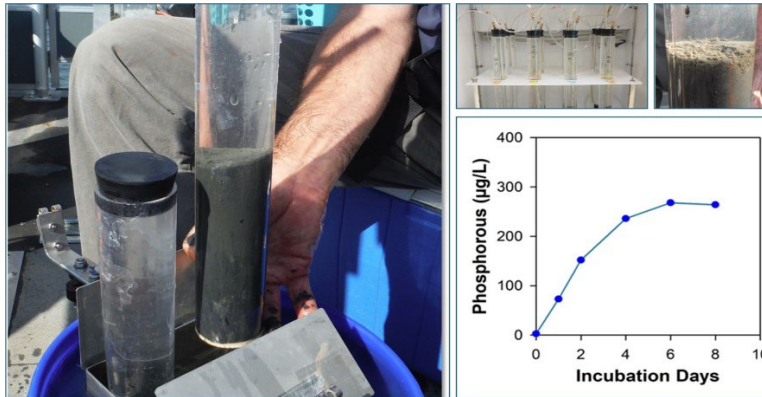


QUALITY ASSURANCE PROJECT PLAN

Sediment Phosphorus Flux in Massachusetts Lakes



Prepared for:

Watershed Planning Program
Division of Watershed Management, Bureau of Water Resources
Massachusetts Department of Environmental Protection



Prepared by:

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CN 614.0

21 March 2025

Quality Assurance Project Plan for Sediment Phosphorus Flux in Massachusetts Lakes

Version 0

Effective March 2025 to March 2030

Suggested Citation

MassDEP, 2025. Quality Assurance Project Plan for Sediment Phosphorus Flux in Massachusetts Lakes Version 0. CN 614.0, Massachusetts Department of Environmental Protection Bureau of Water Resources, Division of Watershed Management, Watershed Planning Program. Worcester, MA. In cooperation with GEI Consultants.

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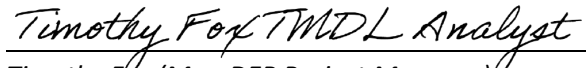
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Acronyms and Abbreviations

cm	Centimeter
COC	Chain-of-Custody
CWA	Clean Water Act
cc/sec	Cubic Centimeter per Second
DIW	Deionized Water
DO	Dissolved Oxygen
LLRM	Lake Loading Response Model
MassDEP	Massachusetts Department of Environmental Protection
m	Meter
µg/l	Micrograms per Liter
µm	Micrometer
µS/cm	MicroSiemens per Centimeter
mg/L	Milligrams per Liter
Mg/m ²	Milligrams per Square Meter
mL	Milliliter
N ₂	Nitrogen Gas
ppm	Parts per Million
pH	Potential of Hydrogen
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
SAP	Sampling and Analysis Plan
SU	Standard Units
TMDL	Total Maximum Daily Load
USEPA	United States Environmental Protection Agency
WPP	Watershed Planning Program

1. Project Management and Data Quality Objectives

1.1. Role of the Generic QAPP

The Commonwealth of Massachusetts Department of Environmental Protection (MassDEP) Watershed Planning Program (WPP) is the responsible agency developing this Quality Assurance Project Plan (QAPP) for implementation of lake bottom sediment nutrient core-flux studies in Massachusetts lakes. A core-flux study involves an experiment to quantify the rate of release of chemical constituents from lake sediment to the overlying water column. Additional discussion of the reasons to measure this rate and its use in lake modeling and management planning is provided in Section 3.

The QAPP includes a general framework and key details for quality control (QC) in conducting the core-flux experiments. This document will serve as the QAPP for future lake sediment nutrient core-flux experiments. The QAPP provides guidance for creation of a project specific Sampling and Analysis Plan (SAP) that may include individual lakes or groups of lakes. A project specific SAP is to be appended to this QAPP.

The QAPP was prepared in accordance with United States Environmental Protection Agency (USEPA) Region 1 guidance (USEPA 2024). Scientific details specific to collecting intact cores of lake sediment and conducting core-flux experiments are based on the contractor's experience in other waters and previous work by other practitioners in lakes across the nation. (Nürnberg 1988, Nürnberg 2024) provides a detailed synthesis of a large body of core-flux experimentation and interpretation from the 1980s to present. Approval of changes to this QAPP, as well as ensuring updates are placed on MassDEP internal file servers and MassDEP webpages, will be the responsibility of the MassDEP Senior Manager.

1.2. Project Organization and Personnel (A7-A10)

The following section provides description of the general framework to organize teams and assign primary roles and responsibilities to team members. The project team includes both MassDEP and contractors, which may include consultants and laboratories. The contractors will designate a person to coordinate with MassDEP and oversee specific tasks detailed in this QAPP. The designated person will be the "Contractor Project Manager" and fulfill those responsibilities. Specific project roles for project participants are summarized in Table 1. Specific personnel and detailed contact information (e-mail address, office phone, cell phone, and work address) assigned to each of these roles will be identified in project specific SAPs that are appended to this QAPP. The typical chain of communication between these roles is provided in Figure 1. Importantly, the Contractor Quality Assurance (QA) Manager must have an independent line of communication to the project's Contractor Project Manager.

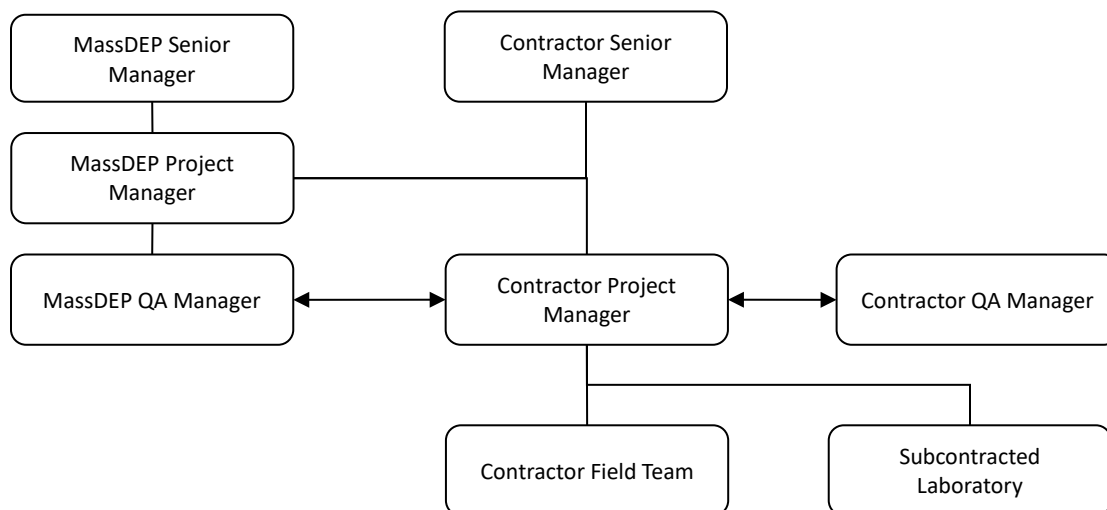
Copies of this QAPP, and any subsequent revisions, will be distributed by the Watershed Planning Program (WPP), Massachusetts Department of Environmental Protection (MassDEP), after approvals have been obtained. The following groups will be made aware of this QAPP:

