Analysis of Phosphorus Concentrations and Loading in the Tan Brook

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Abstract

A land-use based model is being created to analyze total phosphorus in the Tan Brook, a small urban stream that runs through Amherst, Massachusetts. Here, we analyze concentration data collected at 7 locations along the stream length from October 2020- April 2021. We estimate phosphorus loads to the Mill River from these concentrations. The purpose of the modelling and sample collection is to advise on the location of a constructed wetland to treat excessive phosphorus before the Tan Brook discharges into the larger Mill River and then into Lake Warner. A brief literature review was also conducted to discern important design constraints for the constructed wetland. It was ultimately determined that the optimal location for the treatment wetland would be the Campus Pond. Sources of phosphorous are estimated to be from cycling within the Campus Pond, the geese/geese feces surrounding the pond, and urban areas within the Tan Brook Watershed. Important factors for constructed wetland design are substrate material, vegetation, and orientation/configuration of the constructed wetland.

Introduction

Increasing levels of anthropogenic phosphorous in surface waters results in numerous ecological consequences, and a viable method of removing excess nutrients in surface water is needed. A National Water Quality Assessment (NAWQA) study performed in 2004 showed measured concentrations of nitrogen and phosphorus that were 2-10 times higher than USEPA recommended criteria for nutrients in most of the 171 agricultural and urban streams that were studied (Dubrovsky et al, 2010). Phosphorus is a limiting nutrient and therefore is a common component of fertilizer, so it is no surprise that the largest contributor of phosphorus to surface water is via agricultural runoff (Hobbie et al, 2017). The influx of nutrients into water bodies is also heavily related to changes in land use. As natural, biodiverse ecosystems are replaced with impervious surfaces, agriculture, and resource extraction operations, the landscape's ability to provide ecosystem services such as phosphorous sequestration is significantly diminished (Lacher et al, 2018). Further, urban stormwater management approaches, which rely heavily on piped stormwater conveyances, quickly transport nutrients in stormwater directly to the watershed, bypassing ecological sources for phosphorus uptake (Hobbie et al, 2017).

The ecological impacts of excessive nutrient loading are severe. As previously stated, phosphorus is a limiting factor in plant growth on earth due to limited amounts of its bioavailable forms and the energy costs of converting them to these forms. When excessive bioavailable concentrations are introduced to an ecosystem, a corresponding reduction in biodiversity can be seen as organisms with the ability to quickly process phosphorus (phytoplankton and algae) grow rapidly, while organisms that have adapted to exist in very specific concentrations of nutrients die off and/or are pushed out. This issue expresses itself in the form of eutrophication, a phenomenon for which phosphorus is an essential nutrient. Eutrophication is essentially excessive plant growth in a water body resulting from nutrient enrichment. When the sources of nutrient enrichment are anthropogenic, this phenomenon is referred to as 'cultural eutrophication' (Smith, 2003). For the purposes of this analysis, all mentions of eutrophication should be taken to mean 'cultural eutrophication', unless otherwise stated. Eutrophication can have serious impacts on water quality, most notably increased biomass and productivity of various algae, and the shift of some plankton to "bloom-forming species" which in turn contribute to toxic algal bloom formation. The increase in algae and phytoplankton biomass also contributes to decreased oxygen levels as O_2 is consumed by these organisms, and a corresponding loss in fish and other aquatic life. Further, from a drinking water standpoint, eutrophication results in taste, odor and filtration issues (Smith, 2003). As the human population continues to increase, so will the impacts of nutrient loading on the ecosystem and our built world. Indeed, even if production of phosphorus-base fertilizers were to be halted immediately, it has been estimated that legacy amounts of phosphorus would continue to runoff and influence water quality for hundreds of years (Goyette et al, 2018).

With this in mind, the need for accurate models of phosphorus loading into water bodies and solutions for excessive loading is great. One potential solution to the issue of excessive phosphorus loading is the construction of treatment wetlands in the flow paths of degraded rivers and streams. The reasoning behind this is discussed in more detail later in this paper, however the main idea is that we can capitalize on the natural phosphorus sinks created by wetland processes. These processes include both settling and uptake by plants (Griffiths et al, 2020). Understanding these processes and the transport mechanisms that get phosphorus into a water body in the first place is the first step in designing an effective phosphorus removal system.

Locally, Lake Warner in Hadley is a perfect example of a water body that is threatened by excessive nutrient loading. In their 2019 'State of the Lake' Report, the Friends of Lake Warner and the Mill River reported phosphorus levels of up to 50µg/L in July, well in excess of the eutrophic impairment threshold of 25µg/L and the ecological impairment threshold of

8μg/L. Data for the report was collected in May through October of 2019, and represents a continuing and concerning trend of increasing average total phosphorus concentrations (Johnson, 2019). Lake Warner is fed by the Mill River, which is in turn fed by many tributaries, including Tan Brook, which flows from Strong Street in western Amherst and through the University of Massachusetts, Amherst campus before discharging to the Mill River. It is believed that Tan Brook supplies much of the phosphorus to the Mill River due to the surrounding watershed. It is therefore the goal of this study to begin creation of a model to analyze phosphorus loadings from Tan Brook to the Mill River, and to perform a brief literature review regarding the feasibility of a treatment wetland to mitigate any loading.

