

Assessment of Tile Drainage System Impacts to Lake Champlain and Phosphorus Loads  
in Tile Drainage in the Jewett Brook Watershed of St. Albans Bay (Project 15-309)

Amendment 1 to QAPP Version 1.1  
11/23/2016

Section 1. Project Management

1.1 Title and approvals

Assessment of Tile Drainage System Impacts to Lake Champlain and  
Phosphorus Loads in Tile Drainage in the Jewett Brook Watershed of St.  
Albans Bay

Quality Assurance Project Plan, Version 1.0, Amendment 1  
Adding: Task 2-Assessment of Tile Drainage Systems in the Jewett Brook Watershed

Prepared by:  
Stone Environmental, Inc.  
535 Stone Cutters Way  
Montpelier, VT 05602

This project is funded through EPA Grant Number LC96187501 and  
the Great Lakes Fishery Commission FFY16 allocation to LCBP

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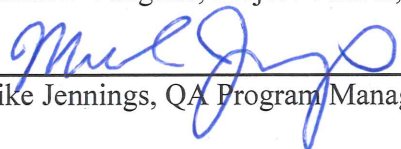
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Matthew Vaughan, Project Officer, LCBP

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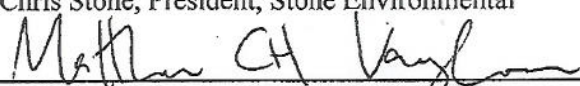
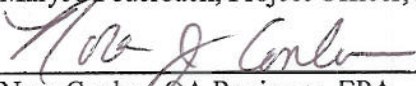
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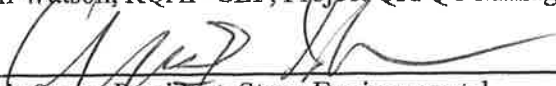
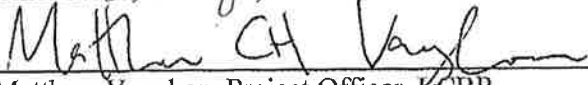
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### 1.4 Project/Task Organization

The diagram in Figure 1 below outlines the primary project participants and their roles in the project, by task. The scope of this QAPP document is currently limited to Tasks 1 (Literature Review Examining Tile Drainage Systems) and 2 (Monitoring and Assessment of Tile Drainage Systems); a second amendment to this QAPP for secondary data work as part of Task 3 will be prepared in at a future point in time.



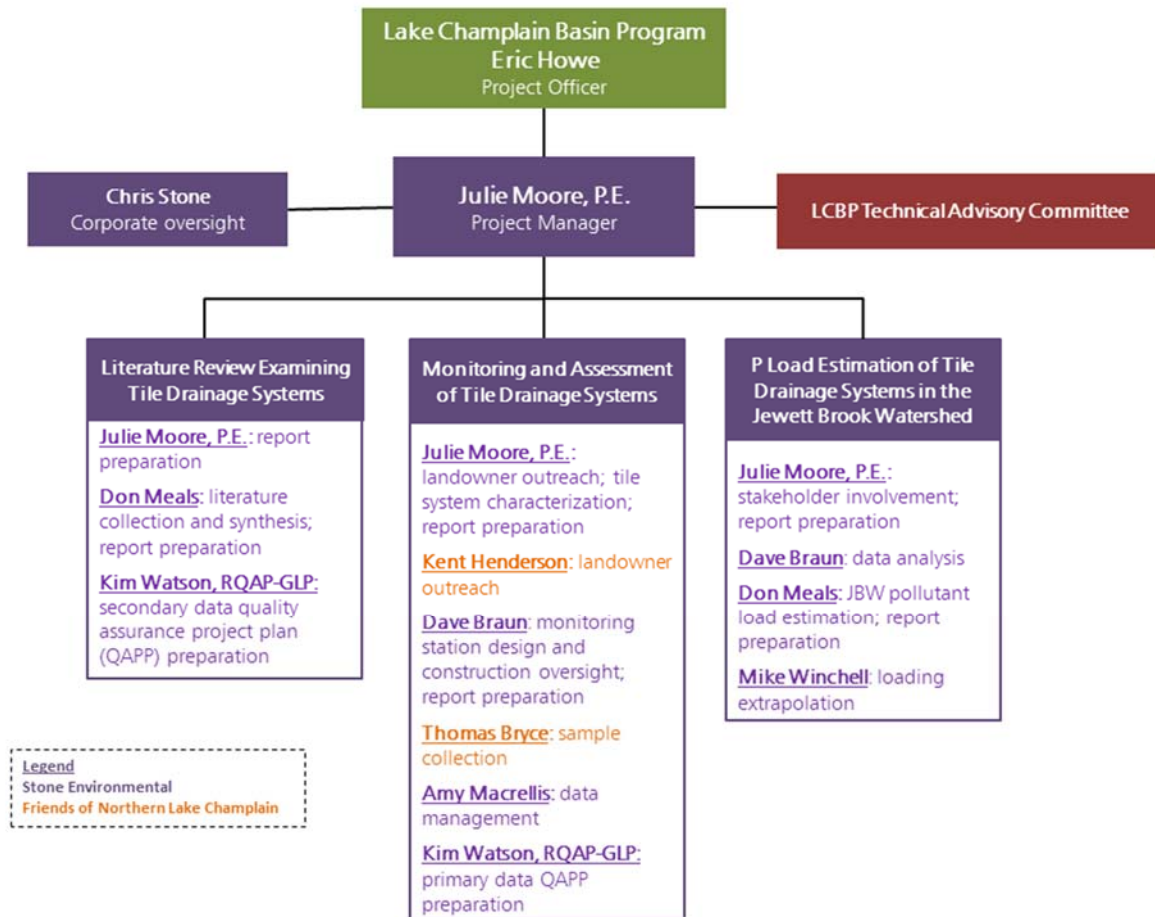


Figure 1: Project Organizational Chart

### Stone Environmental, Inc.:

Staff members from Stone Environmental, Inc. (and their authorized subcontractor) will report to the project manager for technical and administrative direction. Each staff member has responsibility for performance of assigned quality control duties in the course of accomplishing identified sub-tasks. The quality control duties include: completing the assigned task on or before schedule and in a quality manner in accordance with established procedures and documenting and ascertaining that the work performed is technically correct and meets all aspects of the QAPP.

**Table 1: Roles and Responsibilities**

Individual(s) assigned	Responsible for:	Authorized to:
<b>Stone Environmental</b>		
Julie Moore, PE	Project manager, overall study design, landowner outreach, primary contact with the Lake Champlain Basin Program.	Coordinate all aspects of project operations Document and approve all major project changes Manage personnel schedules and assign duties Approve overall study design Conduct site evaluation and characterization activities Interim/Final Report preparation
David Braun	Monitoring station design, construction oversight, monitoring program oversight, non-routine maintenance, data management	Develop and approve final station designs Supervise station construction Repair damage/breakdown in field stations Calibrate and maintain monitoring equipment Oversee collection and handling of water samples Conduct routine operation and maintenance of field stations Perform data QA and reduction Interim/Final Report preparation
Don Meals	Literature review, statistical analysis of monitoring data, and interpretation of results.	Collect and synthesize relevant literature Receive and verify collected data Conduct statistical data analysis Interpret project findings Interim/Final Report preparation
Amy Macrellis	Database development and data management	Develop and maintain data management system Provide data reports and outputs
Mike Winchell	Load extrapolation	Evaluate and apply most-suitable approach for developing load estimates
Kim Watson, RQAP-GLP	Quality review, maintaining the approved QAPP	Evaluate all aspects of project operations for compliance with approved QAPP Resolve QA/QC issues
<b>Subcontractors</b>		
Kent Henderson, Friends of Northern Lake Champlain	Landowner outreach, sample collection	Collect project-related data from participating landowners Collect, handle, and ship water samples Conduct routine operation and maintenance of field stations
Thomas Bryce, Friends of Northern Lake Champlain	Sample collection	Collect, handle, and ship water samples Conduct routine operation and maintenance of field stations

### **1.5 Special Training Requirements/Certifications**

Personnel with considerable expertise and experience in performing the project tasks will conduct all sampling and analysis for the project. Because station operation and maintenance, field data collection, and water sample collection will be done by subcontracted personnel at some sites, initial training will be led by the Stone Environmental Project Manager, or her designee, who will also be responsible for continued coordination of field operations and maintenance of consistency among field sampling personnel. This consistency will be aided by the use of standard checklists and forms for sample retrieval and station maintenance (see Appendix A, Study Specific Procedure). All personnel performing the project tasks will have documented training in their respective duties and shall have read the applicable SOPs. Stone Environmental maintains training records for all staff that document relevant training and SOP review. Laboratory analysis will occur at the Vermont Agriculture and Environmental Laboratory (VAEL) under the direction of the Laboratory Director. No additional specialized training or certifications are necessary for personnel to conduct the project tasks.

## **Section 2. Project Definition and Objectives**

### **2.1 Problem Definition/Background**

Subsurface drainage is an essential agronomic practice on many agricultural fields in the Lake Champlain Basin (LCB), allowing timely equipment access, reduced soil compaction and increased crop yields in fields otherwise too wet to efficiently farm. The combined effects of drawing down the water table and providing rapid conveyance of subsurface water to an outlet can significantly change the hydrologic behavior of a field, generally reducing surface runoff by enhancing infiltration and ground water transmission. Until recently, it was widely believed that, despite hydrologic changes caused by implementation of subsurface drainage, phosphorus (P) losses from agricultural lands occurred primarily via surface runoff and that very little P was lost through subsurface drainage such that tiling a field could reasonably be expected to reduce P losses.

Recent research has revealed that subsurface drainage systems in agricultural fields can discharge significant quantities of P under a wide range of soil characteristics and management practices and should be considered in management strategies seeking to minimize nonpoint source pollution of surface waters.