- MassDEP, WPP staff, QA Manager
- Contractor staff
- Contracted Laboratory (selected staff)

Table 1. Program Roles and Responsibilities Related to Monitoring and Data Use

Organization	Title and/or Primary Role	Responsibilities
MassDEP	Senior Manager	Primary MassDEP staff member responsible for overseeing monitoring work described in the QAPP.
MassDEP	Project Manager	Oversee and manage development of project specific SAP and conduct of study.
MassDEP	Quality Assurance Manager	Overall technical oversight of project data QA/QC and management.
Contractor	Senior Manager	Overall management of administrative and technical work conducted by Contractor staff.
Contractor	Project Manager	Primary person or entity responsible for project meeting materials and development of project specific SAP, conduct of study, and all reporting.
Contractor	QA Manager	Primary person responsible for project QA/QC procedures and is independent from project operations. This includes creation of electronic data deliverables and data validation.
Contractor	Field Team Chief Scientist	Primary person responsible for overseeing the quality of work and data collected in the field. Project Manager may serve as the Chief Scientist.
Contractor	Field Team Project Scientist	Under the direction of the Project Manager and Chief Scientist, the Project Scientist must follow all procedures for field sample collection and conduct of core-flux experiment.
Laboratory	Laboratory Project Manager	Overall lab management and technical oversight regarding the performance of laboratory analysis and submittal of validated data to the Contractor Project Manager in compliance with contractual arrangements.
Laboratory	Laboratory QA Officer	Operate laboratory according to QA/QC program, provide to the Contractor all the necessary containers, preservatives (if required), chain-of-custody (COC) forms to support sample collection, and resolve sample or data analysis issues when they arise.

Figure 1. Organizational Chart



1.3. Project Purpose, Problem Definition, and Background (A4)

1.3.1. Background

The Final Massachusetts Integrated List of Waters for the 2022 Reporting Cycle (MassDEP 2023) lists over 300 lakes as Category 5 with most including total phosphorus as an impairment, each of which require the development of a nutrient Total Maximum Daily Load (TMDL). The TMDLs will define the maximum amount of phosphorus that each waterbody can assimilate while continuing to meet applicable water quality standards. The TMDL will also allocate the maximum allowable load between internal and external sources and provide a framework for the USEPA, MassDEP, and partner organizations to establish and implement nutrient control and management plans with the goal of achieving water quality conditions that support the water quality standards. MassDEP seeks to collect site-specific data to parameterize sediment phosphorus flux coefficients in water quality models that will serve as the linkage analysis for the TMDLs. Nutrient TMDLs require a linkage analysis to relate nutrient load to lake water quality response. The linkage analysis creates a nutrient budget for the lake, accounting for external inflows, flushing to downstream waters, biological uptake, particulate settling to the lake sediment, and release of solubilized forms from the lake benthos. In lakes with low watershed to lake-surface area ratio, release of solubilized nutrients from lake sediments may account for most of the bioavailable phosphorus in the water column during the growing season. Thus, internal

loads can significantly reduce the ability for lakes to assimilate external load and meet surface water quality criteria.

1.3.2. Problem Definition

Excess nutrients in freshwater lakes and ponds are the primary cause for eutrophication and associated impairment of beneficial uses for recreation, aquatic life, and drinking water. Sources of nutrients may include external such as stormwater runoff, groundwater, point source discharges, atmospheric deposition as well as internal such as releases from lake sediment by diffusion or physical resuspension. The legacy of external nutrient loads along with the annual senescence of algae and aquatic plants support nutrient enrichment of lake sediments, and through internal nutrient loading processes, nutrients can be recycled to the overlying water column to support algae production.

Measuring and quantifying internal phosphorus loading from lake sediments is challenging and requires monitoring the diffusion of phosphorus across the sediment/water interface (i.e., phosphorus flux rate at milligrams per square meter per day [$\text{mg}/\text{m}^2/\text{day}$]). There are several approaches to quantifying internal phosphorus loading including 1) high frequency monitoring and modeling of temperature, dissolved oxygen, and phosphorus conditions, both spatially and temporally, 2) in-situ anaerobic/aerobic chambers placed and monitored by scuba divers, 3) sediment sample analysis for phosphorus fractionation and use of literature values relating sediment phosphorus to flux rate, and 4) laboratory-based sediment core-flux experiments that provide estimates of phosphorus flux rates. This QAPP provides the necessary procedures and QC requirements to implement a lake bottom sediment nutrient core-flux experiment for any Massachusetts lake.

Environmental conditions impact the rate of release of solubilized nutrients from lake sediments. Warmer temperatures increase the rate of organic matter decomposition, which can increase the rate of release. Also, dissolved oxygen levels influence the direction of redox reactions, and an increase rate of phosphorus release has been shown to occur with chemical reduction of iron-bound phosphorus (Søndergaard et al., 2003; Anderson et al., 2001; Boström et al., 1988; Nurnberg, 1988). Conversely, during oxidizing conditions, the presence of metals (iron, aluminum, and calcium) in lake sediment provides natural sorption capacity for phosphorus released with organic matter decomposition.

Nurnberg (1988) synthesized data from multiple core-flux experiments under anoxia and found a wide range (e.g., 1-50 $\text{mg}/\text{m}^2/\text{day}$) of measured flux with the extent of ironbound phosphorus being the most important predictive variable in terms of the rate of release. Given this wide range cited in literature, site specific experimentation is useful to support TMDL development or implementation planning. The sediment nutrient flux experiment provides estimates of phosphorus release under oxic and anoxic conditions based on the composition of lake bottom sediment collected as intact cores.

Lastly, thermal stratification in deeper lakes limits exchange of bottom water with the atmosphere and depletion of dissolved oxygen (DO) in the hypolimnion causes anoxic conditions to persist through the period of stratification. Measurement of vertical DO profiles is important to support appropriate extrapolation of oxic and anoxic nutrient flux rates over space (extent of anoxia in the lake bottom) and time (days per year with anoxia in the lake bottom). Thus, discussion of routine monitoring programs including vertical DO profiles is provided in the QAPP to ensure SAPs are developed to collect additional data, when needed, and to use results from core-flux experiments in TMDL development.