Materials and Methods:

Details for specific steps in this analysis will be provided in the following sections. Overall, the procedure for this study was 1) Identify sample sites 2) Collect and analyze samples to determine total phosphorus concentrations 3) Estimate flow rates at each sample site 4) Estimate phosphorus loads at each sample site 5) Calculate export coefficients and compare to Reckhow et al (1980) values.

Methods: Sample Collection and Analysis

Since most of Tan Brook is culverted, the seven sample sites were selected based on the sections that are open to the atmosphere. ArcGIS was used to map the sub-watersheds contributing flow to each of the sites. This map can be seen as **Figure 1** in the Appendix.

Samples were collected monthly and after major rain events from October 2020 to present. Samples were collected in clean amber jars or with a sample bucket which was then poured into an amber jar. In each case, the bucket/jar was rinsed with the sample waters three times prior to final collection. In situ measurements of pH, temperature, and conductivity were also taken. One of the samples is taken at the outlet of the Campus Pond, which is a weir. The height of flow over this weir was also measured at the time of sampling.

The samples were acidified and kept cold until analysis. Total phosphorus concentrations were obtained using the ascorbic acid method (4500-P E in Standard Methods for the Examination of Water and Wastewater) with a persulfate digestion (4500-P B. 3 in Standard Methods). The persulfate digestion serves to convert all phosphate to orthophosphate. The orthophosphate ions react with ammonium molybdate and antimony potassium tartrate in acid to form an antimony-phospo-molybdate complex. The resulting mixture is blue in color, the intensity of which is proportional to the total phosphate concentration (EPA, 1993). We measured the absorbance of each sample using a Hach DR-6000 Spectrophotometer with a wavelength of 880nm. Five standards were also carried through the analysis in triplicates to generate calibration curves. It should be noted that the October/November samples were analyzed using an orthophosphate kit from Hach Company (Hach method 10307, 2019). The remainder of the samples were analyzed using reagents/solutions made in the lab prior to analysis.

Methods: Flow Estimation

Since Tan Brook is such a small stream, no data on streamflow is currently collected. As such, flow estimates were calculated using methods outlined in the USDA Technical Release 55 (USDA, 1986)- “Urban Hydrology for Small Watersheds”, commonly referred to as the “TR-55 method”. The method uses soil type, land cover, and slope to give each watershed a curve number representing the amount of precipitation that will infiltrate into a given area. Precipitation data is then used to generate an estimate for flow rate. The following data layers were obtained from the Massachusetts Bureau of Geographic Information Systems (MassGIS): 2016 Land Cover/Land Use, NRCS SSURGO-Certified Soils (provides soil type and slope), and Digital Elevation Model (1:5,000). The digital elevation model was used to create sub-watersheds for the sampled sites on which the rest of the flow estimates would be based. The sub-watershed map is **Figure 1** in the appendix. Sample site land coverages broken down by watershed is also in the Appendix as **Figure 2.** This data was input into the TR-55 methodology along with precipitation data from the Amherst Wastewater Treatment Plant to yield runoff estimates from the seven sub-watersheds in the Tan Brook watershed.

One issue with the TR-55 method is that it does not provide information on the base flow in the stream. For many of the days that we sampled, it had not rained for several days. For this reason, flow rates in Tan Brook and at each sample site were estimated in the following way. First, flow was calculated over the weir in Site 2 (the Campus Pond outlet) for all days using the weir equation (Aydin et al, 2014):

$$Q = \frac{2}{3} C_d b \sqrt{2g} H^{1.5}$$

Where C_d is a discharge coefficient defined by weir dimensions and flow, b is the length of the weir, g is acceleration due to gravity, and H is the height of flow over the weir. The lowest flow obtained through this calculation for the sampled days was determined to be the “low-flow” condition, where the only inputs to Tan Brook would theoretically be from groundwater. Flow through the remaining six sample sites was determined based on the average percent of the cumulative flow that each site's watershed represented. It was determined that Site 2 on average represented 67% of the total cumulative flow (seen at Site 1). Knowing that in dry weather, the flow over the Site 2 weir was about 11.34 cfs, which represented 67% of the total flow at Site 1, the remaining flow rates at each site were estimated. Flow estimates for each of the sampled days can be found in **Figure 3** in the Appendix. This is certainly a rudimentary way to estimate flow to say the least, and obtaining accurate flow measurements will be paramount in estimating the final phosphorus loads to the Mill River.

Methods: Load Estimation and Comparison to Published Export Coefficients

The phosphorus loads at each sample site and ultimately to the Mill River were calculated using a mass balance with the concentrations, and assuming stead state (dc/dt = 0). The load from consecutive sample sites was also used to determine the incremental loading caused by each sub-watershed. This data was compared with the percent impervious areas within each watershed to see if there was a trend between percent impervious area and phosphorus loads. Finally, export coefficients were calculated using Excel Solver to compare to published export coefficients from Reckhow et al (1980).

