absorbance by the concentration of a standard served as a qualitative representation of the phosphorus content for the sediment samples. Summarized data of the concentrations of associated phosphorus types is located in Table 1, and the actual phosphorus levels are summarized in Table 2.

#### Particle Size Analysis

Particle size analysis was performed so a correlation between the particle size distribution as represented by the median particle size and the amount of phosphorus that the sample contained could be evaluated. Fine grained sediment such as silts and clays can easily bind with phosphorus, but the physical and chemical properties of larger sized sediment reduce the ability of phosphorus to bind to the sediment (Ballantine et al., 2009; Walling et al., 2001). In these instances a lesser amount of phosphorus can be held in the fluvial sediment by organic matter or by ion coatings that have formed around the large particles (Evans et al., 2004). About five grams of sample were placed in acid washed collection tubes, 15 drops of 30% H<sub>2</sub>O<sub>2</sub> were added to the sediment, stirred, and remained uncovered overnight so the reaction had time to be completed to remove any coatings that could have caused particles to clump during the diffraction process. Laser diffraction particle size analysis using a Coulter LS 230 was used to measure the grain sizes and to provide reasoning behind the potential decrease in phosphorus levels at sites with large grain sizes. The treated sediment samples were run through the laser diffracter once, then had two reruns, a total of three times each sample, and the median of the grain size was recorded for the three runs.

#### Land Use Data

Land use land cover data from 2006 was obtained through personal contact with Holly Schulz, a graduate student in 2012. The percent of land use land cover and hectares of land use for each stream segment were used to determine the statistical significance of associations between phosphorus concentrations and land use types. Summarized land use data is located in Table 3.

#### Statistical Analysis

The statistical significance of organic and inorganic phosphorus levels and particle size throughout the Northrup Creek were measured using linear regressions calculated in Minitab, and Kendall Tau correlation coefficients calculated by hand. Kendall Tau correlation coefficients were calculated along with linear regressions because Kendall Tau provides a better measure of association for small sample sizes and mitigates the effect of outliers, both of which characterized the data.

#### Results

#### **Phosphorus-Land Use Correlations**

The initial plan for this study was to analyze the phosphorus data in terms of concentrations of the total for correlations to land use. Once statistical testing revealed no significance using this form of data formatting, the actual phosphorus concentrations were analyzed. Both formats for the analysis of phosphorus data are acceptably used in the field. When the actual phosphorus concentrations were examined, they too did not show any statistical significance, but when the data was graphed, it did show the apparent trends that were expected to occur throughout the creek. Figure 3 through Figure 8 are the graphed phosphorus concentrations of the data listed in Table 2.

#### Total Phosphorus

Total phosphorus concentration as one travels downstream is shown in Figure 3 and Table 1. The residential arm had the highest total phosphorus concentration of 755.13mg/kg at

the headwaters of the stream, which is right next to a farm that regularly applies manure to the surrounding fields. Total phosphorus concentrations decreased in the east arm until the creek entered the village of Spencerport, which once contained a waste water treatment plant. In Spencerport, total phosphorus levels rise to their second highest concentration, 546.52mg/kg. The total phosphorus levels then decrease until they reach the lowest total phosphorus levels rise concentration of 285.13mg/kg near the end of the residential arm. Total phosphorus levels rise slightly by about 50mg/kg at the end of the residential arm at site G, which has 64.5% agricultural land (Table 3). The agricultural arm does not show much variation in total phosphorus concentrations. It has a range of 312.82mg/kg to 404.62mg/kg, less than 100mg/kg of change.

#### **Organic Phosphorus**

The highest concentration of organic phosphorus, 113.79mg/kg at the headwaters of the creek in the residential arm is seen in Figure 4 and Table 2. This location is right near a farm that regularly applies manure to the surrounding fields. Organic phosphorus levels then decrease throughout the creek until they reach the lowest concentration of 22.06mg/kg. Organic phosphorus levels show a small rise of less than 10mg/kg at the end of the residential arm, an area of 64.5% agricultural land. The agricultural arm has a small range of organic phosphorus levels of 23.90mg/kg to 67.99mg/kg. The agricultural arm contains only one site with organic phosphorus concentrations over 40mg/kg, and the residential arm contains three. *Inorganic Phosphorus* 

# The residential arm does have the highest concentration of inorganic phosphorus, 304.44mg/kg, as seen in Figure 5 and Table 2. The agricultural arm has steadily low concentrations of inorganic phosphorus, and some of the concentration patterns do follow the

expected trend. Figure 6 and Table 2 show that the aluminum associated phosphorus concentrations remained under 100mg/kg in both arms, except for at the site nearest the historical input from the waste water treatment plant. Near the waste water treatment plant, the aluminum associated phosphorus concentration rose to its highest, 179.64mg/kg, then decreased to typically observed levels.