In Vermont and across the LCB, little is known about the extent of tile drainage systems, and the potential impacts of tile drainage systems on water quality have not been assessed. To address this knowledge gap, the Project Team will review and synthesize published research documenting P loading impacts of tile drainage systems that can be related to conditions commonly found in the LCB, monitor representative tile drainage systems in the Jewett Brook watershed (JBW), estimate P loading to Jewett Brook from these tile systems, and assess the significance of this loading to the overall P export from the JBW and similar areas of the LCB.

This QAPP applies to both the primary (Task 2) and secondary (Task 1) monitoring and data collection activities described in the project Work Plan.

### **2.2 Project Objectives**

#### **2.2.1 Task 1: Literature Review of Published Research Examining Tile Drainage Systems**

The objective of this task (Task 1: *Literature Review of Published Research Examining Tile Drainage Systems*, as described in the approved project Work Plan) is to synthesize the current state of knowledge of P loading from tile drainage systems from published scientific literature and expert knowledge within the Lake Champlain Region.

The Project Team will identify existing literature and data using a variety of methods, including:

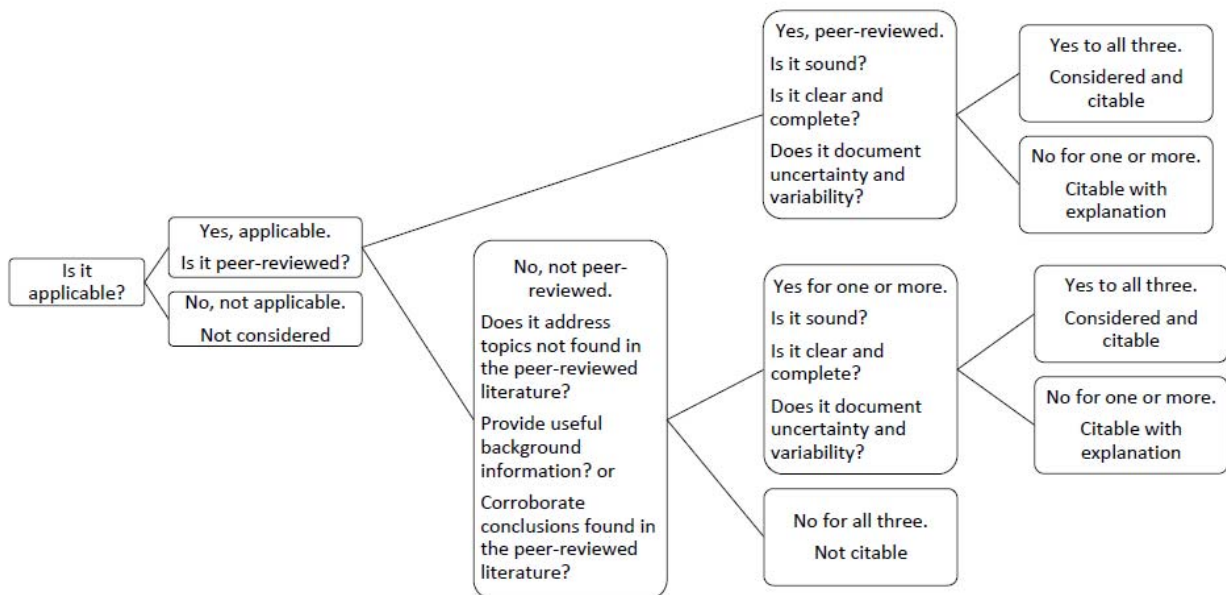
- Search of online scientific databases including but not limited to Web of Science, the National Agricultural Library (AGRICOLA), Elton B. Stephens Co. (EBSCO), and the web search engine Google Scholar;

- Search of federal, state, and stakeholder websites for recent materials (articles, technical papers, reports, and abstracts) and materials addressing topics not covered by sources listed above; and
- Sources proposed by members of the LCBP Technical Advisory Committee (TAC) and other stakeholders/experts within the LCB.

Emphasis will be on peer-reviewed articles, but data from gray literature of suitable quality (see Section 3) will be included to the extent available.

References cited within each reviewed source will be searched for additional resources. If a review article summarizes data from another study or report, the Project Team will obtain the original document so that information is collected from original sources. The search will be repeated with multiple iterations of keywords and in multiple databases until no additional references are identified.

Once the Project Team identifies a potential reference for inclusion in the literature review, they will use the decision process diagrammed in Figure 2 and assess the quality of that reference according to five assessment factors recommended by the EPA's Science Policy Council (US EPA 2003): soundness; applicability and utility; clarity and completeness; uncertainty and variability; and evaluation and review. These factors are described in more detail in Section 3.



**Figure 2. Process for literature screening and inclusion.**

Once an article is qualified, key data from the source will be logged into a set of spreadsheets. The spreadsheets will include fields for all important aspects of the work reported, including full citation, publication date, geographic location, scale, tile drainage system characteristics (e.g., depth, spacing, age), land use, crop and crop management, precipitation and flow, manure and fertilizer applications, soil type, slope, tillage, erosion control, nutrient management, and annual

P concentrations and/or loads. Where papers generate multiple cases (e.g., unique combination of study year, study site, treatment condition, and measured constituent) as individual records, each case will be reported as a separate record.

### **2.2.2 Task 2: Assessment of Tile Drainage Systems in the Jewett Brook Watershed**

The objectives of Task 2 (*Assessment of Tile Drainage Systems in the Jewett Brook Watershed*), as described in the approved project Work Plan, are:

1. To evaluate characteristics of the Jewett Brook Watershed and provide detailed characterization of field areas drained by 12 tile drainage systems selected for monitoring;
2. To measure total and dissolved P concentrations and flow and calculate P loads from 12 representative tile drainage systems in the Jewett Brook Watershed.

## **Section 3. Secondary Data Collection, Review and Evaluation of Available Literature**

### **3.1 Sources of Secondary Data**

The data needed for Task 1 of this project fall under the category of non-direct measurements and may include data from the following types of sources:

#### ***Peer-Reviewed Literature***

- Journal publications
- Reports, white papers, fact sheets, and similar publications developed by federal and state agencies
- Reports on industry-sponsored research, including white papers, fact sheets, and similar publications
- Symposium/conference proceedings

#### ***Non Peer-Reviewed Literature***

- Non peer-reviewed government documents
- Other types
  - Workshop or conference presentations/proceedings
  - Master's/PhD theses (approved)
  - Reports and white papers from private companies, associations, or non-governmental organizations
  - Textbooks
  - Maps
  - Publications with unknown peer-review status

#### ***Datasets***

- Online databases
- Unpublished government data

All data and existing literature will be evaluated using the guidelines given in Section 3.3 of this QAPP. It is expected that information included in the synthesis report will be drawn primarily from peer-reviewed publications. These publications will be viewed generally as containing the most reliable information, particularly if all of the criteria in Table 2 are met. High reliability will be ascribed to publications with high levels of review and evaluation and where extensive tabulation of supporting information is often available. Similarly, some agencies (e.g., EPA, USGS, etc.) are known to follow extensive quality assurance and review procedures for documents they produce.

Non peer-reviewed publications may provide useful information as long as they enhance understanding from peer-reviewed sources, or if peer-reviewed sources prove too scarce or insufficient to answer certain research questions by themselves. Because workshop and conference papers may be abbreviated, and may present works-in-progress, these are not expected to form the sole basis of conclusions presented in the report. Generally, these publications may be of most use to support results presented from peer-reviewed work, to identify promising ideas of investigation and to discuss further in-depth work needed.

Once information for this report has been collected and reviewed for adequate quality (see Section 3.2 Data Quality Requirements below), the Project Team will develop a draft narrative report and other deliverables (see Section 3.6). Any further data sources that become available during the course of the project will be vetted for utility for the final deliverable as well as for quality.

### 3.2 Secondary Data Quality Requirements

Literature and data identified in the course of the search strategy above will be evaluated using the five assessment factors outlined by the Science Policy Council in *A Summary of General Assessment Factors for Evaluating the Quality of Scientific and Technical Information* (US EPA, 2003): Applicability and Utility; Evaluation and Review; Soundness; Clarity and Completeness; and Uncertainty and Variability. Those factors are defined by the following criteria:

**Table 2. Criteria for each quality factor used for assessing data and literature.**

<b>Factor</b>	<b>Criteria</b>
Applicability	Document provides information useful for assessing the magnitude of P loading from tile drainage, agronomic or site factors influencing P loss through tile drainage, or documents the effectiveness of measures to reduce or avoid potential P losses in tile drainage.  Work and results reported are relevant to the environmental conditions found in the Champlain region (e.g., soil types, climate, and representative agronomic practices).
Review	Document has been peer-reviewed.
Soundness	Document relies on sound scientific principles and approaches, and conclusions are consistent with data presented.



Clarity/completeness	Document provides underlying data, assumptions, procedures, and measured parameters, as applicable, as well as information about sponsorship and author affiliations.
Uncertainty/variability	Document identifies uncertainties, variability, sources of error and/or bias and properly reflects them in any conclusions drawn.

Our objective will be to include literature that conforms in full to all five criteria. However, from previous search efforts, we have learned that the preponderance of literature on some topics does not fully conform to some aspect of the outlined criteria. For instance, there are many white papers and reports in technical areas in which independent peer-review is not standard practice or is not well documented. Should non-peer reviewed references address topics not found in the peer reviewed literature, provide useful background information, or corroborate conclusions in the peer reviewed literature, we may cite them with clear explanation. The same kind of explanation will also be offered should references be cited that do not fully conform to one of the other criteria.