Results

Analysis of samples for total phosphorus revealed a general increase in concentrations at Sites 2,3,4 which represent the pond samples. Interestingly, there is a subsequent decrease at Site 1, which will be discussed further in the following section. Concentration data can be found in the Appendix in **Figures 4a-4c.** Similarly, both cumulative and incremental loading at each of the sample sites increased as expected through Site 2, then decreased significantly at Site 1, which was closest to the Mill River. Cumulative loading was compared with the Reckhow et al 1980 estimates to reveal a large disparity between estimated and observed loading using this method. This data is represented in **Figure 5** of the Appendix. In calculating export coefficients for this watershed, the stream-based sample sites (4 through 7) were all relatively close, however the pond sample sites (2 and 3) were significantly different- usually by an order of magnitude or more. When comparing calculate export coefficients to published coefficients, therefore, the remainder of this section will focus on Sites 4 through 7. In comparing the Reckhow export coefficients with our calculated export coefficients, it was determined that Reckhow's coefficients were relatively accurate for bare land, wetlands, shrubs, and water land types. Reckhow export coefficients were significantly different than calculated coefficients for forests, grassland, developed open space, and impervious areas. It should also be noted that Excel Solver was unable to estimate export coefficients for Site 1 since there was a decrease in loads from Site 2 to Site 1. **Figure 6** in the Appendix shows the calculated export coefficients compared to Reckhow's published coefficients. Incremental loading rates compared with the percent impervious coverage in each watershed are shown in **Figure 7** in the Appendix, showing impervious cover and loading both increasing, until Site 2, where the phosphorus load increases significantly and the percent impervious decreases.

Discussion

Phosphorus Loading and Concentration

Concentrations of phosphorus (see **Figures 4a-**4c) were regularly above the eutrophic threshold of 20µg/L (Chapra, 2008). This was especially true in the fall and spring months, perhaps due to an increase in organic matter getting into the Brook or increased photosynthesis within the Brook. Phosphorus concentrations typically reached a peak in the Campus Pond samples (Sites 2, 3 and 4) and then decreased at Site 1. Interestingly, the maximum concentration across all samples, 180µg/L, was measured in the winter, on January 5, though this appears to be an outlier. Concentrations of 170µg/L were observed in both October and November, and 130µg/L was observed in April. Concentrations in the same season are relatively consistent, with more variability occurring between samples taken in different seasons.

In their 2019 report, the Friends of Lake Warner (FoLW) included a measured concentration of 70µg/L at the Tan Brook outlet (current Site 1) and 35µg/L at the inlet of Campus Pond (current Site 4). The current study revealed concentrations from 27 µg/L (measured on November 21) to 130 µg/L (measured on October 13 and 29 and April 21). The average measured concentration was 68µg/L for this site. At the Campus Pond Inlet (Site 4), concentrations ranged from 18µg/L (measured on February 8) to 170 µg/L (measured on October 13 and 29). The average concentration at this site was 72µg/L While the average concentration is very close to the FoLW data at Site 1, there is a significant difference in the Site 4 concentrations. It is unclear when the FoLW samples were collected, which could impact concentrations. It is also possible that flow patterns have changed since 2019. Facilities personnel at the University of Massachusetts confirmed that maintenance has been performed in the past few years to direct more flow to the Campus Pond. It should be noted that the

FoLW data was analyzed at UMass' Environmental Lab, who confirmed that samples were analyzed using the same ascorbic acid method with a persulfate digestion.

As can be seen in **Figure 5**, the Tan Brook is responsible for loading 3,000kg/yr of phosphorus into the Mill River. This is an excessive amount given the smaller nature of the Tan Brook watershed, and which requires remediation. The apparent loading from each sub-watershed (**Figure 7**) shows an interesting trend, as mentioned in the Results section. The average cumulative load trended upwards until Site 2, then decreased significantly at Site 1. This could be due to inaccurate flow estimates in the Site 1 watershed or artificially high concentration data at Site 2. Artificially high concentrations could be due to turbulent water at the Site 2 weir stirring up phosphorus in the sediments, which are then analyzed. It is also possible, but unlikely due to the makeup of the watershed, that there is a tremendous phosphorus sink between Sites 1 and 2.

Analyzing export coefficients can help us understand the role of land use in phosphorus loading. **Figure 6** shows the highest export coefficients across all watersheds occur for impervious areas, developed open spaces, and grasslands. From a loading perspective, this says that more phosphorus will be coming into the Tan Brook from these sources per hectare than other land coverages. Interestingly, the export coefficients can also provide clues that processes other than surface runoff are taking place to impact phosphorus loading. The export coefficients for the Campus Pond samples (Sites 1 and 2) are significantly higher than the Brook samples (Sites 4 through 7), by an order of magnitude or more. This may indicate the significance of processes such as cycling within the campus pond. Essentially, *if* the phosphorus in the Campus Pond is all coming from runoff, the impervious areas and other land uses around the pond are somehow discharging more than 10 times the amount of phosphorus compared to their counterparts in other watersheds. The argument that phosphorus is getting to Sites 2 and 3 by way of processes other than land use is strengthened by **Figure 7**, which shows the percentage of impervious areas within each watershed alongside the incremental loading from each. Site 2 breaks the trend of increasing loading with increasing impervious- as we see a decrease in impervious and an increase in loading.

