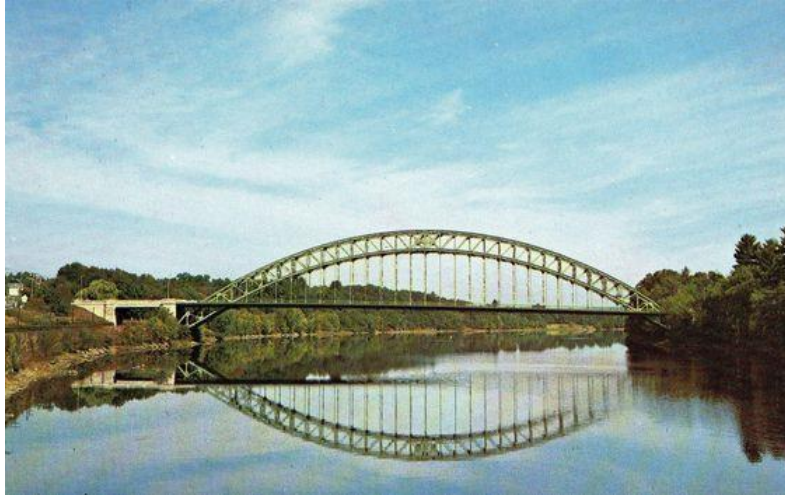


## Addressing Point and Nonpoint Source Phosphorus Loads at Selected Sites in Tyngsborough, Massachusetts



(Source: Cosgro, 2020)

A Major Qualifying Project Report  
Submitted to the Faculty of  
Worcester Polytechnic Institute  
in partial fulfillment of the requirements for the  
Degree of Bachelor of Science

By  
Aurora Bas

May 18<sup>th</sup>, 2020

Submitted to:  
Professor Paul Mathisen, Worcester Polytechnic Institute  
Danielle Mucciarone, Tyngsborough Conservation Commission

*This report represents work of a WPI undergraduate student submitted to the faculty as evidence of completion of a degree requirement. WPI routinely publishes these reports on its website without editorial or peer review. For more information about the projects program at WPI, see <http://www.wpi.edu/Academics/Projects>*

## Abstract

The source identification of phosphorous in the Merrimack River, within the town of Tyngsborough's borders, is needed to satisfy a requirement for Tyngsborough's Municipal Separate Storm Sewer System (MS4) Permit. This report includes methods for mitigation of phosphorus runoff, selection of sites potentially contributing excess phosphorus, methods to address current elevated phosphorus levels, and methods to conduct phosphorous data collection. The goal of this report is to provide the first step towards analyzing suspected key problem sites.

## Acknowledgements

I would like to thank my sponsor, Danielle Mucciarone from the Tyngsborough Conservation Commission, without whom this project would not have been possible. Mrs. Mucciarone's support and expertise were consistently helpful throughout the research and development phases, and her inspiring passion for this topic encouraged me to move forward in my efforts. I would also like to thank my advisor, Professor Paul Mathisen from Worcester Polytechnic Institute, for his guidance and direction with this project.

I would like to thank my family, Christophe Bas, Natana DeLong-Bas, and Gabriel Bas, among all my extended family, for their support and encouragement during this project. I would also like to thank my bunny, Pearl, for chewing on my notes daily to remind me to put my distractions away and focus on this project.

I would also like to thank Worcester Polytechnic Institute for providing the opportunity to engage in this meaningful project, which will serve as the foundation for future phosphorus-related projects in my beloved hometown. I would also like to thank Central Catholic High School for providing me with the knowledge and discipline to pursue my university studies, which led me to this opportunity. Without the education I received from both of these institutions, this project would not have been made available to me. The opportunity to engage in a project that personally interests me, satisfies a graduation requirement, and makes a difference in my hometown is a true gift for which I am grateful.

## Authorship

### ***Aurora Bas***

Ms. Bas, a Worcester Polytechnic Institute Environmental Engineering student, was the sole author of this report in its entirety, aside from the appendices. She coordinated with Danielle Mucciarone of the Tyngsborough Conservation Commission to develop this project, which is a continuation of Ms. Bas' work as a Stormwater Project Intern.

### ***Cecilia Schroeder***

Ms. Schroeder, a Worcester Polytechnic Institute Environmental Engineering student, assisted with the development of the original project proposal, which may be found in Appendix I.

## Capstone Design Statement

To satisfy accreditation requirements set by the Accreditation Board for Engineering and Technology (ABET) and meet the design requirements of the Major Qualifying Project (MQP) for the Department of Civil and Environmental Engineering at Worcester Polytechnic Institute (WPI), this project includes a Capstone Design Experience. This requires students to present an engineering design which applies engineering tools and principles, consistent analysis, and a list of potential constraints within the proposed project.

The design for this project included the determination of preventive measures to minimize phosphorus discharge from a number of sites identified as potential sources of contamination to the Merrimack River, and development of a sampling and monitoring plan to assess phosphorus loadings in the future. The analysis included identification of water, soil, and leaf sampling procedures methods to address phosphorus reduction in the Merrimack River, site monitoring plans, and estimations for phosphorus loads originating from selected sites. These serve as the first step in any future phosphorus-related projects in the town of Tyngsborough, Massachusetts for the purpose of meeting NPDES MS4 Permit regulations and addressing elevated phosphorus levels in the Merrimack River within Tyngsborough's borders.

### *Project Constraints*

This project is designed to be implemented by the Tyngsborough Conservation Commission and respects town budgets, staff limitations, and legal requirements. The project included considerations of a variety of constraints, such as health and safety, environmental, and sustainability concerns.

### *Health and Safety Considerations*

This project is designed to reduce phosphorus loading in the Merrimack River, which provides drinking water to four communities. Because the health and safety of the public is the top priority of the town, it is critical to analyze current levels of phosphorus and reduce them to the legally permitted level.

*Environmental and Sustainability Considerations*

In addition to protecting the public, the recommendations for treatment were proposed with regulatory limitations in mind (some chemical treatments were not permitted for sale or use in Massachusetts due to pesticide regulations) and the well-being of the aquatic life who inhabit the Merrimack River. The recommendations for site monitoring were made to prevent phosphorus loads from contaminating the river to dangerous levels that would lead to eutrophication or dead zones.

Because phosphorus data were not available, the proposed sampling and treatment methods were selected and developed based on knowledge of the town budget, ability to access the sites, and estimations of site runoff flow. This project provides a baseline for future projects, which should be appropriately adapted based on the parameters and constraints of each site.

## Professional Licensure Statement

All Civil and Environmental engineers must abide by the National Society of Professional Engineer's Code of Ethics, which requires engineers to perform all duties with honesty, integrity, and the understanding that engineering directly affects quality of life for all people. Engineers have a responsibility to keep the public safe and should only participate in projects for which they are qualified.

Professional licensure within the field of engineering is important for protecting the safety of the public. Licensed professional engineers acquire this state-regulated level of prestige by meeting specific requirements in education, work experience, and exams. The two exams that provide the opportunity to become licensed are the Fundamentals of Engineering (FE), which is designed for graduates from an EAC/ABET-accredited program, and Principles and Practice of Engineering (PE) exams, and engineers who have worked for four years under the direction of a licensed PE.

The FE, or Fundamentals of Engineering, exam is the first step towards becoming a professional engineer. The NCEES provides the computer-based FE in seven different engineering disciplines year-round at NCEES-approved Pearson VUE test centers. The exam takes six hours to complete and includes 110 questions. The Environmental FE requires knowledge of mathematics, probability and statistics, ethics and professional practice, engineering economics, materials science, environmental science and chemistry, risk assessment, fluid mechanics, thermodynamics, water resources, water and wastewater, air quality, solid and hazardous waste, and groundwater and soils. These are all basic subjects that, without proper knowledge thereof, could negatively impact the safety design of a project.

The PE, or Principles and Practice of Engineering, exam is designed for engineers who have a minimum of four years' post-graduate work experience in their appropriate discipline. The NCEES provides the computer-based PE year-round at NCEES-approved Pearson VUE testing centers. The exam takes nine hours to complete and includes 80 questions. The Environmental PE requires knowledge of water, air, solid and hazardous waste, site assessment and remediation, environmental health and safety, and associated engineering principles. These are all important areas in which environmental engineers should demonstrate appropriate competency.

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## Chapter 1: Introduction

Phosphorus is a naturally occurring element typically found in low concentrations, serving as a key component in cell formation and fundamental biological and chemical processes. Research in the environmental and water quality realms have consistently shown that high phosphorus concentrations are detrimental to the well-being of a water body and the aquatic life that depend upon it. Excess phosphorus in a water body promotes the process of eutrophication, by which plants and algae experience excessive growth and fill up a water body, and the presence of dead zones, where all dissolved oxygen is depleted and no life can survive. Additionally, phosphorus can enter drinking water systems, potentially harming residents who receive from that supply. In excess, phosphorus can negatively contribute to water quality, aquatic life, and overall ecosystem health.

To combat the impact of pollutants such as phosphorus on surface water bodies, the National Pollutant Discharge Elimination System (NPDES) permit program was created in 1972 in response to the Clean Water Act and, authorized by the EPA, regulates point source water pollution (*Massachusetts Small MS4 General Permit*, 2020). The Clean Water Act Section 402 and Code of Federal Regulations § 122.1 (b) requires permits for any point source discharge to water bodies in the United States, which is the guideline by which NPDES abides. These point sources include municipal/industrial wastewater treatment plants, concentrated animal feeding operations, Municipal Separate Storm Sewer Systems (MS4s), and other potential sources of nutrient pollution (Carpenter, 1998). The town of Tyngsborough, MA is working to meet the requirements of the MS4 Permit. If phosphorus levels within Tyngsborough are found not to comply with the requirements of the permit, the permit will be revoked, and Tyngsborough will be fined (*Massachusetts Small MS4 General Permit*, 2020).

The goal of this project is to ensure that Tyngsborough is able to keep its MS4 Permit, to protect the well-being of the general environment, aquatic life, and water bodies, and to serve as the baseline for any phosphorus-related projects by providing a series of recommendations for analysis and treatment. The specific goal of this project is to provide suggestions for preventive measures to minimize phosphorus introduction into the Merrimack River, recommend methods to deal with pre-existing elevated phosphorus levels, identify potential problematic site selection within

Tyngsborough, and develop monitoring plans to assess phosphorus levels and effectiveness of treatment. These topics are covered in a way to ensure that the town of Tyngsborough can properly assess whether the requirements of the NPDES MS4 Permit, which allows the town of Tyngsborough to discharge from the existing stormwater infrastructure, are satisfied. It also provides information on approaches for remediation and treatment if the data show otherwise.

To meet the project goal, the main objectives of this particular project were to:

1. Use aerial maps to identify potential sources of phosphorus discharge into the Merrimack River
2. Determine theoretical phosphorus loading from Tyngsborough using current zoning loadings provided in the Massachusetts Small MS4 General Permit, Appendix F
3. Use Tyngsborough topography GIS data to analyze slopes and determine where to collect samples at nonpoint sources
4. Identify and develop appropriate plans to reduce phosphorus levels in the Merrimack River within the town of Tyngsborough's borders, specifically at the selected sites (these plans may be found in Chapter 5)

This report will serve as the baseline for any phosphorus-related projects, providing a series of recommendations which can then be revised or fine-tuned with repeat site visits and data analyses. These recommendations include determining where to conduct sampling for point and nonpoint phosphorus sources, how to mitigate phosphorus addition into the water, and how to address pre-existing elevated phosphorus levels in the Merrimack.

This report contains a list of nine site selections within Tyngsborough where sampling needs to be conducted (Chapter 4), estimated TMDLs for most of these sites (Chapter 4), recommended preventive measures to minimize phosphorus loads (Chapter 5), a monitoring plan to consistently collect phosphorus data (Chapter 5), and recommendations for products to address existing phosphorus in the Merrimack River (Chapter 5).

## Chapter 2: Background

This section includes an explanation of the need for phosphorus in the environment, how it enters water bodies, effects of an imbalance of phosphorus in natural systems, identification of dead zones, threats posed by cyanobacteria, sources of point and nonpoint source phosphorus contamination, and why elevated phosphorus levels need to be addressed and monitored.

### 2.1 Water Quality in the Merrimack River

Water quality in the Merrimack River is important for a variety of reasons, namely that it is the second largest river in New England (spanning 5,014 square miles), provides critical habitat for both plant and animal species (such as the bald eagle, a threatened species in Massachusetts), and supplies public drinking water for four communities. It has also been identified by the United States Forest Service as the fourth most threatened watershed due to loss of private forested lands, which serve to absorb nutrient and sediment runoff prior to it reaching the river. The greatest phosphorus contributors throughout the river have been identified as municipal wastewater (60%) and runoff from developed lands (21%) (“Environmental Challenges for the Merrimack River”, 2020).

The EPA has identified several main issues with water quality in the Merrimack River, including high bacteria and nutrient concentrations, illicit and untreated sewage discharges, litter, cyanobacteria blooms, and discharge from combined sewer overflows. Currently, untreated sewage has been identified as the primary source of bacteria pollution; other sources also include polluted runoff, runoff from fertilization, animal waste, industrial cleaning operations, and wastewater discharged from facilities without tertiary treatment (during which phosphorus is broken down). To identify whether Tyngsborough is contributing to these elevated levels of phosphorus contamination in the Merrimack River and whether the town can keep its MS4 Permit (which is designed to minimize harmful discharge into a water body), it is important to conduct a series of sampling analyses.

Although there have been case studies and research done on the Merrimack River as a whole, there is not a lot of information available for the segment that runs specifically through Tyngsborough’s

borders. There is currently no information available regarding Total Maximum Daily Loads (TMDLs) listed for phosphorus (though there are TMDLs listed for pathogens). Testing from January 2019 through March 2019 showed that *E. coli* bacteria levels were found to have decreased while other contaminants were found to exceed EPA standards (such as bromodichloromethane, chloroform, dibromoacetic acid, dibromochloromethane, dichloroacetic acid, haloacetic acids, total trihalomethanes, and trichloroacetic acid) (Tyngsborough Water District, 2019). Tyngsborough's Annual Water Quality Report for Reporting Year 2019 does not include any data on phosphorus levels (*Annual Water Quality Report: Reporting Year 2019, 2019*). The most recent phosphorus information available is from 2016 and indicated a declining trend in phosphorus concentration:

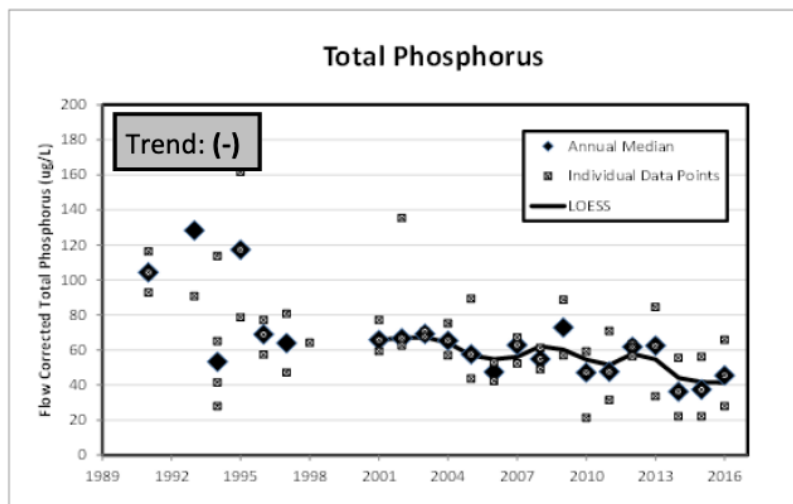


Figure 1: Total Phosphorus in the Merrimack River within Tyngsborough from 1989-2016  
 (“Merrimack River, Tyngsborough, MA”, 2016)

It is unclear how these data were taken, but they were taken at the 01-MER station in Tyngsborough (see Figure 3) by the New Hampshire Department of Environmental Services. Testing from 2012-2016 showed that pH levels displayed an improving trend and received a ‘fair’ overall rating, although the levels were still high.



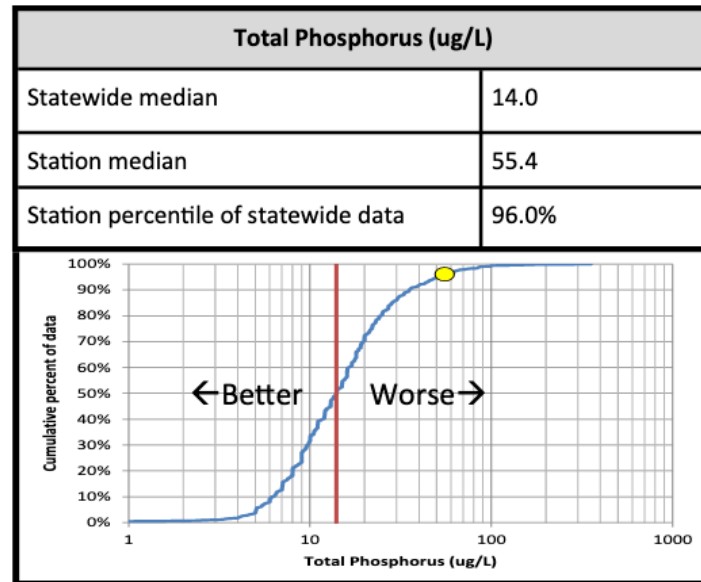


Figure 2: Total Phosphorus ( $\frac{ug}{L}$ ) Comparison (“Merrimack River, Tyngsborough, MA”, 2016)

Although Figure 1 shows a declining trend in phosphorus concentration in the Merrimack River within Tyngsborough’s borders, Figure 2 shows that these values do not meet regulations. Therefore, it is necessary to determine where these loads originate and take more current data.

## 2.2 Total Maximum Daily Loads (TMDLs)

A Total Maximum Daily Load (TMDL) is defined by the Massachusetts Department of Environmental Protection as “the maximum amount of a pollutant that a waterbody can accept and still meet the state’s Water Quality Standards for public health and healthy ecosystems...[it] is the sum of loads that are allowable from all contributing point and nonpoint sources of pollution” (*The Basics of Total Maximum Daily Loads (TMDLs)*). There is a standard process by which TMDLs are developed uniquely for each waterbody. This process includes:

1. Problem identification (what kind of pollutant it is)
2. Identification of target values, which should follow Water Quality Standards
3. Source assessment, which is the aim of this report
4. Determination of how much pollutant loading can occur within Water Quality Standards
5. Determination of needed reductions for both point sources and nonpoint sources

6. Public participation, by which stakeholders are permitted to comment and make recommendations
7. Reception of approval from Massachusetts Department of Environmental Protection
8. Reception of EPA approval, as required by the Federal Clean Water Act (in this case, the New England Regional Office of the EPA, Region 1, must approve them)
9. Consistent monitoring to ensure that TMDLs are effective and being met

Currently, the only TMDLs given are for ponds in the area. Nutrient TMDLs need to be established for impaired waterbodies per MassDEP standards (*TMDL Information*). They may be calculated by:

$$TMDL = \Sigma WLA + \Sigma LA + MOS$$

Where: WLA = Sum of wasteload allocations (point sources)  $\left(\frac{\text{mass of pollutant}}{\text{unit time}}\right)$

LA = Sum of load allocations (nonpoint sources)  $\left(\frac{\text{mass of pollutant}}{\text{unit time}}\right)$

MOS = Margin of safety

Documented phosphorus data within Tyngsborough specifically is extremely difficult to find. Figures 1 and 2 were the only recent relevant data available, so the cumulative database is relatively empty. While these data acquired from the 01-MER station (the only site at which phosphorus is monitored, shown in Figure 3) are helpful in a general sense, it does not give context for where the problem areas really are (since it is only at one location). As such, more data need to be collected at multiple sites (identified in Chapter 4) at both point and nonpoint sources. Tentative contributing sites were identified for this report, but will require further testing to better comprehend where there may be issues and to calculate accurate TMDLs. Following the site selection listed in Chapter 4, samples should be collected via procedures in Chapter 5, and TMDLs should be calculated according to that data.

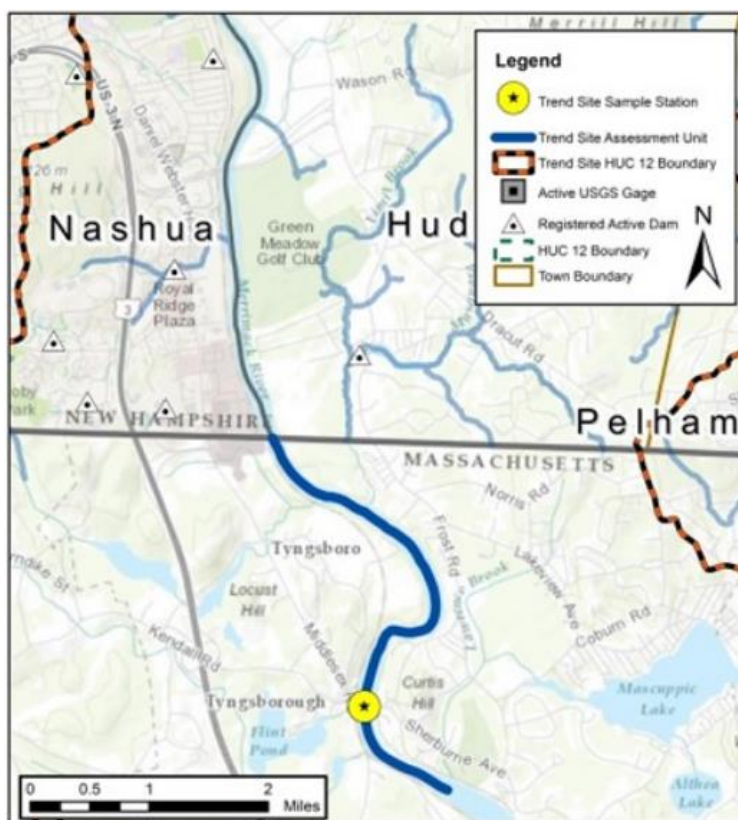


Figure 3: 01-MER Station in Tyngsborough (“Merrimack River, Tyngsborough, MA”, 2016)

### 2.3 Phosphorus and How it Enters the Environment

Phosphorus is a naturally occurring element found in rocks and other mineral deposits, often renewed with the uplift of continental rock. This phosphorus is released as phosphate ions, which are soluble in water and can then mineralize. Phosphates ( $\text{PO}_4^{3-}$ ) are then formed and exist in three forms: orthophosphate, metaphosphate (polyphosphate), or organically bound phosphate; they occur in living and decaying remains of both plants and animals. They can also be introduced through man-made applications, such as fertilizers.

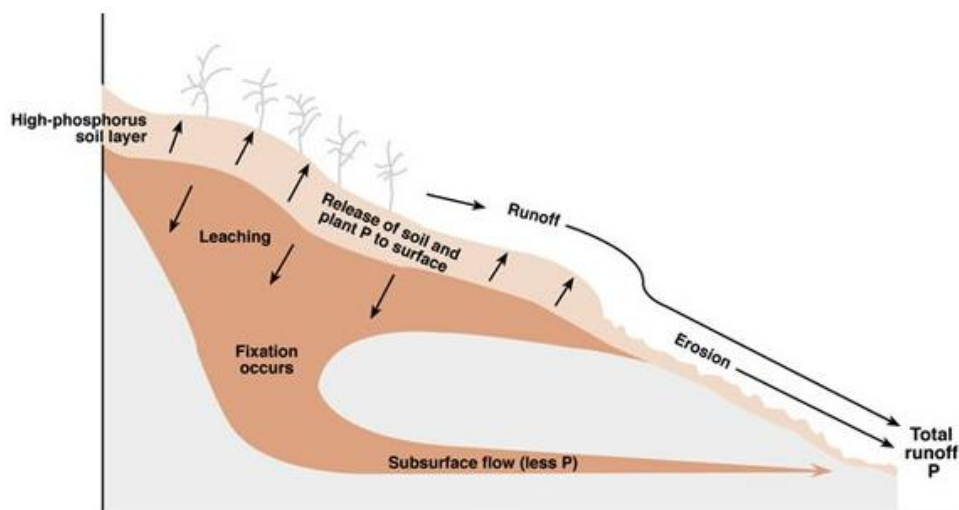


Figure 4: Natural Process by which Phosphorus can Enter a Water Body (Sharpley)

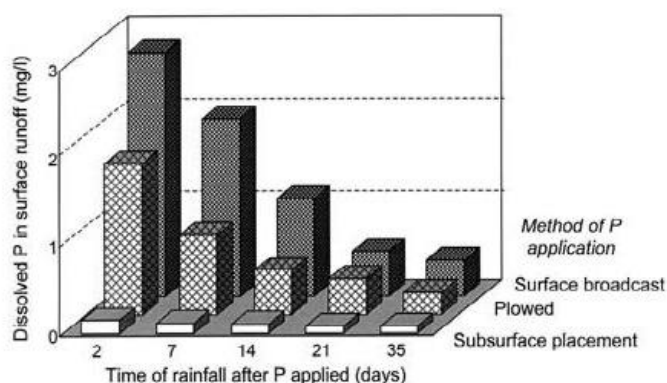


Figure 5: Dissolved P in Surface Runoff after Rainfall (*Septic Systems Contribution to Phosphorus in Shallow Groundwater: Field-Scale Studies Using Conventional Drainfield Designs*, 2017)

In addition to fertilizer usage, there are other ways that phosphorus can enter a water body. For example, it can enter groundwater through leaking septic systems, which is currently a problem in Tyngsborough's commercial district that borders Nashua. This is especially prevalent in areas with high groundwater tables and can occur with either drip dispersal or gravel trench systems (see Figures 6 and 7). Currently, an estimated 25% of the US population is on septic, so it is important to understand, monitor, and mediate how nutrient-rich effluent enters the groundwater and affects the water bodies into which it flows (*Septic Systems Contribution to Phosphorus in Shallow Groundwater: Field-Scale Studies Using Conventional Drainfield Designs*, 2017).

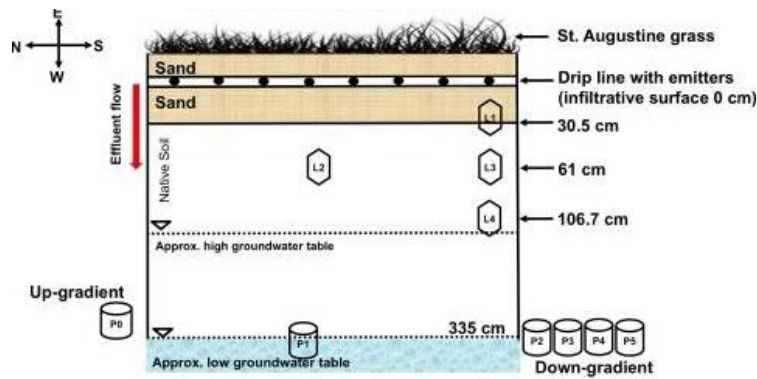


Figure 6: Drip Dispersal Drainfield (*Septic Systems Contribution to Phosphorus in Shallow Groundwater: Field-Scale Studies Using Conventional Drainfield Designs*, 2017)

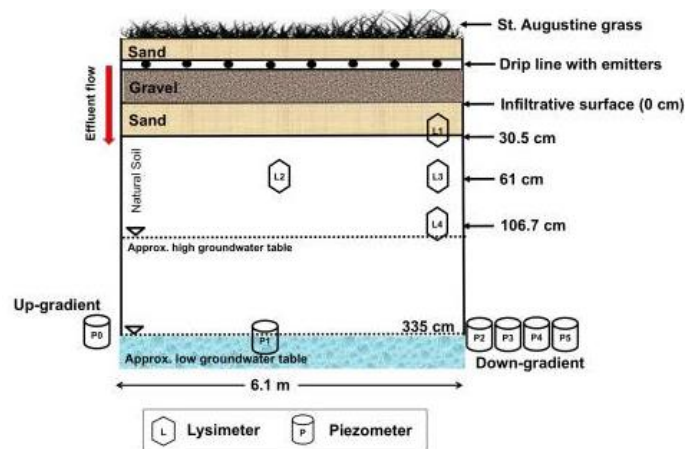


Figure 7: Gravel Trench Drainfield (*Septic Systems Contribution to Phosphorus in Shallow Groundwater: Field-Scale Studies Using Conventional Drainfield Designs*, 2017)

## 2.4 The Role of Phosphorus in Balanced and Imbalanced Systems

Orthophosphates are typically produced via natural processes in the water, but untreated/partially treated sewage, runoff, and fertilizers contribute to their presence in the environment. This form is usable for plants and can be measured by testing for total phosphate. Phosphates are necessary for formation of adenosine triphosphate (ATP), deoxyribonucleic acid (DNA), and ribonucleic acid (RNA), which are all critical for forming cell membranes, plant walls, and cellular energy (*Phosphorus and Water*). ATP is important for the storage and usage of energy, and is also involved in the Krebs Cycle (the process by which living cells generation energy during aerobic

respiration), shown in Figure 8. DNA and RNA are both chains of nucleotides that are essential for coding, decoding, regulation, and expression of genes.