1.3.3. Role of the Project-Specific SAP

Project specific SAPs are appended to this QAPP. Successful implementation of the SAP shall guide the field collection of sediment cores from lake bottoms to be used in laboratory-based experiments for the quantification of site-specific phosphorus release rates under oxic and anoxic conditions. The resulting site-specific phosphorus release rates are intended to be used to parameterize lake water quality models (e.g., LLRMs) that serve as linkage analyses in TMDLs or otherwise used for implementation planning.

1.4. Project Task Description and Schedule (A5)

Four general tasks are identified to plan and implement a lake bottom sediment phosphorus core-flux experiment in Massachusetts, including 1) develop a sampling and analysis plan, 2) field collection of sediment samples, 3) conduct of a core-flux experiment, and 4) develop a report of findings.

1.4.1. Task 1: Develop Sampling and Analysis Plan (SAP)

A project-specific SAP must be developed to be appended to this QAPP. The SAP provides documentation of sampling locations, field methodologies, laboratory procedures, and analytical requirements for the collection of sediment cores, incubation of cores, and collection of samples from overlying water to quantify site-specific phosphorus release rates. Selection of sites for collection of sediment samples should best represent the deep zones of the lake and may include more than one site especially in large (>500 surface acre) lakes or where there are multiple deep zones near different tributaries or areas that experience different periods of anoxia.

The SAP must also identify specific personnel to fill each of the roles identified in Table 1 and provide a project schedule, including selection of a laboratory to contract with for chemical analyses. Collection of sediment for intact cores shall be performed between May 1–September 30. During these months, bacterial communities in the lake bottom will be most representative of activity during periods of more frequent anoxia in lake bottoms as well as warmer water temperatures. Project specific schedules must be included in the SAP with key milestones for the general tasks described in this section of the QAPP.

1.4.2. Task 2: Field Collection of Sediment Samples

In this task the sampling design and detailed procedures included in the approved SAP are implemented. Field collection of sediment cores will be performed in a manner that preserves the sediment/water interface of each core from collection to transport to laboratory for controlled experiments. During field sampling events, vertical water quality profiles will be measured using a multi-parameter sonde. Samples will be collected within 1 meter (m) above the lake bottom for laboratory analysis of total phosphorus. In addition, the field team will collect 2 gallons of water (referred to as replacement water in subsequent sections of this QAPP) within 1 m above the lake bottom for use during the laboratory incubation experiments. Sediment samples may also be collected to evaluate bulk baseline physical and chemical characteristics. Lastly, if sediment analysis is included in the project specific SAP, a subsample of the top 10 centimeters (cm) of sediment will be homogenized and placed into amber glass sample jars using a clean, stainless-steel spoon. Section 2.2 provides additional detail for sampling procedures to be followed.

1.4.3. Task 3: Conduct of a Core-Flux Experiment

In the laboratory, treatment cores will be incubated under controlled temperature simulating bottom water temperature and maintained in the dark with minimal light exposure during the experiment. Pressurized gas will be delivered to each chamber to maintain the target DO conditions. Nitrogen gas (N₂), buffered with carbon dioxide (CO₂), is used to purge DO from each anoxic treatment core to maintain low DO conditions (< 2 mg/L) and ambient air is bubbled to maintain > 5 mg/L DO in oxic treatment cores. Water samples will be collected from the overlying water column in each core using a syringe connected to a dedicated sampling port according to the schedule in the project-specific SAP. The same sampling port will be used to deliver replacement water to the core of equal volume of the water sample. Overlying water samples will be analyzed for total phosphorus and orthophosphate concentrations.

1.4.4. Task 4: Develop Report of Findings

A report of findings will be developed to describe the implementation of the project-specific SAP. The report of findings must document the following:

- Calculation of flux rates: Phosphorus release rates will be calculated by determining the slope of phosphorus mass over time in each core. The estimate of mass in the overlying water must be adjusted for the mass removed during subsampling of the overlying water column and for the mass added with replenish water to maintain a consistent water volume in each core.

Equation 1. The nutrient flux rate is estimated as follows:

$$F_p = \frac{m}{A}$$

$$M_i = (C_i \times V_i) - (C_i \times V_{sub}) + (C_0 \times V_{rep})$$

Where, F_p is the phosphorus flux rate in mg/m²/day, m = the slope of the best fit line of nutrient mass (M_i) over time, accounting for daily adjustments from the mass removed during water subsampling. Mass removed during subsampling ($C_i \times V_{sub}$) is based on concentration in the core on day i (C_i) multiplied by the volume of water removed for sampling (V_{sub}) and mass added with replenishment water ($C_0 \times V_{rep}$) based on concentration in Day zero replenishment water (C_0) multiplied by the volume of water added to replenish core (V_{rep}), and A = the area of the sediment surface (m²).

Extrapolation of daily flux rates to site-specific lake conditions for either anoxic or oxic conditions requires DO measurement to characterize the frequency and extent of anoxic conditions. Alternatively, flux rates estimated for oxic and anoxic conditions in the lake bottom can be added to lake water quality models to simulate annual phosphorus load associated with releases from lake bottom sediments. Estimation of internal phosphorus load using results of the core-flux experiment is not required to be included in the report of findings but should be whenever practicable.

- The report of findings will include details of QC samples and documentation of procedures in conformance with the methods described in this QAPP.

- The report of findings will also include descriptions of the subject lakes, selected sites for core-flux experimentation, vertical profiles of DO, pH, temperature, and conductivity, and plots of analytical data for phosphorus and other chemical analytes. All raw data from the experiment will also be included as tabular results in an appendix to the report of findings.

1.5. Data Quality Objectives (A6)

The data quality objectives (DQOs) for this study will be achieved if the sediment cores and water quality data can be used to determine the phosphorus flux rate for lake sediment under controlled laboratory conditions. Data quality objectives can be described in terms of the following performance indicators: precision, accuracy and bias, representativeness, comparability, and completeness.

1.5.1. Sensitivity

Sensitivity refers to the capability of a method or instrument to discriminate between measurement responses within the expected ranges reported in Table 2. In the field and core experiment laboratory, the sensitivity of water quality sonde instruments shall achieve the desired resolution for field or laboratory sondes (Table 2). In the analytical chemistry laboratory, the sensitivity of analytical methods identified in Section 2.5 (Analytical Methods) shall be sufficient to measure analytes at or above the detection and reporting limits identified for analytes listed in Table 3 to meet DQOs. Notably, some analytical laboratories can reliably achieve detection or reporting limits less than those identified herein given their method/instrument combination, and in those cases the lower detection or reporting limits will be identified in the corresponding SAP.