The process for considering literature sources for inclusion is described in the decision tree shown in Figure 2 above. Any limitations and gaps in data included in the final deliverables for this project will be fully disclosed within the report, and it will be noted that these data should be used with caution. For example, certain datasets or published research may only cover a limited window in time but still be crucial to complement or provide a perspective for other available work. Data developed from laboratory or plot studies may be difficult to extrapolate to field or watershed scale. Even if data do not fully satisfy all the quality criteria, they may represent the best available knowledge for that particular topic and may not only provide a glimpse into current conditions, but also point to the need for improved data collection efforts to help refine recommendations of future projects.

### 3.3 Secondary Data Review and Evaluation

The quality of the secondary data will be determined according to the decision tree shown in Figure 2 and based on data quality requirements defined in Section 3.2 of this document. Unless the Project Team identifies specific issues or shortcomings in the reported work, data from peer-reviewed journal articles will be assumed to have been generated, analyzed, and reported according to acceptable quality standards. Data from non peer-reviewed sources will be evaluated according to procedures outlined above and reported with appropriate caveats.

All tables and figures created from existing literature and data sources will undergo an appropriate review process to ensure that the data were correctly transcribed. This process will include checking the created tables and figures against the original sources. The report text associated with the selected citations will be checked against the original sources to ensure that the report text accurately reflects the information in the original source. Electronic copies of all sources used in the literature will be included in project deliverables (see Section 3.6).

### **3.4 Documentation of Data Sources and Records**

All published research accessed for this project to inform the final deliverables developed for this project will be considered for data quality as described in Section 3.2 and documented in the final report if used. More detailed information about the data source and interpretation methods will be documented by the Project Team and available upon request, as noted in Section 3.6.

### **3.5 Data Validation**

The reporting of accurate project data will generally be ensured by carefully conducting and clearly expressing data reduction (if and when needed) and visual inspection of data before synthesizing for the final report. Specifically:

- A copy of every original source will be saved in a separate folder where it will not be edited in the event the integrity of the working datasets is compromised.
- Working data will be stored in spreadsheet format and will include all relevant raw data.
- Data manipulation will be minimized to decrease the chances of inadvertently introducing errors; such manipulations will be limited to unit conversion, summation of intermediate values (e.g., seasonal) to annual values, and the like. In rare cases, it may be necessary to visually interpret numerical values from graphs if the data are not reported in tabular form. Any such manipulations will be documented and checked by a member of the Project Team who did not perform the original manipulation. All formulas, along with units and conversion factors, will be shown in the spreadsheet; in addition, the formulas will be visible in each cell containing the reduced values.
- Transcribed data, calculations, tables and figures will be checked in accordance with Stone's standard operating procedure; SEI-4.14.2 Quality Control Check On Transcribed Data, Data Calculations, Figures, And Tables.

In-house documentation of assembled datasets will be reviewed to verify references to the use and limitations of the data.

### **3.6 Records Management**

Secondary data and publications collected by Project Team used in the final deliverables for this project will be stored on the Stone server in Montpelier, VT. Techniques used to interpret and display data in the report will also be documented by the Project Team and stored on the server and available to the public upon inquiry. All data published in the final project deliverables will be cited to its original source in the final publication. The data will be provided to the LCBP.

### **3.7 Disclaimers**

References and data sources that do not strictly meet the criteria listed in Section 3.2 may still be included in the synthesis report at the discretion of the Project Team, particularly with respect to data that have not undergone external peer review (e.g., data collected by states or industry). The literature review leader is responsible for deciding to include these data, documenting the rationale for inclusion and providing all available background information on these data in order to place these results in the appropriate context.

As stated previously, any limitations in data quality will be fully disclosed with the final report deliverables. If a decision is made to use data of unknown quality, this will be indicated in a disclaimer that will be added to any project deliverable. The disclaimer will read: “These data are of unknown quality and presented here for illustrative purposes only. No inferences regarding the impacts of tile drainage on water quality in the Lake Champlain Basin should be made based on these data until their quality can be determined.

## **Section 4. Primary Data Collection Activities for Select Tile Drain Systems in the JBW**

### **4.1 Study Location**

The Jewett Brook Watershed (JBW) is in the Town of St. Albans, Vermont. Jewett Brook flows to St. Albans Bay, a eutrophic bay of Lake Champlain (see Map 1). Monitoring stations will be constructed near the outfalls of the 12 tile drainage systems selected for monitoring in the JBW. Equipment will be installed at the edge of the farm field above the ditch or stream to which the tile drain discharges.

### **4.2 Monitoring Site Selection**

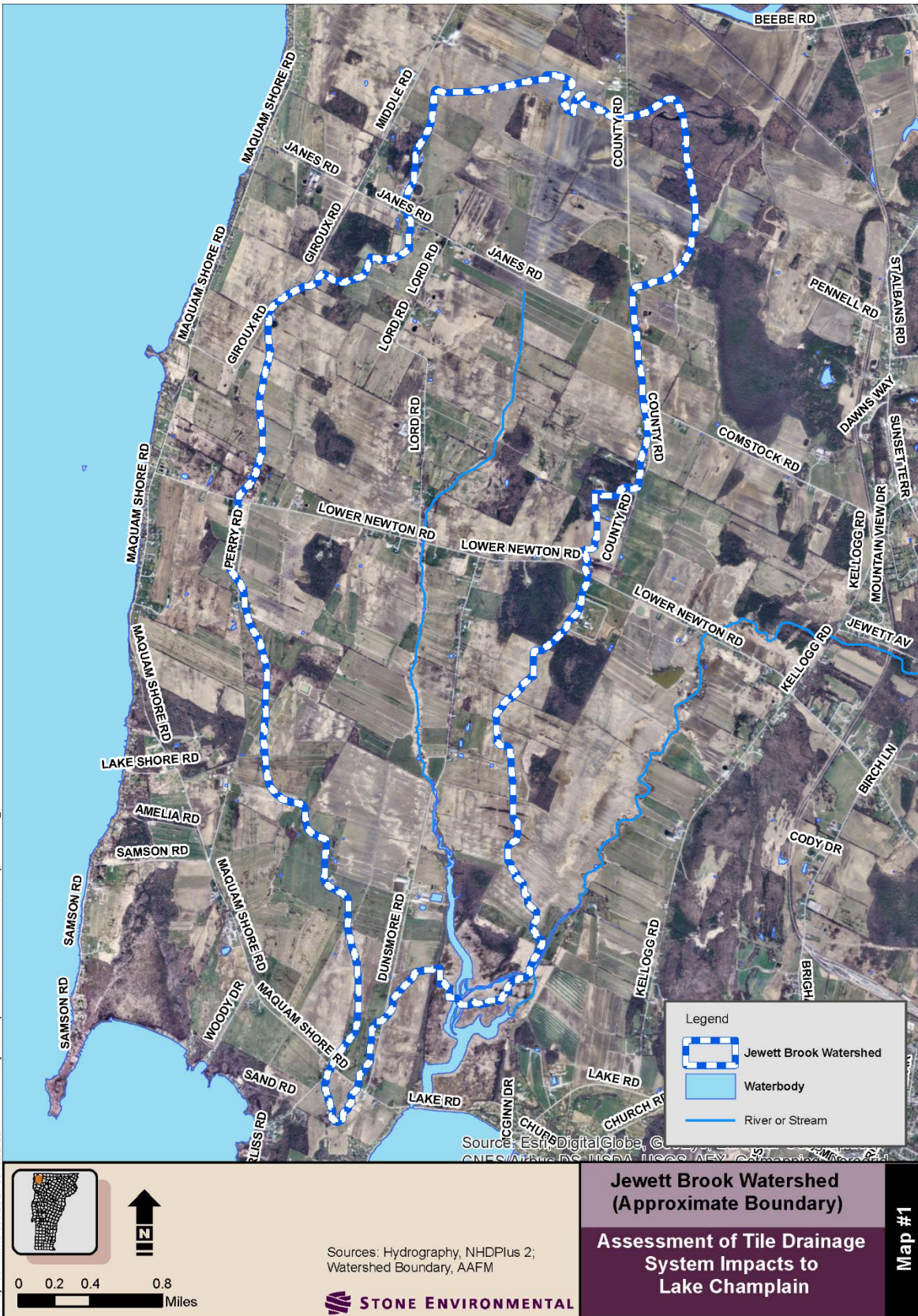
Through a comprehensive outreach effort to farmers and agricultural agents operating in the Jewett Brook Watershed (JBW), Stone secured agreements with 6 of the 11 farmers believed to crop tile-drained land in the Jewett Brook Watershed to allow for monitoring of selected tile drain outlets. Taken together, 18 tile drain systems were identified across these farmers’ managed lands. Several of these tile drains are clearly not suitable for monitoring. The main reason certain tile drains were determined to be unsuitable is that they drained very small areas (<5 acres) and will thus produce relatively little drainflow. Most of these tile drains were in fact dry when visited this past summer (2016). One other tile drain was eliminated from consideration because it was installed primarily to drain barn roof runoff via surface inlets. After excluding these unsuitable tile drains, we identified 15 tile drains that could potentially be monitored, although several of these have obvious drawbacks, including 2 with known surface inlets (standpipes and/or rock inlets). Given that the number of tile drain outlets available for monitoring is only slightly higher than the number to be monitored, no formal site selection criteria need be established. Unfortunately, farmer cooperation and practical realities will necessarily supersede efforts to intentionally represent a range of field conditions (e.g., cropping system, soil type, hydrologic soil group, soil test P, and age, layout, and depth of tile drain system) in the watershed.

### **4.3 Characterization of Tile Drained Field Areas**

The best available geographic data for the JBW will be assembled and reviewed, including cropping patterns and soils data. In characterizing these fields, producer confidentiality will be strictly maintained. Statistics regarding cropping patterns in the watershed (acreage in permanent corn or hay production or in specific rotations) and dominant soil types and slope classes, for land with and without tile drainage will be summarized without attribution to individual farmers or land ownership.