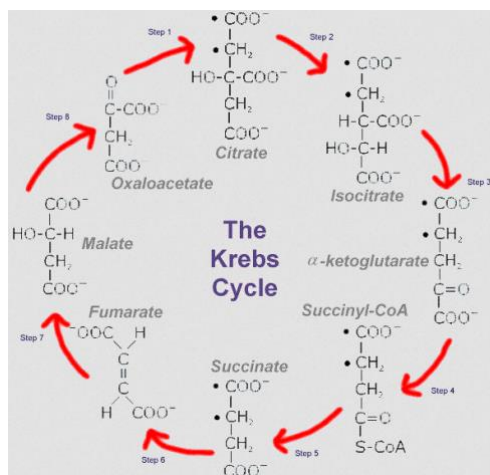


Figure 8: The Krebs Cycle (Oram, 2020)

While phosphates are non-toxic to humans and animals, they can pose health threats if present in high concentrations, typically through the form of digestive issues, and can cause eutrophication of water bodies over just a few decades. In general, phosphate stimulates growth of plankton and aquatic plants, which serve as the base of the food chain; because of the increase in algae and phytoplankton populations due to more available phosphorus, there will be an overall increase in the frequency of photosynthesis. Additionally, phytates, which are indigestible, will be more readily available, and they reduce absorption of other nutrients and wind up in sewage and waterways.

While increased phosphate levels will initially increase overall productivity and biodiversity of an aquatic system, it will eventually lead to a build-up of phosphate in the water. This accelerates the aging process of the water body and causes eutrophication, which is “enhanced production of primary producers resulting in reduced stability of the ecosystem” (Oram, 2020). The aging process often results in major water quality fluctuation and blooms of cyanobacteria. In short, eutrophication creates an imbalance in the consumption and production processes in an ecosystem, with a higher rate of production, as shown in Figure 9. To combat this, more phytoplankton and vegetation arise at a rate higher than what can be consumed in the ecosystem, which leads to anoxic water (via decomposition), lower biodiversity, lower available dissolved oxygen, and toxic algal blooms. Generally, development of plankton depends on availability of light, nutrient



concentrations, and the presence of organic solutes, in addition to temperature and pH ranges. With more nutrients available, there are fewer limitations on their growth.

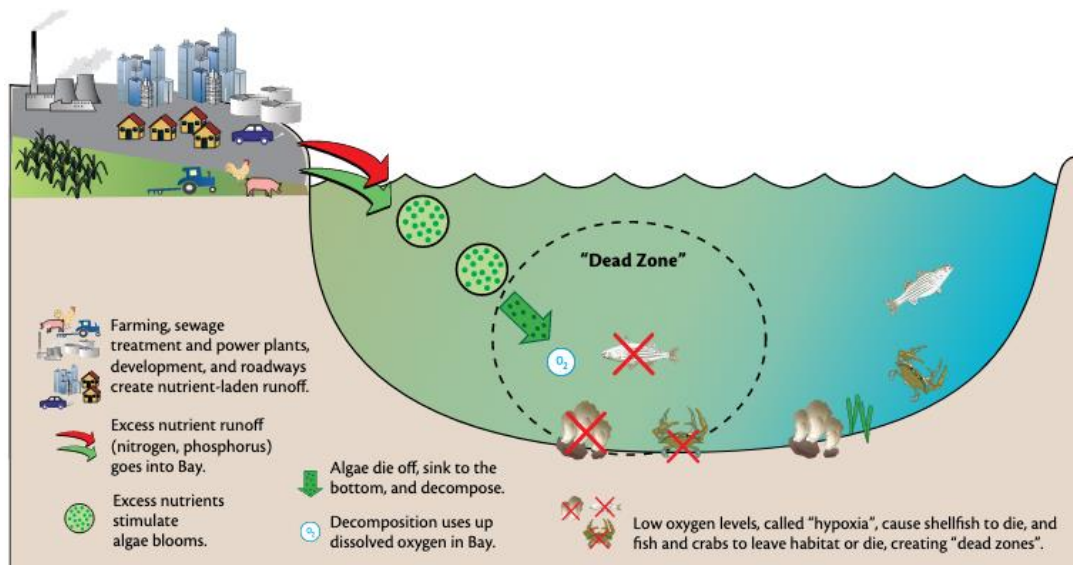


Figure 9: Processes contributing to severely low dissolved oxygen levels (hypoxia) in the Chesapeake Bay (*What Forecasting Dead Zones Teaches Us about Chesapeake Bay*, 2018)

There are two main conditions under which natural cycles function: aerobic (with oxygen) and anaerobic (without oxygen). Under aerobic conditions, an excess of phosphate creates an imbalance in natural cycles with an overproduction of water plants and algae. It also causes lower-level plants to die when surface-level plants and algae block sunlight from reaching lower depths. Bacteria then decompose the organic waste, which consumes oxygen, and releases more phosphate. Under anaerobic conditions, addition of phosphates may cause all of the oxygen to be consumed by bacteria trying to decompose organic waste. Because the initial conditions are different, the end products are also different, such as carbon being converted to methane gas and sulfur being converted to hydrogen sulfide gas (some of which will be precipitated as iron sulfide). The iron phosphate precipitate will eventually be released from the sediments, making the phosphate available and perpetuating the growth and decay cycle. This significantly accelerates the eutrophication process.

## 2.5 Cyanobacteria (Blue-Green Algae) and Dead Zones

Cyanobacteria are single-celled prokaryotes often found in freshwater areas with high concentrations of nutrients and temperatures. These algae, which form from the aforementioned

imbalance of elevated phosphorus levels, arise in huge blooms that can cause skin irritation, liver damage, and even death. They also usurp available dissolved oxygen, suffocating aquatic organisms by causing hypoxic/anoxic conditions, which lead to dead zones, shown in Figure 10.

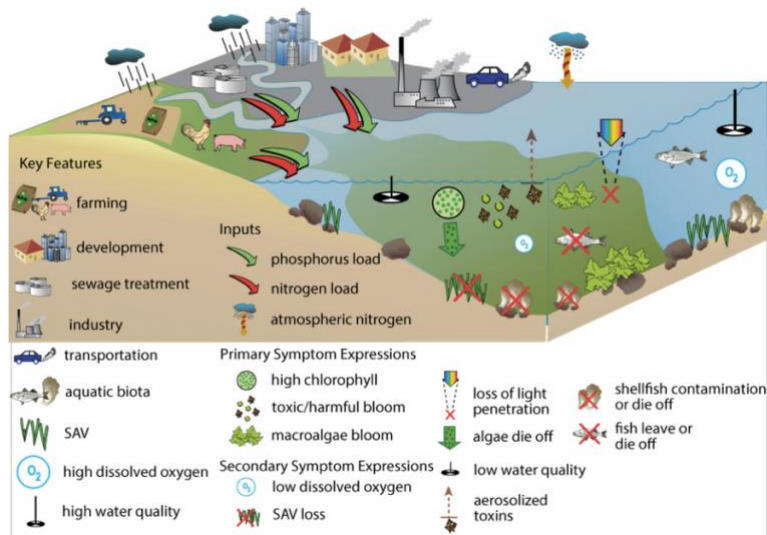


Figure 10: Forecasting dead zones in the Chesapeake Bay (*What Forecasting Dead Zones Teaches Us about Chesapeake Bay*, 2018)

Dead zones can be identified both visually and chemically. Initially, various sampling (which should be done regularly for reporting water quality to satisfy MS4 Permit requirements) can show warning signs that a water body is imbalanced or becoming unhealthy (such as low dissolved oxygen and high concentrations of contaminants). As time goes on, these areas become devoid of life and become clear.

## 2.6 Real-Life Application

As stated previously, the presence of phosphorus in small concentrations is critical for the basics of cell formation and biological processes. However, excess phosphorus, which is supposed to be the limiting reactant, encourages overproduction of algae and plant life, which utilize oxygen in both life and death (*Indicators: Phosphorus*, 2017). Minimizing phosphorus application and runoff is important not only to the environment, but also for town budgets, which may not have the funds necessary to continuously provide treatment for high phosphorus concentrations. It is also important to ensure that the town is abiding by its NPDES MS4 permit in order to continue legally discharging into the Merrimack River.



The addition of phosphorus via fertilizer has been identified as resulting in higher agricultural yield. On average, it is estimated that 15 million tons of phosphorus are lost annually in agriculture (primarily due to erosion runoff) and another 8 million tons are lost via runoff from arable land (Guignard, 2017). Case studies, such as one done in Cape Cod, Massachusetts, also show that phosphorus migrates with groundwater flow, which then discharges into surface water (*Phosphorus and Water*). While wetlands serve as natural ‘sinks’ for phosphorus, there are many wetlands in the United States that have either been drained or negatively affected in a way that makes them not as efficient as they were in their original state.

## 2.7 Point Source and Nonpoint Source Pollution

Phosphorus comes from many different sites and may be classified as entering ground or surface water through either point sources or nonpoint sources (which are usually responsible for about 90% of phosphorus runoff) (Carpenter, 1998). Table 1 identifies several sources of point and nonpoint pollution.

Table 1: Sources of Point and Nonpoint Pollution (Carpenter, 1998)

Sources of Point and Nonpoint Pollution	
Point Sources	Nonpoint Sources
<ol style="list-style-type: none"> <li>1. Wastewater effluent (municipal and industrial)</li> <li>2. Runoff from waste disposal sites, mines, oil fields, and animal feed lots directed to single discharge</li> <li>3. Storm sewer outfalls from cities with more than 100,000 people</li> <li>4. Runoff from construction directed to single discharge</li> <li>5. Overflows from combined storm/sanitary sewers</li> </ol>	<ol style="list-style-type: none"> <li>1. Runoff from agriculture, pastures, urban areas with populations of less than 100,000 people</li> <li>2. Leakage from failed septic systems</li> <li>3. Logging, wetland conversion, and atmospheric deposition</li> </ol>

The benefit of point source pollution is that they are typically continuous (constantly contributing) and therefore easier to trace and identify, while nonpoint source pollution can come from large areas which are difficult to control and narrow down the cause of runoff. Despite the difficulty, it is important to identify, sample, and address any possible high contributors.

## Chapter 3: Methodology

The goal of this project was to ensure that Tyngsborough is able to keep its MS4 Permit, to protect the well-being of the general environment, aquatic life, and water bodies, and to serve as the baseline for any phosphorus-related projects by providing a series of recommendations for analysis and treatment. Several key objectives were identified to meet this goal and make this report useful and successful:

1. Use aerial maps to identify potential sources of phosphorus discharge into the Merrimack River
2. Determine theoretical phosphorus loading from Tyngsborough using current zoning loadings provided in the Massachusetts Small MS4 General Permit, Appendix F
3. Use Tyngsborough topography GIS data to analyze slopes and determine where to collect samples at nonpoint sources
4. Identify and develop appropriate plans to reduce phosphorus levels in the Merrimack River within the town of Tyngsborough's borders, specifically at the selected sites (these plans may be found in Chapter 5)

This section will include the reasoning behind which sites were selected, which include both point and nonpoint phosphorus sources. Additionally, recommended sites at nonpoint sources were determined using Tyngsborough's topography GIS data.

### 3.1 Site Selection

As a first step in understanding the phosphorus loads entering the Merrimack River from Tyngsborough, a series of probable site sources were identified. Because there was no sampling done for this particular project, phosphorus loads from the sites had to be estimated. Sites were selected based on local knowledge of the area (based on twenty years of living around these locations) and recommendations for generic potential sources based on EPA and ESA data. These sites either border the Merrimack River or drain in such a way that the runoff is directed towards the river via impervious surfaces; they are presented via satellite imagery (updated in 2020). The main criteria for selecting these particular sites include:

1. Ongoing construction sites along the Merrimack River
2. Widespread clear-cut areas along the Merrimack River
3. Areas alongside the Merrimack River with little-to-no vegetation or barriers
4. Past and present landfill sites
5. Locations which have runoff into local waterbodies which flow directly into the Merrimack River
6. Areas with septic systems

### 3.1.1 Active Construction Sites

While the town of Tyngsborough's website has a "Town Projects" page, it is not up-to-date (the last project reported was on June 10<sup>th</sup>, 2019, even though there are many other ongoing projects). Therefore, the construction sites identified were based on personal knowledge of the duration of the project and proximity to the Merrimack River.

### 3.1.2 Clear-Cut Sites

Both selected sites are country clubs (Vesper Country Club and Tyngsboro Country Club) located right along the Merrimack River. Neither of these locations has disclosed any information regarding their pesticide/herbicide/fertilizer use or waste, so it is difficult to quantify just how much phosphorus they may be contributing.

### 3.1.3 Former Landfill Sites

It is known that landfill sites can leach into groundwater systems which then flow into surface waters. Given the decomposition that can occur within landfills, it is possible that there is phosphorus (among other elements) that may still be flowing into the Merrimack via groundwater flow. There are two main former landfill sites that were identified as potentially posing issues.

### 3.1.4 Agricultural Site

Parlee Farms, which has been around since 1987, is located right along the Merrimack River in Tyngsborough. It is a fruit orchard and does not produce any dairy products, although there are a few animals on the property (such as goats, rabbits, and chickens). The farm is owned by Farmer Mark, who has implemented Integrated Pest Management (IPM) methods, crop rotation, and

annual soil and tissue analyses to monitor crop health. Additionally, Parlee Farm has a Network for Environment and Weather Applications (NEWA) weather station that transmits data to Cornell University to model and forecast when to make changes in pest management to avoid over-treatment. Despite these methods, Parlee's still utilizes organic-based and synthetic pesticides. While the crop health may be monitored, it is not stated whether water close to that area is monitored for elevated nutrient levels.

### 3.1.5 Septic System Site

The relevant area with known septic system infrastructure is in Tyngsborough's commercial district located along the border with Nashua, NH. It is likely that, because many restaurants are on septic, there is some phosphorus contribution to the Merrimack, which runs behind the buildings located in this area. The land is sloped at such an angle that there is a direct path from where these systems are to the river. There is no vegetation in this area to mitigate the runoff from the roads or leakage from the septic systems.

## 3.2 Phosphorus Load Estimates

Even though there is no current collection of phosphorus load data, estimates for TMDLs can be calculated based on data provided in the Massachusetts Small MS4 General Permit, estimates for phosphorus concentrations in runoff from different kinds of sites (see Table 3), and area values for each of the sites (see Table 2). The area values were multiplied by the estimated annual phosphorus load per land area to find an estimated load for each site. For these calculations, the following equation was used to estimate phosphorus loading for each of the sites with known areas:

$$TMDL = \Sigma WLA + \Sigma LA + MOS$$

Where: WLA = Sum of wasteload allocations (point sources)  $(\frac{\text{mass of pollutant}}{\text{unit time}})$

LA = Sum of load allocations (nonpoint sources)  $(\frac{\text{mass of pollutant}}{\text{unit time}})$

MOS = Margin of safety (estimated at 20%)

## 3.3 Recommended Sampling Locations Based on Topography (GIS)

Nonpoint sources do not discharge to a single location, so it can be difficult to determine where to conduct water sampling. The best way to estimate where the runoff may be flowing to can be done

by analyzing topography data; Tyngsborough has a publicly accessible GIS database available online, which provided the contour maps used to narrow down where sampling should be performed. The phosphorus concentrations from these sites can be measured using primarily soil and leaf analyses (which would involve testing kits and potentially sending data off for lab analysis) or water sampling at the runoff locations identified through slope analysis. The contour maps available through the GIS database provide information on the sites' terrains, particularly the slope distribution. Because of gravity, the water will run to the points of lowest elevation, which is where sampling should be done to measure the phosphorus runoff from the sites.

### 3.4 Reducing Phosphorus Levels in the Merrimack River

Reducing phosphorus levels in a river is more complex than in a water body with a limited area (such as a pond). Regardless, elevated phosphorus concentrations still negatively affect the water quality and overall health of the ecosystem, which need to be addressed. Since wastewater facilities and various sites discharge into the river, it is necessary to develop reduction plans for both sets of sources. Wastewater facilities can be treated chemically prior to discharging into the Merrimack River, and sites can implement physical treatment (such as silt fences) and phosphorus reduction plans (such as applying less fertilizer); the methods proposed in Chapter 5 incorporate these considerations.

## Chapter 4: Results

This section covers a series of identified potential sources of high phosphorus contribution and estimates for phosphorus loads. The site selections were chosen based on the Methodology (see Chapter 3) and are organized by location rather than by importance (i.e. the first site is located closest to the Nashua, NH/Tyngsborough, MA border, and the last site located is closest to the Tyngsborough, MA/Lowell, MA/North Chelmsford, MA border). Additionally, this section includes recommendations for areas at nonpoint sources where runoff should be sampled based on topography data and estimates for the phosphorus loads.

### 4.1 Site Selection

For reference, Figure 11 shows an overview map of Tyngsborough, including the town boundary and the 01-MER sampling station:

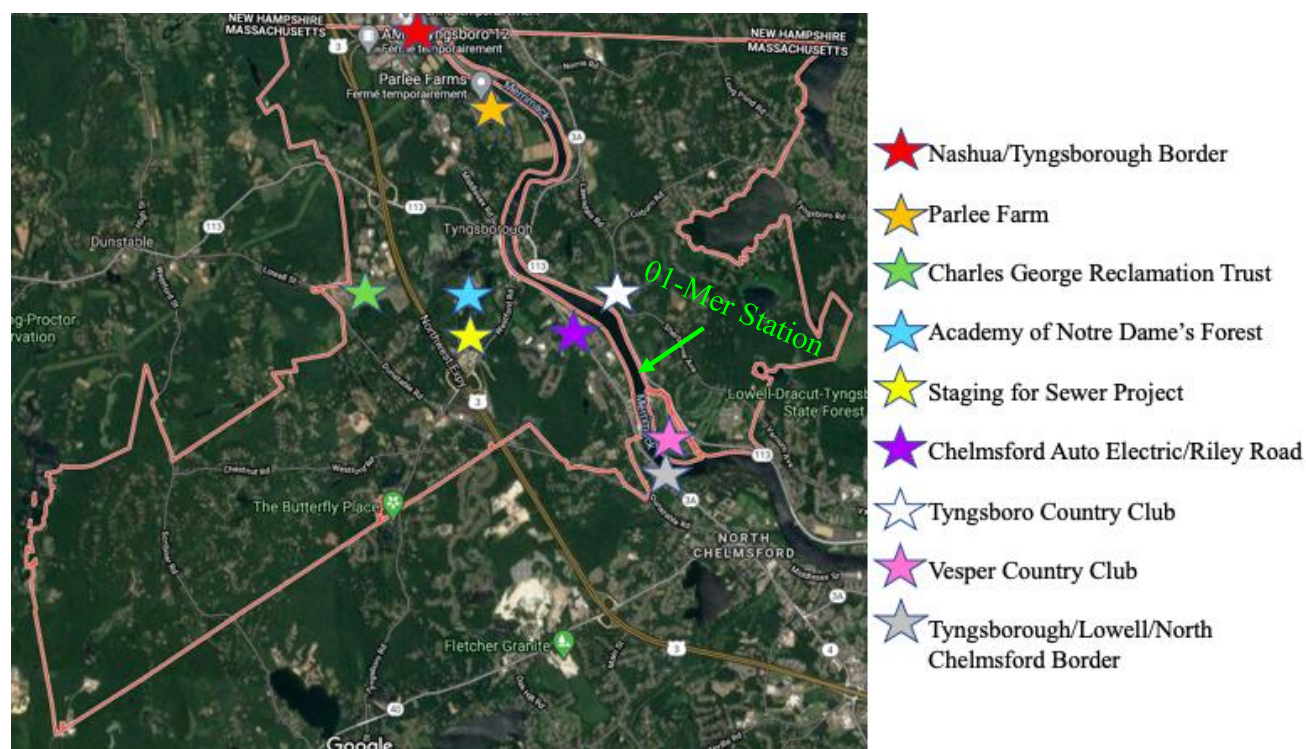


Figure 11: Town of Tyngsborough Border with Starred Selected Sites and 01-MER Station

The town border is important to analyze for a variety of reasons. First, the Merrimack River runs behind a major commercial district in Nashua (which usually means lots of construction, paving of parking lots/roads, seasonal road treatment, such as ice melt, and runoff from parking

lots/roads). Second, the commercial district was built on top of a former landfill that can leach directly into the Merrimack. Third, it is necessary to sample the influent at the border to get initial conditions and compare these data to those collected at other points to see whether this commercial area is a significant contributor to elevated phosphorus levels. Lastly, this area is known to use septic systems, which the EPA has identified as a regular source of phosphorus runoff.

#### 4.1.1 Nashua, New Hampshire and Tyngsborough, Massachusetts Border on Merrimack River and Parlee Farm

Parlee Farm is shown in Figure 12. It is common knowledge that farms use fertilizers to ensure high crop yield. The use of fertilizers is known to provide a certain amount of necessary nutrients to the crops with the rest leaving the area in the form of runoff. For Parlee Farm, the runoff runs directly into the Merrimack. It would be wise to sample near this location to see whether the quantity of fertilizer being used is negatively contributing to higher phosphorus levels.



Figure 12: Nashua, New Hampshire and Tyngsborough, Massachusetts Border on Merrimack River (left) and Parlee Farm (right)

#### 4.1.2 Charles George Reclamation Trust

Charles George Reclamation Trust, shown in Figure 13, is a former landfill and hazardous waste site that released an estimated 1000 pounds of mercury and 2500 cubic yards of chemical waste into groundwater that contaminated wells at the Cannongate Condominium, Flint Pond Marsh, and



Flint Pond. It was found that several aquatic species in these areas contained high levels of mercury and arsenic. Although it now serves as a solar farm, there is still potential for leaching into Flint Pond (which is severely polluted), which feeds into the Merrimack River.



Figure 13: Charles George Reclamation Trust

#### 4.1.3 Academy of Notre Dame Forest and Staging for Sewer Project Phase II

Figure 14 shows the Academy of Notre Dame Forest and the staging area for Tyngsborough's Sewer Project Phase II. The forest on the Academy of Notre Dame's property was formerly packed full of plant and animal diversity until the property, which was originally part of the Academy of Notre Dame's campus, was illegally sold to an outside company which cleared out the majority of the vegetation. Given that this area is on a very steep hill near the bottom of a commercial district, there is much less of a natural sink for nutrient runoff (with similar reasons to those at the NH/MA border). This road provides a direct pathway to the Merrimack, with only a railroad track separating the river from the road.

The staging site has undergone a series of changes over the last decade. It was initially left as wild land (as is displayed in Figure 14) but was cleared years ago; it was then allowed to regrow to a secondary succession state, and was cleared again during summer 2019 for staging of equipment and vehicles for Tyngsborough's Phase II of the sewer project (which is moving Tyngsborough's commercial district on the border with Nashua from septic to town sewer. The leaching of septic systems into the Merrimack is certainly a concern given the area but is actively being addressed).





Figure 14: Academy of Notre Dame Forest (left) and Staging for Sewer Project Phase II (satellite image not up-to-date) (right)

#### 4.1.4 Chelmsford Auto Electric and Riley Road

Figure 15 shows the site located between Chelmsford Auto Electric and Riley Road, which is situated right along the Merrimack River. There has been ongoing construction in this area for a few years, which is known to contribute to elevated mineral and nutrient deposition in surrounding water bodies. The lack of vegetation minimizes the natural filtration of phosphorus, nitrogen, and other elements prior to entering the Merrimack River, thus contributing to higher phosphorus loads.

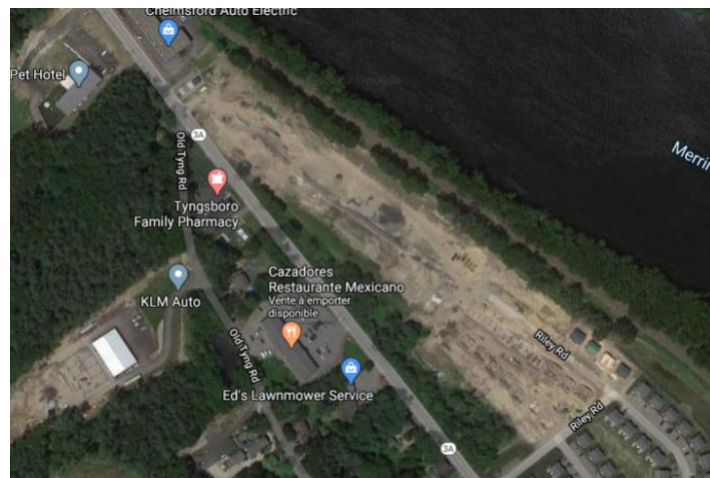


Figure 15: Chelmsford Auto Electric and Riley Road

#### 4.1.5 Tyngsboro Country Club and Vesper Country Club

Figure 16 shows the Tyngsboro and Vesper Country Clubs. Country clubs are well known for their use of fertilizers to maintain high quality turf. Additionally, most country clubs utilize a sprinkler/irrigation system to keep up the appearance of the turf. The combination of frequent phosphorus-containing fertilizers and frequent irrigation is the perfect recipe for highly concentrated phosphorus runoff. With little-to-no natural vegetative barriers on the flat landscape, this runoff flows directly into the Merrimack River.