1.5.2. Precision

Precision is the degree of mutual agreement between or among independent measurements of a similar property. Analytical chemistry measurements will be sufficiently precise to ensure detection of phosphorus within the expected environmental and experimental range. Precision will be measured using Relative Percent Difference (RPD) between duplicates with a 20 percent acceptance range. Field duplicates will be collected, representing at least 10 percent of the total environmental chemistry samples collected. In the core experiment laboratory, duplicates will be collected, representing at least five percent of the total core-flux chemistry samples collected. The Project Manager will check other data to ensure that they are of sufficient precision to meet DQOs.

1.5.3. Accuracy and Bias

Accuracy is the degree of mutual agreement of a measurement with a known value and includes systematic error (bias) of both sampling and analytical operations. Bias results in the distortion of the measurement process, which results in errors in one direction. In the field, accuracy will be assessed through the adherence to all instrument calibration, sample handling, preservation, and sample hold time. The bias component will be assessed using equipment blanks, representing at least 10 percent of the environmental samples collected. In the core experiment laboratory, equipment blanks will be collected, representing at least five percent of the total core-flux chemistry samples collected. The

Project Manager will check other data to ensure that they are of sufficient accuracy and do not contain an unreasonable level of bias to meet DQOs.

In the analytical chemistry laboratory, accuracy and bias will be assessed through the analysis of matrix spikes (MS), laboratory control samples (LCS), blanks, and the percent recovery criteria of control samples and matrix spiked samples. Acceptable criteria limits for this project are provided in Table 3.

1.5.4. Representativeness

Representativeness is the degree to which data accurately and precisely represents an environmental condition targeted for sampling. In the field, sediment cores will be representative of internal nutrient loading conditions if cores are collected in accordance with methodology described herein and from locations in each pond that experience low dissolved oxygen conditions during a portion of the year. Depending upon sediment composition, the upper 10-centimeter (cm) layer is typically considered the active layer where microbial-mediated reduction of iron-bound and manganese-bound phosphorus occurs. Therefore, each core should contain at least 15 cm of sediment to fully capture this layer. If the sediment thickness is less, then the core should be visually inspected to evaluate any layering, and collection of another core should be considered. If the substrate layer is less than 10 cm, then the core will be discarded, and collection of another core will be performed. Site-specific field conditions such as sediment composition (e.g., sand and gravel), organic debris, or depth of refusal may influence sediment core collection, which may require moving to a different location.

In the core-flux laboratory, sediment core incubation conditions are representative of natural conditions observed in each pond and the oxic and anoxic release rates from the sediment cores are representative of internal phosphorus loading conditions for each sampling location. The Project Manager will check other data to ensure that they are adequately representative of the environmental conditions targeted to sample and will meet DQOs.

1.5.5. Comparability

Comparability expresses the confidence with which one data set can be compared to another and is dependent upon the study design and implementation of the project's quality assurance plan. Sediment cores collected from different sampling locations will be sufficiently comparable, provided samples are collected in accordance with the methodology described herein and that the integrity of the water/sediment interface is maintained during collection, transport, and the duration of the core-flux experiment. Deviations from the established methodology will be noted by field/laboratory personnel.

In the core-flux laboratory, the flux rates will be sufficiently comparable between and within locations/treatment factors if experimental conditions (e.g., oxic or anoxic) are maintained for each core for the duration of the experiment. The Project Manager will check other data to ensure that they are sufficiently comparable to meet DQOs.

1.5.6. Completeness

Completeness is expressed as a percentage of valid and useable data obtained compared to the amount that was expected. In the field, the collection of sediment cores and bottom water will be considered

complete if at least 80 percent of the desired number of samples are collected from each waterbody. If samples cannot be obtained as planned, the field personnel will notify the Project Manager, and alternatives will be considered to improve the completeness of the field data. Any deviations will be noted in the field book and report.

In the core-flux laboratory, the experiment will be considered complete if at least 80 percent of the desired number of samples are collected from each core over the duration of the experiment; however, all samples from Day 0 must be collected for the experiment to be considered complete. Deviations from the sampling design will be noted by field/laboratory personnel. The Project Manager will check other data to ensure that they are sufficiently complete to meet DQOs.

Quality control extends throughout the entire study beyond the initial data collection, into data management and reporting. Collection of QC samples during the core-flux incubation period shall represent approximately 10 percent of the total number of core-flux samples collected for the experiment. Other field- or laboratory-based sonde data shall be collected in a manner that results in sufficiently accurate and unbiased results that reflect the true value of the parameter based on the manufacturer's specifications for the sonde. Sondes shall provide minimum levels of accuracy and reporting shown in Table 2.

Table 2. Multiparameter Performance Objectives

Parameter	Method	Units ¹	Resolution	Expected Range	Precision Objective	Accuracy Objective
Temperature	SM 2550 B	°C	0.01	0-30	± 0.2	± 0.1
Dissolved Oxygen	SM 4500 O G	mg/L	0.01	0-14	± 0.2	± 0.1
Specific Conductance	SM 2510 B	µS/cm	0.1	25-500	10%	± 0.5%
pH	SM 4500 H+ B	SU	0.01	5-9	± 0.2	± 0.1

Notes:

1. °C = Degrees Celsius, mg/L = Milligrams per Liter, µS/cm = MicroSiemens per Centimeter; SU = Standard Units

Water samples collected from the overlying water column in each core will be submitted to an analytical laboratory capable of achieving a minimum detection limit of 10 micrograms per liter (µg/L) or less for total phosphorus with sufficient precision and accuracy to be evaluated based on analytical laboratory quality controls (Table 3). Other analytical parameters that may be of interest for measurement in a core-flux experiment include dissolved orthophosphate, ammonia, total nitrogen, dissolved and total iron, and dissolved and total manganese. Detection limits for reporting for these supplemental analytes are also included in Table 3.

Table 3. Laboratory Performance Objectives

Analyte ¹	Units	Detection Limits	Reporting Limits	Expected Range	Precision Objective	Accuracy Objective
Total Phosphorus	mg/L	0.01	0.03	0.005 – 1.0	± 20 %	80-120 %
Orthophosphate as P	mg/L	0.01	0.03	0.005 – 1.0	± 20 %	90-110 %
Ammonia as N	mg/L	0.023	0.075	0.025 – 1.0	± 20 %	80-120 %
Nitrate-Nitrite as N	mg/L	0.0463	0.1	0.05 – 1.0	± 20 %	90-110 %
Total Kjeldahl Nitrogen	mg/L	0.066	0.3	0.7 – 2.0	± 24 %	78-122 %
Dissolved Iron	mg/L	0.009	0.05	0.01 – 1.0	± 20 %	80-120 %
Dissolved Manganese	mg/L	0.0016	0.01	0.01 – 1.0	± 20 %	80-120 %

Notes:

1. Acceptable analytical methods are presented in Section 2.5 Analytical Methods (B2)

Following initial receipt of analytical laboratory data, a review of all raw data and laboratory reports will be performed. Raw valid data will then be entered into an internal database. A 100% QA check of the entered data against the laboratory reports and associated raw data will be performed before proceeding with subsequent analysis and reporting. Subsequent steps will include the creation of spreadsheets for statistical analysis and graphing and summary tables for the report of findings. Each of these steps requires a 100% QA check as well to ensure proper transcription, reporting units, analysis parameters and methods, and use of significant figures. Any data and associated conclusions included in the report of findings itself will also undergo a 100% QA check against the raw data and summary tables.