Discerning additional sources of phosphorus to Sites 2 and 3 is no small task. Loads from cycling need to be accounted for in addition to land use inputs. Given the small size of the Site 2 and 3 watersheds- which account for just 3% of the total Tan Brook watershed area between them, it would be easy to discount land use and attribute all loading to cycling and other internal pond processes. However, the pond and the large grassy field surrounding it are frequently filled with scores of geese. Goose feces in the field (which contributes to the pond via runoff) and in the pond itself likely contribute a non-trivial amount of nutrients, including phosphorus, to the pond. It is possible that simply removing the geese would significantly reduce the phosphorus loads to the Mill River. In any case, separating the land use loading (geese included) from the cycling could help inform on the effectiveness of sediment reduction strategies such as dredging the pond.

Literature Review

Given that there is a clearly significant phosphorus load coming from the Tan Brook to the Mill River, our team also looked into strategies for mitigating this load.vIn this section, we shift focus from data analysis to a brief review of current research into constructed wetlands for nutrient removal. As previously stated, constructed wetlands have the ability to mimic and enhance natural processes for phosphorus removal. There are several configurations that are commonly used in treatment wetlands, the most prevalent of which are vertical subsurface flow, horizontal subsurface flow, and surface flow (Luederitz et al, 2001). For phosphorus removal, several studies highlighted the advantages of horizontal subsurface flow wetlands, due to increased hydraulic residence times (HRT) and interactions with a substrate media in the wetland (Dell'Osbel et al, 2020). This interaction with substrate media is critical, as adsorption has been shown to be the main pathway for phosphorus removal (Mann, 1990). Knowing the importance of adsorption makes selection of an effective substrate material a critical step in wetland design. The ideal substrate would therefore have high capacity for adsorption- i.e particles with a large surface area and favorable polarity/polar sites. A pilot study in Brazil made use of a removable crushed brick filter, where the crushed brick came from nearby construction waste (Dell'Osbel et al, 2020). In addition, constructed wetland design should consider water velocity at the wetland surface and outlets. Because phosphorus is readily carried in sediments, resuspension of these sediments can reintroduce phosphorus into the water (Griffiths et al, 2020).

accumulated over time in bottom sediments, and cycling is likely impacting concentrations.

Given this information, the best location for a constructed wetland is likely the campus pond itself. Locating the wetland here would not only treat phosphorus before it reaches the exceedingly high concentrations that we see from the sampling, but also help to deter the geese. A secondary site would could be in the west of campus at the confluence of Tan Brook and the Mill River, near the heating plant. Locating the wetland here would treat flow before it gets to the Mill River and maintain the Campus Pond as a centerpiece of campus. That being said, Tan Brook is about 8 feet below existing grade in this area, presenting another engineering challenge.

Conclusions and Further Research

It is clear that Tan Brook is contributing excessive phosphorus to the Mill River. Major sources of nutrients appear to be the Campus Pond and the resident geese, as well as impervious areas within the sub-watersheds. Forests and grasslands within the sub-watersheds also appear to contribute more phosphorus than initially estimated. With this in mind, the ideal solution to nutrient loading in the Mill River/Lake Warner would encompass watershed-scale best management practices to limit/decrease impervious surfaces, as well as treatment prior to discharge. A constructed wetland could be a feasible option for treatment with proper design considerations and maintenance. Design of the wetland should maximize HRT, utilize a highly adsorbant and locally available substrate, and minimize water velocity, especially near the outlet. Based on the data we have collected so far, ideal location for a constructed wetland from a water treatment perspective could be the campus pond itself.

Moving forward, getting accurate flow data is of paramount importance for our load estimates. Concentration data will continue to be collected for Tan Brook. This will make loading estimates more robust and reveal any seasonal trends in phosphorus concentrations. Additional data will also help tune export coefficients and help with the ultimate goal of creating a predictive model for phosphorus loading in the system. Our team will also continue looking into the role of nutrient cycling versus land use loading to the Campus Pond.