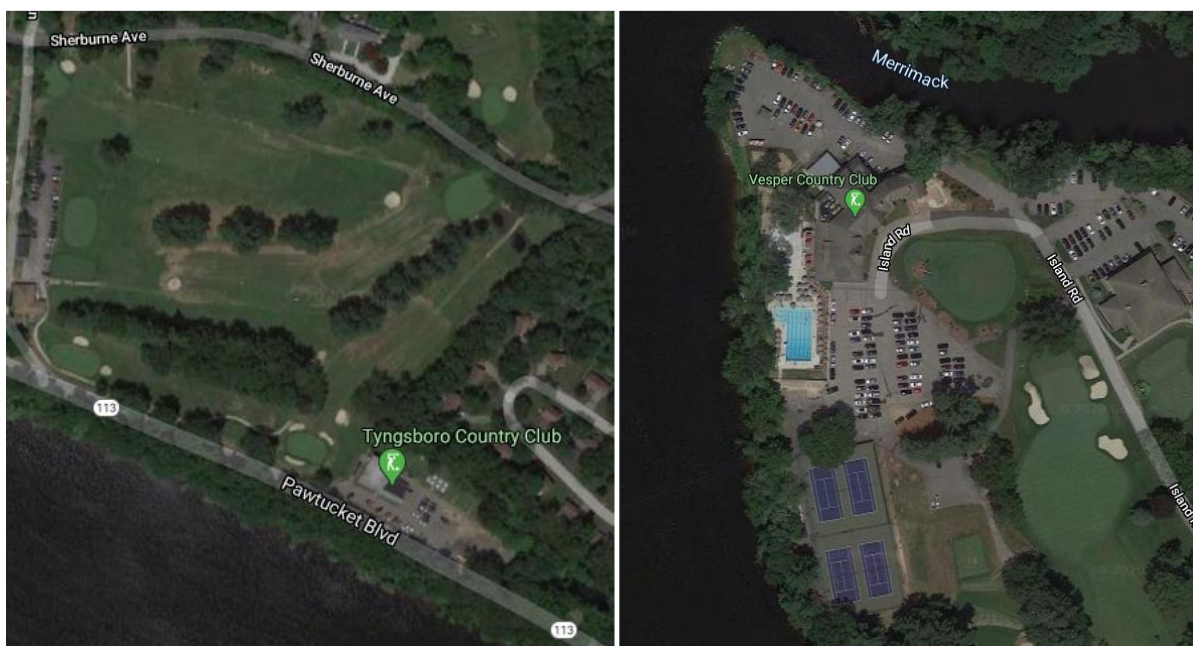


Figure 16: Tyngsboro Country Club (left) and Vesper Country Club (right)

Located on Tyngs Island, Vesper Country Club, formerly a boat club, is surrounded on two sides by the Merrimack River. The Tyngsboro Country Club is bordered on only one side by the Merrimack. Both of these locations have massive parking lots, high visitor traffic, and runoff that flows directly into the river, as there is practically no natural barrier between the terrain and the water.

#### 4.1.6 Tyngsborough/Lowell/North Chelmsford Border

Figure 17 shows an overview of Tyngsborough's town border in relation to the Merrimack River. Just as it is critical to sample the influent to measure what Tyngsborough is receiving, it is

important to sample the effluent as well to monitor what Tyngsborough is discharging. If the influent phosphorus concentration is higher than the effluent concentration, this suggests that Nashua, NH, may be contributing more phosphorus than Tyngsborough is. However, if the effluent phosphorus concentration is higher than the influent concentration, this suggests that Tyngsborough may be significantly contributing to elevated phosphorus levels. This will be a difficult area to sample due to the border alignment, but it should be done nonetheless. The sampling done at the end of Tyngs Island should suffice for this site. It is recognized that the loads from Tyngsborough may be difficult to discern from samples at locations upstream and downstream of Tyngsborough.

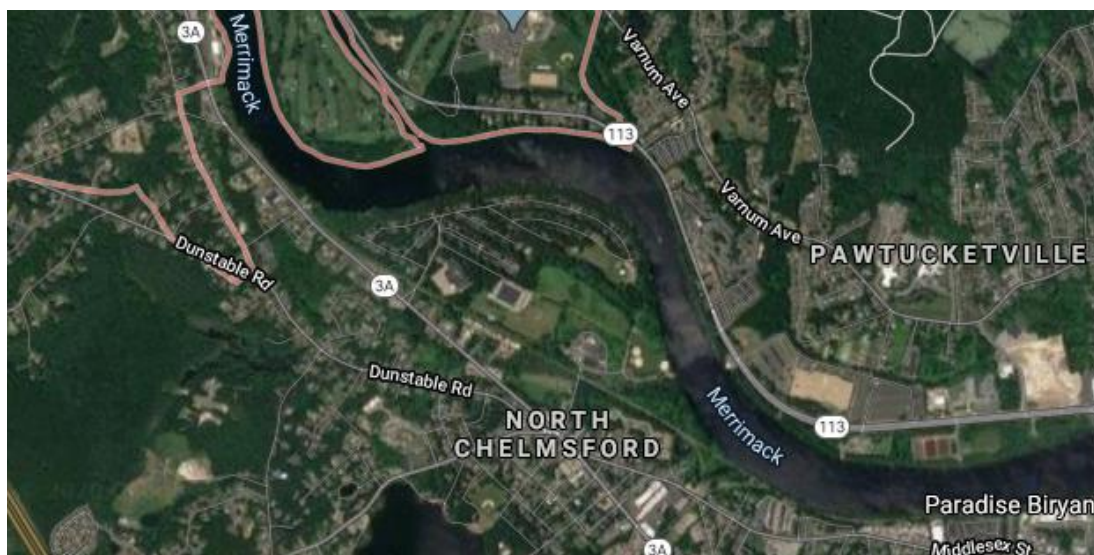


Figure 17: Tyngsborough/Lowell/North Chelmsford Border

Sampling at both ends of the Tyngsborough border is critical for getting baseline conditions and an estimate of whether Tyngsborough is contributing to higher phosphorus levels and will provide data determining whether Tyngsborough's effluent into Lowell meets legal requirements. However, it would be inaccurate to assume that there is no ongoing issue with additional phosphorus in the river solely based on data collection at two locations. It is thus important to conduct a series of sampling collections at multiple sites over the span of the river to ensure that the data taken provides peaks and lows of phosphorus levels to better narrow down where to implement more effective preventive measures and begin site cleanup.



## 4.2 General Phosphorus Loads for Each Site

This section includes TMDL calculations for all sites whose areas have been determined.

### 4.2.1 Site Areas

Area can be estimated for sites by either satellite imagery (with scale) or by land surveyors; due to financial limitations for this project, the area estimations will be done via satellite imagery and known lot sizes will be taken from Tyngsborough's GIS database and the sites' websites ("Town of Tyngsborough, MA", 2020). Area estimations cannot be calculated for measurements at the borders or for the staging of the sewer project, since the satellite imagery has not been updated. Known areas given from business sites are listed as such; all area values are listed in Table 2.

#### 4.2.1.1 Chelmsford Auto Electric/Riley Road Site

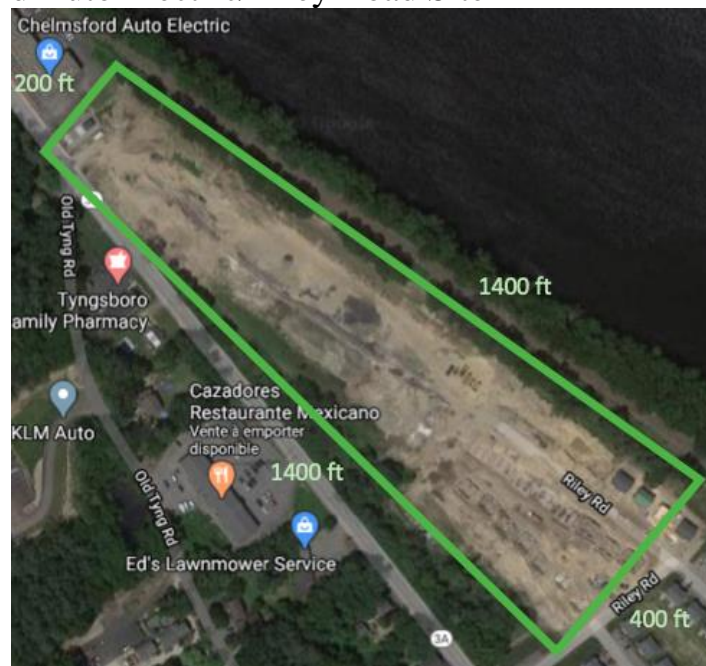


Figure 18: Chelmsford Auto Electric/Riley Road Area Plot Estimation

The shape of the site in Figure 18 is approximately equal to the dimensions of a trapezoid. Using the scale provided on Google maps, the area of this site may be estimated as:

$$\text{Area of a Trapezoid} = \frac{a + b}{2} \times h$$

$$a^2 + b^2 = c^2 \rightarrow a^2 + 400^2 = 1400^2 \rightarrow h = 1341.64 \text{ ft}$$

$$\text{Land Area} = \frac{400 \text{ ft} + 200 \text{ ft}}{2} \times 1341.64 \text{ ft} = 402,492 \text{ ft}^2 \rightarrow 9.24 \text{ acres}$$

#### 4.2.1.2 Academy of Notre Dame Forest



Figure 19: Academy of Notre Dame Forest Area Plot Estimation

The Academy of Notre Dame campus spreads across 200 acres (“Town of Tyngsborough, MA”, 2020), but there is no estimate given for the area of the forest alone. Because there is no information given about the property boundaries, the forest area was estimated by subtracting the area that the school buildings cover from the total acreage (the areas that were subtracted are outlined in green in Figure 19). The school building and tennis courts can be approximated as rectangles, while the baseball fields, track field, and parking lot can be approximated as a collective ellipse.

$$\text{Area of a Rectangle} = l \times w$$

$$\text{Area}_1 = 233.33 \times 100 = 23,333 \text{ ft}^2$$

$$\text{Area}_2 = 500 \times 300 = 150,000 \text{ ft}^2$$

$$\text{Area of Ellipse} = \pi \times a \times b$$

$$\pi \times 1100 \times 600 = 2,073,451.15 \text{ ft}^2$$

$$\text{Total Non – Forested Area} = 2,246,784.15 \text{ ft}^2 \rightarrow 51.58 \text{ acres}$$

$$\text{Total Forested Area} = 200 - 51.58 = 148.42 \text{ acres}$$

Table 2: Areas for Site Selection

Site	Lot Size (acres)
Nashua/Tyngsborough Border	--
Parlee Farm	93
Charles George Reclamation Trust	69
Academy of Notre Dame Forest	148
Staging for Sewer Project	--
Chelmsford Auto Electric/Riley Road	9
Tyngsboro Country Club	19
Vesper Country Club	178
Tyngsborough/Lowell/North Chelmsford Border	--

#### 4.2.2 Phosphorus Load Estimates

The following equation is typically used to estimate phosphorus loading for sites with known areas and point and nonpoint source allocations:

$$TMDL = \Sigma WLA + \Sigma LA + MOS$$

Where: WLA = Sum of wasteload allocations (point sources)  $\left(\frac{\text{mass of pollutant}}{\text{unit time}}\right)$

LA = Sum of load allocations (nonpoint sources)  $\left(\frac{\text{mass of pollutant}}{\text{unit time}}\right)$

MOS = Margin of safety

For this report, the equation was revised to fit the known data (areas and estimates of average phosphorus runoff values in pounds per acre); Table 2 contains the area values used to find the TMDLs. Because there is no specific data available, there are estimates that can be used for these calculations based on previously collected phosphorus runoff data from the Eutrophication case study (Lee, 1973). Table 3 provides estimates of total phosphorus loads from each designated zoning area, but does not list the expected runoff value for each site.

Table 3: Phosphorus Loading Based on Zoning Districts in Tyngsborough (*Massachusetts Small MS4 General Permit, 2020*)

<b>Zone</b>	<b>Phosphorus Load (<math>\frac{lbs}{year}</math>)</b>
Industrial	1799
Commercial	817
Low Density Residential	3236
Medium Density Residential	173
High Density Residential	17

#### 4.2.2.1 Parlee Farm

The New England Tree Fruit Management Guide (2014) tests various orchard soils, compares the phosphorus values to their harvest yield, and compiles information to make recommendations for phosphorus levels. The goal is to educate farmers based on real results to prevent over-treatment; additionally, there are leaf analyses that may be performed to provide an average percent of nutrient usurpation. Leaf analyses performed across New England suggest that the desired phosphorus level for fruit orchard plants is between 0.13-0.33%.

Although Parlee Farm does not state on their website how much fertilizer is applied annually, estimates show that runoff from agricultural sites contains about 0.003 lbs of phosphorus per acre annually (Lee, 1973). Because Parlee Farm covers 93 acres, this means that the phosphorus from runoff is approximately 0.279 lbs of phosphorus every year. It is located in an R1 zoning district, which is classified as low density residential.

$$TMDL = (\text{Site Area} \times \text{Phosphorus in } \frac{lbs}{acre}) + (20\% \text{ of Est. Phosphorus Runoff})$$

$$TMDL = (93 \text{ acres} \times 0.003 \frac{lbs}{acre}) + 0.2(0.279 \frac{lbs}{year})$$

$$TMDL = 0.33 \frac{lbs}{year}$$

#### 4.2.2.2 Charles George Reclamation Trust

Charles George Reclamation Trust is located in the R1 low density residential zoning district. The phosphorus source at this site is likely from groundwater, since it is a former landfill. It is estimated that groundwater contributes an average of 0.059 lbs of phosphorus per acre annually (Lee, 1973).

$$TMDL = (69 \text{ acres} \times 0.059 \frac{\text{lbs}}{\text{acre}}) + 0.2(4.071 \frac{\text{lbs}}{\text{year}})$$

$$TMDL = 5 \frac{\text{lbs}}{\text{year}}$$

#### 4.2.2.3 Academy of Notre Dame Forest

The Academy of Notre Dame is located in the B2 zoning district, which is in the business and commercial district. For this estimate, this will be considered as a commercial area. Urban runoff is estimated as 0.8 lbs of phosphorus per acre annually (Lee, 1973).

$$TMDL = (148 \text{ acres} \times 0.8 \frac{\text{lbs}}{\text{acre}}) + 0.2(118.736 \frac{\text{lbs}}{\text{year}})$$

$$TMDL = 142 \frac{\text{lbs}}{\text{year}}$$

#### 4.2.2.4 Chelmsford Auto Electric/Riley Road

The plot between Chelmsford Auto Electric and Riley Road is located in the I1 district, which is industrial, and is bordered by a B1 zoning district (business and commercial), which will be considered a commercial area. Urban runoff is estimated as 0.8 lbs of phosphorus per acre annually (Lee, 1973).

$$TMDL = (9 \text{ acres} \times 0.8 \frac{\text{lbs}}{\text{acre}}) + 0.2(7.392 \frac{\text{lbs}}{\text{year}})$$

$$TMDL = 9 \frac{\text{lbs}}{\text{year}}$$

#### 4.2.2.5 Tyngsboro Country Club

Tyngsboro Country Club is not classified within the categories listed in Table 4. However, it is surrounded by R1 and R3 zoning districts, which are low and high density residential zones. Rural runoff is estimated as 1.975 lbs of phosphorus per acre annually (Lee, 1973).



$$TMDL = (19 \text{ acres} \times 1.975 \frac{\text{lbs}}{\text{acre}}) + 0.2(37.15 \frac{\text{lbs}}{\text{year}})$$

$$TMDL = 45 \frac{\text{lbs}}{\text{year}}$$

#### 4.2.2.6 Vesper Country Club

Vesper Country Club is listed in an R1 (low density residential) zoning area. Rural runoff is estimated as 1.975 lbs of phosphorus per acre annually (Lee).

$$TMDL = (178 \text{ acres} \times 1.975 \frac{\text{lbs}}{\text{acre}}) + 0.2(351.313 \frac{\text{lbs}}{\text{year}})$$

$$TMDL = 422 \frac{\text{lbs}}{\text{year}}$$

### 4.3 Recommended Sampling Locations Based on Topography (GIS)

Although these locations may not be completely accurate, they are the best estimations that can be made without doing repetitive site visits. This section will focus on nonpoint sources, since sampling at point sources can be done at outfalls. The classifications of each location are specified in Table 4.

Table 4: Selected Site Classification

Site	Classification
Nashua/Tyngsborough Border	--
Parlee Farm	Nonpoint Source
Charles George Reclamation Trust	Nonpoint Source
Academy of Notre Dame Forest	Nonpoint Source
Staging for Sewer Project	Point Source
Chelmsford Auto Electric/Riley Road	Point Source
Tyngsboro Country Club	Nonpoint Source
Vesper Country Club	Nonpoint Source
Tyngsborough/Lowell/North Chelmsford Border	--

As is the nature with contour maps, data is not always listed directly on the lines in each plot; the lines were traced to find the slope values, often located further away from the sites. Based on

comparisons of these values, sampling locations for these sites were determined and indicated with stars. Stars indicate areas to sample for runoff effluent (lower elevations or water bodies on site).

#### 4.3.1 Parlee Farm

Parlee Farm is on a generally uniform slope that directs runoff into the Merrimack River, as shown in Figure 20. Initial soil and leaf analyses can also be conducted at these locations. Calculations in sampling results can help determine whether phosphorus runoff is infiltrating soil and effluent near the Merrimack River.



Figure 20: Contour Map for Parlee Farm

#### 4.3.2 Charles George Reclamation Trust and Academy of Notre Dame Forest

Runoff from Charles George Reclamation Trust, shown in Figure 21, flows into Flint Pond, which flows into the Merrimack River, so it is important to sample the effluent from this site. The terrain is clearly not as uniform as with Parlee Farm, but the issue with this site is more in the groundwater discharge rather than from the surface. Runoff from the Academy of Notre Dame Forest, also shown in Figure 21, was previously mitigated by plentiful vegetation which has since been mostly cleared. It can now flow into either Flint Pond or Uptons Pond, both of which flow into the Merrimack River. It is therefore necessary to sample at the indicated locations to understand the phosphorus loading from this site.

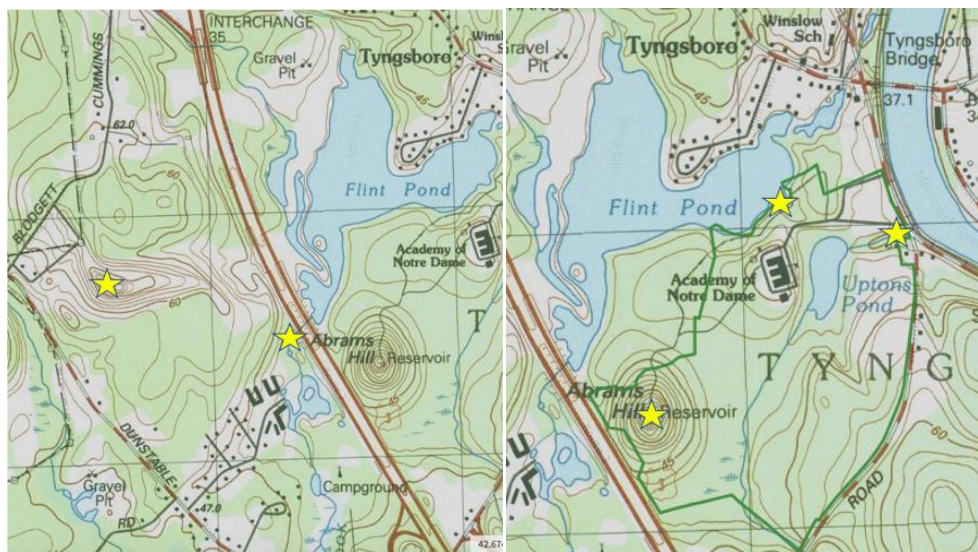


Figure 21: Contour Maps for Charles George Reclamation Trust (left) and for Academy of Notre Dame Forest (right)

#### 4.3.3 Tyngsboro Country Club and Vesper Country Club

Contour maps for both the Tyngsboro and Country Clubs are shown in Figure 22. The Tyngsboro Country Club borders the Merrimack River, so runoff on this site nearly directly flows right into it; a low elevation point can provide information for how much phosphorus is being directed towards the Merrimack River. For Vesper Country Club, which consists of a lot on Tyngs Island and an additional lot on the mainland, the likelihood of elevated phosphorus loading in the Merrimack is high. The site on Tyngs Island is at the edge of the island, which is also at the bottom of a slope. The other two sites are located at entrances to water bodies closest to the downstream end of the land plot.



Figure 22: Contour Maps for Tyngsboro Country Club (left) and Vesper Country Club (right)

## Chapter 5: Recommendations for Reducing Phosphorus Loads and Sampling Plan

This section covers recommendations to minimize phosphorus runoff, generic sampling procedures, sampling for Tyngsborough sites specifically, ways to address pre-existing phosphorus levels in the Merrimack River, and recommendations for site monitoring. Each of these sections covers both point and nonpoint source phosphorus loads.

### 5.1 Selected Site Classification

Because the aforementioned recommendations and procedures are based upon what kind of site is being addressed, it is necessary to classify the category into which the selected sites fall. As a reminder:

Table 4: Selected Site Classification

Site	Classification
Nashua/Tyngsborough Border	--
Parlee Farm	Nonpoint Source
Charles George Reclamation Trust	Nonpoint Source
Academy of Notre Dame Forest	Nonpoint Source
Staging for Sewer Project	Point Source
Chelmsford Auto Electric/Riley Road	Point Source
Tyngsboro Country Club	Nonpoint Source
Vesper Country Club	Nonpoint Source
Tyngsborough/Lowell/North Chelmsford Border	--

### 5.2 Preventive Measures for Point and Nonpoint Sources

Preventive measures are designed to identify a potential source of a problem and implement methods to mitigate or control the problem from reaching dangerous or unfixable levels. Financially, nitrogen and phosphorus pollution combined are detrimental to the US economy, diminishing property values and recreational uses of water at a loss of \$2.2 billion per year. Toxic algal blooms cost an additional \$82 million annually, primarily impacting public health and commercial fisheries. Currently, the EPA and MassDEP's NPDES Permit No. MA0100633 (2019) sets an average monthly limit of  $1.08 \frac{mg}{L}$  of phosphorus for areas discharging into the Merrimack River.

### 5.2.1 Point Sources

As noted previously, the majority of phosphorus in the Merrimack River has been identified as sourcing from sewer and wastewater infrastructure. Tyngsborough is in the process of replacing septic systems in its commercial district right along the Nashua/Tyngsborough border with connections to town sewer. Additionally, the application of alum and ferric chloride coagulants in wastewater treatment facilities can efficiently remove phosphorus, which have a removal efficiency of 89-93% at  $90 \frac{mg}{L}$  (and can also effectively remove total suspended solids and turbidity) (Ebeling, 2003). While initially expensive, this investment can reduce fines from the EPA and help to meet NPDES and MS4 Permit standards. Sites with directed nutrient runoff are also considered point sources and can be remediated through silt fences and catch basin inserts (such as the type displayed in Figure 23), which filter out nutrients in the catch basin prior to fully entering the stormwater drainage system.

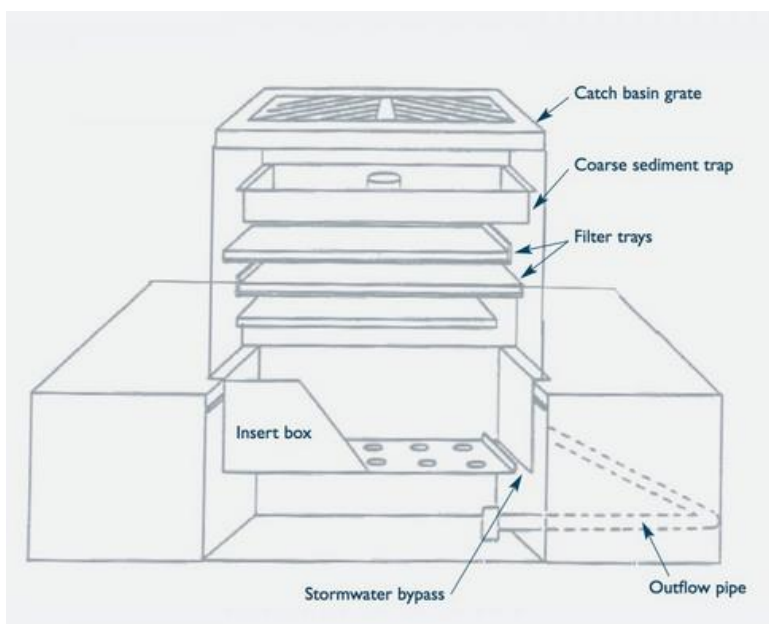


Figure 23: Example of Tray-Type Catch Basin Insert (Dickson, 2018)

Although there are no selected outfalls to sample for the chosen sites, future projects which map outfalls throughout Tyngsborough can use this data to limit phosphorus introduction into the Merrimack River at suspected problem outfalls.

Even though direct implementation of methods at sites to limit phosphorus introduction into wastewater is ideal, these methods are not always completely effective; therefore, it is important

to address phosphorus which has already made its way into wastewater effluent (and can discharge into the Merrimack River). One option to address phosphorus in effluent is a polymeric hydrogel, which can decrease phosphorus levels in wastewater effluents by 99% to less than 0.01 ppm. This gel is a novel phosphate binding crosslinked polyallylamine (PAA•HCl), which was formulated by crosslinking the chains with epichlorohydrin, and binds to phosphate anions in wastewater effluent; they can also be regenerated by the release of phosphorus with a 1N NaOH solution (Kioussis). Studies have shown that using alum and ferric chloride in coagulation-flocculation treatment are very efficient at removing total suspended solids and phosphorus, with 89-93% removal at  $90 \frac{mg}{L}$  doses after only five minutes of settling (Ebeling, 2003).

### 5.2.2 Nonpoint Sources

While each site will have a different prevention plan, there are general recommendations that can be made and implemented across fertilizer-dependent sites (i.e. agriculture) or sites with nutrient runoff (such as country clubs or construction sites):

1. Conducting soil and/or leaf tests to determine whether soils could use reduced phosphorus or even solely nitrogen-based fertilizers
2. Applying fertilizers in a restricted fashion
3. Using silt fences to minimize runoff
4. Installing infiltration basins near man-made impervious surfaces
5. Planting forests and riparian vegetation along riverbanks and shorelines and restoring wetlands, which will decrease the nutrient concentrations flowing into water bodies (case studies have shown that this has a success rate of reducing phosphorus loads by 50-85%)

When it comes to using fertilizers, there are efficient and ‘smart’ ways to minimize runoff through careful application that don’t require soil analysis data. These can include:

1. Using slow-release or enhanced efficiency fertilizers (such as Nutralene, Nitroform, Polyon, Duration, UMAXX, and HYDREXX, which can be used for decreasing phosphorus input since they primarily deliver nitrogen) (Torsiello, 2015)
2. Not treating around environmentally sensitive areas (such as around water)

3. Not applying within 48 hours of expected rainfall
4. Using light irrigation post-application
5. Not applying during late fall on dormant grass
6. Using multiple low-dose applications over a longer period of time instead of a high dose over just a few applications

There are a few other ways to prevent phosphorus runoff post-application. While limiting phosphorus input is the first step, it is important to address phosphorus in effluent. One option to address this involves landscape filters. Using funds from the USGA, researchers at Oklahoma State University designed replaceable landscape filters which prevent dissolved phosphorus from entering water bodies (Sharpley). The filter is made of steel slag material, which is a by-product of separating metal from raw ore (*Prevent Phosphorus from Leaving the Golf Course*, 2015). It is able to remove and bind to phosphorus (via ligand exchange) up to a range of 25-33%. These filters are considered phosphorus sorbing materials (PSMs) and work best when placed in drainage ditches; however, they do need to be replaced over time, as their efficiency (demonstrated in Figure 24) decreases with less available calcium, aluminum, and iron on the surface of the filter.