Calcium associated phosphorus was the most abundant bound phosphorus to be analyzed in this study. The calcium concentrations comprised a large percentage of the total phosphorus levels, ranging from 43.08% to 72.74% (Table 1). Overall, the concentrations and trend of calcium associated phosphorus contributed to the greatest majority of total phosphorus levels throughout the creek and thus had the greatest impact on total phosphorus levels (Figure 7). *Particle Size Analysis* 

The median particle size was found to have a statistically significant correlation to the concentration of total phosphorus in the creek, thus providing evidence that the collected sediment should have provided a good source of phosphorus levels. Median particle sizes ranged from 8.31µm to 18.30µm (Table 1), and could be classified as fine to medium sized silt using the Wentworth sediment grain size scale (Wentworth, 1922). At the two sites where multiple samples were collected to represent sediment across the channel, the standard deviation for the mean particle size at site D was 0.82 and at site G the standard deviation was 1.81, revealing small changes in sediment size across the stream channel, thus validating the first sampling technique that inferred sediment across the channel could be represented as a homogenized sample (Table 1).

Statistical Analysis of Results

The first set of statistical analyses outlined in Table 4 and Table 5 were performed and showed no statistically significant correlation between land use and phosphorus levels, so further statistical testing was performed. Upon further evaluation of the data, the two stream arms of the Northrup Creek were designated as the west agricultural arm and the east residential arm based on land use percentages (Figure 2) (Table 3). Overall, land use land cover data was compared to the percentages of phosphorus (Table 1) and phosphorus concentrations (Table 2) using the percentage of land type and hectares of land type within each stream segment (Table 3). All phosphorus concentrations were treated as the response or dependent variable, while land use land cover data was the predictor or independent variable. A significance level of 0.10 was used for all statistical comparisons and analyses.

#### **Organic Phosphorus Statistics**

Multiple statistical tests were performed to determine if there was a correlation between agricultural land and organic associated phosphorus concentrations. Tests of the percentage of agricultural land versus the percentage of organic associated phosphorus had no statistically significant results. The linear regression had an r<sup>2</sup> value of 1.4%, showing that only 1.4% of the variation in the percentage of organic phosphorus was attributed to the percentage of agricultural land in each stream segment. The null hypothesis for the regression stated that there was no correlation between the percentage of agricultural land and the percentage of organic phosphorus. The calculated p-value of 0.730 led to the accepting of the null hypothesis and the conclusion that the slope of the regression line was statistically equivalent to zero, there was no statistically significant relationship between the percentage of agricultural land and the percentage of organic phosphorus (Table 4). The Kendall Tau correlation coefficient null hypothesis stated that no correlation existed between the percentage of agriculture and the

percent of organic phosphorus. The calculated tau value of 0.16 was smaller than the critical value for 0.418 provided by the Distribution-Free Statistical Tests (Bradley, 1968), resulting in the accepting of the null hypothesis and the conclusion that there is not a statistically significant correlation between the percent of agricultural land and the percent of organic phosphorus (Table 5).

Tests of the percentage of agricultural land versus the concentration of organic associated phosphorus had no statistically significant results. The linear regression had an  $r^2$  value of 1.0% in the east arm and 6.9% in the west arm, showing that only 1.0% and 6.9% of the variation in the concentration of organic phosphorus was attributed to the percentage of agricultural land in each stream segment. The null hypothesis for the regression stated that there was no correlation between the percentage of agricultural land and the concentration of organic phosphorus. The calculated p-value of 0.830 in the east arm and 0.669 in the west arm led to the accepting of the null hypothesis and the conclusion that the slope of the regression line was statistically equivalent to zero, there was no statistically significant relationship between the percentage of agricultural of organic phosphorus (Table 6). Due to a lack of support for the statistical significance of the percentage of land being correlated to phosphorus concentrations, a Kendall Tau correlation was not calculated.