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APPENDIX

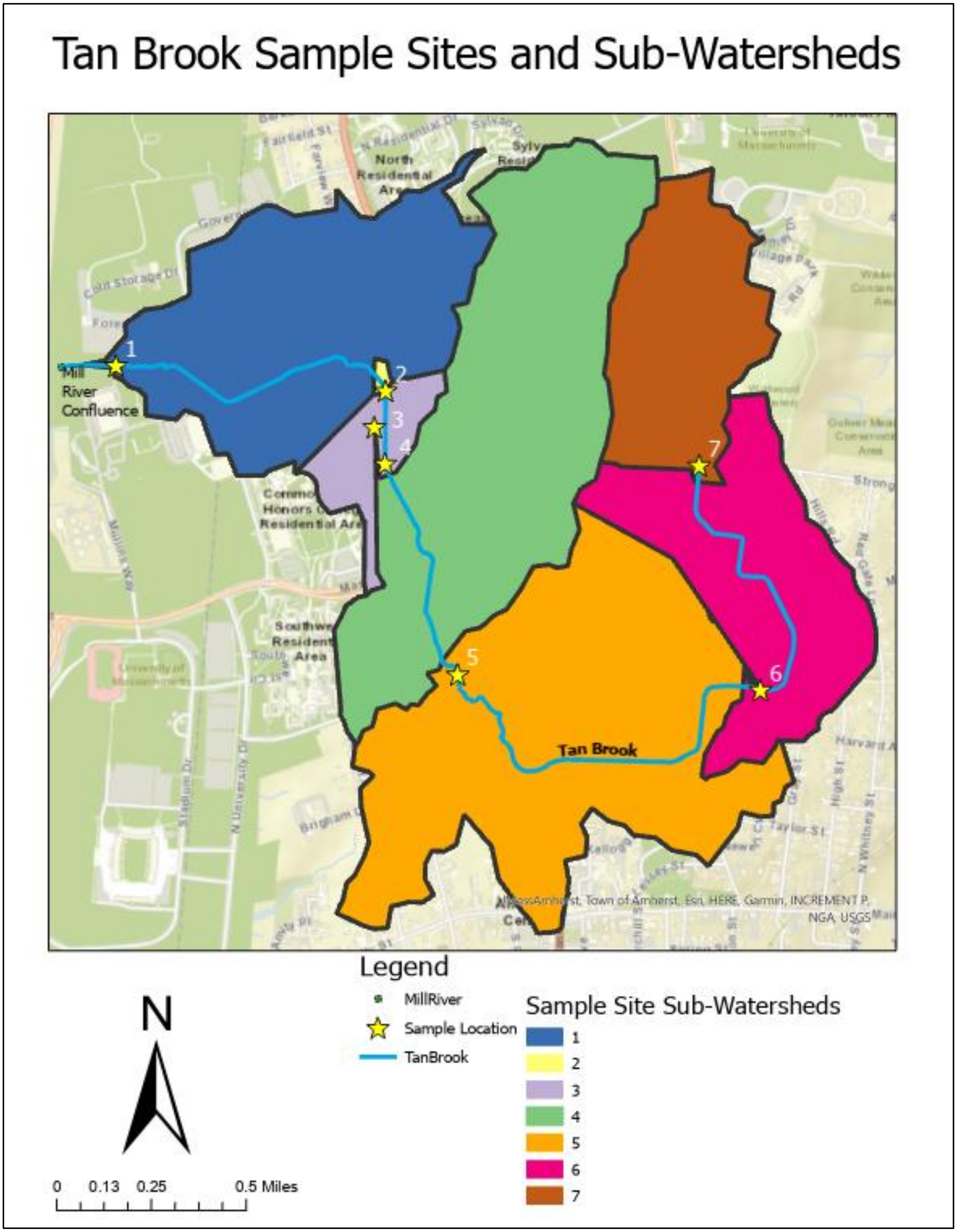


Figure 1: Tan Brook Sample Sites and Sub-Watersheds

Land Cover	Site 1	2	3	4	5	6	7
Bare Land	0.02	0.00	0.00	0.04	0.12	0.06	0.29
Deciduous Forest	3.74	0.98	3.83	19.91	13.43	25.65	31.90
Developed Open Space	22.10	54.10	28.43	21.62	27.26	27.62	16.54
Evergreen Forest	4.85	0.00	3.43	12.49	24.44	13.42	17.84
Grassland	0.00	0.00	0.18	6.02	0.66	4.69	2.05
Impervious	69.30	44.55	53.54	39.33	33.05	26.27	18.49
Palustrine Emergent Wetland	0.00	0.00	0.00	0.06	0.00	0.00	7.56
Scrub/Shrub	0.00	0.00	0.00	0.42	0.00	0.00	0.10
Water	0.00	0.37	10.59	0.12	0.00	0.00	0.45