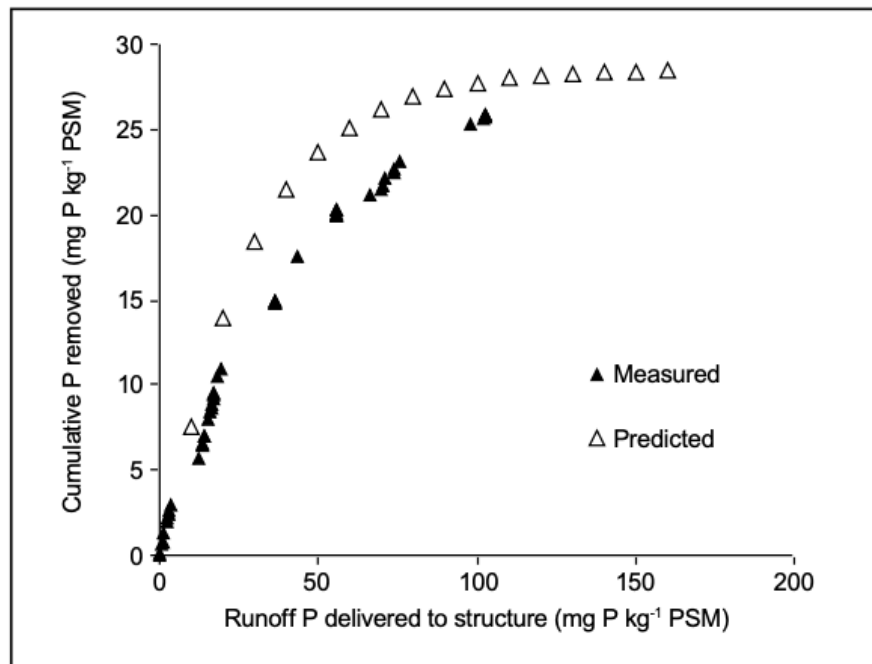


Figure 24: Cumulative P Removed vs. Runoff P Delivered to  $\frac{1}{4}$  inch Steel Slag Sieve over 5 Months (Sharpley)

### 5.3 Final Phosphorus Loads and Percent Reductions

This section demonstrates the estimated efficiency of phosphorus reduction using the methods proposed in Section 5.2. Final phosphorus loads and percent reduction values are critical for understanding the impact of the proposed treatment method(s). Final phosphorus loads may be calculated by:

$$\text{Final Phosphorus Load} = \left(1 - \frac{\text{Percent Reduction}}{100}\right) \times \text{Initial Phosphorus Load}$$

#### 5.3.1 Parlee Farm

Studies have shown that the implementation of water erosion controls (such as silt fences) can reduce phosphorus loads by approximately 23% (Faucette, 2008); recalling the initial TMDL, the final phosphorus load can then be calculated as:

$$\begin{aligned}\text{Final Phosphorus Load} &= (1 - 0.23) \times 0.33 \frac{\text{lbs}}{\text{year}} \\ \text{Final Phosphorus Load} &= 0.25 \frac{\text{lbs}}{\text{year}}\end{aligned}$$

#### 5.3.2 Charles George Reclamation Trust

Planting forests and riparian vegetation along water bodies (in this case, along Flint Pond) have shown to reduce phosphorus loads by 50-85%. Recalling the initial TMDL, the final phosphorus load may be calculated as:

$$\begin{aligned}\text{Final Phosphorus Load} &= (1 - 0.675) \times 5 \frac{\text{lbs}}{\text{year}} \\ \text{Final Phosphorus Load} &= 2 \frac{\text{lbs}}{\text{year}}\end{aligned}$$

#### 5.3.3 Academy of Notre Dame Forest

Planting forests and riparian vegetation have shown to reduce phosphorus loads by 50-85%. Recalling the initial TMDL, the final phosphorus load may be calculated as:



$$\text{Final Phosphorus Load} = (1 - 0.675) \times 142 \frac{\text{lbs}}{\text{year}}$$

$$\text{Final Phosphorus Load} = 46 \frac{\text{lbs}}{\text{year}}$$

#### 5.3.4 Chelmsford Auto Electric/Riley Road

Studies have shown that the implementation of catch basin inserts can reduce total phosphorus in wastewater by approximately 40%. Recalling the initial TMDL, the estimated phosphorus reduction is:

$$\text{Final Phosphorus Load} = (1 - 0.4) \times 9 \frac{\text{lbs}}{\text{year}}$$

$$\text{Final Phosphorus Load} = 5 \frac{\text{lbs}}{\text{year}}$$

#### 5.3.5 Tyngsboro Country Club

Replaceable steel slag landscape filters are estimated to have a phosphorus reduction of 25-33%; recalling the initial estimated TMDL, the final phosphorus load may be estimated as:

$$\text{Final Phosphorus Load} = (1 - 0.29) \times 45 \frac{\text{lbs}}{\text{year}}$$

$$\text{Final Phosphorus Load} = 32 \frac{\text{lbs}}{\text{year}}$$

#### 5.3.6 Vesper Country Club

Replaceable steel slag landscape filters are estimated to have a phosphorus reduction of 25-33%; recalling the initial estimated TMDL, the final phosphorus load may be estimated as:

$$\text{Final Load} = (1 - 0.29) \times 422 \frac{\text{lbs}}{\text{year}}$$

$$\text{Final Phosphorus Load} = 300 \frac{\text{lbs}}{\text{year}}$$

## 5.4 Soil Sampling Procedure

There are many soil testing kits available, but it is important to ensure that the selected kit(s) measure phosphorus and not just other parameters (such as moisture). Garden Helpful compiled a list of the top ten most reliable and accurate soil test kits, which were selected based on a collection of reviews; however, only a few tests actually measure phosphorus (and other parameters) (Dalpiaz, 2020).

### 5.4.1 Soil Testing Procedure

Table 5 provides information for five out of the top ten soil testing kits; these five were chosen based on their ability to test for phosphorus at the minimum.

Table 5: Information about Soil Testing Kits

<b>Soil Testing Kit</b>	<b>Tests For</b>	<b>Pros</b>	<b>Cons</b>
Soil Savvy Test Kit	pH, N, P, K, Ca, Mg, S, Na, Fe, Mn, Zn, Cu, B, Al	Professional accuracy	Takes time to receive lab results
Luster Leaf 1601 Rapitest Test Kit for Soil	pH, N, P, K	High efficiency	Procedure is a bit complex
Luster Leaf 1605 Rapitest Digital Soil Tester	pH, N, P, K	High efficiency & accuracy	N/A
Whitetail Institute Laboratory Soil Test Kit	pH, N, P, K, Ca, Mg	Professional accuracy	Takes about a week to receive lab results
Environmental Concepts 1663 Professional Soil Test Kit	pH, N, P, K	High accuracy	Procedure is a bit complex

#### 5.4.1.1 Soil Savvy Test Kit

This kit simply requires the user to place a portion of soil in a provided jar and mail it in the included pre-paid postage envelope. The results will then be sent off to the UNIBEST laboratory and results will be made available either online or to a listed email address.

#### 5.4.1.2 Luster Leaf 1601 Rapitest Test Kit for Soil

For this kit, the user should take a sample two or three inches below the soil surface without contaminating the sample (by using gloves). The sample should be placed into a container, mixed with water, and partially transferred to the color comparator. The analysis is then done by adding

powder from the appropriate capsule (each element that can be measured has its own colored testing kit) and comparing the result to the color indicator on the righthand side.

#### 5.4.1.3 Luster Leaf 1605 Rapitest Digital Soil Tester

This kit utilizes LED digital technology and an optical calibration system to read test colors that can be difficult to distinguish with the human eye. The user should take a sample two or three inches below the soil surface, place the sample into a test tube, slide the test tube into the optical chamber, and push the appropriate button (each element that can be measured has its own button). Once the results are displayed, the included tester booklet gives recommendations for fertilizers.

#### 5.4.1.4 Whitetail Institute Laboratory Soil Test Kit

The basic procedure for this kit involves taking ten to twenty samples of the first three to six inches of sub-surface soil per plot by using a spade and bucket. The samples should be mixed thoroughly, and all big plant pieces and rocks should be removed. The sample should then be placed into the provided soil sample bag up to the fill line. The samples and a form indicating whether the goal is to maintain or establish a new plot (and the kind of crop if this is the case) should be sent to Whitetail Institute Laboratories, which will provide soil analysis results and recommendations for fertilizers via email or letter within 24-48 hours of their reception time.

#### 5.4.1.5 Environmental Concepts 1663 Professional Soil Test Kit

This kit is liquid based and does not require lab testing. The sample should be taken two to four inches below the soil surface, placed into a clean container, broken up by either a spoon or trowel, and left to dry. Rocks and other big organic matter should then be removed, and the sample should be placed into a test tube, and the appropriate reagent should be added (indicated in the included instruction manual, which is not fully available online). It will take an estimated ten minutes for the results to show. They can then be analyzed via instructions provided in the manual.

### 5.4.2 Leaf Analysis Procedure

To determine whether the phosphorus applied is the appropriate amount, a leaf analysis test can be performed. This involves analyzing nutrient concentrations in selected leaf samples and

comparing them to identified “ideal” levels; if the concentrations are close to the comparison values, then the tree is considered to be at optimal growth, fruit yield, and quality. The recommended time frame to conduct this procedure is between July 15<sup>th</sup> through August 15<sup>th</sup> because this is the time during which elemental concentrations are relatively stable. Samples are to be taken from fifty trees (Heckman, 2001). The best selection for leaves has the following:

1. Grows on healthy limbs that are at 45 to 60° angles away from the trunk
2. Not from suckers or water sprouts
3. Not contaminated with dust, soil, insects, or disease
4. Not fresh plant tissue

To perform a proper analysis, the following steps should be taken:

1. Choose leaves based on the aforementioned parameters
2. Place the leaves in a clean paper bag
3. Air dry the samples for two to three days in the open
4. Send samples to Rutgers Cooperative Research & Extension, New Jersey Agricultural Experiment Station
5. Compare results to Figure 25

### Standard Values Used For Interpreting Results of Tree Fruit analysis

Rutgers Soil and Plant Analysis Laboratory

Element	Apple	Pear	Peach	Apricot	Plum	Cherry, Sour	Cherry, Sweet
<b>MACRONUTRIENT NORMAL RANGE %</b>							
Nitrogen (N)		2.20-2.80	3.25-4.00	2.00-2.50	2.40-3.00	2.60-3.00	2.10-3.00
Low req <sup>1</sup>	1.75-2.00						
High req <sup>2</sup>	2.00-2.25						
Phosphorus(P)	0.20-0.30	0.11-0.25	0.20-0.40	0.13-0.35	0.14-0.25	0.16-0.22	0.16-0.50
Potassium(K)	1.25-1.75	1.00-2.00	1.50-2.00	2.50-3.00	1.60-3.00	1.60-2.10	2.50-3.00
Calcium(Ca)	1.20-1.60	1.00-1.50	1.50-2.25	1.60-2.50	1.50-3.00	1.50-2.60	2.00-3.00
Magnesium(Mg)	0.25-0.40	0.25-0.50	0.30-0.60	0.30-1.20	0.30-0.80	0.30-0.75	0.30-0.80
<b>MICRONUTRIENT NORMAL RANGE, ppm</b>							
Baron(B)	25-50	20-70	25-75	25-70	25-60	20-55	20-100
Copper(Cu)	5-20	5-20	5-20	5-25	6-16	8-28	5-50
Iron(Fe)	100-300	60-250	100-200	70-150	100-250	100-200	100-200
Manganese(Mn)	40-100	30-100	50-150	25-100	40-160	40-60	40-200
Molybdenum(Mo)		20-100			20-200		
Zinc(Zn)	20-50	25-200	20-60	20-100	20-50	20-50	20-50

<sup>3</sup> Stayman, Turley, McIntosh, Jerseyred, Gravenstein, Starr, Summer Pippin, and Britemac have low nitrogen requirements.

<sup>2</sup> Red Delicious, Rome Beauty, Golden Delicious, and Jonathan have high nitrogen requirements.

Figure 25: Standard Values Used for Interpreting Results of Tree Fruit Analysis (Heckman, 2001)

#### 5.4.3 Proposed Sampling Procedure for Tyngsborough

Sampling should be prepared and analyzed according to Standard Method for the Examination of Water and Wastewater 4500-P (which may be found in Appendix II) at each of the sites listed in Section 4.3. These sites should be inspected under both dry and wet weather conditions; a wet weather event is classified as a storm during which more than 0.1 inch of rain falls within 72 hours. Data should be collected on at least a monthly basis, but more frequently if appropriate weather conditions permit.

It is important to collect data consistently in order to determine the initial conditions, appropriate treatment, and whether the treatment is effective (which is assessed via phosphorus reduction).

The data collected using the proposed sampling methods will eventually be used to calculate the current phosphorus export rate through (*Massachusetts Small MS4 General Permit*, 2020):

$$P_{exp} \left( \frac{mass}{year} \right) = P_{base} \left( \frac{mass}{year} \right) - \left[ P_{Sred} \left( \frac{mass}{year} \right) + P_{NSred} \left( \frac{mass}{year} \right) \right] + P_{DEVinc} \left( \frac{mass}{year} \right)$$

Where:  $P_{exp}$  = Current phosphorus export rate from chosen PCP area

$P_{base}$  = Baseline phosphorus export rate

$P_{Sred}$  = Yearly phosphorus reduction from implemented structural controls

$P_{NSred}$  = Yearly phosphorus reduction from implemented non-structural controls

$P_{DEVinc}$  = Yearly phosphorus increase resulting from development since 2005

The Massachusetts Small MS4 General Permit requires that the  $P_{exp}$  must be reduced by  $30 \frac{kg}{year}$  or:

$$P_{exp} \leq P_{allow} \left( \frac{mass}{year} \right) + (P_{RR} \times 0.80)$$

Where:  $P_{allow}$  = Applicable Allowable Phosphorus Load

$P_{RR}$  = Phosphorus Reduction Requirement

Location-wise, the only area where phosphorus has consistently been tested is at the 01-MER station, which is approximately two-thirds of the way down the Merrimack within Tyngsborough (“Merrimack River, Tyngsborough, MA”, 2016); while this may provide some helpful upstream data, it does not necessarily help identify where phosphorus levels are an issue or where the excess originates.

## 5.5 Sampling Plan

Sampling procedures for point and nonpoint sources will differ based on landscape and inherent differences in runoff flow. Sampling is much more easily done at point sources, such as wastewater effluent and construction sites directed into one discharge location, than at nonpoint sources, which can discharge to and from a widespread area. Point source sampling can be completed at outfalls, while nonpoint sources will require a more comprehensive water sampling plan (such as

downstream sampling), which can be supplemented by soil and leaf analysis to estimate phosphorus loads.

### 5.5.1 Point Sources

Beginning in June 2019, efforts have been made to map the stormwater drainage system for the town to locate infrastructure and discharge outfalls. The data recovered during this process is collected as GIS data and plugged into a town database; this process has slowed down due to a staff shortage, but there are plans to continue this analysis. The generic procedure for mapping this information involves:

1. Visiting each street to locate catch basins, culverts, and noticeable outfalls
2. Recording the coordinates using a GPSMAP 64s
3. Directly transferring the data into the town's stormwater GIS database

With the complete map, predictions can be made to figure out how the infrastructure is connected (there is currently no up-to-date plan for this, with the Tyngsborough Highway Department cleaning out 1400 catch basins per year and only 800 catch basins on file). Outfall delineations can then be estimated, which will make point source phosphorus identification much more feasible, particularly with respect to discharging into the Merrimack River. Regarding the illegal discharge and leaking from septic systems, Tyngsborough has begun a project to address the existing septic system infrastructure in its commercial district along the Nashua, NH border. The project is currently in Phase II and will replace the septic systems with town sewer.

### 5.5.2 Nonpoint Sources

Nonpoint sources are more difficult to sample due to the widespread area and potential for runoff on so many locations. The best place to begin analyzing how much phosphorus is potentially being used is to interview each of the site owners and request statistics of annual waste and fertilizer use. This will make for more accurate TMDLs, which can then be compared to sampling data to set appropriate phosphorus reduction levels. When possible, streams running through the site can be sampled and assessed to calculate even more precise TMDLs. The sampling procedures described in Section 5.5.3 should be implemented for the sites listed in Section 4.3.

## 5.6 Addressing Pre-existing Phosphorus Levels

While prevention methods are necessary to prevent further rising nutrient levels, it is also important to address the phosphorus that has already made its way into a water body. Whether from point or nonpoint sources, reducing phosphorus levels can be achieved through either inactivation or physical removal. There is currently no ideal way to completely achieve one hundred percent inactivation or removal, but there are methods which have proven to be successful at reduction.

There are several technologies available that can be used to manage existing phosphorus levels. These can include mechanical dredging, aeration, alum treatment, and other chemical treatments (*Improving Pond Water Quality Through Phosphorus Reduction*, 2014). Because there is currently no available data to determine where the most negatively affected area(s) in the Merrimack River is/are, there is no way to predict the span of the treatment necessary to reduce current phosphorus levels. Once the potential problem sites have been verified as either problematic or non-problematic (via sample analysis), it will be easier to determine what solutions are most viable depending on the severity of the issue.

### 5.6.1 Mechanical Dredging

Mechanical dredging is the most direct way to remove sediment build-up, but it is very expensive and environmentally disruptive. This method would likely have more success in smaller-scale, severely impaired water bodies, but can be used if the phosphorus levels found in the Merrimack River are dangerously excessive.

### 5.6.2 Aeration

Aeration can be done in combination with either naturally occurring or inoculated bacteria, which can accelerate organic matter decay and prevent a build-up of excess nutrients. This should be done in addition to other treatments for more severe cases rather than relied upon as the only solution.



### 5.6.3 Alum Treatment

Alum treatment can be done in water and wastewater treatment facilities and in water bodies. It works in a water body by controlling phosphorus release from sediment and inactivating it. This treatment is typically most successful at a pH range of four to six (compared to a typically phosphorus-rich water, which usually has a pH range of seven to eight). This process requires repeat application since one treatment does not permanently deactivate phosphorus.

### 5.6.4 Phoslock

Phoslock has shown to inactivate phosphorus in a more effective and safe way compared to alum. It is comprised of a lanthanum modified bentonite clay, which is applied to a water surface as either a granule or a slurry (*Phoslock (55#) SKU PHOSLOCK055*, 2020). It reacts with free (very reactive) phosphorus and adsorbs the molecules to form rhabdophane; the unreacted lanthanum then imbeds into bentonite granules, which will then settle to the bottom of the water body, forming a permeable layer that will continuously bond to and sequester phosphorus as it is released from sediments. Phoslock works in a pH range of four to eleven and under anoxic conditions and is nontoxic to aquatic organisms. Phoslock claims include 1 kg phosphorus inactivation per 100 kg of Phoslock used; this product does require annual reapplication, as is the case with nearly all chemical treatments. After conducting sampling, it is possible to directly calculate necessary application, which is harder to do with alum. However, due to pesticide regulations, this product is prevented from being used in Connecticut, Massachusetts, New Hampshire, New York, Maine, Rhode Island, and Vermont but can be used in other locations.

### 5.6.5 Naturalake Bioscience MD Pellets

Naturalake Bioscience MD Pellets are slow-release probiotics that sink to the bottom of a water body and penetrate the sediment build-up (*Naturalake Biosciences MD Pellets (30lb Pail)*, 2020). They release biostimulants and specific bacterial cultures to accelerate the decay of organic debris, which reduces the available internal nutrient reserve at the bottom of the water. The pellets are flexible and can work over an entire water body or smaller areas such as shorelines and coves. Additionally, they break down floating vegetation, but do not kill aquatic plants or algae. This product is permitted in Massachusetts, so it can be used within Tyngsborough's borders.

### 5.6.6 Naturalake Biosciences Nature's Blend

Naturalake Biosciences Nature's Blend is a dry probiotic with psychrophilic, neutrophilic, and mesophilic microorganisms, along with biostimulants, that can efficiently cycle out both nitrogen and phosphorus excess (*Naturalake Biosciences Nature's Blend (30lb Pails, 1lb Pks)*, 2020). This formula works best between 14.4-25.6°C and is sprayed over the surface of the water; it is designed to work quickly and rapidly reverse any negative effects from the treatment. This product is permitted in Massachusetts, so it can be used within Tyngsborough's borders.

## 5.7 Site Monitoring

It is critical to better understand phosphorus loading throughout the watershed; one way to address this includes the development of an annual monitoring plan to collect consistent data to assess whether the preventive and treatment methods used are successful. This would include different approaches for point and nonpoint sources.

### 5.7.1 Point Sources

Each year, samples should be taken at known outfalls (per the aforementioned procedure in Chapter 5) to assess whether chemical treatment is successful at reducing phosphorus concentrations; since chemical treatments require repetitive application, the samples should initially be taken regularly to develop a treatment timeline and avoid overtreatment. Overtreatment is costly, unnecessary, and potentially harmful (as saturation can cause unwanted byproducts). If any physical treatment is implemented, samples should also be taken post-treatment after an appropriate time period to determine its effectiveness.

### 5.7.2 Nonpoint Sources

Soil analyses should be conducted at identified problem sites to determine whether phosphorus levels have increased or decreased (since phosphorus can still enter water bodies through groundwater), and water sampling should be conducted at identified locations. Leaf analyses should also be conducted to determine the actual absorption of phosphorus compared to what is applied; this calculation can save money on application/treatment products and eventually reduce

the amount applied. Consistent data collection is the best way to determine whether preventive methods and treatment are successful.

## Chapter 6: Conclusions and Recommendations

During the process of conducting analyses for this report, the following were determined:

1. A list of nine site selections within Tyngsborough where sampling needs to be conducted
2. Estimated TMDLs for most of these sites, using data from the Massachusetts Small MS4 General Permit, Appendix F
3. Recommended preventive measures to minimize phosphorus loads and a monitoring plan to consistently collect data to analyze whether phosphorus levels are meeting requirements for the discharge permit and whether prevention and treatment are effective
4. Recommendations for products to address existing phosphorus in the Merrimack River

Because no specific information on phosphorus concentrations or loads were available for this project, calculations were completed based on estimations. The values for these estimations were pre-determined in the Massachusetts Small MS4 General Permit and estimated based on known values from case studies in other locations. These values and the analyses should be verified based on sampling procedures identified in Chapter 5.

One main challenge of this project involved TMDLs for the selected sites. There is not a lot of information available for Tyngsborough specifically to make the most accurate calculations; this project certainly opens up opportunities for future phosphorus-related projects, which should be done consistently and annually to make sure that phosphorus loads at the identified sites are meeting regulations. Other sites may also be identified and sampled based on the procedures mentioned in Chapter 5.

Initial sample collections, complete mapping of the stormwater drainage system (especially outfalls), and implementation of site monitoring plans will be critical for developing an appropriate database for phosphorus concentrations. Any improvements to the procedures should be determined based on conducting site visits and actual collection.

## References

- “4500-P.” *Standard Methods for the Examination of Water and Wastewater: Supplement to the 16. Edition*, American Public Health Association, 1988, pp. 146–162.
- Annual Water Quality Report: Reporting Year 2019*. Tyngsborough Water District, 2019.
- The Basics of Total Maximum Daily Loads (TMDLs)*. Mass.gov, [www.mass.gov/guides/the-basics-of-total-maximum-daily-loads-tmdls](http://www.mass.gov/guides/the-basics-of-total-maximum-daily-loads-tmdls).
- Brunner, J.f. “Integrated Pest Management in Tree Fruit Crops.” *Encyclopedia of Agriculture and Food Systems*, 2014, doi:10.1016/b978-0-444-52512-3.00175-3.
- Carpenter, Stephen R., et al. “Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen.” *Issues in Ecology*, vol. 3, 1998.
- Cosgro, Matthew D. “Postcard: Tyngsboro Bridge over the Beautiful Merrimack River between Lowell, Massachusetts and Nashua, New Hampshire.” *Nashua City Station Railroad History*, 2020, [www.nashuacitystation.org/resource/9304014350/](http://www.nashuacitystation.org/resource/9304014350/).
- Dalpiaz, Joe. *The 10 Best Soil Test Kits - (2020 Reviews & Guide)*. Garden Helpful, 16 Feb. 2020, gardenhelpful.com/best-soil-test-kits/.
- Dickson, David. *Catch Basin Inserts*. University of Connecticut, 4 Oct. 2018, ctstormwatermanual.nemo.uconn.edu/11-design-guidance/catch-basin-inserts/.
- Ebeling, James M., et al. “Evaluation of Chemical Coagulation–Flocculation Aids for the Removal of Suspended Solids and Phosphorus from Intensive Recirculating Aquaculture Effluent Discharge.” *Aquacultural Engineering*, vol. 29, no. 1-2, Oct. 2003, pp. 23–42., doi:10.1016/s0144-8609(03)00029-3.
- “Environmental Challenges for the Merrimack River.” Environmental Protection Agency, 20 Feb. 2020, [www.epa.gov/merrimackriver/environmental-challenges-merrimack-river](http://www.epa.gov/merrimackriver/environmental-challenges-merrimack-river).
- Guignard, Maïté S., et al. “Impacts of Nitrogen and Phosphorus: From Genomes to Natural Ecosystems and Agriculture.” *Frontiers in Ecology and Evolution*, vol. 5, 2017, doi:10.3389/fevo.2017.00070.
- Faucette, L. B., et al. “Sediment and Phosphorus Removal from Simulated Storm Runoff with Compost Filter Socks and Silt Fence.” *Journal of Soil and Water Conservation*, vol. 63, no. 4, 2008.
- Heckman, Joseph. *Leaf Analysis for Fruit Trees*. Rutgers Cook College, Dec. 2001, documents.crinet.com/AgSource-Cooperative-Services/Agronomy-&-Feed/LeafAnalysis.pdf .

- Improving Pond Water Quality Through Phosphorus Reduction*. SOLitude Lake Management, 19 Mar. 2014, [www.solitudelakemanagement.com/blog/improving-pond-water-quality-through-phosphorus-reduction](http://www.solitudelakemanagement.com/blog/improving-pond-water-quality-through-phosphorus-reduction).
- Indicators: Phosphorus*. Environmental Protection Agency, 7 July 2017, [www.epa.gov/national-aquatic-resource-surveys/indicators-phosphorus](http://www.epa.gov/national-aquatic-resource-surveys/indicators-phosphorus).
- Kioussis, Dimitri R., et al. "Phosphate Binding Polymeric Hydrogels for Aquaculture Wastewater Remediation." *Aquacultural Engineering*, vol. 19, no. 3, 1999, pp. 163–178., doi:10.1016/s0144-8609(98)00049-1.
- Lee, G.F., "Eutrophication," Transactions of the Northeast Fish and Wildlife Conference, pp 39-60 (1973).
- Massachusetts Small MS4 General Permit*. Environmental Protection Agency, 28 Apr. 2020, [www.epa.gov/npdes-permits/massachusetts-small-ms4-general-permit](http://www.epa.gov/npdes-permits/massachusetts-small-ms4-general-permit).
- "Merrimack River, Tyngsborough, MA." *River Monitoring Network Condition Report*, no. RM-003, 2016.
- Naturalake Biosciences MD Pellets (30lb Pail)*. SOLitude Lake Management, 2020, [www.aeratorsaquatics4lakesnponds.com/Products/Naturalake-Biosciences-MD-Pellets-\(30lb-pail\)\\_\\_\\_AF-VSMDP030.aspx](http://www.aeratorsaquatics4lakesnponds.com/Products/Naturalake-Biosciences-MD-Pellets-(30lb-pail)___AF-VSMDP030.aspx).
- Naturalake Biosciences Nature's Blend (30lb Pails, 1lb Pks)*. SOLitude Lake Management, 2020, [www.aeratorsaquatics4lakesnponds.com/Products/Naturalake-Biosciences-Nature%e2%80%99s-Blend-\(30lb-pails-1lb-pks\)\\_\\_\\_AF-NB030-1LB.aspx](http://www.aeratorsaquatics4lakesnponds.com/Products/Naturalake-Biosciences-Nature%e2%80%99s-Blend-(30lb-pails-1lb-pks)___AF-NB030-1LB.aspx).
- Nutrient Indicators Dataset*. Environmental Protection Agency, 30 Jan. 2019, [www.epa.gov/nutrient-policy-data/nutrient-indicators-dataset](http://www.epa.gov/nutrient-policy-data/nutrient-indicators-dataset).
- Nutrient Permitting*. Environmental Protection Agency, 5 July 2017, [www.epa.gov/npdes/nutrient-permitting](http://www.epa.gov/npdes/nutrient-permitting).
- Oram, Brian. *Phosphate in Surface Water Streams Lakes*. Water Research Center, 2020, [water-research.net/index.php/phosphate-in-water](http://water-research.net/index.php/phosphate-in-water).
- Phoslock (55#) SKU PHOSLOCK055*. SOLitude Lake Management, 2020, [www.aeratorsaquatics4lakesnponds.com/Products/Phoslock-\(55\)\\_\\_\\_PHOSLOCK055.aspx](http://www.aeratorsaquatics4lakesnponds.com/Products/Phoslock-(55)___PHOSLOCK055.aspx).
- Phosphorus and Water*. United States Geological Survey, [www.usgs.gov/special-topic/water-science-school/science/phosphorus-and-water?qt-science\\_center\\_objects=0#qt-science\\_center\\_objects](http://www.usgs.gov/special-topic/water-science-school/science/phosphorus-and-water?qt-science_center_objects=0#qt-science_center_objects).