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in Tile Drainage in the Jewett Brook Watershed of St. Albans Bay (Project 15-309)

Amendment 1 to QAPP Version 1.1  
11/23/2016





Detailed information will be obtained for fields served by the 12 tile outlets selected for monitoring. Extent of drained area, drain spacing, tile depth, and system construction and age will be defined based on information provided by the landowner; soil types, slope, cropping system, and manure/fertilizer inputs within the drained area will also be documented. Phosphorus application rates and soil test P data will be assembled from nutrient management plans and interviews with the participating farmers and/or their technical service providers.

Project personnel will communicate with landowners at the monitoring sites on a regular basis, both to obtain agronomic management information and to provide information about project results on an ongoing basis.

#### **4.4 Monitoring System Design**

At each of the 12 selected tile drains, drainflow will be recorded continuously and flow-proportional composite water samples will be collected approximately weekly to provide total phosphorus (TP), total dissolved phosphorus (TDP), and total nitrogen (TN) concentration data representing the preceding period. Weekly discharge and weekly composite sample data will be used to compute weekly P and N loads; flow, concentration, and load data will be aggregated to calculate flow volume, distributions of TP, TDP, and TN concentrations, and cumulative TP, TDP, and TN loads at outflows by season and over the entire monitoring period. Field visits to retrieve and process composite water samples will be conducted each week when the monitored tile drain is flowing. The sampling schedule may be influenced by weather and agronomic considerations, including collecting more frequent samples during certain farm operations such as manure or fertilizer application.

#### **4.5 Monitoring Duration and Frequency**

Construction of the monitoring stations will occur after corn harvest in the fall of 2016 so that vehicles can reach the station locations. System operation, sample collection, and sample analysis will continue from November 2016 through November 2017. Stations will remain operational though dry periods, although samples will obviously not be collected if tile outlets cease flowing. During the winter of 2016-17, autosamplers will be turned off to avoid damage. However, weekly grab samples will be collected from the tile drains when discharge occurs.

Weekly retrieval, processing, and analysis of flow-proportional composite water samples will provide data representing an event mean concentration (EMC) for each constituent for the preceding period. Samples will be retrieved on the same day each week, to the maximum extent practicable.

The sampling schedule will be influenced by weather and agronomic considerations; however, we expect the following general schedule of monitoring activities:

1. Monitoring systems installation completed and sampling initiated in November 2016.
2. System operation, sample collection, and sample analysis will continue from November 2016 through November 2017 with the exception of January – March 2017 when continuous monitoring may be suspended due to freezing conditions.

## 4.6 Pollutants of Concern

The principal pollutant of concern is phosphorus. In addition to the potential impacts of P on immediate receiving waters, P is the primary cause of eutrophication-related impairments in Lake Champlain. Nitrogen losses are also of concern. Both N and P losses are also undesirable from an agronomic standpoint.

### 4.6.1 Constituents to be monitored

All water samples will be analyzed for TP, TDP, and TN.

## 4.7 Sampling Procedures

Monitoring and sampling methods will be consistent for the duration of the study period. Trained personnel will be responsible for satisfactory sampling operations, maintenance of monitoring stations, and processing of field data. Field personnel will be responsible for recording failures of sampling systems and taking corrective actions.

Table 3 summarizes the number and type of samples that are anticipated in this study. The estimates of samples intended for TP, TDP, and TN analysis are based on weekly sample collection at all monitoring stations over the 12-month monitoring period. We assumed that, on average, tile drains would flow 42 weeks per year (no discharge would be present on 10 weekly sampling visits due to dry or frozen conditions). During most weekly sampling events, we assumed that a single set of sample splits will be processed. On one in four sampling events, we assumed two carboys would need to be processed into two sample splits per analyte. A minimum of 10% additional QC samples are included in the sample estimates.

The estimated number of samples at all stations was calculated as:

	12 stations
x	42 weeks (assumes tile outlets are not flowing 12 weeks per year)
x	1.25 samples per event per station (assumes a single set of splits will be taken most weeks and two sets of splits will be taken roughly one week out of four)
x	1.1 accounts for 10% field duplicates
=	693 Total estimated samples per analyte

**Table 3. Sample types to be collected**

Analytical Parameters	Sample Container	Number of Samples	Sample Preservation	Hold Time (days)
TP <sup>1</sup>	Polyethylene bottle (composite) / 60-mL glass vial (aliquot for lab)	700	None	28
TDP <sup>1</sup>	Polyethylene bottle (composite) / 60-mL glass vial (aliquot for lab)	700	Filtered (0.45 µm) in field	28
TN	Polyethylene bottle (composite) / 50-mL plastic centrifuge tube, blue cap (aliquot for lab)	700	Cool (<6°C), 0.1 mL H <sub>2</sub> SO <sub>4</sub>	28
1. VAEL employs an EPA-approved variant of standard methods wherein samples for phosphorus analysis are digested in the same glass storage vial in which they are collected. No acidification is necessary.				

#### **4.7.1 Water sampling instrumentation**

ISCO 6712 and 3700 automatic samplers will be used to collect samples of drainage water from each of the selected tile drains. The autosamplers will be programmed to withdraw sample aliquots on a flow-proportional basis, according to the frequency of flow pulses received from the flowmeter. The sampling frequency will be constant during the collection of each weekly composite sample. The autosampler will sequentially fill four 10-L polyethylene carboys. When the first carboy is filled, the autosampler will begin dispensing sample aliquots to the second carboy, and so on until either the fourth carboy is filled or the sampling program is stopped. The flow proportional sampling frequency at each station will be adjusted seasonally with the goal of obtaining an average of approximately 5 L of sample per week (one half-full carboy), which will minimize the risk of under-sampling during large flow events (total sample capacity = 40 L).

At free-flowing outlets where flumes are used to measure discharge, sample lines will be affixed to the flume. At non-free flowing outlets (e.g., those which experience submerged conditions), the sample line will be inserted approximately 10 feet into the outlet pipe in order to avoid sampling tile drainflow that has mixed with the receiving water. Discharge monitoring is discussed in more detail in Section 4.8.

#### **4.7.2 Collection of water samples**

Approximately weekly, field technicians will visit each station to process water samples according to the Study Specific Procedure included as Appendix A. If the tile line has not flowed, no sample will have been collected; this will be noted on the Sample Retrieval Form (Appendix A).

Collected water samples will be transported on ice to VAEL in Burlington, VT, approximately 20 km/25 min from the monitoring sites, within the stated holding times for each analyte. Samples will be tracked using a Chain of Custody form (Appendix A) that will be completed by the sampler and will accompany all water samples delivered to VAEL. The Chain of Custody form includes sample IDs, number of containers of each sample being sent to the lab, and the analyses requested. Once the water samples are accepted by VAEL, they will be subject to the lab's internal tracking system.

#### **4.8 Discharge Measurement**

Depending on the elevation of the tile drain outlet relative to the water surface in the receiving ditch or stream, one of two types of flow monitoring installations will be made. Where submergence of the tile drain outlet is unlikely, an appropriately sized flume with ultrasonic level sensor will be installed at the outlet. Where the outlet is likely to become submerged during high water levels, an excavation will be made to install a magnetic flowmeter within a pipe loop constructed in a section of the tile line above the outfall.

##### **4.8.1 Discharge measurement at free-flowing outlets**

The primary hydraulic device used at free-flowing (not submerged) tile outlets will be an appropriately-sized H-flume or Palmer-Bowlus flume. Each flume will be bolted to a rectangular



approach channel. A baffle wall at the front of the approach will allow the drain tile to be inserted into the flume/approach. Through the life of the monitoring program, the flume will be kept level through regular adjustments using a system of turnbuckles and threaded rods.

An ultrasonic water level sensor (ISCO 2110 Ultrasonic Flow Module) will be mounted over the flume to continuously measure stage (water level). The stated accuracy of this instrument is the greater of  $\pm 0.00396$  m or 0.00256 m per foot (0.305 m) from the calibration point. Level data will be converted to discharge rate based on the established hydraulic rating of the flume. These data will be used in calculation of discharge corresponding to each weekly sample and in calculation of pollutant export.

#### **4.8.2 Discharge measurement at non-free-flowing outlets**

To monitor flow at the tile drain outlets which are submerged or likely to become submerged at high water levels, a trap or loop will be constructed in the pipeline to ensure full-pipe flow and a pipeline flowmeter will be installed in the trap section. This method will require excavation of a trench along the drain tile to install the pipe trap and flowmeter. A short section of pipe will be cut out and replaced with rigid pipe and fittings, forming a trap. A Krohne Waterflux 3000 electromagnetic flowmeter will be installed in the trap section, cabled to a signal converter (Krohne IFC 100) mounted above ground in an instrument enclosure. This sensor has outstanding accuracy at high flow rates (less than  $\pm 0.3\%$  in a 6-inch diameter pipe at flows above 300 gallons per minute) and better accuracy at low flows than any similar pipeline flowmeter (for example, 3% in a 6-inch diameter pipe at 5 gallon per minute). The sensor is rated for full submergence and direct burial.

#### **4.9 Testing and measurement protocols**

All water samples will be analyzed by the standard methods of the Vermont Agriculture and Environmental Laboratory. These methods and relevant data quality objectives, assessment procedures, and reporting limits are described in the VAEL's Quality Systems Manual, Revision 23, dated December 18, 2015. Methods of analysis are summarized in Table 4.

**Table 4. Analytical methods**

<b>Sample Matrix</b>	<b>Analytical Parameter</b>	<b>Lab</b>	<b>Method</b>
Water	TP	VAEL	4500-P H
Water	TDP	VAEL	4500-P H
Water	TN	VAEL	4500-N C-modified

References: Standard Methods for the Examination of Water and Wastewater; 21st Ed. 2005.