Both field and laboratory QC samples (e.g., duplicates and blanks) will be collected at a minimum 10 percent rate of total sample collection and submitted to the laboratory for the same analysis of total phosphorus and other supplemental analytes for QC purposes. Precision of duplicates will be measured using Relative Percent Difference (RPD). The potential for field-based bias due to field contamination will be evaluated using deionized water (DIW) equipment blanks. Laboratory bias will be evaluated using laboratory QC standards for method blanks and matrix spikes along with reported percent recovery.

1.6. Special Trainings and Certification (A11)

The special training or certification courses required for the QAPP include boating safety, and at least one member of field crew must have completed Red Cross medical and first aid training and possess a current certification (training every two years). The Contractor Project Manager is responsible for including documentation of special training and certifications in the project folder.

Most sample collection will require the operation of a boat and basic safety training should be completed prior to the field effort to collect sediment samples. The vessel used for the study must meet all basic safety requirements associated with the size as prescribed in:

- Coast Guard Safety Equipment for Boats | West Marine
<https://www.westmarine.com/west-advisor/DIY-Safety-Equipment.html>

State guidelines for clean and safe boating must be followed. Prior to initiation of field sampling activities, the Contractor Project Manager must review the following:

- Massachusetts Boating Law Summary | Mass.gov
<https://www.mass.gov/info-details/massachusetts-boating-law-summary>
- CZ-Tip - Simple Steps to Clean Boating in Massachusetts | Mass.gov
<https://www.mass.gov/info-details/cz-tip-simple-steps-to-clean-boating-in-massachusetts>

Personnel involved with collection of sediment samples should have at least two years of professional experience in conducting limnological field surveys. The Contractor Project Manager will provide all personnel involved in field sample collection or data analysis with copies of this QAPP and project specific SAP for review. The Field Team Leader is responsible for following all safety requirements, boating rules, and sampling procedures referenced in this QAPP.

Analytical laboratories that are responsible for producing chemistry data for tests listed under MassDEP's laboratory certification program will maintain certification through MassDEP, or equivalent agency in other states, for analysis of water samples, as applicable to the analytes processed under this QAPP. While the use of certified laboratories is encouraged, it is not required for analytes under this QAPP.

1.7. Documentation and Records Management (A12)

The Contractor Project Manager shall retain approved versions of the QAPP with the project-specific SAP appended to this QAPP. Changes to the QAPP and or SAP documents shall indicate a revision number and be provided to MassDEP. The Contractor Project Manager shall provide copies of revised documents to the Project Team listed in Table 1.

The final report of findings shall include all field data and laboratory data along with COC forms, laboratory analytical reports, and electronic data deliverables for samples analyzed in the laboratory. The Contractor QA Manager shall review all analytical laboratory reports for completeness and will notify the Contractor Project Manager of any omissions or inaccuracies. If corrections are made to field notebooks, COC forms, or laboratory reports, any change shall be documented and initialed by the responsible party, and the Contractor Project Manager and MassDEP Project Manager shall be notified. All project related information shall be stored in a shared folder such as an online drive accessible by all parties identified in Table 1.

2. Sampling and Analysis Plan

2.1. Experimental Design (B1)

This section of the QAPP provides general procedures to be followed for the conduct of a core-flux experiment. The overall design of a lake sediment nutrient core-flux experiment involves the development of a SAP by the Contractor Project Manager that identifies site locations, names of key personnel, waterbody specific information and objectives, provides details about the number of replicates, list of analytes, reference to QC requirements, and generates project specific forms such as CoCs and field and laboratory data entry sheets. The project-specific SAPs are to be appended to this QAPP.

Key steps in the implementation of a core-flux experiment include:

- Selection of sites for lake bottom sediment sample collection
- Collection of sediment cores
- Transport of intact cores to a laboratory
- Controlling temperature and DO conditions in a laboratory setting
- Measurement of physicochemical parameters in overlying water
- Subsampling of overlying water for chemical analysis
- Analysis of results
- Development of a report of findings

2.2. Field Methods (B2)

A general set of procedures for field methods to collect intact sediment cores and water for use in the experiment is provided below. The Contractor Project Manager and Field Team Leader will follow these procedures unless modified within the project specific SAP.

At each sampling location, determine the maximum water depth and collect vertical water quality profile data (i.e., temperature and DO) using a calibrated multi-parameter sonde from near surface to near sediment, without disturbing the sediment. These data shall provide a snapshot of environmental conditions prior to collecting a bottom water sample or sediment core. Measurement depths shall begin at the 0.5 m from the surface, 1 m, 2 m, and every meter there after until within 1 m of the sediment interface.

Next, grab water samples from a bottom-layer are collected prior to collecting any sediment cores. Use a Van Dorn sampler, peristaltic pump, or similar water sampling device to collect water samples within 1 m from the lake bottom for laboratory analysis of total phosphorus. The field team will collect and additional 2 gallons of water (referred to as replacement water in subsequent sections of this QAPP) within 1 m above the lake bottom for later use during the laboratory incubation experiments. All water samples shall be filtered through a 0.2 micrometer (μm) filter to remove organic matter, algae, and

bacteria. Collect the filtrate for the experiment and store in appropriately labeled 1-gallon cubitainers (minimum of two). Depending upon the clarity of the water, pre-filtration using either a 10 μm , 5 μm , or 1 μm may be necessary to remove particulates before filtering through the 0.2 μm filter.