- Prevent Phosphorus from Leaving the Golf Course*. United States Golf Association, 19 Mar. 2015, [www.usga.org/course-care/prevent-phosphorus-from-leaving-the-golf-course-21474859739.html](http://www.usga.org/course-care/prevent-phosphorus-from-leaving-the-golf-course-21474859739.html).
- Scrubbing Phosphorous from Runoff Water*. United States Golf Association, 7 Mar. 2016, [www.usga.org/content/usga/home-page/course-care/turfgrass-and-environmental-research/research-updates/scrubbing-phosphorous-from-runoff-water.html](http://www.usga.org/content/usga/home-page/course-care/turfgrass-and-environmental-research/research-updates/scrubbing-phosphorous-from-runoff-water.html).
- Septic Systems Contribution to Phosphorus in Shallow Groundwater: Field-Scale Studies Using Conventional Drainfield Designs*. Public Library of Science, doi:10.1371/journal.pone.0170304.g001.
- Sharpley, Andrew N., et al. "Phosphorus Loss from Land to Water: Integrating Agricultural and Environmental Management." *Plant and Soil*, vol. 237, no. 2, 2001, pp. 287–307., doi:10.1023/a:1013335814593.
- Sharpley, Andrew, and Douglas Beegle. *Managing Phosphorus for Agriculture and the Environment*. Pennsylvania Nutrient Management Program (Penn State Extension), <https://extension.psu.edu/programs/nutrient-management/educational/soil-fertility/managing-phosphorus-for-agriculture-and-the-environment>.
- TMDL Information*. Department of Environmental Conservation, [dec.vermont.gov/watershed/map/tmdl](http://dec.vermont.gov/watershed/map/tmdl).
- Topographic Map Symbols*. United States Geological Survey, [pubs.usgs.gov/gip/TopographicMapSymbols/topomapsymbols.pdf](http://pubs.usgs.gov/gip/TopographicMapSymbols/topomapsymbols.pdf).
- Torsiello, John. "Talking N, P and K." *Golf Course Industry*, 12 Nov. 2015, [www.golfcourseindustry.com/article/gci1115-documenting-fertilizer-usage/](http://www.golfcourseindustry.com/article/gci1115-documenting-fertilizer-usage/).
- "Town of Tyngsborough, MA." Town of Tyngsborough, 2020.
- Tyngsborough Water District*. Environmental Working Group, 2019, [www.ewg.org/tapwater/system.php?pws=MA3301000](http://www.ewg.org/tapwater/system.php?pws=MA3301000).
- U.S. Department of Agriculture, Natural Resources Conservation Service. 2017. Effects of Conservation Practices on Phosphorus Loss from Farm Fields: A National Assessment Based on the 2003-06 CEAP Survey and APEX Modeling Databases. 100 pp.
- Water Quality: the Merrimack River*. Northern Middlesex Stormwater Collaborative, [www.nmstormwater.org/merrimack-river-water-quality](http://www.nmstormwater.org/merrimack-river-water-quality).
- What Forecasting Dead Zones Teaches Us about Chesapeake Bay*. University of Maryland Center for Environmental Science, 14 Feb. 2018, [www.umces.edu/news/what-forecasting-dead-zones-teaches-us-about-chesapeake-bay](http://www.umces.edu/news/what-forecasting-dead-zones-teaches-us-about-chesapeake-bay).

## Appendix I. Submitted Proposal for MQP

### **Chapter 1: Introduction and Background**

Phosphorus in small concentrations is necessary for basic cell functions and growth, but can be harmful to aquatic ecosystems when present in high concentrations. It is therefore important to identify sources of excess phosphorus and methods to address it.

#### **1.1 How Phosphorus Enters and Changes in the Environment**

Phosphorus is a naturally occurring element that is found in soil and water. Humans typically utilize phosphorus to enhance the growth of crops via fertilizers. When it rains, excess fertilizer is carried into waterways (Manuel, 2014). Multiple forms of phosphorus occur in aquatic ecosystems, both dissolved and particulate. More specifically, some forms can include reactive phosphorus or insoluble phosphorus. Phosphorus is rarely present in its elemental form; rather, it usually occurs as organic or inorganic phosphate (US EPA, 2012).

The phosphorus cycle describes how phosphorus changes and moves through aquatic ecosystems. Plants absorb dissolved phosphorus and convert it from an inorganic compound to organic compound. When these plants are consumed, animals introduce organic phosphorus to their systems. When these animals excrete waste, the organic phosphorus is transformed back into inorganic phosphorus through decomposition by bacteria. Plants then re-absorb the inorganic phosphorus, and the cycle continues. Movement of water transports the phosphorus, while consumption by plants or animals renders it stationary (US EPA, 2012).

Phosphorus enters water systems mainly due to human activities. Large amounts of phosphorus are found in fertilizers, as well as the waste of farm animals. When it rains, phosphorus is carried into waterways. In addition, wastewater plant systems can release excess amounts of phosphorus if wastewater is treated improperly. Phosphorus can also enter the ecosystem through



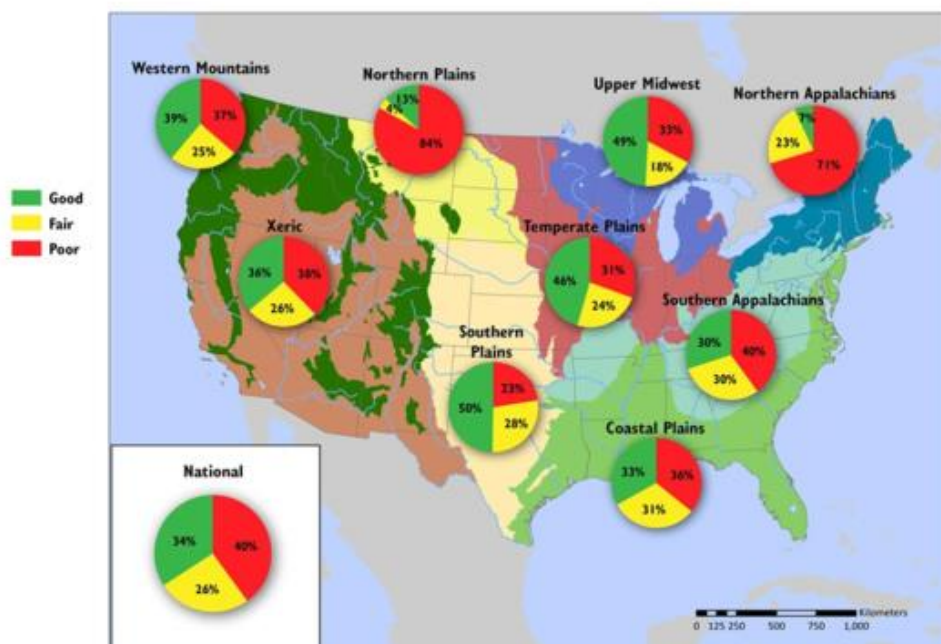
home activities. Fertilizer from gardens contains phosphorus, as does pet waste, soaps, and detergents. Paving stones, roofing shingles, sidewalks, and driveways can also contribute to the amount of phosphorus that leaches into stormwater (US EPA, 2019 a). Phosphorus also enters water systems naturally through soil erosion. This erosion can occur during a typical rainfall event or during flooding, which is known as bank erosion (USGS, n.d.). Both organic and inorganic phosphorus can be dissolved in the water or attached to other particles, known as suspension (US EPA, 2012).

## **1.2 Effects of Phosphorus Pollution**

The effects of phosphorus pollution are threefold: humans, the environment, and the economy are impacted (US EPA, 2019 b). Similar to its function on land, fertilizers also accelerate the growth of algae in water (Manuel, 2014). This elevated growth commonly leads to eutrophication, which causes the algae grow to unsustainable levels and kill fish, lower the pH of the water, deplete oxygen, and block sunlight (NOAA, 2019; Manuel, 2014). In addition, eutrophication can also lead to the creation of dead zones, which is commonly known as hypoxia. These are areas where the oxygen is so depleted that aquatic organisms cannot survive (US EPA, 2019 c). The area of these hypoxic zones has increased over 30% between 1995 and 2007. One such example is the dead zone that occurs in the Gulf of Mexico, which covers nearly 5500 square miles in size (Manuel, 2014). Humans can also come into direct contact with toxic algae, leading to an array of health problems (US EPA, 2019 d). Such health problems include vomiting, diarrhea, fever, and liver damage (Manuel, 2014). Furthermore, when water containing toxic algae is treated, treatment chemicals react with the algae to form toxic dioxins- which are a major health concern (US EPA, 2019 d). Lastly, the presence of nutrients in water systems can raise water treatment costs and lead to losses in tourism, real estate, and commercial fishing (US EPA, 2019 e).

### 1.3 Areas Affected by Phosphorus Pollution

Areas affected by phosphorus pollution include lakes, rivers, coasts, bays, ground water, and drinking water. According to the Environmental Protection Agency (EPA), almost 20% of 50,000 lakes in the United States were contaminated with phosphorus or nitrogen (US EPA, 2019 f). In addition, the EPA found that 40% of rivers and streams across the United States were also contaminated with phosphorus (Manuel, 2014). Pollution from these lakes and streams eventually makes its way to coasts, bays, and estuaries. Over 65% of coastal areas and over 30% of estuaries in the United States are affected by this pollution (US EPA, 2019 g). Lastly, phosphorus can end up in the water that humans drink through polluted waterways. Streams and rivers are easily identifiable as potentially polluted systems; however, phosphorus can also pollute groundwater systems. Water soaks through the ground and collects excess phosphorus, transporting it into the groundwater that many humans rely on to survive (US EPA, 2019 g). Figure 1 shows the resulting widespread phosphorus pollution across United States river and streams.



*Figure 1: Phosphorus Pollution in U.S. Rivers and Streams (Manuel, 2014)*

#### **1.4 Phosphorus Measurement and Management**

The different forms of phosphorus found in aquatic ecosystems are measured in multiple ways. Total orthophosphate, which is the phosphorus molecule itself, is measured using the ascorbic acid method. A reagent with ascorbic acid is added to the sample, and the sample turns blue. The concentration of orthophosphate is proportional to the intensity of the color. This test measures both dissolved and suspended orthophosphate. Testing for total phosphorus measures orthophosphate, condensed phosphate, and organic phosphate that are both dissolved and suspended. The sample is heated and acidified in order to convert all forms of phosphate to orthophosphate. The concentration of phosphate in the sample is then determined using the previously mentioned ascorbic acid method. Dissolved phosphorus is measured by filtering the sample and then analyzing it using the ascorbic acid method, and insoluble phosphorus is calculated by subtracting the dissolved phosphorus from the total phosphorus concentration (US EPA, 2012).

One way to limit the amount of pollutants entering aquatic systems is by establishing Total maximum daily loads (TMDLs). A TMDL is a regulation of the maximum amount of a pollutant that an aquatic ecosystem can sustain and still meet federal standards. Impaired water bodies are identified on a state by state basis, and individual TMDLs are established for each water body. TMDLs are also established for individual pollutants, and the Environmental Protection Agency (EPA) must approve the plan. Due to the thoroughness required to monitor water bodies and establish TMDLs, such plans can take years or even decades to implement (Manuel, 2014).

Best management practices (BMPs) are also used to help reduce the amount of pollutants entering aquatic ecosystems. These BMPs are physical or cultural controls implemented within a

community, and they can be either structural or non-structural. Structural BMPs include stormwater controls such as detention basins, vegetative swales, and constructed wetlands. These constructs act as filtration mechanisms for stormwater. Non-structural BMPs include practices such as leaf litter collection, proper pet waste disposal, and the use of fertilizers that do not contain phosphorus. Such practices prevent pollutants from entering the water in the first place (Manuel, 2014; Marsh 2011).

### **1.5 Tyngsborough's Contribution to Phosphorus Pollution**

The National Pollutant Discharge Elimination System (NPDES) was created in response to the Clean Water Act in 1972. This permit system was implemented in order to control the levels of pollutants entering the water. The Massachusetts MS4 General Permit is a subset of the NPDES program. This type of permit regulates pollutants within a similar region, such as Massachusetts (US EPA, 2016 a). There are many contributors to phosphorus pollution along the Merrimack. The top contributors are municipal wastewater at 60% and runoff from developed areas at 21% (Northern Middlesex Stormwater Collaborative, n.d.). Unfortunately, as Figure 2 shows, phosphorus is not consistently measured when testing water quality.

Waterbody that receives flow from the MS4 and segment ID if applicable	Number of outfalls into receiving water segment	Chloride	Chlorophyll-a	Dissolved Oxygen/DO Saturation	Nitrogen	Oil & Grease/PAH	Phosphorus	Solids/ TSS/ Turbidity	E. coli	Enterococcus	Other pollutant(s) causing impairments
Althea Lake	4	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Mercury
Bridge Meadow Brook MA84A-34	44	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Unknown
Flint Pond MA 84012	3	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Mercury in Fish, Non-Native Aquatic Plants, Aquatic Plants (TMDL Required)
Lake Mascuppic MA 84037	17	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	Mercury in Fish, Non-Native Aquatic Plants, Aquatic Plants (TMDL not required)
Lawrence Brook MA84A-20	17	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Non-Native Aquatic Plants
Locust Pond and tribs MA 84031 (not in MS4)	6	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Mercury in Fish (TMDL Required)
Long Pond MA 84032	4	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Mercury in Fish, Non-Native Aquatic Plants, Aquatic Plants
Massapoag Pond MA 84087	4	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Mercury in Fish, Non-Native Aquatic Plants, Aquatic Plants (TMDL Required)
Merrimack River MA 84A-01	28	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	Mercury in Fish, Faecal Coliform (TMDL Required)
Scarlet Brook MA 84A-01	3	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	Unknown
Snake Meadow Brook	3	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Unknown
Uptons Pond MA 84075	2	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Unknown
Deep Brook	5	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	Unknown
Merrimack Trib Tyng Road MA 84A-01	5	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Unknown, assume e. coli
Merrimack Trib Kendall Road MA 84A-01	8	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Unknown, assume e. coli
		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
Total	134	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	
		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	

Figure 2: Past data for impaired water bodies in Tyngsborough (updated June 30th, 2019)  
(Tyngsborough 2018 Annual Water Quality Report)

## Chapter 2: Methodology

The goal of this project is to determine whether Tyngsborough is contributing to elevated phosphorus levels in the Merrimack River. In collaboration with the Tyngsborough Conservation Commission, we will propose a plan to manage and reduce the amount of phosphorus entering the Merrimack River. This project is to be done in compliance with requirements set forth by the MS4 Permit (which allows Tyngsborough to discharge stormwater). To accomplish this, we have identified four main objectives:

*Objective 1:* Determine the theoretical phosphorus loading from Tyngsborough using current zoning and phosphorus loadings provided in the Massachusetts General MS4 Permit.

*Objective 2:* Analyze previously collected data samples from impaired water bodies in Tyngsborough (provided by Danielle Mucciarone, Tyngsborough Conservation Director).

*Objective 3:* Using MapGEO and aerial maps, identify potential source(s) of phosphorus discharge into the Merrimack River.

*Objective 4:* Identify and develop an appropriate plan to reduce phosphorus pollution throughout the town of Tyngsborough, specifically at the aforementioned sites.

In this chapter, we state our objectives and the methodology we used to achieve them. We describe how we determined the theoretical phosphorus loading in Tyngsborough, and we analyze the available data on current Tyngsborough phosphorus pollution. We identify other sources of phosphorus pollution based on MapGEO and aerial maps. Finally, we describe a set of control methods to reduce phosphorus pollution.

## **2.1 Objective 1: Determine the theoretical phosphorus loading from Tyngsborough using current zoning and phosphorus loadings provided in the Massachusetts General MS4 Permit**

For this objective, we used the information provided in the Massachusetts MS4 General Permit to determine the theoretical phosphorus loadings stemming from each zone in Tyngsborough. In order to do this, we first used MapGEO to measure the area of each zoning district in Tyngsborough. We then used Table 1-1 from Appendix F of the Massachusetts MS4 General Permit to determine the annual composite phosphorus load export rates (PLER). We calculated the loading by multiplying the area of the zoning district by the PLER for each district (US EPA, 2016 b). An example of this calculation for the industrial zone is shown below:

$$Load_{industrial} = 2.179 \text{ mi}^2 \times \left( \frac{640 \text{ acre}}{1 \text{ mi}^2} \right) \times 1.29 \text{ lb/ac/yr} = 1798.98 \text{ lb/yr}$$

From these calculations, we found the phosphorus loading for each zoning district:

Table 1: Phosphorus Loading Based on Zoning Districts in Tyngsborough

Zone	Phosphorus Load (lb/yr)
Industrial	1798.98
Commercial	817.38
Low density residential	3236.35
Medium density residential	172.83
High density residential	16.67

We can see that the greatest phosphorus loads come from the industrial and low density residential zones. It is therefore important to focus on these areas when developing a plan to reduce phosphorus pollution, explained further in Section 2.4.

## **2.2 Objective 2: Analyze previously collected data samples from impaired water bodies in Tyngsborough**

The Massachusetts Water Resources Report from 2017 (Phase III) states that, while “there are no enforceable numeric water quality standards for total phosphorus in [...] Massachusetts [...] EPA suggests that total phosphorus concentrations in streams not exceed 100 µg/L” (Nutrients ES-2). Additionally, the recommended threshold for rivers entering lake/reservoir is 50 µg/L and 25 ug/L for lakes. Typically, phosphorus levels increase going from upstream to downstream, with wet weather values higher than those of dry weather.

## **2.3 Objective 3: Using MapGEO and aerial maps, identify potential source(s) of phosphorus discharge into the Merrimack River**

For this objective, we used MapGEO to identify tributaries that lead into the Merrimack River. Since it would not be feasible to examine every tributary and potential source of phosphorus leading into the Merrimack, we decided to choose a subbasin to analyze that would contribute

larger phosphorus loads to the river. The main criteria for this was that the subbasin should encompass zoning districts attributed with the highest phosphorus loads- which were the industrial light and low density residential zones. We then had to identify a subbasin that was mostly within the town boundaries, so that we could be more certain of where the phosphorus originated. After applying these criteria, we decided to focus our studies on a subbasin located in a residential zone in the northeast part of Tyngsborough (see Figure 3). Phosphorus pollution can make its way to the Merrimack through this subbasin via Lawrence Brook.

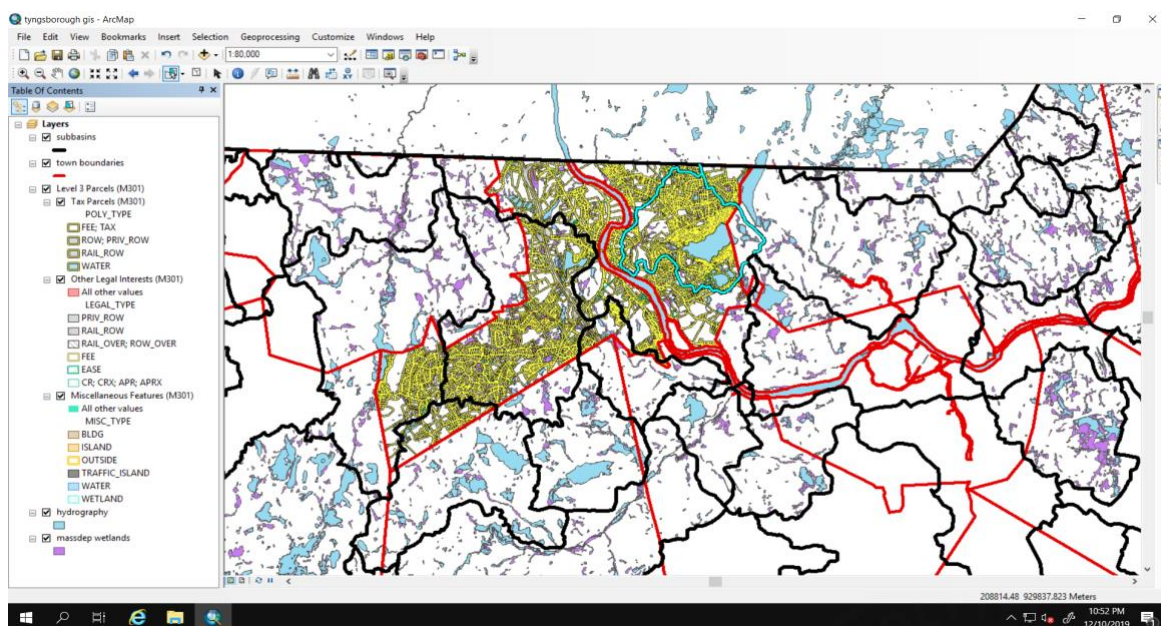


Figure 3: Chosen Subbasin for Analysis in Tyngsborough (seen highlighted in blue)

## 2.4 Objective 4: Identify and develop an appropriate plan to reduce phosphorus pollution throughout the town of Tyngsborough, specifically at the aforementioned sites

Plans will differ depending on the kind of site, but will include reduction in phosphorus application and methods to address runoff.

### 2.4.1 Non-Structural BMPs

Non-structural BMPs are practices that a government body can implement in order to prevent excess phosphorus from entering the stormwater systems. Under the Massachusetts MS4



General Permit, these non-structural BMPs include an enhanced sweeping program, catch basin cleaning, and an organic waste and leaf litter collection program (US EPA 2014).

The enhanced sweeping program is performed by sweeping impervious surfaces, such as parking lots, throughout the year. Credits for implementing this program may be calculated as:

**(1) Enhanced Sweeping Program:** The permittee may earn a phosphorus reduction credit for conducting an enhanced sweeping program of impervious surfaces. Table 2-2 below outlines the default phosphorus removal factors for enhanced sweeping programs. The credit shall be calculated by using the following equation:

$$\text{Credit}_{\text{sweeping}} = \text{IA}_{\text{swept}} \times \text{PLE}_{\text{IC-land use}} \times \text{PRF}_{\text{sweeping}} \times \text{AF} \quad \text{(Equation 2-1)}$$

**Where:**

$\text{Credit}_{\text{sweeping}}$	=	Amount of phosphorus load removed by enhanced sweeping program (lb/year)
$\text{IA}_{\text{swept}}$	=	Area of impervious surface that is swept under the enhanced sweeping program (acres)
$\text{PLE}_{\text{IC-land use}}$	=	Phosphorus Load Export Rate for impervious cover and specified land use (lb/acre/yr) (see Table 2-1)
$\text{PRF}_{\text{sweeping}}$	=	Phosphorus Reduction Factor for sweeping based on sweeper type and frequency (see Table 2-3).
$\text{AF}$	=	Annual Frequency of sweeping. For example, if sweeping does not occur in Dec/Jan/Feb, the AF would be 9 mo./12 mo. = 0.75. For year-round sweeping, AF=1.0 <sup>1</sup>

*Figure 4: Enhanced Sweeping Program*

Catch basin cleaning is the process of removing debris from BMPs. Catch basins should be cleaned frequently enough such that the storage capacity is no less than 50% of the total storage capacity.

**(2) Catch Basin Cleaning:** The permittee may earn a phosphorus reduction credit,  $Credit_{CB}$ , by removing accumulated materials from catch basins (i.e., catch basin cleaning) in the Watershed such that a minimum sump storage capacity of 50% is maintained throughout the year. The credit shall be calculated by using the following equation:

$$Credit_{CB} = IA_{CB} \times PLE_{IC-land\ use} \times PRF_{CB} \quad \text{(Equation 2-2)}$$

**Where:**

$Credit_{CB}$	=	Amount of phosphorus load removed by catch basin cleaning (lb/year)
$IA_{CB}$	=	Impervious drainage area to catch basins (acres)
$PLE_{IC-land\ use}$	=	Phosphorus Load Export Rate for impervious cover and specified land use (lb/acre/yr) (see Table 2-1)
$PRF_{CB}$	=	Phosphorus Reduction Factor for catch basin cleaning (see Table 2-4)

*Figure 5: Catch Basin Cleaning*

Organic waste collection is the process of removing waste from landscaping, organic debris, and leaf litter. These wastes are collected from impervious surfaces from which runoff proceeds to nearby water bodies.

**(3) Enhanced Organic Waste and Leaf Litter Collection program:** The permittee may earn a phosphorus reduction credit by performing regular gathering, removal and disposal of landscaping wastes, organic debris, and leaf litter from impervious surfaces from which runoff discharges to the TMDL waterbody or its tributaries. In order to earn this credit (Credit<sub>leaf litter</sub>), the permittee must gather and remove all landscaping wastes, organic debris, and leaf litter from impervious roadways and parking lots at least once per week during the period of September 1 to December 1 of each year. Credit can only be earned for those impervious surfaces that are cleared of organic materials in accordance with the description above. The gathering and removal shall occur immediately following any landscaping activities in the Watershed and at additional times when necessary to achieve a weekly cleaning frequency. The permittee must ensure that the disposal of these materials will not contribute pollutants to any surface water discharges. The permittee may use an enhanced sweeping program (e.g., weekly frequency) as part of earning this credit provided that the sweeping is effective at removing leaf litter and organic materials. The Credit<sub>leaf litter</sub> shall be determined by the following equation:

$$\text{Credit}_{\text{leaf litter}} = (\text{Watershed Area}) \times (\text{PLE}_{\text{IC-land use}}) \times (0.05) \quad \text{(Equation 2-3)}$$

**Where:**

Credit <sub>leaf litter</sub>	= Amount of phosphorus load reduction credit for organic waste and leaf litter collection program (lb/year)
Watershed Area	= All impervious area (acre) from which runoff discharges to the TMDL waterbody or its tributaries in the Watershed
PLE <sub>IC-land use</sub>	= Phosphorus Load Export Rate for impervious cover and specified land use (lbs/acre/yr) (see Table 2-1)
0.05	= 5% phosphorus reduction factor for organic waste and leaf litter collection program in the Watershed

*Figure 6: Enhanced Organic Waste and Leaf Litter Collection Program*

## 2.4.2 Structural BMPs

Structural BMPs are constructed in order to reduce the phosphorus load once it enters the stormwater system. Under the Massachusetts MS4 General Permit, these structural BMPs include infiltration trenches, infiltration basins, bio-filtration practice, gravel wetland system, porous pavement, dry pond or detention basin, and dry water quality swale/grass swale (US EPA, 2016 b).