#### **4.10 Quality Assurance/ Quality Control (QA/QC)**

##### **4.10.1 Quality objectives and criteria for measurement data**

The project data-quality objective is to collect, provide, maintain, analyze, display, and document valid water quantity and quality data. The monitoring information that will be collected to support project objectives will meet the quality assurance objectives outlined in this

section. Data quality will be measured in terms of accuracy and precision, completeness, representativeness, comparability, completeness, and traceability.

Table 5 summarizes data quality requirements associated with the sampling program and the accuracy and precision levels reported by the analytical laboratory for each parameter. The analytical laboratory for the water samples is VAEL, which is currently located on the University of Vermont campus in Burlington. VAEL is accredited by the National Environmental Laboratory Accreditation Conference Institute (TNI) for the specified water quality parameters. Discharge measurement will document the rate and total quantity of drain flow over the course of the study. Analysis of flow-proportional water samples will provide mean concentrations of each monitored constituent. Mass of each monitored constituent will be computed from interval and total discharge volumes and constituent concentrations. To ensure data quality objectives are met, all sampling activities will be well-documented and will occur in accordance with the specifications presented in this QAPP.

For the QC samples, field duplicates will be collected of TP, TDP, and TN samples. Duplicates will be collected on a rotating basis among stations. Samples from one or two stations will be collected in duplicate on every event, such that at least 10% of the total sample load is collected in duplicate. Grab samples collected during the winter months will be collected in duplicate according to the same scheme used for the composite sample splits.

**Table 5. Data quality requirements and assessments**

Matrix	Parameter	Units	PQL <sup>1</sup>	Accuracy <sup>2</sup>	Accuracy protocol	Precision Lab/Field <sup>3</sup>	Precision protocol	Method Range
Water	TP	µg/L	5 µg/L	85-115%	Spike recovery	15/20	Field duplicate	5 – 200 µg/L
Water	TDP	µg/L	5 µg/L	85-115%	Spike recovery	15/20	Field duplicate	5 – 200 µg/L
Water	TN	mg/L	0.1 mg-N/L	85-115%	Spike recovery	10/20	Field duplicate	0.05 – 2.0 mg-N/L

1. Practical Quantitation Limits (PQL) is the lower limit of quantitation (reporting).
2. Accuracy for analytical parameters is expressed as Percent Recovery of Sample Matrix Spike. Analyte Percent Recovery acceptance criteria are method specified limits or generated from historical laboratory data. Recoveries are matrix/sample dependent.
3. Laboratory Analytical Duplicate Relative Percent Difference (RPD) acceptance criteria/Field Duplicate RPD acceptance criteria.

#### 4.10.2 Accuracy

Accuracy is defined as a measure of how close a result is to the true value. For physical/chemical parameters, accuracy is generally assessed through the analysis of spiked samples, with results expressed as percent recovery. VAEL's Quality Systems Manual, Revision 23, provides acceptance criteria for spiked sample results for each analyte tested. Calibration procedures, blank samples, and sample handling protocols provide additional information used to evaluate the accuracy of each analytical procedure.

#### 4.10.3 Precision

Precision is defined as a measure of the reproducibility of individual measurements of the same property under a given set of conditions. Precision is generally assessed through field and

laboratory duplicate analyses. In this case, duplicate analysis will be conducted on splits of field-collected composite samples. The most commonly used measure of precision is the relative percent difference (RPD). The formula for calculating the Relative Percent Difference is:

$$RPD = 100 * \text{Absolute Value}(X_1 - X_2) / ((X_1 + X_2) / 2)$$

where  $X_1$  and  $X_2$  are the two measurements being compared.

The method RPD is provided for the key analytical parameters in Table 5. Field duplicates will be prepared and delivered to the laboratory at a minimum rate of 10%.

#### **4.10.4 Representativeness**

In the context of this study, representativeness expresses the degree to which the data gathered by the project accurately and precisely represent field conditions. By continuously measuring discharge and collecting flow-proportional samples for chemical analysis, the data gathered will accurately represent water and pollutant export under true field conditions.

Data representativeness for primary source data for this project will be accomplished through implementing standard sampling procedures and analytical methods which are appropriate for the intended data uses.

#### **4.10.5 Comparability**

Comparability expresses the confidence with which one data set can be compared to another. Comparability of the field measurements is ensured by adhering to consistent standard sampling techniques and protocols. Such consistency will be reinforced by training and supervision of field staff (see Section 1.5). Comparability of laboratory measurements is ensured through following VAEL's Quality Systems Manual, Revision 23, dated December 18, 2015, and the respective SOP for a given analyte.

#### **4.10.6 Completeness**

Completeness is a measure of the percentage of planned samples collected or the percentage of usable data points per measurement, with a usable result defined as one that meets criteria for accuracy, precision, and representativeness. Project specific completeness goals account for all aspects of sample handling, from collection through reporting. The minimum completeness objective for the key parameters measured in tile flow is determined to be 95 percent.

$$\% \text{ Completeness} = \# \text{ of Usable Points} / \text{Total \# of Data Points Collected} \times 100$$

A usable result is defined as a result that meets all criteria for accuracy, precision, and representativeness.

#### **4.10.7 Traceability**

Traceability is defined as the ability to trace the generation of each analytical result from sample collection through analysis and reporting. To accomplish this, all activities must be fully documented. Specific requirements will be met for documenting operation and maintenance of

field instrumentation, sample tracking, analytical methodology including NIST traceable standards, record-keeping, data reduction procedures, and data presentation; these requirements are described elsewhere in this document. The data quality objective for traceability with respect to all primary data analyses for all samples is 100 percent.

#### **4.11 Quality Control Requirements**

All data acquired or generated will be fully documented as to original source, quality, and history.

Field quality control sampling will consist of the following:

- At least 10% of composite sample splits will be duplicated in the field by collecting a second aliquot from the churn splitter for delivery to the lab.
- No travel blanks will be collected because the parameters are not susceptible to cross contamination during shipment.

Data from field duplicates will be accepted if the RPD is less than or equal to 20%; in such cases, the mean of accepted field duplicates will be used to represent data from the sample involved. In cases where the RPD of field duplicates exceeds 20%, the data may be deemed unusable.

Sampling QC excursions are evaluated by the Project Manager. Field duplicate sample results are used to assess the entire sampling process, including environmental variability; therefore the arbitrary rejection of results based on predetermined limits is not practical. The professional judgment of the Project Manager or her designee will be relied upon in evaluating results. Rejecting sample results based on wide variability is a possibility. Notations of field duplicate excursions and blank contamination will be noted in the final report.

#### **4.12 Instrument/Equipment Calibration and Frequency**

Field analytical equipment that may be used in this project includes instruments for measuring water stage and flow rate. Calibration procedures for the equipment will follow manufacturer instructions.

Instrument and equipment calibration for water analysis will be routinely carried out by VAEI under their EPA approved Quality Systems Manual, Revision 23, dated December 18, 2015.

#### **4.13 Data Acquisition Requirements for Non-direct Measurements**

Sources of supplementary data considered in this project may include weather data obtained from a local NWS cooperating station. Such data may be used to compare contemporary weather conditions against long-term averages or normals. These data will be accepted as valid if officially published by the NWS. Second, historical soil and manure test data from the farm's nutrient management plan (if available) may be reviewed to help characterize site soils and agronomic management. Soil and manure samples for this purpose are typically collected by certified crop management consultants and analyses are performed through the UVM Agricultural and Environmental Testing Laboratory. The data reported in this manner will be

accepted as valid if it is contained in a nutrient management plan recognized by the AAFM. Farm records maintained by the participating farmers will be reviewed for information regarding management of the study fields. Collection of these data by the farmer meets record keeping requirements of Vermont AAFM. Additional supplemental data sources used include published topographic data and soils mapping based on the USDA-NRCS county soil surveys.

The supplementary data will not contribute directly to project decision-making, with the exception of field agronomic practices data recorded by the participating farmer.

#### **4.14 Data Summaries**

Summary data tables will be prepared for each station using the procedures described in Section 4.16. These tables will include total discharge, mass export, and mean concentrations of all monitored constituents. Using these summary data tables, descriptive statistics (range, mean, median, standard deviation, coefficient of variation) will be calculated by station. These summary data tables and statistical summaries will be stored electronically on Stone Environmental's servers, which are backed up daily to a Unitrends backup appliance. Once per week the most recent backup will be written to a drive which is taken to a storage vault offsite.

#### **4.15 Methods for Data Acquisition and Storage**

To protect personally identifiable information (PII) in any publications or public discussions of project results, the study site will be identified by an alphanumeric code consisting of the abbreviation "JBT" (Jewett Brook Tile) followed by a number between 1 and 12 (i.e., JBT01 through JBT12). Once data are reported to LCBP, they will be subject to standard measures required to protect participants' PII.

The Stone Environmental Project Manager or her designee will be responsible for organization and oversight of data generation, disbursement, processing and storage so that the data will be documented, accessible and secure for the foreseeable time period of its use. The VAEL director has the same responsibility for the laboratory data and information s/he generates.

Standard sample retrieval forms (Appendix A) will be used to document sample location, station and field conditions, date and time of collection, and personnel responsible for collection for all samples collected in the field. A Chain of Custody form (Appendix B) will be used by the laboratories to confirm sample delivery. VAEL will complete log-in sheets to document sample receipt and condition. Copies of all field sheets will be maintained in the project file at the offices of Stone Environmental.

Analytical data from VAEL will be transmitted in electronic format to the Project Manager or her designee after all internal review has been completed.

Data from the flowmeters and autosamplers will be automatically pushed to Stone's computer server every 30 minutes. These raw electronic data will be maintained on the server for the duration of the project and will be viewable in near real-time through a web user interface. These

data will be extracted into Access databases, Excel workbooks, and *R* for manipulation and preparation of data summaries.