Tests of the hectares of agricultural land versus the concentration of organic associated phosphorus had no statistically significant results. The linear regression had an  $r^2$  value of 16.4% in the east arm, and 0.1% in the west arm, showing that only 16.4% and 0.1% of the variation in the concentration of organic phosphorus was attributed to the hectares of agricultural land in each stream segment. The null hypothesis for the regression stated that there was no correlation between the hectares of agricultural land and the concentration of organic

phosphorus. The calculated p-value of 0.368 in the east arm and 0.959 in the west arm led to the accepting of the null hypothesis and the conclusion that the slope of the regression line was statistically equivalent to zero, there was no statistically significant relationship between the hectares of agricultural land and the concentration of organic phosphorus (Table 7). The Kendall Tau correlation coefficient null hypothesis stated that no correlation existed between the hectares of agriculture and the concentration of organic phosphorus. The calculated tau value of -0.238 in the east arm and -0.200 in the west arm was smaller than the critical value for 0.619 and 0.800 respectively provided by the Distribution-Free Statistical Tests (Bradley, 1968), resulting in the accepting of the null hypothesis and the conclusion that there is not a statistically significant correlation between the hectares of agricultural land and the conclusion that there is not organic phosphorus (Table 8).

#### Inorganic Phosphorus Statistics

The same series of statistical tests were performed to determine if there was a correlation between residential land and inorganic associated phosphorus concentrations. Tests of the percentage of residential land versus the percentage of inorganic associated phosphorus had no statistically significant results. The linear regression had an  $r^2$  value of 0.2%, showing that only 0.2% of the variation in the percentage of inorganic phosphorus was attributed to the percentage of residential land in each stream segment. The hypothesis statement and alpha value for the linear regression can be referenced in Table 4. A p-value of 0.907 led to the accepting of the null hypothesis and the conclusion that the line is statistically equal to zero, there is no statistically significant relationship between the percentage of residential land and the percent of inorganic phosphorus (Table 4). The Kendall Tau hypothesis can be referenced in Table 5. The calculated tau value of -0.05 was smaller than the critical value for 0.418 (Bradley, 1968), resulting in the accepting of the null hypothesis and the conclusion that there is not a statistically significant correlation between the percent of residential land and the percent of inorganic phosphorus (Table 5).

Tests of the percentage of residential land versus the concentration of inorganic associated phosphorus had no statistically significant results. The linear regression had an r<sup>2</sup> value of 19.6% for the east arm and 9.6% for the west arm, showing that only 19.6% and 9.6% of the variation in the concentration of inorganic phosphorus was attributed to the percentage of residential land in each stream segment. The hypothesis statement and alpha value for the linear regression can be referenced in Table 6. A p-value of 0.319 in the east arm and 0.611 in the west arm led to the accepting of the null hypothesis and the conclusion that the line is statistically equal to zero, there is no statistically significant relationship between the percentage of residential land and the concentration of inorganic phosphorus (Table 6). Due to a lack of support for the statistical significance of the percentage of land being correlated to phosphorus concentrations, a Kendall Tau correlation was not calculated.

Tests of the hectares of residential land versus the concentration of inorganic associated phosphorus had no statistically significant results. The linear regression had an  $r^2$  value of 51.4% for the east arm and 26.6% for the west arm, showing that 51.4% and 26.6% of the variation in the concentration of inorganic phosphorus was attributed to the hectares of residential land in each stream segment. The hypothesis statement and alpha value for the linear regression can be referenced in Table 7. A p-value of 0.070 for the east arm led to the rejecting of the null hypothesis and the conclusion that the line is not statistically equal to zero, there is a statistically significant relationship between the hectares of residential land and the concentration of inorganic phosphorus in the east arm (Table 7). The p-value in the west arm was 0.374 which