Infiltration trenches are shallow troughs with a top layer of stone. Stormwater runoff filters through the bottom of the trench into the water table. These trenches can remove between 40-70% of total phosphorus from stormwater. The area that drains into these trenches should not be greater than five acres (MassDEP, 2008).

Infiltration basins are similar to infiltration trenches. They are built over permeable soils, and water infiltrates through through the basin into the water table. Infiltration basins remove 60-70% of total phosphorus from the water. These basins can serve a larger area of up to 15 acres (MassDEP, 2008).

Biofilter swales are grassy troughs that rely on gravity to separate out sediment, rather than filtration. Total phosphorus removal is between 85-94% (MassDEP, 2008). Gravel wetland systems are a type of constructed wetlands. They use gravel as a filter for sediment. The design of gravel wetland systems also allows vegetation to grow, which helps filter pollutants further. Constructed wetlands remove 40-50% phosphorus (MassDEP, 2008). Porous pavement has more air voids, which allows water to pass through the pavement layer and filter to the soil. The percentage of nutrient removal is unknown (MassDEP, 2008). Dry detention ponds or basins are used to hold stormwater in order to allow sediment to settle and prevent downstream flooding. These BMPs remove 10-30% total phosphorus (MassDEP, 2008). Dry water quality swales are open, grassy channels designed to hold large volumes of water during flood periods. Dry swales are underlaid by a drainage system. These BMPs can remove 20-90% of total phosphorus from stormwater (MassDEP, 2008).

#### **2.4.3 Semi-Structural BMPs**

Semi-structural BMPs can also be used to reduce phosphorus loads in stormwater. Examples of these semi-structural BMPs include impervious area disconnection through storage, impervious area disconnection, conversions of impervious area to permeable pervious area, and soil amendments to enhance permeability of pervious areas (US EPA, 2016 b).

## References

- Manuel, J. (2014, November). Nutrient Pollution: A Persistent Threat to Waterways. Retrieved November 1, 2019, from <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4216153/>.
- Marsh, Janette. (2011). BMPs & Management Measures: Structural & Nonstructural [PDF file]. Retrieved November 29, 2019 from <https://www3.epa.gov/region1/npdes/stormwater/ma/2014AppendixF-Attachment1.pdf>.
- MassDEP. (2008). Structural BMP Specifications for the Massachusetts Stormwater Handbook [PDF file]. Retrieved November 29, 2019 from <https://www.mass.gov/files/documents/2016/08/qi/v2c2.pdf>.
- NOAA. (2019, June 12). What is eutrophication? Retrieved November 1, 2019, from [https://www.epa.gov/sites/production/files/2015-10/documents/thurs1\\_02measures\\_0.pdf](https://www.epa.gov/sites/production/files/2015-10/documents/thurs1_02measures_0.pdf).
- Northern Middlesex Stormwater Collaborative. (n.d.). Water Quality. Retrieved from <http://www.nmstormwater.org/merrimack-river-water-quality>.
- US EPA. (2016). About NPDES. Retrieved December 7, 2019 from <https://www.epa.gov/npdes/about-npdes>.
- US EPA. (2016). Appendix F: Requirements for Discharges to Impaired Waters with an Approved TMDL [PDF file]. Retrieved November 21, 2019 from <https://www3.epa.gov/region1/npdes/stormwater/ma/2016fpd/appendix-f-2016-ma-sms4-gp.pdf>.
- US EPA. (2012, March 6). 5.6 Phosphorus. Retrieved November 1, 2019, from <https://archive.epa.gov/water/archive/web/html/vms56.html>.
- US EPA. (2019, February 4). Sources and Solutions. Retrieved November 1, 2019, from <https://www.epa.gov/nutrientpollution/sources-and-solutions>.

US EPA. (2019, February 4). The Effects of Nutrient Pollution. Retrieved November 1, 2019, from <https://www.epa.gov/nutrientpollution/effects>.

US EPA. (2019, April 15). The Effects: Environment. Retrieved November 1, 2019, from <https://www.epa.gov/nutrientpollution/effects-environment>.

US EPA. (2019, April 15). The Effects: Human Health. Retrieved November 1, 2019, from <https://www.epa.gov/nutrientpollution/effects-human-health>.

US EPA. (2019, February 4). The Effects: Economy. Retrieved November 1, 2019, from <https://www.epa.gov/nutrientpollution/effects-economy>.

US EPA. (2019, April 18). Where This Occurs: Lakes and Rivers. Retrieved November 1, 2019, from <https://www.epa.gov/nutrientpollution/where-occurs-lakes-and-rivers>.

US EPA. (2019, April 18). Where This Occurs: Coasts and Bays. Retrieved November 1, 2019, from <https://www.epa.gov/nutrientpollution/where-occurs-coasts-and-bays>.

US EPA. (2019, April 15). Where this occurs: Ground Water and Drinking Water. Retrieved November 1, 2019, from <https://www.epa.gov/nutrientpollution/where-occurs-ground-water-and-drinking-water>.

USGS. (n.d.). Phosphorus and Water. Retrieved November 1, 2019, from [https://www.usgs.gov/special-topic/water-science-school/science/phosphorus-and-water?qt-science\\_center\\_objects=0#qt-science\\_center\\_objects](https://www.usgs.gov/special-topic/water-science-school/science/phosphorus-and-water?qt-science_center_objects=0#qt-science_center_objects).

## Appendix II. Standard Method 4500-P

4-146

INORGANIC NONMETALS (4000)

### 4500-P PHOSPHORUS\*

#### 4500-P A. Introduction

##### 1. Occurrence

Phosphorus occurs in natural waters and in wastewaters almost solely as phosphates. These are classified as orthophosphates, condensed phosphates (pyro-, meta-, and other polyphosphates), and organically bound phosphates. They occur in solution, in particles or detritus, or in the bodies of aquatic organisms.

These forms of phosphate arise from a variety of sources. Small amounts of orthophosphate or certain condensed phosphates are added to some water supplies during treatment. Larger quantities of the same compounds may be added during laundering or other cleaning, because these materials are major constituents of many commercial cleaning preparations. Phosphates are used extensively in the treatment of boiler waters. Orthophosphates applied to agricultural or residential cultivated land as fertilizers are carried into surface waters with storm runoff and to a lesser extent with melting snow. Organic phosphates are formed primarily by biological processes. They are contributed to sewage by body wastes and food residues, and also may be formed from orthophosphates in biological treatment processes or by receiving-water biota.

Phosphorus is essential to the growth of organisms and can be the nutrient that limits the primary productivity of a body of water. In instances where phosphate is a growth-limiting nutrient, the discharge of raw or treated wastewater, agricultural drainage, or certain industrial wastes to that water may stimulate

the growth of photosynthetic aquatic micro- and macroorganisms in nuisance quantities.

Phosphates also occur in bottom sediments and in biological sludges, both as precipitated inorganic forms and incorporated into organic compounds.

##### 2. Definition of Terms

Phosphorus analyses embody two general procedural steps: (a) conversion of the phosphorus form of interest to dissolved orthophosphate, and (b) colorimetric determination of dissolved orthophosphate. The separation of phosphorus into its various forms is defined analytically but the analytical differentiations have been selected so that they may be used for interpretive purposes.

Filtration through a 0.45- $\mu\text{m}$ -pore-diam membrane filter separates dissolved from suspended forms of phosphorus. No claim is made that filtration through 0.45- $\mu\text{m}$  filters is a true separation of suspended and dissolved forms of phosphorus; it is merely a convenient and replicable analytical technique designed to make a gross separation. Prefiltration through a glass fiber filter may be used to increase the filtration rate.

Phosphates that respond to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample are termed "reactive phosphorus." While reactive phosphorus is largely a measure of orthophosphate, a small fraction of any condensed phosphate present usually is hydrolyzed unavoidably in the procedure. Reactive phosphorus occurs in both dissolved and suspended forms.

Acid hydrolysis at boiling-water temperature converts dissolved and particulate condensed phosphates to dissolved or-

\* Approved by Standard Methods Committee, 1999.  
Joint Task Group: (4500-P.J)—William Nivens (chair), Prem H. Arora, Lori J. Emery, James G. Poff, Steven C. Schindler; 20th Edition (4500-P.G, H, I)—Scott Stueg (chair), Bradford R. Fisher, Owen B. Mathre, Theresa M. Wright.

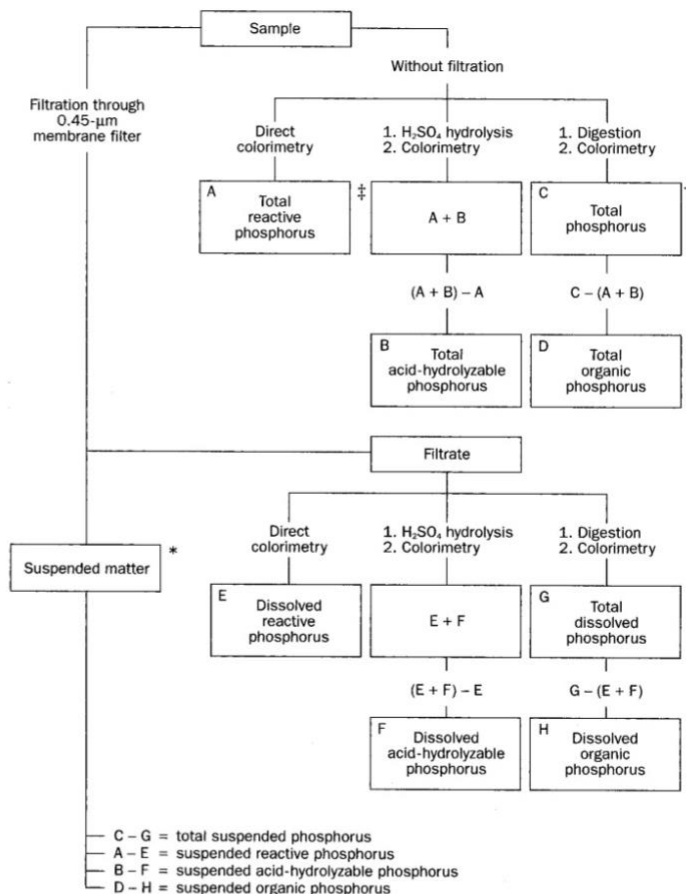


Figure 4500-P:1. Steps for analysis of phosphate fractions.

\* Direct determination of phosphorus on the membrane filter containing suspended matter will be required where greater precision than that obtained by difference is desired. Digest filter with  $\text{HNO}_3$  and follow by perchloric acid. Then perform colorimetry.

† Total phosphorus measurements on highly saline samples may be difficult because of precipitation of large quantities of salt as a result of digestion techniques that drastically reduce sample volume. For total phosphorus analyses on such samples, directly determine total dissolved phosphorus and total suspended phosphorus and add the results.

‡ In determination of total dissolved or total suspended reactive phosphorus, anomalous results may be obtained on samples containing large amounts of suspended sediments. Very often results depend largely on the degree of agitation and mixing to which samples are subjected during analysis because of a time-dependent desorption of orthophosphate from the suspended particles.

thophosphate. The hydrolysis unavoidably releases some phosphate from organic compounds, but this may be reduced to a

minimum by judicious selection of acid strength and hydrolysis time and temperature. The term "acid-hydrolyzable phosphorus" is preferred over "condensed phosphate" for this fraction.

The phosphate fractions that are converted to orthophosphate only by oxidation destruction of the organic matter present are considered "organic" or "organically bound" phosphorus. The severity of the oxidation required for this conversion depends on the form—and to some extent on the amount—of the organic phosphorus present. Like reactive phosphorus and acid-hydrolyzable phosphorus, organic phosphorus occurs both in the dissolved and suspended fractions.

The total phosphorus as well as the dissolved and suspended phosphorus fractions each may be divided analytically into the three chemical types that have been described: reactive, acid-hydrolyzable, and organic phosphorus. Figure 4500-P:1 shows



TABLE 4500-P.I. PRECISION AND BIAS DATA FOR MANUAL PHOSPHORUS METHODS

Method	Phosphorus Concentration			No. of Laboratories	Relative Standard Deviation %	Relative Error %
	Orthophosphate $\mu\text{g/L}$	Polyphosphate $\mu\text{g/L}$	Total $\mu\text{g/L}$			
Vanadomolybdophosphoric acid	100			45	75.2	21.6
	600			43	19.6	10.8
	7000			44	8.6	5.4
Stannous chloride	100			45	25.5	28.7
	600			44	14.2	8.0
	7000			45	7.6	4.3
Ascorbic acid	100			3	9.1	10.0
	600			3	4.0	4.4
	7000			3	5.2	4.9
Acid hydrolysis + vanadomolybdophosphoric acid		80		37	106.8	7.4
		300		38	66.5	14.0
		3000		37	36.1	23.5
Acid hydrolysis + stannous chloride		80		39	60.1	12.5
		300		36	47.6	21.7
		3000		38	37.4	22.8
Persulfate + vanadomolybdophosphoric acid			210	32	55.8	1.6
			990	32	23.9	2.3
			10 230	31	6.5	0.3
Sulfuric-nitric acids + vanadomolybdophosphoric acid			210	23	65.6	20.9
			990	22	47.3	0.6
			10 230	20	7.0	0.4
Perchloric acid + vanadomolybdophosphoric acid			210	4	33.5	45.2
			990	5	20.3	2.6
			10 230	6	11.7	2.2
Persulfate + stannous chloride			210	29	28.1	9.2
			990	30	14.9	12.3
			10 230	29	11.5	4.3
Sulfuric-nitric acids + stannous chloride			210	20	20.8	1.2
			990	17	8.8	3.2
			10 230	19	7.5	0.4

the steps for analysis of individual phosphorus fractions. As indicated, determinations usually are conducted only on the unfiltered and filtered samples. Suspended fractions generally are determined by difference; however, they may be determined directly by digestion of the material retained on a glass-fiber filter.

### 3. Selection of Method

*a. Digestion methods:* Because phosphorus may occur in combination with organic matter, a digestion method to determine total phosphorus must be able to oxidize organic matter effectively to release phosphorus as orthophosphate. Three digestion methods are given in Section 4500-P.B.3, 4, and 5. The perchloric acid method, the most drastic and time-consuming method, is

recommended only for particularly difficult samples such as sediments. The nitric acid-sulfuric acid method is recommended for most samples. By far the simplest method is the persulfate oxidation technique. Persulfate oxidation is coupled with ultraviolet light for a more efficient digestion in an automated in-line digestion/determination by flow injection analysis (4500-P.I).

The persulfate oxidation method in Section 4500-P.J renders a digestate that can be analyzed for both total nitrogen and total phosphorus. This procedure can be used for both parameters because it occurs over a broad pH range. During the initial stage of the digestion, sample pH is alkaline ( $\text{pH} > 12$ ); during the final stage, sample pH becomes acidic. As a result, nitrogenous compounds are oxidized to nitrate and phosphorus compounds to orthophosphate.

It is recommended that persulfate oxidation methods be checked against one or more of the more drastic digestion techniques and be adopted if identical recoveries are obtained.

*b. Colorimetric method:* Three methods of orthophosphate determination are described. Selection depends largely on the concentration range of orthophosphate. The vanadomolybdophosphoric acid method (C) is most useful for routine analysis in the range of 1 to 20 mg P/L. The stannous chloride method (D) or the ascorbic acid method (E) is more suited for the range of 0.01 to 6 mg P/L. An extraction step is recommended for the lower levels of this range and when interferences must be overcome. Automated versions of the ascorbic acid method (F, G, and H) also are presented. Careful attention to procedure may allow application of these methods to very low levels of phosphorus, such as those found in unimpaired fresh-water systems.

Ion chromatography (4110) and capillary ion electrophoresis (4140) are useful for determination of orthophosphate in undigested samples.

#### 4. Precision and Bias

To aid in method selection, Table 4500-P:1 presents the results of various combinations of digestions, hydrolysis, and colorimetric techniques for three synthetic samples of the following compositions:

Sample 1: 100  $\mu\text{g}$  orthophosphate phosphorus ( $\text{PO}_4^{3-}\text{-P/L}$ ), 80  $\mu\text{g}$  acid-hydrolyzable phosphate phosphorus/L (sodium hexametaphosphate), 30  $\mu\text{g}$  organic phosphorus/L (adenylic acid), 1.5 mg  $\text{NH}_3\text{-N/L}$ , 0.5 mg  $\text{NO}_3^-\text{-N/L}$ , and 400 mg  $\text{Cl}^-\text{/L}$ .

Sample 2: 600  $\mu\text{g}$   $\text{PO}_4^{3-}\text{-P/L}$ , 300  $\mu\text{g}$  acid-hydrolyzable phosphate phosphorus/L (sodium hexametaphosphate), 90  $\mu\text{g}$  organic phosphorus/L (adenylic acid), 0.8 mg  $\text{NH}_3\text{-N/L}$ , 5.0 mg  $\text{NO}_3^-\text{-N/L}$ , and 400 mg  $\text{Cl}^-\text{/L}$ .

Sample 3: 7.00 mg  $\text{PO}_4^{3-}\text{-P/L}$ , 3.00  $\mu\text{g}$  acid-hydrolyzable phosphate phosphorus/L (sodium hexametaphosphate), 0.230

mg organic phosphorus/L (adenylic acid), 0.20 mg  $\text{NH}_3\text{-N/L}$ , 0.05 mg  $\text{NO}_3^-\text{-N/L}$ , and 400 mg  $\text{Cl}^-\text{/L}$ .

#### 5. Sampling and Storage

If dissolved phosphorus forms are to be differentiated, filter sample immediately after collection. Preserve by freezing at or below  $-10^\circ\text{C}$ . In some cases 40 mg  $\text{HgCl}_2\text{/L}$  may be added to the samples, especially when they are to be stored for long periods before analysis. CAUTION: *HgCl<sub>2</sub> is a hazardous substance; take appropriate precautions in disposal; use of HgCl<sub>2</sub> is not encouraged.* Do not add either acid or  $\text{CHCl}_3$  as a preservative when phosphorus forms are to be determined. If total phosphorus alone is to be determined, add  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  to  $\text{pH}<2$  and cool to  $4^\circ\text{C}$ , or freeze without any additions.

Do not store samples containing low concentrations of phosphorus in plastic bottles unless kept in a frozen state because phosphates may be adsorbed onto the walls of plastic bottles.

Rinse all glass containers with hot dilute  $\text{HCl}$ , then rinse several times in reagent water. Never use commercial detergents containing phosphate for cleaning glassware used in phosphate analysis. More strenuous cleaning techniques may be used.

#### 6. Bibliography

- BLACK, C.A., D.D. EVANS, J.L. WHITE, L.E. ENSMINGER & F.E. CLARK, eds. 1965. *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*. American Soc. Agronomy, Madison, Wisc.
- JENKINS, D. 1965. A study of methods suitable for the analysis and preservation of phosphorus forms in an estuarine environment. SERL Rep. No. 65-18, Sanitary Engineering Research Lab., Univ. California, Berkeley.
- LEE, G.F. 1967. Analytical chemistry of plant nutrients. *In* Proc. Int. Conf. Eutrophication, Madison, Wisc.
- FITZGERALD, G.P. & S.L. FAUST. 1967. Effect of water sample preservation methods on the release of phosphorus from algae. *Limnol. Oceanogr.* 12:332.

## 4500-P B. Sample Preparation

For information on selection of digestion method (§s 3 through 5 below), see 4500-P.A.3a.

#### 1. Preliminary Filtration

Filter samples for determination of dissolved reactive phosphorus, dissolved acid-hydrolyzable phosphorus, and total dissolved phosphorus through  $0.45\text{-}\mu\text{m}$  membrane filters. A glass fiber filter may be used to prefilter hard-to-filter samples.

Wash membrane filters by soaking in distilled water before use because they may contribute significant amounts of phosphorus to samples containing low concentrations of phosphate. Use one of two washing techniques: (a) soak 50 filters in 2 L distilled water for 24 h; (b) soak 50 filters in 2 L distilled water for 1 h, change distilled water, and soak filters an additional 3 h. Membrane filters also may be washed by running several 100-mL portions of distilled water through them. This procedure

requires more frequent determination of blank values to ensure consistency in washing and to evaluate different lots of filters.

#### 2. Preliminary Acid Hydrolysis

The acid-hydrolyzable phosphorus content of the sample is defined operationally as the difference between reactive phosphorus as measured in the untreated sample and phosphate found after mild acid hydrolysis. Generally, it includes condensed phosphates such as pyro-, tripoly-, and higher-molecular-weight species such as hexametaphosphate. In addition, some natural waters contain organic phosphate compounds that are hydrolyzed to orthophosphate under the test conditions. Polyphosphates generally do not respond to reactive phosphorus tests but can be hydrolyzed to orthophosphate by boiling with acid.

After hydrolysis, determine reactive phosphorus by a colorimetric method (C, D, or E). Interferences, precision, bias, and sensitivity will depend on the colorimetric method used.

*a. Apparatus:*

*Autoclave or pressure cooker*, capable of operating at 98 to 137 kPa.

*b. Reagents:*

1) *Phenolphthalein indicator aqueous solution*.

2) *Strong acid solution*: Slowly add 300 mL conc  $\text{H}_2\text{SO}_4$  to about 600 mL distilled water. When cool, add 4.0 mL conc  $\text{HNO}_3$  and dilute to 1 L.

3) *Sodium hydroxide*, NaOH, 6*N*.

*c. Procedure*: To 100-mL sample or a portion diluted to 100 mL, add 0.05 mL (1 drop) phenolphthalein indicator solution. If a red color develops, add strong acid solution dropwise, to just discharge the color. Then add 1 mL more.

Boil gently for at least 90 min, adding distilled water to keep the volume between 25 and 50 mL. Alternatively, heat for 30 min in an autoclave or pressure cooker at 98 to 137 kPa. Cool, neutralize to a faint pink color with NaOH solution, and restore to the original 100-mL volume with distilled water.

Prepare a calibration curve by carrying a series of standards containing orthophosphate (see colorimetric method C, D, or E) through the hydrolysis step. Do not use orthophosphate standards without hydrolysis, because the salts added in hydrolysis cause an increase in the color intensity in some methods.

Determine reactive phosphorus content of treated portions, using Method C, D, or E. This gives the sum of polyphosphate and orthophosphate in the sample. To calculate its content of acid-hydrolyzable phosphorus, determine reactive phosphorus in a sample portion that has not been hydrolyzed, using the same colorimetric method as for treated sample, and subtract.

## 3. Perchloric Acid Digestion

*a. Apparatus:*

1) *Hot plate*: A 30- × 50-cm heating surface is adequate.

2) *Safety shield*.

3) *Safety goggles*.

4) *Erlenmeyer flasks*, 125-mL, acid-washed and rinsed with distilled water.

*b. Reagents:*

1) *Nitric acid*,  $\text{HNO}_3$ , conc.

2) *Perchloric acid*,  $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ , purchased as 70 to 72%  $\text{HClO}_4$ , reagent-grade.

3) *Sodium hydroxide*, NaOH, 6*N*.

4) *Methyl orange indicator solution*.

5) *Phenolphthalein indicator aqueous solution*.

*c. Procedure*: CAUTION—Heated mixtures of  $\text{HClO}_4$  and organic matter may explode violently. Avoid this hazard by taking the following precautions: (a) Do not add  $\text{HClO}_4$  to a hot solution that may contain organic matter. (b) Always initiate digestion of samples containing organic matter with  $\text{HNO}_3$ . Complete digestion using the mixture of  $\text{HNO}_3$  and  $\text{HClO}_4$ . (c) Do not fume with  $\text{HClO}_4$  in ordinary hoods. Use hoods especially constructed for  $\text{HClO}_4$  fuming or a glass fume eradicator\* connected to a water pump. (d) Never let samples being digested with  $\text{HClO}_4$  evaporate to dryness.

Measure sample containing the desired amount of phosphorus (this will be determined by whether Method C, D, or E is to be

used) into a 125-mL erlenmeyer flask. Acidify to methyl orange with conc  $\text{HNO}_3$ , add another 5 mL conc  $\text{HNO}_3$ , and evaporate on a steam bath or hot plate to 15 to 20 mL.

Add 10 mL each of conc  $\text{HNO}_3$  and  $\text{HClO}_4$  to the 125-mL conical flask, cooling the flask between additions. Add a few boiling chips, heat on a hot plate, and evaporate gently until dense white fumes of  $\text{HClO}_4$  just appear. If solution is not clear, cover neck of flask with a watch glass and keep solution barely boiling until it clears. If necessary, add 10 mL more  $\text{HNO}_3$  to aid oxidation.

Cool digested solution and add 1 drop aqueous phenolphthalein solution. Add 6*N* NaOH solution until the solution just turns pink. If necessary, filter neutralized solution and wash filter liberally with distilled water. Make up to 100 mL with distilled water.

Determine the  $\text{PO}_4^{3-}$ -P content of the treated sample by Method C, D, or E.

Prepare a calibration curve by carrying a series of standards containing orthophosphate (see Method C, D, or E) through digestion step. Do not use orthophosphate standards without treatment.

## 4. Sulfuric Acid-Nitric Acid Digestion

*a. Apparatus:*

1) *Digestion rack*: An electrically or gas-heated digestion rack with provision for withdrawal of fumes is recommended. Digestion racks typical of those used for micro-kjeldahl digestions are suitable.

2) *Micro-kjeldahl flasks*.

*b. Reagents:*

1) *Sulfuric acid*,  $\text{H}_2\text{SO}_4$ , conc.

2) *Nitric acid*,  $\text{HNO}_3$ , conc.

3) *Phenolphthalein indicator aqueous solution*.

4) *Sodium hydroxide*, NaOH, 1*N*.

*c. Procedure*: Into a micro-kjeldahl flask, measure a sample containing the desired amount of phosphorus (this is determined by the colorimetric method used). Add 1 mL conc  $\text{H}_2\text{SO}_4$  and 5 mL conc  $\text{HNO}_3$ .

Digest to a volume of 1 mL and then continue until solution becomes colorless to remove  $\text{HNO}_3$ .

Cool and add approximately 20 mL distilled water, 0.05 mL (1 drop) phenolphthalein indicator, and as much 1*N* NaOH solution as required to produce a faint pink tinge. Transfer neutralized solution, filtering if necessary to remove particulate material or turbidity, into a 100-mL volumetric flask. Add filter washings to flask and adjust sample volume to 100 mL with distilled water.

Determine phosphorus by Method C, D, or E, for which a separate calibration curve has been constructed by carrying standards through the acid digestion procedure.

## 5. Persulfate Digestion Method

*a. Apparatus:*

1) *Hot plate*: A 30- × 50-cm heating surface is adequate.

2) *Autoclave*: An autoclave or pressure cooker capable of developing 98 to 137 kPa may be used in place of a hot plate.

3) *Glass scoop*, to hold required amounts of persulfate crystals.

*b. Reagents:*

\* GFS Chemical Co., Columbus, OH, or equivalent.



- 1) *Phenolphthalein indicator aqueous solution.*
  - 2) *Sulfuric acid solution:* Carefully add 300 mL conc  $\text{H}_2\text{SO}_4$  to approximately 600 mL distilled water and dilute to 1 L with distilled water.
  - 3) *Ammonium persulfate*,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , solid, or potassium persulfate,  $\text{K}_2\text{S}_2\text{O}_8$ , solid.
  - 4) *Sodium hydroxide*, NaOH, 1N.
  - c. *Procedure:* Use 50 mL or a suitable portion of thoroughly mixed sample. Add 0.05 mL (1 drop) phenolphthalein indicator solution. If a red color develops, add  $\text{H}_2\text{SO}_4$  solution dropwise to just discharge the color. Then add 1 mL  $\text{H}_2\text{SO}_4$  solution and either 0.4 g solid  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  or 0.5 g solid  $\text{K}_2\text{S}_2\text{O}_8$ .
- Boil gently on a preheated hot plate for 30 to 40 min or until a final volume of 10 mL is reached. Organophosphorus compounds such as AMP may require as much as 1.5 to 2 h for complete digestion. Cool, dilute to 30 mL with distilled water, add 0.05 mL (1 drop) phenolphthalein indicator solution, and neutralize to a faint pink color with NaOH. Alternatively, heat for 30 min in an autoclave or pressure cooker at 98 to 137 kPa.