After vertical profiles of field measured parameters and water is collected for chemical analysis and for replacement water, sediment sampling may begin. The following procedures are recommended for the collection of sediment samples in a manner that preserves the sediment/water interface and maintains a consistent volume of sediment in each oxic/anoxic treatment replicate. A modified Ekman dredge (i.e., tall and weighted) or similar box corer shall be used to collect a sediment grab sample, ideally sampling the top 15 to 20 cm thick layer of lake bottom sediment. Before lowering the dredge, determine water depth, and slowly lower the device until refusal (*Do Not* let the dredge free fall). Use a weighted messenger to activate the closure mechanism and slowly retrieve the dredge to within 0.5 m depth below the water's surface. Before removing the dredge from the water, position a 7-gallon bucket in the water below the dredge so that the dredge remains under water while being brought aboard the boat. This procedure preserves the integrity of each sediment sample by eliminating any drainage from the dredge and allows for sediment subsampling to occur under water, eliminating any exposure of the sediment to air. Once at the surface, the sediment sample will be inspected for acceptability. An acceptable grab is characterized by an even surface with minimal disturbance, little or no leakage of overlying water, and a penetration depth of at least 10 cm with at least 80 percent of the surface intact. Grabs not meeting these criteria shall be discarded and noted as a failed attempt. Site-specific field conditions such as sediment composition (e.g., sand and gravel), organic debris, or depth of refusal may influence sediment core collection, which may require moving to a different location. When collecting additional cores, reposition the boat by at least 3 meters so it is not directly over the previous location. Once a successful grab is retrieved, the sample will be photographed and noted for physical characteristics, including percent recovery, penetration depth, sediment composition, and color.

While the sediment grab sample is still submerged, four, 2 × 24-inch acrylic tubes are gently inserted into the sediment grab sample to collect replicate cores for phosphorus flux experiments. Once all four core tubes are inserted into the sediment sample, the top of each core tube is plugged with a #10 rubber bung to allow for the slight repositioning of each core for extraction. Hydrostatic suction will allow for the core tube to be partially released from the surrounding sediment without losing the sediment from the bottom of the core tube. Before completely removing the core from the surrounding sediment, gently insert a #9.5 rubber bung into the bottom of the core tube. This process requires coordination with a second person to release the top bung to balance the displacement volume of the bottom bung as it is inserted, allowing water to escape the top of the core tube. Once the bottom bung is in place, fully remove the core tube from the sediment grab sample and place an end cap on the core tube. Wipe off the core tube and use electrical tape to secure the end cap, then replace the top #10 bung. Repeat these steps to collect the three remaining sediment cores. This approach maintains a consistent amount of sediment and overlying water column in each replicate core. At each sampling location, four sediment cores will be subsampled from the sediment sample. Lastly, lake water is carefully added to each core tube, without disturbing the sediment interface, to remove any headspace in the tube. Notably, the lake water in the core tube will be replaced in the laboratory so this water does not need to be collected from near the lake bottom. In the field, core tubes shall be stored in an upright and secured position, within water, and covered to minimize any heating or exposure to sunlight. Transport the cores to the laboratory.

2.3. Laboratory Experiment Methods (B2)

In the laboratory, the phosphorus flux experiment follows the methodology discussed in the Journal of Visualized Experiments (Ogdahl et al. 2014) to estimate the anoxic phosphorus release rate. Use a peristaltic pump to remove the overlying water column from each core and replace with 0.2 μm filtered replacement water from the cubitainer. Remove all but the last 2 to 3 cm of water in the core tube to maintain the integrity of the sediment interface, then slowly add filtered site water to the core tube. Incubate the sediment cores at the average temperature of the bottom water of all three waterbodies to maintain a consistent thermal regime for the duration of the study. Depending upon the seasonal timing of sediment collection, the experimental temperature may be adjusted to reflect mid-summer water temperature. Use a temperature data logger placed inside a separate container of water to record incubator temperature for the duration of the experiment.

Replace the top #10 rubber bung with one that contains two holes. In one hole, place either the ambient air line or buffered nitrogen gas line depending upon treatment factor, and in the second hole place the sampling port. The sampling port shall be positioned in the overlying water column at mid-depth. Repeat with each core tube. The gas distribution lines shall be calibrated to deliver approximately 0.5 cubic centimeters per second (cc/sec) to each treatment. Nitrogen gas (N_2) is buffered with 350 parts per million (ppm) of carbon dioxide to maintain stable pH condition in the anoxic treatments. The holes in the top bung allow for gas displacement without pressurizing the core tubes.

Water samples shall be collected at Day 0, the time of water replacement for each core, and from the overlying water column on subsequent days of the experiment as specified in the SAP (e.g., Day 1, 2, 4, and 6). Use a 100 milliliter (mL) Luer-tip syringe to connect to the Luer-tip sampling port and withdraw the desired sample volume needed for analysis of DO, pH, total phosphorus, and orthophosphate content. Two syringes shall be dedicated for each site, one for sample collection and one for replacement of 0.2 μm filter water. The sample collection syringe shall be rinsed with DIW between sample collection (e.g., oxic/anoxic treatment cores and sample days). For DO and pH analysis, use a field-based sonde that will fit into the core tube or collect approximately 50 mL sample volume for laboratory bench scale probes. If a field-based sonde is used, remove the top bung and measure DO and pH sample after the phosphorus samples are removed, but before the replenish water is added to the core. This will prevent displacement of water from the core tube. If bench sondes are used, remove the minimum sample volume needed for DO and pH analysis through the sampling port. The analytical laboratory should require less than 200mL of water for chemical analyses. Replace the total sample volume removed for analyses with 0.2 μm filtered water and note the sample volume in the field book. Following the last day of sample collection, measure the height and volume of the overlying water column in each core (e.g., use volume of a cylinder), and areal cross-section of the core tube, and volume of sediment in each core. The water volume and cross-section measurements are required to estimate the flux rate, and the volume of sediment is used for informational purposes.

2.4. Sample Handling and Chain of Custody (B7)

All samples collected will be labeled in a clear and precise way for proper identification and tracking in the laboratory. The labels will contain the appropriate information for the sample and depending on

sample type, this information may include station location, date of collection, incubation day, treatment factor, analytical parameter(s), and method of preservation.

All sample containers will be placed in a cooler for transfer to the laboratory. The following outlines the packaging procedures that will be followed for shipping of samples.

- Preferably blue ice should be used to keep samples cool, but when wet ice is used, pack it in zip locked, double plastic bags. Seal the drain plug of the cooler to prevent melting ice from leaking out of the cooler.
- Check screw caps for tightness.
- Ensure sample labels adhere to the bottles
- Place samples in a sturdy cooler(s) lined with a large plastic trash bag. Enclose the appropriate COC(s) in a zip-lock plastic bag affixed to the underside of the cooler lid.
- Fill empty space in the cooler with bubble wrap or packing paper to prevent movement and breakage during shipment.
- Each ice chest will be securely taped shut with strapping tape with appropriate shipping label attached.

All sample shipments or transfers of coolers containing samples shall be accompanied by a COC record. Request a PDF fillable COC form from the analytical laboratory and accurately complete the form. If multiple coolers are sent to a single laboratory on a single day, COC form(s) will be completed and sent with the samples for each cooler.