Figure 2: Sample site land coverage percentages

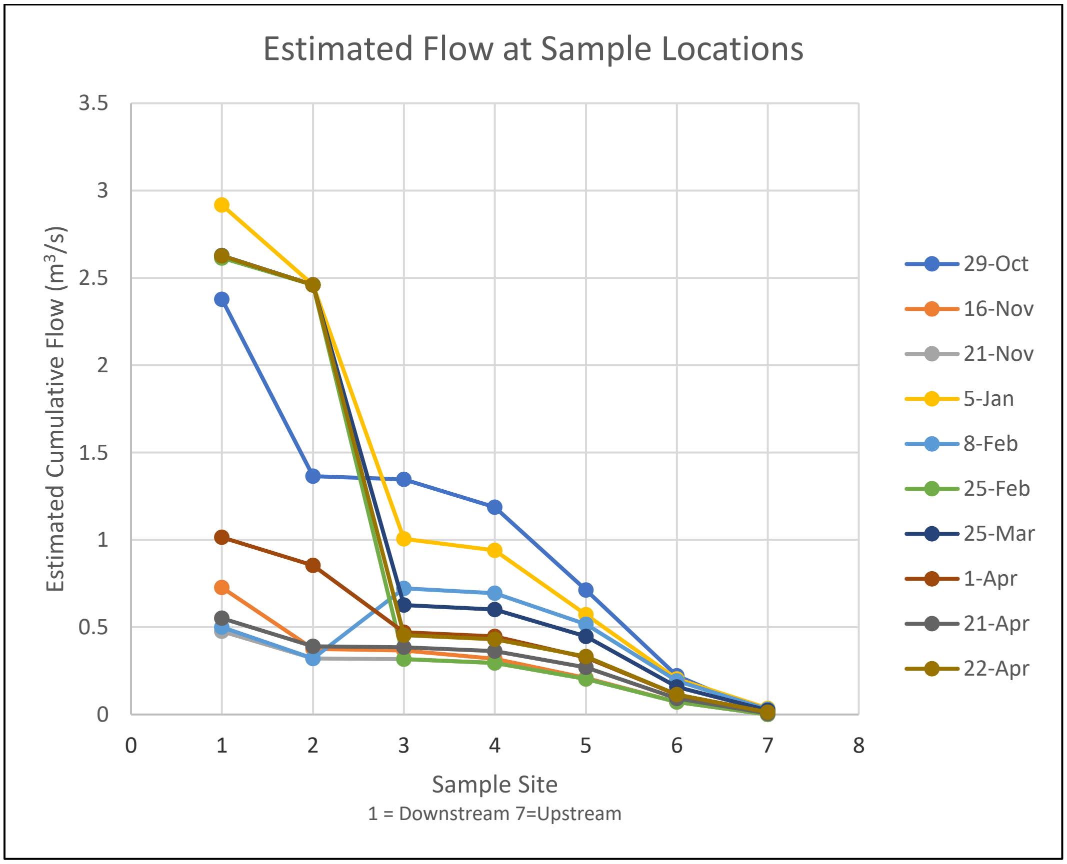


Figure 3: Estimated cumulative flow at each sample site

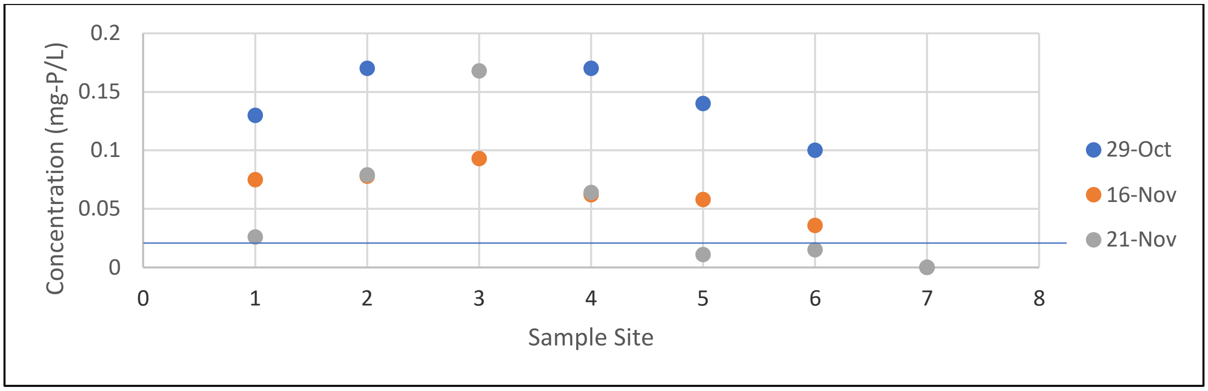


Figure 4a: Measured total phosphorus concentrations (mg-P/L) for samples taken in October and November of 2020. The eutrophic threshold of 20µg/L (Chapra, 2008) is also shown in blue.