Cool, add 0.05 mL (1 drop) phenolphthalein indicator solution, and neutralize to a faint pink color with NaOH. Make up to 100 mL with distilled water. In some samples a precipitate may form at this stage, but do not filter. For any subsequent subdividing of the sample, shake well. The precipitate (which is possibly a calcium phosphate) redissolves under the acid conditions of the colorimetric reactive phosphorus test. Determine phosphorus by Method C, D, or E, for which a separate calibration curve has been constructed by carrying standards through the persulfate digestion procedure.

#### 6. Bibliography

- LEE, G.F., N.L. CLESCERI & G.P. FITZGERALD. 1965. Studies on the analysis of phosphates in algal cultures. *J. Air Water Pollut.* 9:715.
- SHANNON, J.E. & G.F. LEE. 1966. Hydrolysis of condensed phosphates in natural waters. *J. Air Water Pollut.* 10:735.
- GALES, M.E., JR., E.C. JULIAN & R.C. KRONER. 1966. Method for quantitative determination of total phosphorus in water. *J. Amer. Water Works Assoc.* 58:1363.

### 4500-P C. Vanadomolybdophosphoric Acid Colorimetric Method

#### 1. General Discussion

- a. *Principle:* In a dilute orthophosphate solution, ammonium molybdate reacts under acid conditions to form a heteropoly acid, molybdophosphoric acid. In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed. The intensity of the yellow color is proportional to phosphate concentration.
- b. *Interference:* Positive interference is caused by silica and arsenate only if the sample is heated. Negative interferences are caused by arsenate, fluoride, thorium, bismuth, sulfide, thiosulfate, thiocyanate, or excess molybdate. Blue color is caused by ferrous iron but this does not affect results if ferrous iron concentration is less than 100 mg/L. Sulfide interference may be removed by oxidation with bromine water. Ions that do not interfere in concentrations up to 1000 mg/L are  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{U}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{AsO}_3^-$ ,  $\text{Br}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{CN}^-$ ,  $\text{IO}_3^-$ ,  $\text{SiO}_4^{4-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ , pyrophosphate, molybdate, tetraborate, selenate, benzoate, citrate, oxalate, lactate, tartrate, formate, and salicylate. If  $\text{HNO}_3$  is used in the test,  $\text{Cl}^-$  interferes at 75 mg/L.
- c. *Minimum detectable concentration:* The minimum detectable concentration is 200  $\mu\text{g P/L}$  in 1-cm spectrophotometer cells.

#### 2. Apparatus

- a. *Colorimetric equipment:* One of the following is required:
    - 1) *Spectrophotometer*, for use at 400 to 490 nm.
    - 2) *Filter photometer*, provided with a blue or violet filter exhibiting maximum transmittance between 400 and 470 nm.
- The wavelength at which color intensity is measured depends on sensitivity desired, because sensitivity varies tenfold with wavelengths 400 to 490 nm. Ferric iron causes interference at

low wavelengths, particularly at 400 nm. A wavelength of 470 nm usually is used. Concentration ranges for different wavelengths are:

P Range mg/L	Wavelength nm
1.0-5.0	400
2.0-10	420
4.0-18	470

- b. *Acid-washed glassware:* Use acid-washed glassware for determining low concentrations of phosphorus. Phosphate contamination is common because of its absorption on glass surfaces. Avoid using commercial detergents containing phosphate. Clean all glassware with hot dilute HCl and rinse well with distilled water. Preferably, reserve the glassware only for phosphate determination, and after use, wash and keep filled with water until needed. If this is done, acid treatment is required only occasionally.

c. *Filtration apparatus and filter paper.\**

#### 3. Reagents

- a. *Phenolphthalein indicator aqueous solution.*
- b. *Hydrochloric acid*, HCl, 1 + 1.  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$ , or  $\text{HNO}_3$  may be substituted for HCl. The acid concentration in the determination is not critical but a final sample concentration of 0.5N is recommended.
- c. *Activated carbon.†* Remove fine particles by rinsing with distilled water.

\* Whatman No. 42 or equivalent.

† Darco G60 or equivalent.

*d. Vanadate-molybdate reagent:*

1) *Solution A:* Dissolve 25 g ammonium molybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , in 300 mL distilled water.

2) *Solution B:* Dissolve 1.25 g ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ , by heating to boiling in 300 mL distilled water. Cool and add 330 mL conc HCl. Cool Solution B to room temperature, pour Solution A into Solution B, mix, and dilute to 1 L.

*e. Standard phosphate solution:* Dissolve in distilled water 219.5 mg anhydrous  $\text{KH}_2\text{PO}_4$  and dilute to 1000 mL; 1.00 mL = 50.0  $\mu\text{g PO}_4^{3-}\text{-P}$ .

## 4. Procedure

*a. Sample pH adjustment:* If sample pH is greater than 10, add 0.05 mL (1 drop) phenolphthalein indicator to 50.0 mL sample and discharge the red color with 1 + 1 HCl before diluting to 100 mL.

*b. Color removal from sample:* Remove excessive color in sample by shaking about 50 mL with 200 mg activated carbon in an erlenmeyer flask for 5 min and filter to remove carbon. Check each batch of carbon for phosphate because some batches produce high reagent blanks.

*c. Color development in sample:* Place 35 mL or less of sample, containing 0.05 to 1.0 mg P, in a 50-mL volumetric flask. Add 10 mL vanadate-molybdate reagent and dilute to the mark with distilled water. Prepare a blank in which 35 mL distilled water is substituted for the sample. After 10 min or more, measure absorbance of sample versus a blank at a wavelength of 400 to 490 nm, depending on sensitivity desired (see ¶ 2a above). The color is stable for days and its intensity is unaffected by variation in room temperature.

*d. Preparation of calibration curve:* Prepare a calibration curve by using suitable volumes of standard phosphate solution and proceeding as in ¶ 4c. When ferric ion is low enough not to interfere, plot a family of calibration curves of one series of standard solutions for various wavelengths. This permits a wide

latitude of concentrations in one series of determinations. Analyze at least one standard with each set of samples.

## 5. Calculation

$$\text{mg P/L} = \frac{\text{mg P (in 50 mL final volume)} \times 1000}{\text{mL sample}}$$

## 6. Precision and Bias

See Table 4500-P:1.

## 7. Bibliography

- KITSON, R.E. & M.G. MELLON. 1944. Colorimetric determination of phosphorus as molybdovanadophosphoric acid. *Ind. Eng. Chem., Anal. Ed.* 16:379.
- BOLTZ, D.F. & M.G. MELLON. 1947. Determination of phosphorus, germanium, silicon, and arsenic by the heteropoly blue method. *Ind. Eng. Chem., Anal. Ed.* 19:873.
- GREENBERG, A.E., L.W. WEINBERGER & C.N. SAWYER. 1950. Control of nitrite interference in colorimetric determination of phosphorus. *Anal. Chem.* 22:499.
- YOUNG, R.S. & A. GOLLEGE. 1950. Determination of hexametaphosphate in water after threshold treatment. *Ind. Chem.* 26:13.
- GRISWOLD, B.L., F.L. HUMOLLER & A.R. MCINTYRE. 1951. Inorganic phosphates and phosphate esters in tissue extracts. *Anal. Chem.* 23:192.
- BOLTZ, D.F., ed. 1958. *Colorimetric Determination of Nonmetals*. Interscience Publishers, New York, N.Y.
- AMERICAN WATER WORKS ASSOCIATION. 1958. Committee report. Determination of orthophosphate, hydrolyzable phosphate, and total phosphate in surface waters. *J. Amer. Water Works Assoc.* 50:1563.
- JACKSON, M.L. 1958. *Soil Chemical Analysis*. Prentice-Hall, Englewood Cliffs, N.J.
- ABBOT, D.C., G.E. EMSDEN & J.R. HARRIS. 1963. A method for determining orthophosphate in water. *Analyst* 88:814.
- PROFT, G. 1964. Determination of total phosphorus in water and wastewater as molybdovanadophosphoric acid. *Limnologia* 2:407.

## 4500-P D. Stannous Chloride Method

## 1. General Discussion

*a. Principle:* Molybdophosphoric acid is formed and reduced by stannous chloride to intensely colored molybdenum blue. This method is more sensitive than Method C and makes feasible measurements down to 7  $\mu\text{g P/L}$  by use of increased light path length. Below 100  $\mu\text{g P/L}$  an extraction step may increase reliability and lessen interference.

*b. Interference:* See Section 4500-P.C.1b.

*c. Minimum detectable concentration:* The minimum detectable concentration is about 3  $\mu\text{g P/L}$ . The sensitivity at 0.3010 absorbance is about 10  $\mu\text{g P/L}$  for an absorbance change of 0.009.

## 2. Apparatus

The same apparatus is required as for Method C, except that a pipetting bulb is required for the extraction step. Set spectrophotometer at 625 nm in the measurement of benzene-isobutanol ex-

tracts and at 690 nm for aqueous solutions. If the instrument is not equipped to read at 690 nm, use a wavelength of 650 nm for aqueous solutions, with somewhat reduced sensitivity and precision.

## 3. Reagents

*a. Phenolphthalein indicator aqueous solution.*

*b. Strong-acid solution:* Prepare as directed in Section 4500-P.B.2b2).

*c. Ammonium molybdate reagent I:* Dissolve 25 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 175 mL distilled water. Cautiously add 280 mL conc  $\text{H}_2\text{SO}_4$  to 400 mL distilled water. Cool, add molybdate solution, and dilute to 1 L.

*d. Stannous chloride reagent I:* Dissolve 2.5 g fresh  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 mL glycerol. Heat in a water bath and stir with a glass rod to hasten dissolution. This reagent is stable and requires neither preservatives nor special storage.

*e. Standard phosphate solution:* Prepare as directed in Section 4500-P.C.3e.

## PHOSPHORUS (4500-P)/Ascorbic Acid Method

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*f. Reagents for extraction:*

1) *Benzene-isobutanol solvent:* Mix equal volumes of benzene and isobutyl alcohol. (CAUTION—This solvent is highly flammable.)

2) *Ammonium molybdate reagent II:* Dissolve 40.1 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in approximately 500 mL distilled water. Slowly add 396 mL ammonium molybdate reagent I. Cool and dilute to 1 L.

3) *Alcoholic sulfuric acid solution:* Cautiously add 20 mL conc  $\text{H}_2\text{SO}_4$  to 980 mL methyl alcohol with continuous mixing.

4) *Dilute stannous chloride reagent II:* Mix 8 mL stannous chloride reagent I with 50 mL glycerol. This reagent is stable for at least 6 months.

## 4. Procedure

*a. Preliminary sample treatment:* To 100 mL sample containing not more than 200  $\mu\text{g}$  P and free from color and turbidity, add 0.05 mL (1 drop) phenolphthalein indicator. If sample turns pink, add strong acid solution dropwise to discharge the color. If more than 0.25 mL (5 drops) is required, take a smaller sample and dilute to 100 mL with distilled water after first discharging the pink color with acid.

*b. Color development:* Add, with thorough mixing after each addition, 4.0 mL molybdate reagent I and 0.5 mL (10 drops) stannous chloride reagent I. Rate of color development and intensity of color depend on temperature of the final solution, each  $1^\circ\text{C}$  increase producing about 1% increase in color. Hence, hold samples, standards, and reagents within  $2^\circ\text{C}$  of one another and in the temperature range between 20 and  $30^\circ\text{C}$ .

*c. Color measurement:* After 10 min, but before 12 min, using the same specific interval for all determinations, measure color photometrically at 690 nm and compare with a calibration curve, using a distilled water blank. Light path lengths suitable for various concentration ranges are as follows:

Approximate P Range mg/L	Light Path cm
0.3–2	0.5
0.1–1	2
0.007–0.2	10

Always run a blank on reagents and distilled water. Because the color at first develops progressively and later fades, maintain

equal timing conditions for samples and standards. Prepare at least one standard with each set of samples or once each day that tests are made. The calibration curve may deviate from a straight line at the upper concentrations of the 0.3 to 2.0-mg/L range.

*d. Extraction:* When increased sensitivity is desired or interferences must be overcome, extract phosphate as follows: Pipet a 40-mL sample, or one diluted to that volume, into a 125-mL separatory funnel. Add 50.0 mL benzene-isobutanol solvent and 15.0 mL molybdate reagent II. Close funnel at once and shake vigorously for exactly 15 s. If condensed phosphate is present, any delay will increase its conversion to orthophosphate. Remove stopper and withdraw 25.0 mL of separated organic layer, using a pipet with safety bulb. Transfer to a 50-mL volumetric flask, add 15 to 16 mL alcoholic  $\text{H}_2\text{SO}_4$  solution, swirl, add 0.50 mL (10 drops) dilute stannous chloride reagent II, swirl, and dilute to the mark with alcoholic  $\text{H}_2\text{SO}_4$ . Mix thoroughly. After 10 min, but before 30 min, read against the blank at 625 nm. Prepare blank by carrying 40 mL distilled water through the same procedure used for the sample. Read phosphate concentration from a calibration curve prepared by taking known phosphate standards through the same procedure used for samples.

## 5. Calculation

Calculate as follows:

*a. Direct procedure:*

$$\text{mg P/L} = \frac{\text{mg P (in approximately 104.5 mL final volume)} \times 1000}{\text{mL sample}}$$

*b. Extraction procedure:*

$$\text{mg P/L} = \frac{\text{mg P (in 50 mL final volume)} \times 1000}{\text{mL sample}}$$

## 6. Precision and Bias

See Table 4500-P:I.

## 4500-P E. Ascorbic Acid Method

## 1. General Discussion

*a. Principle:* Ammonium molybdate and antimony potassium tartrate react in acid medium with orthophosphate to form a heteropoly acid—phosphomolybdic acid—that is reduced to intensely colored molybdenum blue by ascorbic acid.

*b. Interference:* Arsenates react with the molybdate reagent to produce a blue color similar to that formed with phosphate.

Concentrations as low as 0.1 mg As/L interfere with the phosphate determination. Hexavalent chromium and  $\text{NO}_2^-$  interfere to give results about 3% low at concentrations of 1 mg/L and 10 to 15% low at 10 mg/L. Sulfide ( $\text{Na}_2\text{S}$ ) and silicate do not interfere at concentrations of 1.0 and 10 mg/L.

*c. Minimum detectable concentration:* Approximately 10  $\mu\text{g}$  P/L. P ranges are as follows:



Approximate P Range mg/L	Light Path cm
0.30–2.0	0.5
0.15–1.30	1.0
0.01–0.25	5.0

## 2. Apparatus

*a. Colorimetric equipment:* One of the following is required:

1) *Spectrophotometer*, with infrared phototube for use at 880 nm, providing a light path of 2.5 cm or longer.

2) *Filter photometer*, equipped with a red color filter and a light path of 0.5 cm or longer.

*b. Acid-washed glassware:* See Section 4500-P.C.2b.

## 3. Reagents

*a. Sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, 5N:* Dilute 70 mL conc H<sub>2</sub>SO<sub>4</sub> to 500 mL with distilled water.

*b. Antimony potassium tartrate solution:* Dissolve 1.3715 g K(SbO)C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> · ½H<sub>2</sub>O in 400 mL distilled water in a 500-mL volumetric flask and dilute to volume. Store in a glass-stoppered bottle.

*c. Ammonium molybdate solution:* Dissolve 20 g (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> · 4H<sub>2</sub>O in 500 mL distilled water. Store in a glass-stoppered bottle.

*d. Ascorbic acid, 0.1M:* Dissolve 1.76 g ascorbic acid in 100 mL distilled water. The solution is stable for about 1 week at 4°C.

*e. Combined reagent:* Mix the above reagents in the following proportions for 100 mL of the combined reagent: 50 mL 5N H<sub>2</sub>SO<sub>4</sub>, 5 mL antimony potassium tartrate solution, 15 mL ammonium molybdate solution, and 30 mL ascorbic acid solution. *Mix after addition of each reagent.* Let all reagents reach room temperature before they are mixed and mix in the order given. If turbidity forms in the combined reagent, shake and let stand for a few minutes until turbidity disappears before proceeding. The reagent is stable for 4 h.

*f. Stock phosphate solution:* See Section 4500-P.C.3e.

*g. Standard phosphate solution:* Dilute 50.0 mL stock phosphate solution to 1000 mL with distilled water; 1.00 mL = 2.50 µg P.

## 4. Procedure

*a. Treatment of sample:* Pipet 50.0 mL sample into a clean, dry test tube or 125-mL erlenmeyer flask. Add 0.05 mL (1 drop) phenolphthalein indicator. If a red color develops add 5N H<sub>2</sub>SO<sub>4</sub> solution dropwise to just discharge the color. Add 8.0 mL combined reagent and mix thoroughly. After at least 10 min but no more than 30 min, measure absorbance of each sample at 880 nm, using reagent blank as the reference solution.

*b. Correction for turbidity or interfering color:* Natural color of water generally does not interfere at the high wavelength used. For highly colored or turbid waters, prepare a blank by adding all reagents except ascorbic acid and antimony potassium tartrate to the sample. Subtract blank absorbance from absorbance of each sample.

*c. Preparation of calibration curve:* Prepare individual calibration curves from a series of six standards within the phosphate ranges indicated in § 1c above. Use a distilled water blank with the combined reagent to make photometric readings for the calibration curve. Plot absorbance vs. phosphate concentration to give a straight line passing through the origin. Test at least one phosphate standard with each set of samples.

## 5. Calculation

$$\text{mg P/L} = \frac{\text{mg P (in approximately 58 mL final volume)} \times 1000}{\text{mL sample}}$$

## 6. Precision and Bias

The precision and bias values given in Table 4500-P:I are for a single-solution procedure given in the 13th edition. The present procedure differs in reagent-to-sample ratios, no addition of solvent, and acidity conditions. It is superior in precision and bias to the previous technique in the analysis of both distilled water and river water at the 228-µg P/L level (Table 4500-P:II).

## 7. References

- EDWARDS, G.P., A.H. MOLOF & R.W. SCHNEEMAN. 1965. Determination of orthophosphate in fresh and saline waters. *J. Amer. Water Works Assoc.* 57:917.

TABLE 4500-P:II. COMPARISON OF PRECISION AND BIAS OF ASCORBIC ACID METHODS

Ascorbic Acid Method	Phosphorus Concentration, Dissolved Orthophosphate µg/L	No. of Labora- tories	Relative Standard Deviation %		Relative Error %	
			Distilled Water	River Water	Distilled Water	River Water
13th Edition <sup>1</sup>	228	8	3.87	2.17	4.01	2.08
Current method <sup>2</sup>	228	8	3.03	1.75	2.38	1.39

2. MURPHY, J. & J. RILEY. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27:31.

## 8. Bibliography

SLETTEN, O. & C.M. BACH. 1961. Modified stannous chloride reagent for orthophosphate determination. *J. Amer. Water Works Assoc.* 53: 1031.

STRICKLAND, J.D.H. & T.R. PARSONS. 1965. A Manual of Sea Water Analysis, 2nd ed. Fisheries Research Board of Canada, Ottawa.

## 4500-P F. Automated Ascorbic Acid Reduction Method

### 1. General Discussion

*a. Principle:* Ammonium molybdate and antimony potassium tartrate react with orthophosphate in an acid medium to form an antimony-phosphomolybdate complex, which, on reduction with ascorbic acid, yields an intense blue color suitable for photometric measurement.

*b. Interferences:* As much as 50 mg  $\text{Fe}^{3+}$ /L, 10 mg Cu/L, and 10 mg  $\text{SiO}_2$ /L can be tolerated. High silica concentrations cause positive interference.

In terms of phosphorus, the results are high by 0.005, 0.015, and 0.025 mg/L for silica concentrations of 20, 50, and 100 mg/L, respectively. Salt concentrations up to 20% (w/v) cause an error of less than 1%. Arsenate ( $\text{AsO}_4^{3-}$ ) is a positive interference.

Eliminate interference from  $\text{NO}_2^-$  and  $\text{S}^{2-}$  by adding an excess of bromine water or a saturated potassium permanganate ( $\text{KMnO}_4$ ) solution. Remove interfering turbidity by filtration before analysis. Filter samples for total or total hydrolyzable phosphorus only after digestion. Sample color that absorbs in the photometric range used for analysis also will interfere. See also Section 4500-P.E.1b.

*c. Application:* Orthophosphate can be determined in potable, surface, and saline waters as well as domestic and industrial

wastewaters over a range of 0.001 to 10.0 mg P/L when photometric measurements are made at 650 to 660 or 880 nm in a 15-mm or 50-mm tubular flow cell. Determine higher concentrations by diluting sample. Although the automated test is designed for orthophosphate only, other phosphorus compounds can be converted to this reactive form by various sample pretreatments described in Section 4500-P.B.1, 2, and 5.

### 2. Apparatus

*a. Automated analytical equipment:* An example of the continuous-flow analytical instrument consists of the interchangeable components shown in Figure 4500-P.2. A flow cell of 15 or 50 mm and a filter of 650 to 660 or 880 nm may be used.

*b. Hot plate or autoclave.*

*c. Acid-washed glassware:* See Section 4500-P.C.2b.

### 3. Reagents

*a. Antimony potassium tartrate solution:* Dissolve 0.3 g  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$  in approximately 50 mL distilled water and dilute to 100 mL. Store at 4°C in a dark, glass-stoppered bottle.

*b. Ammonium molybdate solution:* Dissolve 4 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 100 mL distilled water. Store in a plastic bottle at 4°C.

*c. Ascorbic acid solution:* See Section 4500-P.E.3d.

*d. Combined reagent:* See Section 4500-P.E.3e.

*e. Dilute sulfuric acid solution:* Slowly add 140 mL conc  $\text{H}_2\text{SO}_4$  to 600 mL distilled water. When cool, dilute to 1 L.

*f. Ammonium persulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , crystalline.*

*g. Phenolphthalein indicator aqueous solution.*

*h. Stock phosphate solution:* Dissolve 439.3 mg anhydrous  $\text{KH}_2\text{PO}_4$ , dried for 1 h at 105°C, in distilled water and dilute to 1000 mL; 1.00 mL = 100  $\mu\text{g}$  P.

*i. Intermediate phosphate solution:* Dilute 100.0 mL stock phosphate solution to 1000 mL with distilled water; 1.00 mL = 10.0  $\mu\text{g}$  P.

*j. Standard phosphate solutions:* Prepare a suitable series of standards by diluting appropriate volumes of intermediate phosphate solution.

### 4. Procedure

Set up manifold as shown in Figure 4500-P.2 and follow the general procedure described by the manufacturer.

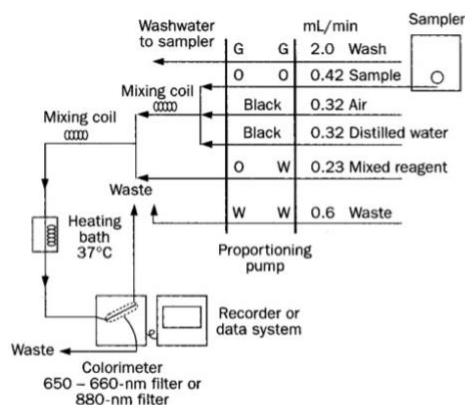


Figure 4500-P.2. Phosphate manifold for automated analytical system.



Add 0.05 mL (1 drop) phenolphthalein indicator solution to approximately 50 mL sample. If a red color develops, add  $\text{H}_2\text{SO}_4$  (3e) dropwise to just discharge the color.

#### 5. Calculation

Prepare standard curves by plotting response of standards processed through the manifold against P concentration in standards. Compute sample P concentration by comparing sample response with standard curve.

#### 6. Precision and Bias

Six samples were analyzed in a single laboratory in septuplicate. At an average  $\text{PO}_4^{3-}$  concentration of 0.340 mg/L, the average deviation was 0.015 mg/L. The coefficient of variation

was 6.2%. In two samples with added  $\text{PO}_4^{3-}$ , recoveries were 89 and 96%.

#### 7. Bibliography

- HENRIKSEN, A. 1966. An automatic method for determining orthophosphate in sewage and highly polluted waters. *Analyst* 91:652.
- LOBBING, L.B. & R.L. BOOTH. 1973. Evaluation of the AutoAnalyzer II; A progress report. In *Advances in Automated Analysis: 1972 Technicon International Congress*. Vol. 8, p. 7. Mediad, Inc., Tarrytown, N.Y.
- U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020, National Environmental Research Center, Cincinnati, Ohio.
- U.S. ENVIRONMENTAL PROTECTION AGENCY. MDQARL Method Study 4, Automated Methods. National Environmental Research Center, Cincinnati, Ohio.

### 4500-P G. Flow Injection Analysis for Orthophosphate

#### 1. General Discussion

*a. Principle:* The orthophosphate ion ( $\text{PO}_4^{3-}$ ) reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex that absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

Also see Sections 4500-P.A, B, and F, and Section 4130, Flow Injection Analysis (FIA).

*b. Interferences:* Remove large or fibrous particulates by filtering sample through glass wool. Guard against contamination from reagents, water, glassware, and the sample preservation process.

Silica forms a pale blue complex that also absorbs at 880 nm. This interference is generally insignificant because a silica concentration of approximately 30 mg/L would be required to produce a 0.005 mg P/L positive error in orthophosphate.

Concentrations of ferric iron greater than 50 mg/L cause a negative error due to competition with the complex for the reducing agent ascorbic acid. Treat samples high in iron with sodium bisulfite to eliminate this interference, as well as the interference due to arsenates.

Glassware contamination is a problem in low-level phosphorus determinations. Wash glassware with hot dilute HCl and rinse with reagent water. Commercial detergents are rarely needed but, if they are used, use special phosphate-free preparations.

Also see Section 4500-P.F.

#### 2. Apparatus

*Flow injection analysis equipment* consisting of:

- FIA injection valve* with sample loop or equivalent.
- Multichannel proportioning pump.*
- FIA manifold* (Figure 4500-P:3) with tubing heater and flow cell. Relative flow rates only are shown in Figure 4500-P:3. Tubing volumes are given as an example only; they may be scaled down proportionally. Use manifold tubing of an inert material such as TFE.

*d. Absorbance detector*, 880 nm, 10-nm bandpass.

*e. Injection valve control and data acquisition system.*

#### 3. Reagents

Use reagent water (>10 megohm) to prepare carrier and all solutions. To prevent bubble formation, degas carrier and buffer with helium. Pass He at 140 kPa (20 psi) through a helium degassing tube. Bubble He through 1 L solution for 1 min. As an alternative to preparing reagents by weight/weight, use weight/volume.

*a. Stock ammonium molybdate solution:* To a tared 1-L container add 40.0 g ammonium molybdate tetrahydrate [ $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ] and 983 g water. Mix with a magnetic stirrer for at least 4 h. Store in plastic and refrigerate.

*b. Stock antimony potassium tartrate solution:* To a 1-L dark, tared container add 3.0 g antimony potassium tartrate (potassium antimonyl tartrate hemihydrate),  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ , and 995 g water. Mix with a magnetic stirrer until dissolved. Store in a dark bottle and refrigerate.