led to the accepting of the null hypothesis and the conclusion that there is not a statistically significant relationship between the hectares of residential land and the concentration of inorganic phosphorus in the west arm (Table 7). The Kendall Tau hypothesis can be referenced in Table 8. The calculated tau value of 0.333 for the east arm was smaller than the critical value of 0.619 (Bradley, 1968), resulting in the accepting of the null hypothesis and the conclusion that there is not a statistically significant correlation between the hectares of residential land and the concentration of inorganic phosphorus in the east arm (Table 8). The calculated tau value of - 0.400 for the west arm was smaller than the critical value of 0.800 (Bradley, 1968), resulting in the accepting of the null hypothesis, resulting in the accepting of the statistically significant correlation between the hectares of residential land and the concentration of inorganic phosphorus in the east arm (Table 8). The calculated tau value of - 0.400 for the west arm was smaller than the critical value of 0.800 (Bradley, 1968), resulting in the accepting of the null hypothesis and the conclusion that there is not a statistically significant correlation between hectares of residential land and the concentration between hectares of residential land and the concentration between hectares of residential land and the concentration of inorganic phosphorus in the west arm (Table 8).

#### Particle Size

Tests of the median particle size and total phosphorus levels were shown to have statistically significant results. The linear regression had an  $r^2$  value of 31.5%, showing that 31.5% of the variation in the levels of total phosphorus was attributed to the median particle size throughout the stream. The null hypothesis for the regression stated that there was no correlation between the median particle size and the levels of total phosphorus. The calculated p-value of 0.072 led to the rejection of the null hypothesis and the conclusion that the slope of the regression line is not statistically equal to zero, there is a statistically significant relationship between median particle size and total phosphorus (Table 4). The Kendall Tau coefficient correlation null hypothesis stated that no correlation existed between the median particle size and the total phosphorus levels. The calculated tau value of 0.45 was larger than the critical value for 0.418 provided by the Distribution-Free Statistical Tests (Bradley, 1968), resulting in the rejection of the null hypothesis and the conclusion that there is a statistically significant correlation between the median particle size and total phosphorus levels (Table 5).

#### Discussion

Several studies have demonstrated that areas of a catchment with a historical and current application of manure to agricultural fields have the highest concentrations of organic phosphorus (Ballantine et al., 2009; Noll et al., 2009). Statistical results from this examination of Northrup Creek showed that agricultural areas of the catchment do not have the highest concentrations of organic phosphorus, but the graphed data does represent the expected apparent trend. When fluvial sediment samples were collected for this study, many farms near the headwaters of the catchment in the residential arm were observed to be applying manure to the agricultural fields, explaining the high concentrations of total phosphorus and organic phosphorus. The agricultural arm contains much of the land designated as agricultural in the northern end of the catchment which is comprised of row crops and orchards. This area does not regularly receive manure applications, and instead uses inorganic chemical fertilizers, explaining the lower total phosphorus and organic phosphorus concentrations. Variations in the agricultural management practices throughout the catchment could be a contributing factor in the uncharacteristic organic phosphorus concentration results.

Further variations in land use practices could be contributing to the uncharacteristic statistical results of an area of residential land with a historical effluent input from a waste water treatment plant not having a correlation to inorganic phosphorus concentrations. The only statistical test that supported the expected trend was the significant linear regression of hectares of residential land and the concentration of inorganic phosphorus. Further statistical analysis with a Kendall Tau correlation proved that the linear regression did not provide a good analysis of the data because the data set contained only seven points, thus negating this finding. Owens and Walling (2002) showed that residential and urbanized areas containing waste water treatment plants had high levels of inorganic phosphorus, and at the time of their study the waste water treatment plants were currently releasing treated effluent into the catchment. The waste water treatment plant which was located in Spencerport, New York, began adding iron salts to reduce phosphorus levels by 85% in 1995, and continued to reduce effluent phosphorus levels until it went offline in 2008 (Sherwood, 1999; Knauf, 2012). This long term decrease and removal of a large source of inorganic phosphorus input likely provided the fluvial sediment enough time to migrate downstream the effects of this large historical input and naturally remove much of the inorganic phosphorus held in the sediment, resulting in the low concentrations of inorganic phosphorus in residential areas. However, this does not explain the distribution of iron manganese concentrations seen in Figure 8, which were highest in areas that also contained the highest organic phosphorus concentrations.