All electronic files on Stone's servers, including raw data pushed from monitoring stations, will be backed up daily to a Unitrends backup appliance. Once per week the most recent backup will be written to a drive which is taken to a storage vault offsite. Paper and electronic files will be archived for a minimum of five years at Stone Environmental following completion of the project.

#### **4.16 Methods of Analyses**

The ISCO 2105ci interface module at each station will record instantaneous discharge rates measured by the flowmeters at five minute intervals. Discharge and sample event mark data will be transmitted automatically to a computer server located at Stone Environmental's offices in Montpelier, VT.

An Access database has been created to import and process analytical data from electronic tables transmitted by VAEL, import and aggregate corresponding event discharge data from the SQL server, and calculate total discharge, constituent mean concentrations, and mass export. This data processing will be performed using a series of database queries that will accomplish the following data manipulations:

1. Analytical results of duplicate samples will be averaged
2. Analytical results will be linked to specific sampling events on a common ID (LabID)
3. The constituent mass corresponding to the collection period of each composite sample (concentration multiplied by associated discharge total) will be calculated
4. Where multiple composite samples are subsampled for analysis (for example, carboys 1 and 2), the partial event constituent masses from #3 will be summed to derive total export for the interval.

There are several common sources of inaccuracy in discharge measurement that we are attempting to minimize through selection of the most appropriate instruments and certain station design innovations. These sources of inaccuracy include submergence of the tile drain outlets, level sensor drift, and flumes becoming non-level. Submergence of many of the outlets will be addressed by ensuring full pipe flow conditions at all times and installing an appropriate flowmeter for this condition. Flume level will be maintained by checking level during every maintenance visit and making appropriate adjustments. In some cases, level and discharge data may warrant adjustments to account for sediment or ice accumulation in monitored pipes and flumes.

The data set used for the primary statistical analyses will include total discharge ( $\text{m}^3$ ) and mean concentration ( $\text{mg/L}$ ) and mass export ( $\text{kg}$ ) for each monitored constituent for each sampling event for each monitored location. Data reported as less than a detection limit will be assigned a value of one-half the detection limit for purposes of data analysis, but will be flagged as below detection in reported concentration data tables. All statistical analyses will be done using version

10.0 of JMP statistical software (SAS Institute). Basic descriptive statistics and exploratory data analysis will be conducted on this data set.

## **Section 5. Assessment and Oversight**

It will be the responsibility of the Project QA Officer to ensure that project QA/QC activities, assessments, and responses are conducted according to this QAPP. The QA Officer (or designee) will have the authority to issue a stop work order upon finding a significant condition that would adversely affect the quality and usability of the data. The QA Officer will document, implement, and verify the effectiveness of corrective actions, such as an amendment to the QAPP, and take steps to ensure that everyone on the distribution list is notified.

Monitoring station readiness will be assessed through routine (minimum of twice weekly) review of flowmeter, sampler, and battery voltage data transmitted in near real-time to a server located at Stone Environmental's office. Several important and not uncommon problems may be detected remotely and quickly using these data, for example, sampler error messages, erroneous autosampling attempts, and low battery voltage. Early detection of these problem conditions will enable timely response by sampling teams to visit the monitoring station in question and correct the problem. Regular maintenance of the monitoring station and instruments will minimize the incidence of instrument malfunctions and other problems. Certain basic maintenance activities will be conducted after sampling event, to clean bulk sample containers, churn splitters, sampler lines, and flumes (if necessary) and to reset the autosampler. Site visits will be conducted for more intensive maintenance activities approximately monthly during the monitoring period. A Routine Maintenance Form will be completed during each maintenance visit (Appendix C). Deficiencies noted will be corrected by the responsible personnel. In the event that corrective action is required that is beyond the training of the maintenance personnel, a Stone Environmental project scientist with expertise in the monitoring systems will diagnose and correct the problem.

The effectiveness of monitoring will be assessed by the responsible sampling personnel at each site using data collected at the time of sample retrieval (Appendix A). Section 4.10 describes several common sources of inaccuracy in discharge measurement and how these will be addressed.

Periodically, when summary data tables are prepared for reporting purposes, the Project Manager or her designee will assess the quality of all discharge and analytical data and will be responsible for verifying/validating all sample tracking information and laboratory analysis data. Any deficiencies will be flagged with a qualifying statement in summary data tables and necessary corrective action will be taken. As part of final report preparation, the Project Manager or her designee will also review field and data management operations for the preceding year for consistency with the requirements outlined in this QAPP.

Internal assessments and response actions with regard to laboratory analysis within VAEL will occur under the terms of the lab's approved Quality Systems Manual (Revision 23). Project



investigators will examine data reports from the laboratory for problems or conditions of concern noted by analysts, based on *Sample Remark Codes*. Examples of such codes are included in Table 6.

**Table 6. Sample remark codes used by VAEL**

<b>Sample Remark Code</b>	<b>Description</b>
B	Reported value is associated with a lab blank contamination.
BH	Reported value may be biased high.
BL	Reported value may be biased low.
E	Estimated Value
D	Dilution resulted in instrument concentration below PQL.
H	Hold time exceeded.
I	Matrix Interference
N	Not processed or processed but results not reported.
O	Outside calibration range, estimated value.
OL	Outside Limit
P	Preservation of sample inappropriate, value may be in error.
S	Surrogate recovery outside acceptance limits.
T	Time not provided
W	Sample warm on arrival, no evidence cooling has begun.

If water quality data are suspect (e.g., flagged by the lab, duplicate RPD too high, unusual extreme concentrations), the first response will be to contact the laboratory and verify that no simple errors have been made. If questions cannot be resolved and suspect concentration data remain, the concentration data may be rejected for that constituent for the sampling event in question.

NEIWPCC may implement, at its discretion, various audits or reviews of this project to assess conformance and compliance to the quality assurance project plan in accordance with the NEIWPCC Quality Management Plan.

Quarterly reports will be submitted to LCBP and NEIWPCC, per the standard LCBP reporting process for review and approval. The LCBP Project Officer will be presented with the final project deliverables and a summary of any QA/QC actions taken before providing final approval to the report.

Any limitations and gaps in data included in the analysis will be fully disclosed within the project final report, and it will be noted that these data should be used with caution.

## **Section 6. Deliverables**

As part of Task 1, Stone will develop and submit a narrative report for LCBP review summarizing all information obtained through the literature review, including an executive summary suitable for wide distribution beyond the scientific community. The deliverables for this project will include:

- The narrative report and executive summary with complete list of references;

- Spreadsheets summarizing detailed information from each literature source; and
- Electronic copies of all sources cited.

As part of Task 2, Stone will produce a report detailing the methods and results of the watershed and drainage area characterization. The memo will document cropping patterns in the JBW (acreage in permanent corn or hay production or in specific rotations) and dominant soil types and slope classes, for land with and without tile drainage, as well as providing descriptive information for the agricultural areas served by each of 12 tile drain systems included in the study. In addition, photo-documentation of each monitoring installation will be submitted.

Stone will also produce a succinct monitoring and assessment report summarizing the methods and results of the watershed and drainage area characterization, and the flow and water quality monitoring. The report will also include an analysis of agronomic and water quality factor associations. GIS layers used or generated to support the analyses will also be provided to LCBP, subject to confidentiality requirements of the Vermont Agency of Agriculture. Total and dissolved P concentrations and loads for each of the 12 monitored tile drainage systems will be summarized in monthly and annual statistics.

In addition to the task-specific deliverables described above, quarterly reports will be submitted to LCBP, per the standard LCBP reporting process for review and approval. Relevant LCBP advisory committees, notably the Technical Advisory Committee, will be presented with the final report deliverables and a summary of any QA/QC actions taken before providing final approval to the report.

## **Section 7. References**

U.S. Environmental Protection Agency. 2003. A Summary of General Assessment Factors for Evaluating the Quality of Scientific and Technical Information. Washington, DC: Office of Research and Development, Science Policy Council; Report No. EPA/100/B-03/001.

**APPENDIX A:**  
**Sampling Procedures and Routine Maintenance for Assessment of Tile Drainage System**  
**Impacts to Lake Champlain and Phosphorus Loads in Tile Drainage in the Jewett Brook**  
**Watershed**

## STUDY SPECIFIC PROCEDURE

### ***Sampling Procedures and Routine Maintenance for Assessment of Tile Drainage System Impacts to Lake Champlain and Phosphorus Loads in Tile Drainage in the Jewett Brook Watershed***

SSP Number: 1

Date Issued: 11/14/16

Version Number: 1

Date of Revision: NA

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#### **OBJECTIVE**

To facilitate collection of high-quality water samples, preventative maintenance of monitoring stations and equipment, and accurate recording of monitoring activities and data.

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#### **POLICIES**

All field staff performing sampling duties for the project must read this SSP and implement the procedures written herein.

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#### **HEALTH AND SAFETY**

A health and safety plan (HASP) was prepared for this project identifying possible health and safety risks involved in field activities, how these risks are to be managed, and responsibilities of project management and staff. This HASP must be read and signed by every direct employee of Stone Environmental engaged in fieldwork for this project. Contractors assisting Stone with sampling and other field activities are not similarly bound by the HASP, but should nonetheless remain alert and responsive to potential health and safety risks. Stone Environmental assumes no responsibility and will accept no liability for the health and safety of personnel who are not direct employees of Stone Environmental.

There are several common health and safety risks which demand particular attention, as follows:

##### **Insects**

Hornets, wasps, bees, and yellow jackets are common in edge-of-field settings in Vermont. These insects may build nests in the monitoring shelters. A spray can of insecticide should be available at each monitoring shelter. Personnel known to be allergic to hornet, wasp, bee, and/or yellow jacket stings should carry with them an EpiPen or similar medication as directed by their physician.

Mosquitos may carry dangerous pathogens including West Nile virus and eastern equine encephalitis. Use repellent and appropriate clothing to minimize mosquito bites.