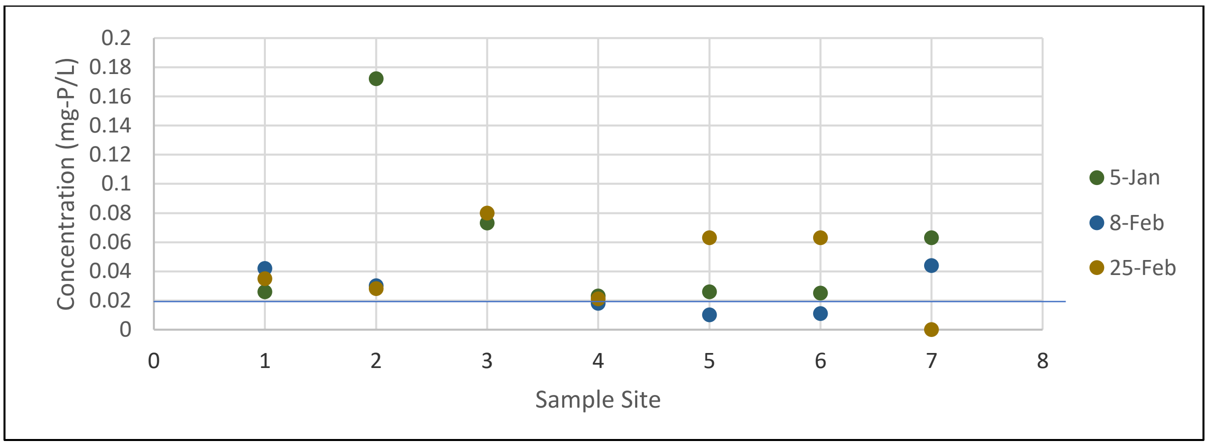


Figure 4b: Measured total phosphorus concentrations (mg-P/L) for samples taken in January and February of 2021. The eutrophic threshold of 20µg/L (Chapra, 2008) is also shown in blue.

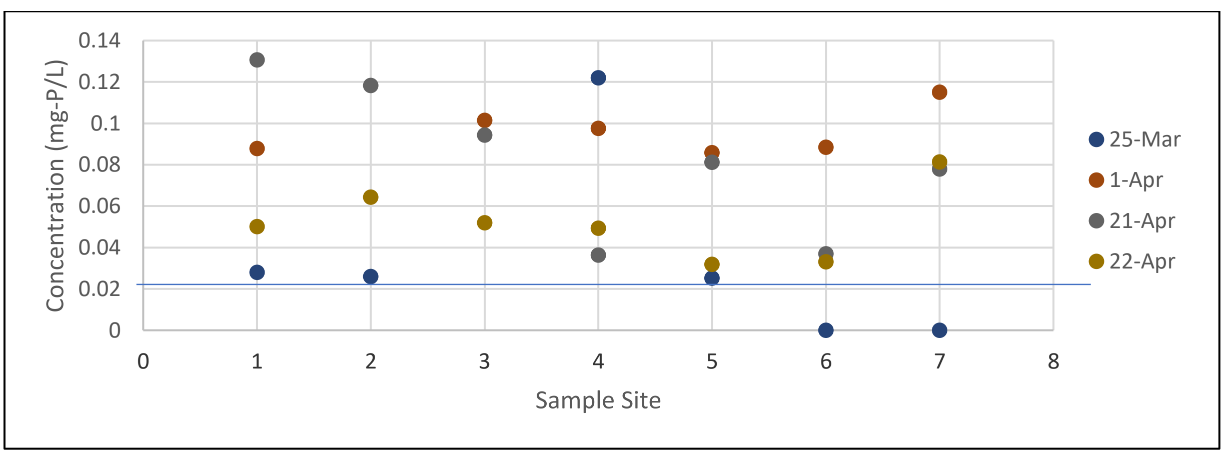


Figure 4c: Measured total phosphorus concentrations (mg-P/L) for samples taken in March and April of 2021. The eutrophic threshold of 20µg/L (Chapra, 2008) is also shown in blue.