Overall, Northrup Creek is a small watershed compared to other watersheds that have been examined in studies which correlated the effect of land use to phosphorus concentrations. The Northrup Creek is only 64km<sup>2</sup>, while watersheds studied by Walling et al., (2001) were 2674-6850km<sup>2</sup>, and 930-1932km<sup>2</sup> (Owens and Walling, 2002). Size may play a part in increasing the difficulty in resolving land use impact on a small stream. Because the Northrup Creek watershed is so small, it is difficult to distinguish segments of the creek as strictly agricultural or residential. Due to this high amount of variation in land use between stream segments, the statistical tests may not have been able to detect the visible trend. In this study of Northrup Creek, high concentrations of calcium associated phosphorus were found throughout the limestone based creek. Numerous examinations of fluvial sediment have shown that local geology has a high level of influence on phosphorus concentrations and that the chemical composition of the surrounding bedrock is reflected in the stream channel sediment (Ballantine et al., 2009; Evans et al., 2004). Similar research done on streams with a limestone or chalk bedrock yielded high calcium associated phosphorus concentrations, validating the Northrup Creek results (Evans & Jones, 2004; Noll et al., 2009). Sediment size and the resulting influence on total phosphorus levels was also a large component of studies by Evans et al. (2004) and Walling et al. (2001), and showed results similar to those in the Northrup Creek in which sediment size influenced the total phosphorus levels stream sediment could hold.

#### Conclusion

The results of the phosphorus fractionation of fluvial sediment in Northrup Creek, a mixed land use watershed, showed that land use does not influence sediment phosphorus concentrations in the Northrup Creek. Agricultural areas of the catchment do not have a significant impact on the levels of organic phosphorus, rejecting the initial hypothesis statement that agricultural areas would have the highest organic phosphorus concentrations. Results also showed that residential areas which include the historical input of effluent from a waste water treatment plant do not have a significant impact on the levels of inorganic phosphorus, rejecting the hypothesis statement that the highest levels of inorganic phosphorus would be found in residential areas with a waste water treatment plant input source. Calcium associated phosphorus levels were high throughout the creek, confirming the hypothesis that high levels of calcium associated phosphorus would be found throughout the creek due to the limestone bedrock. In the

Northrup Creek, land use was not found to have a significant impact on phosphorus content of fluvial sediment, while local geology had the largest and most widespread influence on total phosphorus levels.

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Appendix

Figure 1.

Northrup Creek watershed and sampling locations.



Adapted from a study conducted by Holly Schulz on the Northrup Creek Watershed in which samples were collect at the same sites for both projects (Schulz, 2012). Sites 1-11 are referred to as G, H, F, J, I, E, K, D, B, C, A respectively in this study.

Figure 2.

Northrup Creek watershed with designated agricultural and residential arms of the creek.



Adapted from a study conducted by Holly Schulz on the Northrup Creek Watershed in which samples were collect at the same sites for both projects (Schulz, 2012). Sites 1-11 are referred to as G, H, F, J, I, E, K, D, B, C, A respectively in this study.





Concentrations of total phosphorus in residential and agricultural arms of Northrup Creek.





Concentrations of organic phosphorus in residential and agricultural arms of Northrup Creek.





Concentrations of inorganic phosphorus in residential and agricultural arms of Northrup Creek.

# Figure 6.

Concentrations of aluminum associated phosphorus in residential and agricultural arms of





Concentrations of calcium associated phosphorus in residential and agricultural arms of Northrup



Creek.

Figure 8.

Concentrations of iron manganese associated phosphorus in residential and agricultural arms of Northrup Creek.



# Table 1.

Sediment size and associated phosphorus percentages of total phosphorus levels at each site in

Northrup Creek.

	Site										
Phosphorus	Α	В	С	D	Ε	F	G	Η	Ι	J	K
Туре											
% Org-P	15.07	28.42	9.04	7.39	4.92	9.67	8.76	8.64	18.38	8.23	5.91
% Exch-P	0.096	0.350	0.247	0.562	0.137	0.229	0.215	0.146	0.359	0.229	0.071
% Fe-Mn-	27.59	10.86	14.76	9.67	10.83	16.59	22.17	20.51	20.06	11.07	14.96
Р											
% Al-P	12.72	13.35	32.87	10.24	11.38	9.26	18.59	14.53	11.77	14.18	7.52
% Ca-P	44.52	47.01	43.08	72.14	72.74	64.25	50.27	56.17	49.42	66.29	71.55
% Inorg P	40.32	24.22	47.63	19.90	22.21	25.85	40.76	35.04	31.84	25.26	22.48
Total P	755.14	355.67	546.53	452.08	448.51	285.13	335.90	371.92	369.87	312.82	404.62
(mg/kg)											
Median	14.20	11.60	18.30	12.00	11.90	12.90	12.02	9.09	11.60	8.31	13.60
Particle											
Size (µm)											
Mean	11.90	9.18	12.60	9.55	9.42	9.97	9.24	7.88	9.45	7.15	10.90
Particle											
Size (µm)											
Mean	N/A	N/A	N/A	0.82	N/A	N/A	1.81	N/A	N/A	N/A	N/A
Standard											
Deviation											

## Table 2.

Concentrations of associated phosphorus at each site in Northrup Creek.