Ticks are common in areas bordering agricultural fields. Tick populations should be reduced by mowing work areas. Long pants, tucked into socks, should be worn when possible. Skin and clothing should be checked for ticks upon leaving the field.

### **Plants**

In addition to poison ivy and stinging nettle, personnel must avoid contact with wild parsnip, a new invasive plant in Vermont that can produce a painful and lasting burning of the skin after exposure of affected areas to sunlight. This plant has been seen in the area of the Ferrisburgh monitoring stations and may exist at other stations as well.

### **Severe weather**

Sampling activities will often take place shortly following storm events. Under no circumstances should personnel visit monitoring stations during lightning storms. Personnel should also be alert to high wind or other conditions and avoid exposure.

### **Cold/heat stress**

Personnel will be working under both very cold and very warm conditions in the course of the monitoring program. Standard recommendation for minimizing the risk of heat stress and hypothermia need to be observed.

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## **FLOW PROPORTIONAL COMPOSITE SAMPLING PROCEDURES**

An ISCO 6712 or 3700 autosampler will be operated to collect flow-proportional composite samples during times of the year where conditions are expected to remain above freezing. Approximately weekly, field technicians will visit each station to process the bulk composite samples into appropriate splits.

1. Record information from autosampler display (see attached Sample Retrieval Form). Note that the autosampler may display various error messages, some of which may be important, others not. If the display indicates a warning about excessive pump tubing counts, you may disregard this. If the sampler displays “No Liquid Detected”, this may indicate either that the intake was exposed to air during one or more sampling attempts or that there is a clog in the sampling line. If this warning is displayed, inspect the sampling line for a clog, kink, or ice blockage and otherwise ignore it. For all other warning messages, please contact Stone.
2. Stop the sampling program by pressing the red button to pause the program and then selecting STOP PROGRAM. In certain cases, the sampling program may have been stopped remotely by Stone. Stopping the program remotely can mitigate certain problems and potential risks, such as frozen sampling lines on cold nights.
3. Record approximate sample volumes in each carboy.

4. Select the appropriate carboy(s). Carboy 1 should contain a minimum of 300 mL for sample splits to be prepared for analysis. Since the programmed aliquot volume is 100 mL, three aliquots should produce 300 mL of sample. If three or more sample aliquots were attempted and the volume in carboy 1 is substantially less than 300 mL, then the suction line was likely exposed during pumping, drawing air rather than water. You may also view the sampling report for further information about which sampling attempts were unsuccessful.
5. Fill out and affix labels to the appropriate containers. The correct container for each analyte is given in Table 1.

*Table 1. Sample containers, preservation, and permissible holding times*

Analyte	Container	Preservation	Hold Time (days)
TP	60-mL glass vial	None	28
TDP	60-mL glass vial	Filtered (0.45 µm) in field	28
TN	50-mL plastic centrifuge tube, blue cap	Cool (<6°C), 0.1 mL H <sub>2</sub> SO <sub>4</sub>	28

The Sample ID field is a concatenation of the Site ID (JBT01, JBT02, etc.), the collection date (mmddyy), and the carboy(s) from which sample splits are taken [1, 2, 3, 4, or 1/2 (if the samples from carboys 1 and 2 are added together in the churn splitter)]. See step 7 regarding the sample splitting procedure. The following examples illustrate the sample IDs syntax:

- A sample collected at JBT01 on May 2, 2017 only from carboy 1: **JBT01-050217-1**
- A sample collected at JBT02 on September 27, 2017 by combining the contents of carboys 1 and 2 in the churn splitter: **JBT02-092717-1/2**

6. Put on lab gloves
7. Pour sample from the selected carboy(s) into the churn splitter. Try to swirl the water to suspend sediment as you pour the sample into the churn splitter.

In many cases, only the first carboy will contain sample. If the second carboy also contains sample, this can be added to the churn splitter so long as the combined volume will not exceed 14 liters, the capacity of the churn splitter. For example, if carboy 1 contains 9 liters and carboy 2 contains 4 liters, these can be composited in the churn splitter; and the resulting sample ID would be in the form: SiteID-mmddyy-1/2.

If the combined volume will exceed 14 L, each carboy should be split individually, resulting in two sets of sample splits for analysis.

8. Operate the churn splitter for 5-10 seconds. With sample containers in hand, open the stopcock and let spill on the ground for 1-2 seconds to clear the line. Then prepare:

- a. TP sample split: While operating the churn splitter, fill the glass vial up to the line.
  - b. TN sample split: While operating the churn splitter, fill a blue capped centrifuge tube to the 50 mL line.
  - c. Let the contents of the churn splitter settle for 1-5 minutes.
  - d. TDP sample split: Sample splits for TDP analyses will be filtered in the field by dispensing sample from the churn splitter directly into a filtration apparatus containing a 45-mm Durapore® 0.45- $\mu$ m acetate membrane filter. Use forceps to place a clean filter in the filter holder. Wet the filter with a spray of distilled water. Remove the plunger and attach the filter holder to the syringe. Fill a syringe with settled water from the churn splitter. Squirt approximately 10 mL onto the ground and then fill a glass vial to the 50-mL line. If the filter clogs prematurely, it may be replaced with a new filter and the process repeated.
9. Preservation. Put on safety glasses. Add 1 drop of concentrated sulfuric acid to preserve the TN sample. Place all samples on ice and store on ice or refrigerate until delivery to the laboratory. Clean up acid spills with acid neutralizing solution or copious amounts of water. To use acid neutralizing solution, shake bottle of acid neutralizing solution and cover affected area until bubbling stops.
  10. Washing equipment. The standard washing procedure is for three rinses with distilled water. After each event, the churn splitter, filter holder, and carboys should be washed.
  11. Reinstall carboys in the following clock positions: 1 at 6:00, 2 at 3:00, 3 at 12h, and 4 at 9:00.
  12. Press the red button and select “run program” on the autosampler to ready the station for the next event. Confirm that the sampler program is running.
  13. Complete the Chain of Custody form, including sample IDs, number of containers of each sample being sent to the lab, and the analyses to be performed. The Chain of Custody form must be kept with the samples, either by sticking it into the plastic sleeve taped to the underside of the cooler lid or in a ziplock bag with the samples.
  14. Samples must be delivered to the laboratory within the holding times indicated in Table 1.

---

## GRAB SAMPLING PROCEDURES

The autosampler programs will be stopped during the winter months when temperatures are expected to remain below freezing. During this period, field technicians will visit each station approximately weekly to collect grab samples if tile lines are flowing.

1. Fill out and affix labels to the appropriate containers. The correct container for each analyte is given in Table 1.



2. For grab samples, the Sample ID field is a concatenation of the Site ID (JBT01, JBT02, etc.), the collection date (mmddyy), and the word “GRAB”. The following example illustrate the sample IDs syntax:
  - A grab sample collected at JBT01 on February 2, 2017: **JBT01-020217-GRAB**
3. Grab sample collection.
  - a. Put on lab gloves
  - b. If the air temperature is above freezing:
    - i. Collect samples for TP and TN analysis directly into the sample container. The preferred method is to use the autosampler to pump a sample directly into the sample container, using the manual sample mode. The autosampler pump tubing should be detached from the autosampler housing and a stream of water directed into the sample container. Set the sample volume to 200 mL and dispense the first approximately 5 pump cycles (50 mL) onto the ground, then collect sample up to the fill line on the sample container.
    - ii. Samples for TDP analysis may be dispensed directly into the filtration apparatus containing a 45-mm Durapore® 0.45- $\mu$ m acetate membrane filter. Use forceps to place a clean filter in the filter holder. Wet the filter with a spray of distilled water. Remove the plunger and attach the filter holder to the syringe. Use the autosampler to pump sample into the syringe, using the manual sample mode. The autosampler pump tubing should be detached from the autosampler housing and a stream of water directed into the syringe. Set the sample volume to 200 mL and dispense the first approximately 5 pump cycles (50 mL) onto the ground, then collect approximately 60 mL of sample in the syringe. Squirt approximately 10 mL onto the ground and then fill a glass vial to the 50-mL. If the filter clogs prematurely, it may be replaced with a new filter and the process repeated.
  - c. If the air temperature is below freezing:
    - i. The autosampler may be damaged by ice accumulation. If the tile line continues flowing under freezing conditions, grab samples may be withdrawn using a portable centrifugal pump inserted into the flow metering chamber via a sampling port. Using this pump, sample should be dispensed directly into the sample containers, dispensing the first approximately 50 mL onto the ground, then collecting sample up to the fill line on the sample containers.
    - ii. Because field filtration is not generally successful under freezing conditions, grab samples collected for TDP analysis will be filtered at VAEL. In this case, TDP samples must be brought to VAEL for processing on the day of collection.

4. Preservation. Put on safety glasses. Add 1 drop of concentrated sulfuric acid to preserve the TN sample. Place all samples on ice and store on ice or refrigerate until delivery to the laboratory. Clean up acid spills with acid neutralizing solution or copious amounts of water. To use acid neutralizing solution, shake bottle of acid neutralizing solution and cover affected area until bubbling stops.
5. The filter holder and syringe should be washed by rinsing three times with distilled water after sampling at each station.
6. Complete the Chain of Custody form, including sample IDs, number of containers of each sample being sent to the lab, and the analyses to be performed. The Chain of Custody form must be kept with the samples, either by sticking it into the plastic sleeve taped to the underside of the cooler lid or in a ziplock bag with the samples.
7. Samples must be delivered to the laboratory within the holding times indicated in Table 1.