*c. Working molybdate color reagent:* To a tared 1-L container add 680 g water, then add 64.4 g conc sulfuric acid. CAUTION: This solution becomes very hot! Swirl to mix. When mixture can be handled comfortably, add 213 g stock ammonium molybdate

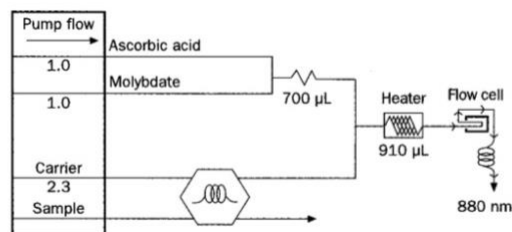


Figure 4500-P:3. FIA orthophosphate manifold.

solution (¶ 3a) and 72.0 g stock antimony potassium tartrate solution (¶ 3b). Shake and degas with helium.

d. *Ascorbic acid solution*: To a tared 1-L container, add 60.0 g granular ascorbic acid and 975 g water. Stir or shake until dissolved. Degas this reagent with helium, then add 1.0 g dodecyl sulfate,  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$ , stirring gently to mix. Prepare fresh weekly.

e. *Stock orthophosphate standard*, 25.00 mg P/L: In a 1-L volumetric flask dissolve 0.1099 g primary standard grade anhydrous potassium phosphate monobasic ( $\text{KH}_2\text{PO}_4$ ) that has been dried for 1 h at 105°C in about 800 mL water. Dilute to mark with water and invert to mix.

f. *Standard orthophosphate solutions*: Prepare orthophosphate standards in desired concentration range, using stock standard (¶ 3e) and diluting with water.

#### 4. Procedure

Set up a manifold equivalent to that in Figure 4500-P:3 and follow method supplied by manufacturer or laboratory standard operating procedure. Use quality control protocols outlined in Section 4020.

#### 5. Calculations

Prepare standard curves by plotting absorbance of standards processed through the manifold versus orthophosphate concentration. The calibration curve is linear.

#### 6. Precision and Bias

a. *Recovery and relative standard deviation*: Table 4500-P:III gives results of single-laboratory studies.

b. *MDL*: A 700- $\mu\text{L}$  sample loop was used in the method described above. Using a published MDL method,<sup>1</sup> analysts ran 21 replicates of a 5.0- $\mu\text{g}$  P/L standard. These gave a mean of 5.26  $\mu\text{g}$  P/L, a standard deviation of 0.264  $\mu\text{g}$  P/L, and MDL of 0.67  $\mu\text{g}$  P/L.

#### 7. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1984. Definition and procedure for the determination of method detection limits. Appendix B to 40 CFR 136 Rev. 1.11 amended June 30, 1986. 49 CFR 43430.

TABLE 4500-P:III. RESULTS OF SINGLE-LABORATORY STUDIES WITH SELECTED MATRICES

Matrix	Sample/Blank Designation	Known Addition mg P/L	Recovery %	Relative Standard Deviation %
Wastewater treatment plant influent	Reference sample*	—	101	—
	Blank†	0.05	96	—
		0.1	95	—
	Site A‡§	0	—	0.7
		0.05	98	—
		0.1	101	—
	Site B‡§	0	—	5
		0.05	75	—
		0.1	91	—
	Site C‡§	0	—	0.6
		0.05	88	—
		0.1	97	—
Wastewater treatment plant effluent	Reference sample*	—	100	—
	Blank†	0.05	96	—
		0.1	96	—
	Site A‡	0	—	0.7
		0.05	94	—
		0.1	96	—
	Site B‡	0	—	0.3
		0.05	94	—
		0.1	99	—
	Site C‡	0	—	0.5
		0.05	109	—
		0.1	107	—
Landfill leachate	Reference sample*	—	98	—
	Blank†	0.05	94	—
		0.1	95	—
	Site A‡#	0	—	0.9
		0.05	105	—
		0.1	106	—
	Site B‡#	0	—	6.7
		0.05	89	—
		0.1	94	—
	Site C‡#	0	—	0.9
		0.05	110	—
		0.1	109	—

\* U.S. EPA QC sample, 0.109 mg P/L.

† Determined in duplicate.

‡ Samples without known additions determined four times; samples with known additions determined in duplicate.

§ Sample dilutions: A - 5-fold; B - 100-fold; C - 10-fold. Typical relative difference between duplicates 0.5%.

|| Sample dilutions: A - 5-fold; B - 20-fold; C - 10-fold. Typical relative difference between duplicates 0.3%.

# Sample dilutions: A - 20-fold; B - 10-fold; C - 20-fold. Typical relative difference between duplicates 1%.

## 4500-P H. Manual Digestion and Flow Injection Analysis for Total Phosphorus

### 1. General Discussion

*a. Principle:* Polyphosphates are converted to the orthophosphate form by a sulfuric acid digestion and organic phosphorus is converted to orthophosphate by a persulfate digestion. When the resulting solution is injected onto the manifold, the orthophosphate ion ( $\text{PO}_4^{3-}$ ) reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex that absorbs light at 880 nm. The absorbance is proportional to the concentration of total phosphorus in the sample.

See Section 4500-P.A for a discussion of the various forms of phosphorus found in waters and wastewaters, Section 4500-P.B for a discussion of sample preparation and digestion, and Section 4130, Flow Injection Analysis (FIA).

*b. Interferences:* See 4500-P.G.1b.

### 2. Apparatus

*Digestion and flow injection analysis equipment consisting of:*

*a. Hotplate or autoclave.*

*b. FIA injection valve with sample loop or equivalent.*

*c. Multichannel proportioning pump.*

*d. FIA manifold (Figure 4500-P:4) with tubing heater and flow cell. Relative flow rates only are shown in Figure 4500-P:4. Tubing volumes are given as an example only; they may be scaled down proportionally. Use manifold tubing of an inert material such as TFE.*

### 3. Reagents

Use reagent water (>10 megohm) for all solutions. To prevent bubble formation, degas carrier and buffer with helium. Pass He at 140 kPa (20 psi) through a helium degassing tube. Bubble He

through 1 L solution for 1 min. As an alternative to preparing reagents by weight/weight, use weight/volume.

Prepare reagents listed in 4500-P.G.3a, b, d, e, and f, and in addition:

*a. Sulfuric acid carrier,  $\text{H}_2\text{SO}_4$ , 0.13M:* To a tared 1-L container add 993 g water, then add 13.3 g conc  $\text{H}_2\text{SO}_4$ . Shake carefully to mix. Degas daily. Prepare fresh weekly.

*b. Molybdate color reagent:* To a tared 1-L container add 694 g water, then add 38.4 g conc  $\text{H}_2\text{SO}_4$ . CAUTION: *The solution becomes very hot!* Swirl to mix. When mixture can be handled comfortably, add 72.0 g stock antimony potassium tartrate (§ G.3b) and 213 g stock ammonium molybdate (§ G.3a). Shake to mix, and degas.

### 4. Procedure

See Section 4500-P.B.4 or 5 for digestion procedures. Carry both standards and samples through the digestion. The resulting solutions should be about 0.13M in sulfuric acid to match the concentration of the carrier. If the solutions differ more than 10% from this concentration, adjust concentration of carrier's sulfuric acid to match that of digested samples.

Set up a manifold equivalent to that in Figure 4500-P:4 and analyze digested samples and standards by following method supplied by manufacturer or laboratory's standard operating procedure. Use quality control protocols outlined in Section 4020.

### 5. Calculations

Prepare standard curves by plotting absorbance of standards processed through the manifold versus phosphorus concentration. The calibration curve is linear.

### 6. Precision and Bias

*a. MDL:* A 780- $\mu\text{L}$  sample loop was used in the method described above. Using a published MDL method,<sup>1</sup> analysts ran 21 replicates of a 3.5- $\mu\text{g}$  P/L standard. These gave a mean of 3.53  $\mu\text{g}$  P/L, a standard deviation of 0.82  $\mu\text{g}$  P/L, and MDL of 2.0  $\mu\text{g}$  P/L. The MDL is limited mainly by the precision of the digestion.

*b. Precision study:* Ten injections of a 100.0- $\mu\text{g}$  P/L standard gave a percent relative standard deviation of 0.3%.

### 7. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1984. Definition and procedure for the determination of method detection limits. Appendix B to 40 CFR 136 Rev. 1.11 amended June 30, 1986. 49 CFR 43430.

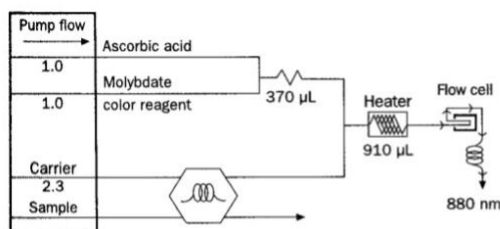


Figure 4500-P:4. FIA total phosphorus manifold.

## 4500-P I. In-line UV/Persulfate Digestion and Flow Injection Analysis for Total Phosphorus

## 1. General Discussion

*a. Principle:* Organic phosphorus is converted in-line to orthophosphate by heat, ultraviolet radiation, and persulfate digestion. At the same time, inorganic polyphosphates are converted to orthophosphate by in-line sulfuric acid digestion. The digestion processes occur before sample injection. A portion of the digested sample is then injected and its orthophosphate concentration determined by the flow injection method described in Section 4500-P.H.1.

See Section 4500-P.A for a discussion of the various forms of phosphorus found in waters and wastewaters, Section 4500-P.B for a discussion of sample preparation and digestion, and Section 4130, Flow Injection Analysis (FIA).

*b. Interferences:* See 4500-P.G.1b.

## 2. Apparatus

*Flow injection analysis equipment* consisting of:

*a. FIA injection valve* with sample loop or equivalent.

*b. Multichannel proportioning pump.*

*c. FIA manifold* (Figure 4500-P:5) with tubing heater, in-line ultraviolet digestion fluidics including a debubbler consisting of a gas-permeable TFE membrane and its holder, and flow cell. Relative flow rates only are shown in Figure 4500-P:5. Tubing volumes are given as an example only; they may be scaled down proportionally. Use manifold tubing of an inert material such as TFE. The block marked "UV" should consist of TFE tubing irradiated by a mercury discharge ultraviolet lamp emitting radiation at 254 nm.

*d. Absorbance detector*, 880 nm, 10-nm bandpass.

*e. Injection valve control and data acquisition system.*

## 3. Reagents

Use reagent water (>10 megohm) for all solutions. To prevent bubble formation, degas carrier and all reagents with helium. Pass He at 140 kPa (20 psi) through a helium degassing tube. Bubble He through 1 L solution for 1 min. As an alternative to preparing reagents by weight/weight, use weight/volume.

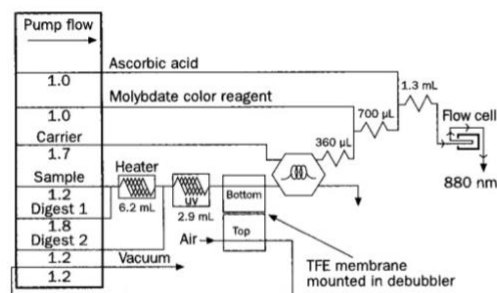


Figure 4500-P:5. FIA in-line total phosphorus manifold.

*a. Digestion reagent 1:* To a tared 1-L container, add 893.5 g water, then slowly add 196.0 g sulfuric acid,  $\text{H}_2\text{SO}_4$ . CAUTION: This solution becomes very hot! Prepare weekly. Degas before using.

*b. Digestion reagent 2:* To a tared 1-L container, add 1000 g water, then add 26 g potassium persulfate,  $\text{K}_2\text{S}_2\text{O}_8$ . Mix with a magnetic stirrer until dissolved. Prepare weekly. Degas before using.

*c. Sulfuric acid carrier, 0.71M:* To a tared 1-L container, slowly add 70 g  $\text{H}_2\text{SO}_4$  to 962 g water. Add 5 g sodium chloride, NaCl. Let cool, then degas with helium. Add 1.0 g sodium dodecyl sulfate. Invert to mix. Prepare weekly.

*d. Stock ammonium molybdate:* To a tared 1-L container add 40.0 g ammonium molybdate tetrahydrate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , and 983 g water. Mix with a magnetic stirrer for at least 4 h. The solution can be stored in plastic for up to 2 months if refrigerated.

*e. Stock antimony potassium tartrate:* To a 1-L dark, plastic, tared container add 3.0 g antimony potassium tartrate (potassium antimony tartrate trihydrate),  $\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2 \cdot 3\text{H}_2\text{O}$ , and 995 g water. Mix with a magnetic stirrer until dissolved. The solution can be stored in a dark plastic container for up to 2 months if refrigerated.

*f. Molybdate color reagent:* To a tared 1-L container add 715 g water, then 213 g stock ammonium molybdate (§ 3e) and 72.0 g stock antimony potassium tartrate (§ 3f). Add and dissolve 22.8 g sodium hydroxide, NaOH. Shake and degas with helium. Prepare weekly.

*g. Ascorbic acid:* To a tared 1-L container add 70.0 g ascorbic acid and 975 g water. Mix with a magnetic stirrer until dissolved. Degas with helium. Add 1.0 g sodium dodecyl sulfate. Mix with a magnetic stirrer. Prepare fresh every 2 d.

*h. Stock orthophosphate standard, 1000 mg P/L:* In a 1-L volumetric flask dissolve 4.396 g primary standard grade anhydrous potassium phosphate monobasic,  $\text{KH}_2\text{PO}_4$  (dried for 1 h at

TABLE 4500-P:IV. RECOVERIES OF TOTAL PHOSPHORUS

Compound	Known Concentration mg P/L	Mean Concentration Recovered mg P/L	Recovery %	Relative Standard Deviation %
Sodium pyrophosphate	10	8.99	90.3	0.5
	2	1.81	90.2	0.6
	0.2	0.19	93.4	1.0
Phenylphosphate	10	10.10	101.5	0.2
	2	2.12	105.0	5.6
	0.2	0.20	101.3	1.0
Trimethylphosphate	10	8.99	90.3	0.2
	2	1.86	92.7	0.3
	0.2	0.18	95.3	1.1
Sodium tripolyphosphate	10	10.61	106.7	1.0
	2	2.14	106.6	0.2
	0.2	0.22	108.9	0.9

TABLE 4500-P:V. COMPARISON OF MANUAL AND IN-LINE TOTAL PHOSPHORUS METHODS

Samples	Concentration by Manual Persulfate Digestion Method mg P/L	Concentration by In-Line Digestion Method mg P/L	Relative Difference %
Influent (I2)	5.93	5.52	-6.9
Influent (I3)	5.03	4.50	-10.5
Influent (I5)	2.14	2.11	-1.4
Influent (I6)	1.88	1.71	-9.0
Effluent (E1)	3.42	2.87	-16.1
Effluent (E2)	3.62	3.55	-1.9
Effluent (E3)	3.26	3.34	+2.4
Effluent (E4)	8.36	8.16	-2.4
Effluent (E5)	0.65	0.71	+9.2
Effluent (E6)	0.74	0.81	+9.5
Phenylphosphate	1.95	1.91	-2.1
Trimethylphosphate	1.87	1.80	-3.7
Sodium pyrophosphate	1.90	1.73	-8.9
Sodium tripolyphosphate	1.84	1.73	-6.0

105°C), in about 800 mL water. Dilute to mark with water and invert to mix. Prepare monthly.

i. *Standard solutions:* Prepare orthophosphate standards in desired concentration range, using stock orthophosphate standards (¶ 3i), and diluting with water. If the samples are preserved with sulfuric acid, ensure that stock standard and diluted standards solutions are of the same concentration.

#### 4. Procedure

Set up a manifold equivalent to that in Figure 4500-P:5 and follow method supplied by manufacturer or laboratory's standard operating procedure. Use quality control procedures described in Section 4020.

#### 5. Calculations

Prepare standard curves by plotting absorbance of standards processed through manifold versus phosphorus concentration. The calibration curve is linear.

Verify digestion efficiency by determining tripolyphosphate and trimethylphosphate standards at regular intervals. In the concentration range of the method, the recovery of either of these compounds should be >95%.

### 4500-P J. Persulfate Method for Simultaneous Determination of Total Nitrogen and Total Phosphorus

#### 1. General Discussion

a. *Principle:* The oxidation of nitrogenous compounds for determining total nitrogen must occur in an alkaline medium. Conversely, the oxidation of phosphorus compounds for deter-

Figure 4500-P:6. Correlation between manual and in-line total phosphorus methods.

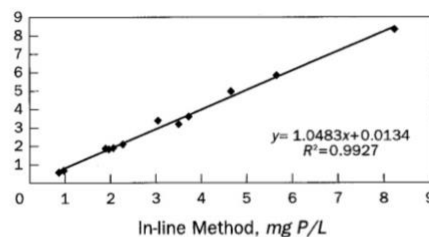


Figure 4500-P:6. Correlation between manual and in-line total phosphorus methods.

#### 6. Precision and Bias

a. *MDL:* A 390-μL sample loop was used in the method described above. Using a published MDL method,<sup>1</sup> analysts ran 21 replicates of a 0.10-mg P/L orthophosphate standard. These gave a mean of 0.10 mg P/L, a standard deviation of 0.003 mg P/L, and MDL of 0.007 mg P/L.

b. *Precision of recovery study:* Ten injections of a 10.0-mg P/L trimethylphosphate standard gave a mean percent recovery of 98% and a percent relative standard deviation of 0.8%.

c. *Recovery of total phosphorus:* Two organic and two inorganic complex phosphorus compounds were determined in triplicate at three concentrations. The results are shown in Table 4500-P:IV.

d. *Comparison of in-line digestion with manual digestion method:* Samples from a wastewater treatment plant influent and effluent and total phosphorus samples at 2.0 mg P/L were determined in duplicate with both manual persulfate digestion followed by the method in Section 4500-P:H and in-line digestion method. Table 4500-P:V gives the results of this comparison, and Figure 4500-P:6 shows the correlation between manual and in-line total phosphorus methods.

#### 7. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1984. Definition and procedure for the determination of method detection limits. Appendix B to 40 CFR 136 Rev. 1.11 amended June 30, 1986. 49 CFR 43430.

mining total phosphorus must occur under acidic conditions. Methods determining total nitrogen have used a persulfate-sodium hydroxide system to oxidize nitrogenous compounds to nitrate. Accordingly, methods determining total phosphorus have used persulfate in an acidic medium.



During the initial stage of the digestion, sample pH is alkaline ( $\text{pH} > 12$ ). In the final stage of the digestion, the sodium hydroxide is consumed, causing sample pH to become acidic ( $\text{pH} < 2$ ). By means of this broad pH range, the method allows for the oxidation of both nitrogen and phosphorus compounds. The digested sample is analyzed for nitrate and orthophosphate, yielding total nitrogen and total phosphorus results.

*b. Selection of nitrate/orthophosphate measurement methods:* Using a dual-channel autoanalyzer that performs nitrate-nitrite by the cadmium reduction method and orthophosphate by the ascorbic acid reduction method, total nitrogen and total phosphorus can be measured simultaneously. Alternatively, other methods for orthophosphate and nitrate can be used.

## 2. Apparatus

Clean all glassware with HCl before use.

*a. Autoclave*, capable of achieving a temperature of  $120^\circ\text{C}$  for a minimum of 120 min.

*b. Glass culture tubes*, 13-mm-OD  $\times$  100-mm-long with autoclavable caps.

*c. Autopipettor*, capable of pipetting a 6.0-mL portion.

*d. Repeating pipettor*, capable of pipetting 1.25-mL portion.

*e. Erlenmeyer flask*, 3000-mL.

*f. Aluminum foil*.

*g. Automated continuous-flow instrument system for nitrate and phosphate determination:* The suggested analytical instruments are described in Sections 4500- $\text{NO}_3^-$ -F and 4500-P.F.

## 3. Reagents

*a. Deionized water*, high-quality, free of phosphorus and nitrogen compounds. Prepare by ion-exchange or distillation methods as directed in 4500- $\text{NH}_3$ -B.3a and 4500- $\text{NO}_3^-$ -B.3a.

*b. Sodium hydroxide, 3N:* Dissolve 120 g low-nitrogen NaOH in 800 mL deionized water in a 1000-mL volumetric flask. Cool and dilute to volume.

*c. Oxidizing reagent:* Dissolve 64 g low-nitrogen ( $<0.001\%$  N) potassium persulfate,  $\text{K}_2\text{S}_2\text{O}_8$ , in 500 mL deionized water. Use low heat if necessary. Add 80 mL 3N NaOH, prepared from low-nitrogen sodium hydroxide, and dilute to 1000 mL. Store in a brown bottle at room temperature.

*d. All of the reagents listed for determining nitrate + nitrite as indicated in Section 4500- $\text{NO}_3^-$ -F.3.*

*e. All of the reagents listed for determining phosphate as indicated in Section 4500-P.F.3.*

*f. Nicotinic acid p-toluenesulfonate stock and working standards:* Dry nicotinic acid p-toluenesulfonate in an oven at  $105^\circ\text{C}$  for 24 h. Dissolve 2.1084 g in deionized water and dilute to 100 mL; 1 mL = 1 mg N. To prepare a working standard, dilute 2.0 mL stock solution to 1000 mL; 1 mL = 2  $\mu\text{g}$  N.

*g. Adenosine triphosphate stock and working standards:* Dissolve 0.6514 g adenosine triphosphate in deionized water and dilute to 1000 mL; 1 mL = 0.1 mg P. To prepare a working standard, dilute 20.0 mL stock solution to 1000 mL; 1 mL = 2  $\mu\text{g}$  P. To prepare a low-range working standard, dilute 1.0 mL stock solution to 1000 mL; 1 mL = 0.1  $\mu\text{g}$  P.

## 4. Procedure

*a. Calibration curve:* Prepare a minimum of five standards over the desired calibration ranges using a stock calibration standard containing both nitrate and orthophosphate. Treat standards in the same manner as samples. Include blanks in calibration curves.

*b. Sample preparation:* If necessary, dilute sample with deionized water so that expected nitrogen and phosphorus concentrations fall within the range of the calibration standards. Samples preserved with acid cannot be analyzed by this digestion method.

*c. Digestion check standards:* Analyze quality-control standards containing organic nitrogen and phosphorus on each analytical run (see *§s 3f* and *g* for suggested standards and preparation procedures). These standards provide reference checks on the calibration and test the efficiency of the digestion.

*d. Digestion:* Pipet 6.0 mL of sample or standard into the culture tubes. Add 1.25 mL oxidizing reagent to each tube using a repeating pipettor. Cover the tubes with loose-fitting plastic caps. Prepare an autoanalyzer wash water in an erlenmeyer flask by adding oxidation reagent to deionized water in the same proportion as was added to the samples. Cover flask with foil. Autoclave samples and wash water for 55 min at  $120^\circ\text{C}$ . Cool to room temperature. Add 0.05 mL of 3N NaOH to each tube before proceeding to nitrate + nitrite and phosphate analyses. Shake to mix. Add same proportion of 3N NaOH to digested wash water.

*e. Final nitrate + nitrite measurement:* Use the automated cadmium reduction method for the determination of nitrate-nitrite after digestion. See Section 4500- $\text{NO}_3^-$ -F. Other nitrate analysis methods may be applicable; however, precision and bias data do not exist for these methods on this matrix at this time.

*f. Final phosphate measurement:* Use the automated ascorbic acid reduction method for the determination of phosphate after digestion. See Section 4500-P.F. Other phosphate analysis methods may be applicable; however, precision and bias data do not exist for these methods at this time.

## 5. Calculation

Prepare nitrogen and phosphorus standard curves by plotting the instrument response of standards against standard concentrations. Compute the nitrogen and phosphorus concentrations by comparing the sample response with the standard curve. Where necessary, multiply sample concentration by the appropriate dilution factor to determine final concentration.

## 6. Quality Control

Use protocols specified in Section 4020 to verify performance. These include daily use of reagent blanks, laboratory-fortified blanks, and known additions. Regulatory analysis may require additional quality control procedures

## 7. Precision and Bias

*a. Total nitrogen:*

1) Nitrogen digestion check standards — Four different organic nitrogen standards (2 mg N/L) were analyzed by a single

laboratory on three separate analytical runs yielding the following results:

Nitrogen Compound	Recovery		Relative	
	Mean mg N/L	of N %	Standard Deviation mg N/L	Standard Deviation %
Urea	2.03	102	0.021	1.0
Ammonium <i>p</i> -toluenesulfonate	1.93	97	0.037	1.9
Glycine <i>p</i> -toluenesulfonate	1.94	97	0.034	1.8
Nicotinic acid <i>p</i> -toluenesulfonate	1.86	93	0.044	2.4

2) Mixed ammonia-nitrate solution — A mixed ammonia-nitrate sample (0.55 mg N/L) was analyzed nine times, yielding the following results:

Nitrogen Compounds	Recovery		Relative	
	Mean mg/L	of N %	Standard Deviation mg/L	Standard Deviation %
Ammonium sulfate & potassium nitrate	0.557	101	0.012	2.1

3) Samples — A single laboratory analyzed five samples in quadruplicate on three separate occasions. Samples analyzed for total nitrogen included surface water and diluted wastewater samples. At an average concentration of 15.0 mg N/L, the average standard deviation was 0.143 mg/L.

*b. Phosphorus:*

1) Adenosine triphosphate solutions — Two concentrations (2 mg P/L and 100 µg P/L) adenosine triphosphate were analyzed by a single laboratory on two separate analytical runs yielding the following results:

Phosphorus Compound	Recovery	
	Mean mg P/L	of P %
Adenosine triphosphate, 2 mg P/L	2.05	103
Adenosine triphosphate, 0.100 µg/L	0.103	103

2) Samples — A single laboratory analyzed five samples in quadruplicate on three separate occasions. Samples were analyzed for total phosphorus over two different calibration ranges. Surface water and diluted wastewater samples were analyzed utilizing a low calibration range (0 to 250 µg P/L, method detection level (MDL) = 2 µg P/L). At an average concentration of 1670 µg P/L, the average standard deviation was 29.4 µg/L. Surface water and undiluted wastewater samples were analyzed using a high calibration range (0 to 6 mg P/L, MDL = 0.05 mg P/L). At an average concentration of 1.97 mg P/L, the average standard deviation was 0.028 mg/L.

## 8. Bibliography

- KOROLEFF, F. 1972. Determination of total nitrogen in natural waters by means of persulfate oxidation. In S.R. Carlberg, ed. New Baltic Montreal. ICES Cooperative Res. Rep., Ser. A, No. 29, p. 73.
- KOROLEFF, F. 1977. Simultaneous persulfate oxidation of phosphorus and nitrogen compounds in water. In K. Grasshoff, Report of the Baltic Intercalibration Workshop. Annex. Interim Commission for the Protection of the Environment of the Baltic Sea, p. 52.
- NYDAHL, F. 1978. On the peroxodisulphate oxidation of total nitrogen in waters to nitrate. *Water Res.* 12: 1123.
- U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Method 365.1 in Methods for Chemical Analysis of Water and Wastes. EPA 600/4-79/020, U.S. Environmental Protection Agency, Cincinnati, Ohio.
- VALDERRAMA, J.C. 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. *Marine Chemistry* 10:109.
- U.S. ENVIRONMENTAL PROTECTION AGENCY. 1987. Handbook of Methods for Acid Deposition Studies: Laboratory Analyses for Surface Water Chemistry. EPA 600/4-87/026, U.S. Environmental Protection Agency, Washington, D.C., p. 1811.
- AMEEL, J.J., R.P. AXLER & C.J. OWEN. 1993. Persulfate Digestion for Determination of Total Nitrogen and Phosphorus in Low Nutrient Waters. Center for Water and the Environmental, Natural Resources Research Inst. *Amer. Environ. Lab.* Oct 1993:2.