	Site										
Phosphorus	Α	В	С	D	Ε	F	G	Η	Ι	J	K
Туре											
(mg/kg)											
Fe-Mn-P	208.36	38.64	80.65	43.69	48.56	47.29	74.47	76.28	74.20	34.64	60.52
Org-P	113.79	101.06	49.42	33.41	22.06	27.57	29.43	32.13	67.99	25.74	23.90
Al-P	96.08	47.49	179.64	46.27	51.03	26.40	62.43	54.02	43.54	44.36	30.41
Ca-P	336.17	167.21	235.46	326.14	326.23	183.20	168.83	208.92	182.79	207.35	289.49
Inorg P	304.44	86.13	260.29	89.97	99.59	73.70	136.90	130.31	117.75	79.00	90.94
Total P	755.13	355.66	546.52	452.08	448.51	285.13	335.89	371.91	369.87	312.82	404.62

### Table 3.

Summarized land use land data for each site in Northrup Creek.

Site	% Ag Land	Hectares Ag Land	% Res Land	<b>Hectares Res Land</b>
Α	13.2	36.5	36.3	100.1
В	47.9	171.5	7.5	27.0
С	46.8	262.6	7.7	43.4
D	3.0	1.1	30.2	11.3
E	31.3	198.1	9.6	60.9
F	26.9	206.7	3.9	30.2
G	64.5	407.1	3.3	20.5
Н	78.3	524.6	1.7	11.3
Ι	48.7	342.4	2.5	17.4
J	36.9	202.9	2.1	11.6
K	35.0	79.3	1.6	3.7

Table 4.

Summarized statistical results from linear regression of percentage of land use and percent of

associated phosphorus concentrations.

Hypothesis	p-value	α	Accept/Reject	Conclusion	$r^2$
Ho: No correlation exists	0.730	0.10	accept	Because p-value	1.4%
between % Ag land and				(0.730)>0.1, accept Ho	
% OP				and conclude that the	
Ha: % Ag land and %				slope of the regression line	
OP are correlated				is zero, there is no	
				significant relationship	
				between % Ag land and %	
				OP	
Ho: No correlation exists	0.907	0.10	accept	Because p-value	0.2%
between % Res land and				(0.907)>0.1, accept Ho	
% IP				and conclude that the line	
Ha: % Res land and % IP				is zero, there is no	
are correlated				significant relationship	
				between % Res Land and	
				% IP	
Ho: No correlation exists	0.072	0.10	reject	Because p-value (0.072)	31.5%
between median particle				<0.1, reject Ho and	
size and total phosphorus				conclude that the slope of	
Ha: Median particle size				the regression line is not	
and total phosphorus are				zero, there is a relationship	
correlated				between median particle	
				size and total phosphorus	

Table 5.

Summarized statistical results from Kendall Tau correlation of percentage of land use and

percent of associated phosphorus concentrations.

Hypothesis	τ	α	Accept/Reject	Conclusion
Ho: no correlation exists	0.16	0.418	accept	Because t(0.16) < CV(0.418),
between % Ag land and %				accept Ho and conclude that there
OP				is not a statistically significant
Ha: a correlation exists				correlation between % Ag land
between % Ag land and %				and % OP.
OP				
Ho: no correlation exists	-0.05	0.418	accept	Because t(-0.05) < CV(0.418),
between % Res land and % IP				accept Ho and conclude that there
Ha: a correlation exists				is not a statistically significant
between % Res Land and %				correlation between % Res land
IP				and % IP.
Ho: no correlation exists	0.45	0.418	reject	Because $t(0.45) > CV(0.418)$ ,
between median particle size				reject Ho and conclude that there
and total phosphorus				is a statistically significant
Ha: a correlation exists				correlation between median
between median particle size				particle size and total phosphorus.
and total phosphorus				

Table 6.