The COC form will identify the contents of each shipment and maintain the custodial integrity of the samples. Generally, a sample is in someone's custody if it is either in someone's physical possession, in someone's view, locked up, or kept in a secured area. The sampling team leader or designee will sign the COC form in the "relinquished by" box and note date and time.

2.5. Analytical Methods (B2)

Water samples collected from the overlying water column in each core will be analyzed by an analytical laboratory capable of achieving a minimum detection limit of 10 µg/L or less for total phosphorus and orthophosphate using one of the acceptable methods in Table 4. Methods for other supplemental analytes are also presented in Table 4.

Table 4. Acceptable Analytical Methods for Chemical Analysis of Core-Flux Samples

Analyte	Methods	Hold Time
Total Phosphorus	EPA 365.1, SM 4500-P E-H, Lachat QC 10-115-01-4-B, FIAlyzer-1000 PO4-W-2-5	28 days
Orthophosphate	EPA 365.1, SM 4500-P E-H, Lachat QC 10-115-01-1-B, -T, FIAlyzer-1000 PO4-W-2-4	48 hours
Ammonia Nitrogen	EPA 350.1, SM 4500 NH3 G, FIAlyzer-1000 NH3-W-1-2	28 days

Analyte	Methods	Hold Time
Nitrate Nitrogen and Nitrite Nitrogen	EPA 353.1, EPA 353.2, SM 4500 NO3 F, FIALyzer-1000 NO3-W-1-1	28 days
Total Iron	EPA 200.7, EPA 200.8, SM 3125 B	180 days
Dissolved Iron	EPA 200.7, EPA 200.8, SM 3125 B	180 days

The analytical results will be used to quantify rates of phosphorus released from the sediment during oxic and anoxic conditions in the overlying water column during controlled laboratory conditions and help parameterize coefficients used in the TMDL model development. These results shall not be used for water quality assessment purposes for any waterbody.

2.6. Quality Control (B4)

QC samples as described in this section shall be collected to support the analysis of the sampling activity and samples collected during the incubation experiment. The site location, core treatment, and type of QC sample shall be identified on the sample label. The Contractor Project Manager must determine the number of QC samples to be collected during the study to achieve a minimum of 10 percent of all samples as QC samples. The method to determine when and from where to collect quality control samples will be specified in the project-specific SAP. In the case of sediment core-flux experiments, most samples will be collected from overlying water within the laboratory incubation. QC water samples will be collected for at least one site on the lake on Day 0 of the experiment. Two gallons of site water will be used throughout the study to replace volume from subsampling to keep the cores full. Given that site water will only be collected on Day 0, a higher rate of QC will be realized (e.g., if a single site is selected for a lake, then the rate of QC sample collection for field samples would be 100 percent).

2.6.1. Field Quality Control Samples

Field QC samples are important to collect because of the large volume of replacement water that will be used every day of the incubation. In addition, flux calculations will be relative to ambient phosphorus on Day 0, which will be comprised of fresh replacement water. Field QC samples shall be submitted as separate water samples to the analytical laboratory and reported accordingly on the data reports. Equipment blank samples shall be collected at the first site sampled in each waterbody before environmental samples are collected. Field Duplicate water samples shall be collected from the first site sampled following the collection of the environmental sample. Specific requirements are outlined below.

Equipment Blank – A blank is prepared in the field or lab by pouring 1 liter (L) of DIW into the sampling equipment and ensuring contact with all parts of the device and sampling process, then collecting water sample aliquots in prelabeled sample bottles. Blank samples are preserved, if any, then sealed, handled, stored, and analyzed for total phosphorus and other supplemental analytes identified in the SAP.

Equipment blanks provide the best overall means of assessing contamination arising from the equipment, ambient conditions, sample containers, transit, and the laboratory. Measurable results reported for the equipment blanks will be examined on a case-by-case basis and adjustments to the process or additional training may be provided as needed to improve quality.

Field Duplicate – A second water sample is collected from the same location/core, in immediate succession, using identical techniques. Duplicate samples are preserved, if any, sealed, handled, stored, and analyzed in the sample manner as the primary sample. Precision of duplicate results is calculated by the relative percent difference (RPD) as defined by 100 times the difference (range) of each duplicate set, divided by the average value (mean) of the set. For duplicate results, D1 and D2, the RPD is calculated from the following Equation 2 and should be within ± 20 percent.

Equation 2. Duplicate Relative Percent Difference

$$RPD = \frac{|D1 - D2|}{\frac{(D1 + D2)}{2}} \times 100$$

2.6.2. Laboratory Quality Control Samples for Core-flux Incubation

Laboratory QC samples will be collected during the incubation phase of the sediment core study and includes Laboratory Blanks and Laboratory Duplicates. Specific requirements are outlined below.

Laboratory Blank - A blank is prepared in the laboratory by using a dedicated sampling syringe to collect and dispense DIW into prelabeled sample bottles. Blank samples are preserved, if any, then sealed, handled, stored, shipped, and analyzed for total phosphorus and other supplemental analytes. The Laboratory Blank is processed the same as a P-flux sample. These blank samples provide information regarding sample bottle preparation, including analytical variability. The SAP will specify dates and incubation chambers for collection of lab blanks.

Laboratory Duplicate – A duplicate sample is collected from the same core, immediately following the collection of the core-flux sample. This sample will vary between sites and treatment factors to provide context on the analytical variability of the overlying water in each core. Process the Laboratory Duplicate the same as a core-flux sample. Precision of duplicate results is calculated by the RPD as presented in Equation 1 above. To reduce the sample volume removed from each core, the duplicate samples should be spread across different cores where multiple analytes are being analyzed. The SAP will specify dates and incubation chambers for collection of lab duplicates.

2.7. Instrument/Equipment Testing, Inspection and Maintenance (B5)

On the date of sediment collection, water quality profiles will be recorded at each sediment collection location at 1 m depth increments using a multi-parameter sonde. The parameters measured will include temperature, pH, specific conductivity, and DO. This information gathered will help understand the potential influence of these parameters on their environment and provide baseline data to compare to the nutrient flux study. Measurement of total phosphorus, orthophosphate, DO, and pH shall be performed on the overlying water within each core to evaluate the effect of treatment controls (i.e., oxic versus anoxic) and whether environmental conditions are being maintained within each core.

Field instrumentation will be calibrated and/or checked in accordance with manufacturer recommendations by the Contractor Project Scientist or Field Team Leader. Upon calibration of the field instrument, if the acceptance criteria are not met then corrective actions need to be performed.

Corrective actions include recalibrating the probe, replacing the probe or consulting with the vendor to resolve the issue. The vendor is responsible for ensuring the field instrumentation is in proper working order and that routine maintenance is performed. During the core-flux experiment, the Contractor Project Scientist will perform calibration checks at the beginning of each overlying water sampling day, which will be recorded and used in tandem with other QC data to assess the accuracy of in situ measurements.