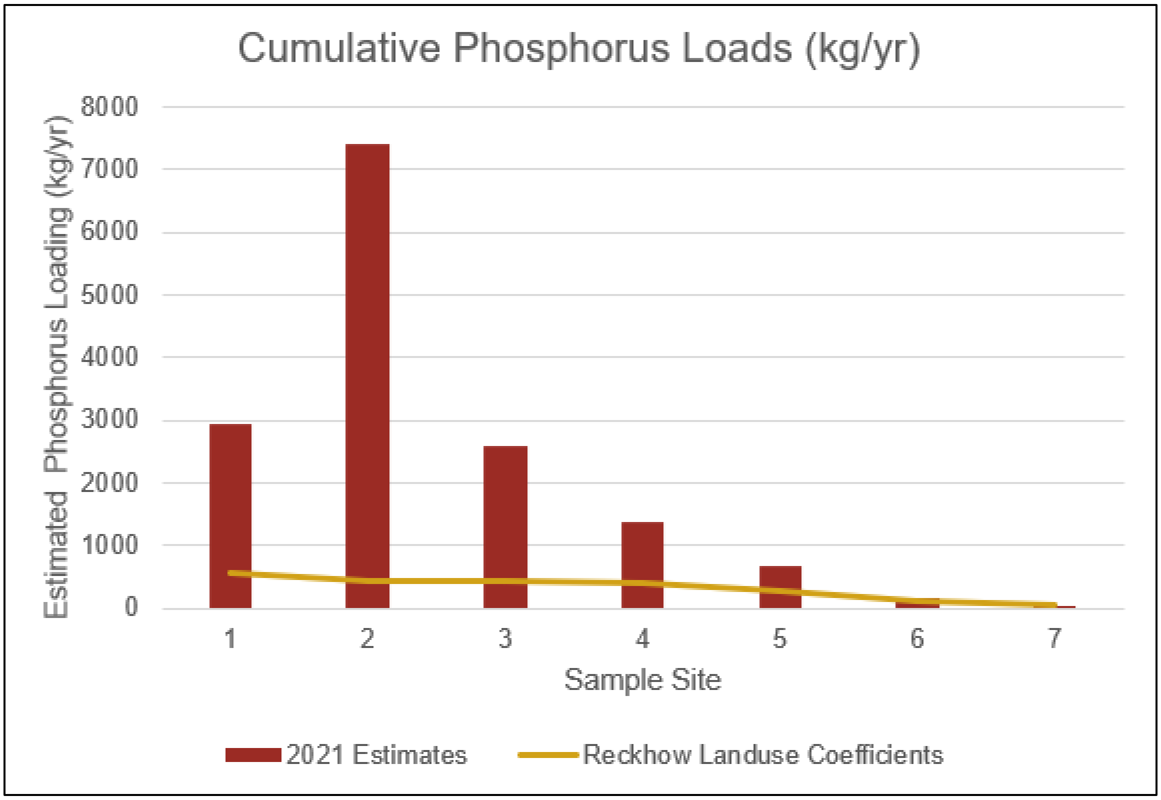
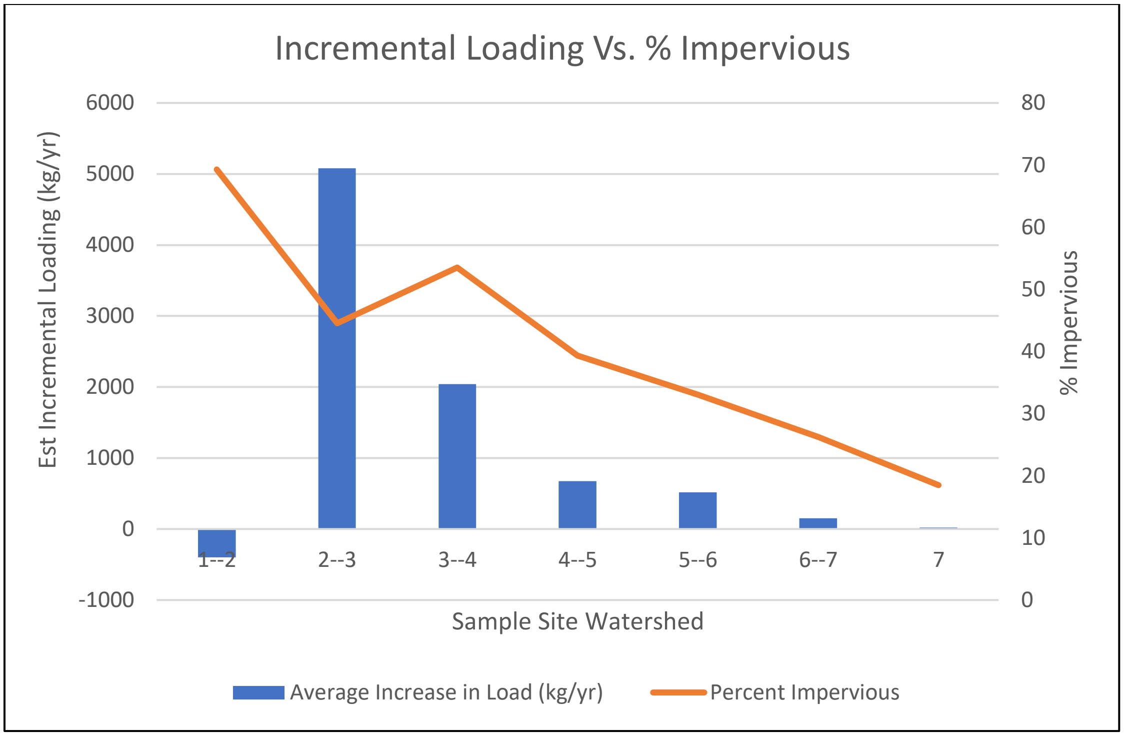


Figure 5 Cumulative phosphorus loads calculated in 2021 versus loads estimated via Reckhow land use export coefficients (Reckhow, 1980)

				Site				
Land Cover	1*	2	3	4	5	6	7	**Reckhow et al Coefficient**
Bare Land				3.25	3.26	3.25	3.24	3.25
Deciduous Forest		112.28	10.85	3.01	1.54	1.53	0.01	0.5
Developed Open Space		6182.77	78.02	3.85	3.24	2.24	0.75	1.134
Evergreen Forest			9.50	1.81	2.12	0.77	0.01	0.236
Grassland			1.63	1.89	1.18	1.32	1.09	1.134
Impervious		5092.12	145.96	6.14	3.74	2.24	0.76	1.19
Wetland				0.11	0.18	0.19	0.01	0.1
Scrub/Shrub				0.35			0.30	0.3
Water		42.88	29.63	1.01			0.99	1.0

Figure 6 Land use export coefficients (kg/ha/yr) calculated for each sampling location compared to Reckhow land use export coefficients (1980)
*Excel Solver could not find solutions for this watershed



<u>Figure 7</u>: Incremental loading by watershed (kg-P/yr) compared to increases in percentage impervious area for each watershed.
Note that the deficit between Sites 1 and 2 was significantly more than what is shown here