Summarized statistical results from linear regression of percentage of land use and concentration

of associated phosphorus.

Hypothesis	p-value-	α	Accept/Reject	Conclusion	$\mathbf{r}^2$
East Ho: No correlation exists between % Ag land and OP Ha: % Ag land and OP are correlated	0.830	0.10	accept	Because p-value (0.830)>0.1, accept Ho and conclude that the slope of the regression line is zero, there is no significant relationship between % Ag land and OP	1.0%
West Ho: No correlation exists between % Ag land and OP Ha: % Ag land and OP are correlated	0.669	0.10	accept	Because p-value (0.669)>0.1, accept Ho and conclude that the slope of the regression line is zero, there is no significant relationship between % Ag land and OP	6.9%
East Ho: No correlation exists between % Res land and IP Ha: % Res land and IP are correlated	0.319	0.10	accept	Because p-value (0.319)>0.1, accept Ho and conclude that the line is zero, there is no significant relationship between % Res Land and IP	19.6%
West Ho: No correlation exists between % Res land and IP Ha: % Res land and IP are correlated	0.611	0.10	accept	Because p-value (0.611)>0.1, accept Ho and conclude that the line is zero, there is no significant relationship between % Res Land and IP	9.6%

Table 7.

Summarized statistical results from linear regression of hectares of land use and concentration of

associated phosphorus.

Hypothesis	p-value	α	Accept/Reject	Conclusion	$r^2$
East	0.368	0.10	accept	Because p-value	16.4%
Ho: No correlation exists			_	(0.368)>0.1, accept Ho	
between hectares Ag				and conclude that the	
land and OP				slope of the regression line	
Ha: Hectares Ag land				is zero, there is no	
and OP are correlated				significant relationship	
				between hectares Ag land	
				and OP	
West	0.959	0.10	accept	Because p-value	0.1%
Ho: No correlation exists				(0.959)>0.1, accept Ho	
between hectares Ag				and conclude that the	
land and OP				slope of the regression line	
Ha: Hectares Ag land				is zero, there is no	
and OP are correlated				significant relationship	
				between hectares Ag land	
				and OP	
East	0.070	0.10	reject	Because p-value	51.4%
Ho: No correlation exists				(0.070)<0.1, reject Ho and	
between hectares Res				conclude that the slope of	
land and IP				the regression line is not	
Ha: Hectares Res land				zero, there is a relationship	
and IP are correlated				between hectares of Res	
				land and IP	
West	0.374	0.10	accept	Because p-value	26.6%
Ho: No correlation exists				(0.374)>0.1, accept Ho	
between hectares Res				and conclude that the line	
land and IP				is zero, there is no	
Ha: Hectares Res land				significant relationship	
and IP are correlated				between hectares Res	
				Land and IP	

Table 8.

Summarized statistical results from Kendall Tau correlation of hectares of land use and

concentrations of associated phosphorus.

Hypothesis	τ	α	Accept/Reject	Conclusion
East	-0.238	0.619	accept	Because t(-0.238) < CV(0.619),
Ho: no correlation exists				accept Ho and conclude that there
between hectares Ag land and				is not a statistically significant
OP				correlation between hectares Ag
Ha: a correlation exists				land and OP.
between hectares Ag land and				
OP				
West	-0.200	0.800	accept	Because t(-0.200) < CV(0.800),
Ho: no correlation exists				accept Ho and conclude that there
between hectares Ag land and				is not a statistically significant
OP				correlation between hectares Ag
Ha: a correlation exists				land and OP.
between hectares Ag land and				
OP				
East	0.333	0.619	accept	Because t(0.333)< CV(0.619),
Ho: no correlation exists				accept Ho and conclude that there
between hectares Res land				is not a statistically significant
and IP				correlation between hectares Res
Ha: a correlation exists				land and IP.
between hectares Res Land				
and IP				
West	-0.400	0.800	accept	Because $t(-0.400) < CV(0.800)$ ,
Ho: no correlation exists				accept Ho and conclude that there
between hectares Res land				is not a statistically significant
and IP				correlation between hectares Res
Ha: a correlation exists				land and IP.
between hectares Res Land				
and IP				