2.8. Inspection/Acceptance of Supplies and Consumables (B6)

Sample collection personnel will complete a bottle order request form with each analytical laboratory to help ensure that the number, type, and condition of sample containers are appropriate for the analyses to be conducted. Additionally, sample collection personnel will also be responsible for visually inspecting sample containers and verifying their cleanliness, integrity, and consistency with the QAPP guidelines before collecting samples for laboratory analysis. Sample containers that are visibly damaged, soiled, or inappropriate for the required analysis will not be used for sample storage.

2.9. Data Management (B7)

All electronic data deliverables, laboratory reports, case narratives, QC reports, email correspondence, or other information generated by an analytical laboratory will be retained by the Contractor Project Manager for at least three years following project completion in the electronic records for the project. This will include preliminary or draft data, in addition to any revisions.

3. Assessment, Response Actions, and Oversight

This section addresses the activities for assessing the effectiveness of the implementation of the SAP and QA/QC activities. The purpose of the assessment is to ensure that SAP and QAPP are implemented as described to ensure project goals are achieved.

3.1. Assessments, Oversight, and Response Actions (C1 and C2)

The Contractor Project Manager will provide oversight for field collection of water quality data and sediment core collection and confirm that the experimental laboratory conditions and water quality data are collected as described in the SAP appended to this QAPP. The Contractor QA Manager will audit field and laboratory notebooks and reported analytical data to ensure data quality objectives are achieved. Any “anomalous” data will be examined in detail to determine whether potential sources or errors were introduced to the process or whether the data reflects environmental or experimental variability. The Contractor QA Manager will communicate any findings with the Contractor Project Manager and discuss options for proceeding with the data or whether additional data may need to be collected. The Contractor Project Manager will determine the final response action, if needed, and communicate decisions with the project team.

As conditions in the field or laboratory may vary, it may become necessary to implement minor modifications to sampling as presented in this QAPP. When appropriate, the Contractor Project Manager and Contractor QA Manager shall notify the MassDEP Project Manager of proposed modifications to the approved QAPP or project specific SAP within 24 hours of a minor change. The modifications will be documented in the report of findings. Minor changes involve adjustments to improve the overall flow of work and will never involve a reduction in the rigor of the project or quality control activities.

3.2. Reports to management (C2)

The Contractor Project Manager will provide routine project updates to the MassDEP Project Manager including field and laboratory updates. These updates will include information on quality assessments of sediment core collection and the phosphorus flux experimental conditions, and any decisions that were made regarding data quality.

4. Data Review and Usability

This section discusses the QA activities that occur once field data are collected and following the collection of phosphorus flux data to determine release rates under oxic and anoxic conditions. Implementation of these activities ensures that the data collected meet the SAP requirements and overall project goals of determining phosphorus release rates from lake sediment under oxic and anoxic conditions.

By following procedures in this QAPP for sample COC, analysis of QC samples, data management and retention, and reporting, the integrity of environmental information will be retained throughout the project lifecycle.

4.1. Data Review and Usability Determination (D1)

The Contractor QA Manager will review field measured data and photographic documentation of sediment cores to verify and validate completeness of data collection, to determine the reasonableness of measured values in the context of environmental variability, and to ensure control limits are achieved as outlined in the SAP. Data that do not meet the completeness or reasonableness criteria will be examined on a case-by-case basis to determine whether the data should be qualified, rejected, or recollected.

The Contractor Laboratory QA Officer shall review the day-to-day laboratory conditions and environmental conditions within the core tubes to ensure that treatment factors are maintained for the duration of the experiment and that water samples are collected per the SAP appended to this QAPP. Documentation of all DO and pH measurements and subsample collections for phosphorus analysis will be made in the laboratory notebook. The Contract QA Officer will review the laboratory notebook after Days 0 and 1 of the experiment and then every other day thereafter.

The analytical laboratory will use their established control limits to accept data generated by their processes and either reject or qualify data that do not meet the control limits for the instrument's precision and accuracy. The Contractor QA Manager shall review the laboratory QC data along with project QC samples and prepare sections of the project report that present RPD calculations from duplicate samples. All data used to calculate phosphorus release rates will first be reviewed for reasonableness based on the expected range of values for the parameter under experimental controls.

4.2. Verification and Validation of Data (D2)

The Contractor Project Manager or designee shall be responsible for verifying that all water quality samples collected are completely and accurately documented on the COC forms before submitting to the analytical laboratory. If there is missing or inaccurate information on the COC forms, the forms shall be corrected immediately upon noticing the error and/or communicated to the analytical laboratory.

The Contractor QA Manager is responsible for making sure that the Field Team Leader completes instrument calibration per the manufacturer's recommendations and documents that field instruments

were calibrated before each field event and day of the incubation experiment. The Laboratory QA Officer shall be responsible for calibrating laboratory instruments and documentation.

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Appendix A – Field and Laboratory Methods

SM-2500B (Field Temperature)
SM 4500 O G (Field Dissolved Oxygen)
SM 2510 B (Field Specific Conductance)
SM 4500 H (Field pH)
EPA 365.1 (Laboratory Total Phosphorus and Orthophosphate)
SM 4500-P E-H (Laboratory Total Phosphorus and Orthophosphate)
Lachat QC 10-115-01-4-B (Laboratory Total Phosphorus)
FIAlyzer-1000 PO4-W-2-5 (Laboratory Total Phosphorus)
Lachat QC 10-115-01-1-B (Laboratory Orthophosphate)
FIAlyzer-1000 PO4-W-2-4 (Laboratory Orthophosphate)
EPA 350.1 (Laboratory Ammonia Nitrogen)
SM 4500 NH3 G (Laboratory Ammonia Nitrogen)
FIAlyzer-1000 NH3-W-1-2 (Laboratory Ammonia Nitrogen)
EPA 353.1 (Laboratory Nitrate Nitrogen and Nitrite Nitrogen)
EPA 353.2 (Laboratory Nitrate Nitrogen and Nitrite Nitrogen)
SM 4500 NO3 F (Laboratory Nitrate Nitrogen and Nitrite Nitrogen)
FIAlyzer-1000 NO3-W-1-1 (Laboratory Nitrate Nitrogen and Nitrite Nitrogen)
EPA 200.7 (Laboratory Total Iron and Dissolved Iron)
EPA 200.8 (Laboratory Total Iron and Dissolved Iron)
SM 3125 B (Laboratory Total Iron and Dissolved Iron)

Appendix B – Sampling and Analysis Plans

Note all Sampling and Analysis Plans under separate cover.