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## **ROUTINE MAINTENANCE**

### **Tasks to be performed by sampler after each sampling event**

1. On the Sample Retrieval Form, record the amount of rainfall collected in any manual gauges and the date and time. Record the amount of rainfall collected in the graduated cylinder to the nearest 0.01 inch then empty it. If water is present in the outer (overflow) cylinder, carefully decant this into the graduated cylinder and add this amount to the first reading. Repeat if necessary until the overflow cylinder is empty.
2. Confirm that the sampler program is running.
3. Confirm that the sampling line and pump tubing are attached.
4. Confirm that the sample carboys are installed properly.
5. Describe field/crop condition.
6. Verify that sufficient sampling supplies (bottles, filters, gloves) remain for at least two sampling events. Notify the Stone project manager if any supplies are low.

### **Tasks to be performed by Stone approximately monthly**

1. Confirm that the sampler program is running.
2. Check the sampling line for any kinks or sags; zip-tie if necessary to maintain a consistent downward slope in the line.
3. Confirm that the sample carboys are installed properly.

4. Check the desiccant cartridges of the flowmeters and 2105ci modules and replace desiccant if necessary.
5. Restock monitoring stations with bottles, sample retrieval forms, labels, filtration supplies, gloves, and distilled water.
6. Refill or replace acid dropper bottles.
7. Cut weeds from around the shelters and flume and along the wingwalls.
8. Describe field/crop condition.

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**AUTHORIZATION**

Written by: \_\_\_\_\_ Date: \_\_\_\_\_

Dave Braun, Water Quality Scientist, Stone Environmental, Inc.

Approved by: \_\_\_\_\_ Date: \_\_\_\_\_

Julie Moore, Project Manager, Stone Environmental, Inc.

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**REVISION HISTORY**

None

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**FORMS**

Assessment of Tile Drainage System Impacts to Lake Champlain and Phosphorus Loads  
in Tile Drainage in the Jewett Brook Watershed of St. Albans Bay (Project 15-309)

Amendment 1 to QAPP Version 1.1  
11/23/2016

### Sample Retrieval Form

Collected by: \_\_\_\_\_

Date: \_\_\_\_\_

Weather: \_\_\_\_\_

Rainfall (if gauge is deployed) \_\_\_\_\_ in.

	Station JBT01	Comment
Station condition	<input type="checkbox"/> OK    Other _____	
Field/crop condition		
<b>SAMPLE COLLECTION</b>		
Type of sample(s) collected (circle)	Composite split    Grab    None	
Sampler display	_____, _____ bottle _____	
Time you stopped the autosampler	_____ AM or PM	
Carboy volume (L)	1:    2:    3:    4:    or NA	
Sample ID assigned	JBT01 – _____ – <u>  1  </u> (Station) – (mmddyy) – (carboy)  JBT01 – _____ – <u>  2  </u> (Station) – (mmddyy) – (carboy)  JBT01 – _____ – <u>  3  </u> (Station) – (mmddyy) – (carboy)  JBT01 – _____ – <u>  4  </u> (Station) – (mmddyy) – (carboy)  JBT01 – _____ – <u> 12 </u> (Station) – (mmddyy) – (carboy)  JBT01 – _____ – _____ (Station) – (mmddyy) – (GRAB)	
Splits collected (circle)	TP    TDP    TN	
Duplicates collected? (circle)	TP    TDP    TN Carboy _____	
<b>RESETTING STATIONS</b>		
STOP then Re-RUN SAMPLING PROGRAM (circle)	Yes    No	
Carboys and churn splitter triple rinsed? (circle)	Yes    No    NA	
Desiccant good? (circle)	Yes    Changed	
Carboys installed properly? (circle)	Yes    No	
Additional comments:		

Assessment of Tile Drainage System Impacts to Lake Champlain and Phosphorus Loads  
in Tile Drainage in the Jewett Brook Watershed of St. Albans Bay (Project 15-309)

Amendment 1 to QAPP Version 1.1  
11/23/2016

### Chain of Custody Form for Water Samples

Stone Project ID: 15-309

Lab Program #:

Stone Contact: Dave Braun, 802-272-8819, dbraun@stone-env.com

Collection Date	Sample ID	Total # of Containers	Analyses Requested (circle those collected)
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN
			TP TDP TN

Sampled by: \_\_\_\_\_  
print name
signature

Amendment 1 to QAPP Version 1.1  
11/23/2016

Technician: \_\_\_\_\_ Date: \_\_\_\_\_

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**APPENDIX B:**  
**Determination of Phosphorus by Flow Injection Analysis 24 8 1-2015**  
**(Acid Persulfate Digestion Method)**

**APPENDIX C:**  
**Determination of Total Nitrogen by Flow Injection Analysis 24 7 1-2015**  
**(Persulfate Digestion Method)**



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## **1.0 Identification of Test Method**

- 1.1 This SOP is for the analysis of Phosphorus either total or dissolved and is based on Standard Methods for the Examination of Water and Wastewater, 21<sup>th</sup> Ed. APHA-AWNA/WPCF Method 4500-P H Manual Digestion and Flow Injection Analysis for Total Phosphorus and Determination of Total Phosphorus by Flow Injection Analysis Colorimetry, QuikChem Method 10-115-01-1-F.
- 1.2 Orthophosphate (SRP) procedure is exactly the same as TP minus digestion. Holding time is 48 hours.

## **2.0 Applicable Matrix/Matrices**

- 2.1 This method determines the amount of phosphorus in drinking, ground, surface water and soil extracts.

## **3.0 Method Detection Limit (MDL)/Limit of Quantitation (LOQ)**

- 3.1 The MDL for both Total Phosphorus and Dissolved Phosphorus is 2.5µg P/L.
- 3.2 The LOQ for both Total Phosphorus and Dissolved Phosphorus is 5µg P/L.

## **4.0 Scope and Application**

- 4.1 This method covers the determination of total phosphorus in drinking water, non-potable water and laboratory DI water. This method determines total phosphorus in non-filtered samples and total dissolved phosphorus in samples that were filtered through a 0.45µm filter. The difference between the result of a sample determined directly and filtered is termed total insoluble phosphorus.
- 4.2 The method is based on reactions that are specific for the orthophosphate ( $\text{PO}_4^{3-}$ ) ion.
- 4.3 The applicable range of the 5 - 200µg P/L.

## **5.0 Summary of Test Method**

- 5.1 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, which absorbs light at 880nm. The absorbance is proportional to the concentration of orthophosphate in the sample. Polyphosphates may be converted to the orthophosphate form by sulfuric acid digestion and organic phosphorus may be converted to orthophosphate by persulfate digestion.

## **6.0 Definitions**

- 6.1 Calibration Blank (CB) - A volume of reagent water in the same matrix as the calibration standards, but without the analyte.
- 6.2 Calibration Standard (CAL) - A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
  - 6.2.1 Continuing Calibration Verifications (CCV and CCB) - Calibration standards analyzed at regular intervals used to monitor the instrument calibration. Refer to section 6.14 for DQM

- 6.2.2 CCV Mid – The CCV Mid is a mid-level calibration standard that is analyzed at the beginning of analysis, after every 10 samples and at the end of analysis.
- 6.2.3 CCV Low – The CCV Low is low-level standard that is two times the PQL (6.11). It is analyzed at the beginning of the run.
- 6.2.4 CCB – A blank calibration standard used to monitor the instrument calibration during analysis. It is analyzed at the beginning of analysis, after every 10 samples and at the end of analysis.
- 6.3 Method Blank (MB) – A laboratory reagent water blank that is treated exactly as a sample, and is used to monitor lab contamination.
- 6.4 Laboratory Control Sample (LCS) – A laboratory reagent blank spiked with known amounts of analyte. The LCS is used to assess the performance of all or a portion of the measurement system. The LCS samples are then analyzed and processed exactly as customer samples.
  - 6.4.1 LCS – Mid – The target analyte concentration is at mid-calibration level.
  - 6.4.2 LCS – Low – The target analyte concentration is at or near the PQL.
- 6.5 Filter Blank (FB) - A laboratory reagent water blank that is treated exactly as a sample, and is used to monitor lab contamination. A filter blank is analyzed only when sample filtration is required at the bench.
- 6.6 Field Split (FS) Sample – An aliquot of a well-mixed sample is poured into two separate containers by field personnel under field conditions. These Duplicates are processed and analyzed independently either as Duplicates (6.7.1) or Matrix Spikes (6.7.2). One of the FS Samples is logged into the lab data system and its corresponding Lab ID# is written on the label of the second FS Sample. The goal for the fiscal year is for the lab to receive 10% of the total sample TP/DP load as FS Samples.
  - 6.6.1 Duplicate – A routine environmental (FS) sample analyzed to obtain a measure of precision.
  - 6.6.2 Matrix Spike (MS) – A sample prepared by adding a known volume of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine recovery efficiency. The added analyte should have the same concentration as the LCS – Mid (6.5.1).
- 6.7 Initial Calibration Verification (ICV) – The ICV is obtained from a source other than the calibration standards. The ICV is a sample to assess the performance of all or a portion of the measurement system. The analyte concentration of the ICV is typically at mid-calibration level. The ICV sample is analyzed and processed exactly as customer samples.
- 6.8 Method Detection Limit (MDL) – The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.
- 6.9 Limit of Detection (LOD) – The LOD is the lowest concentration level that can be statistically different from a blank. The LOD is approximately equal to MDL.
- 6.10 Limit of Quantitation – The LOQ is approximately equal to the PQL. A CCV-Low (6.3.2) is included in each analysis at 1-2 times the PQL.

- 6.11 Practical Quantitation Limit (PQL) – The laboratory reporting limit, which is 2 to 5 times the MDL (6.8).
- 6.12 Proficiency Evaluation (PE) – A certified solution of method analyte to test whether the analyst/laboratory can produce analytical results within specified acceptance criteria.
- 6.13 Digestion Prep Batch – The set of 20 samples, a MB and an LCS all digested at the same time.
- 6.14 Analytical Batch – Digested Phosphorus samples all analyzed at the same time. An analytical batch can include many digestion prep batches (6.14).
- 6.15 Data Quality Management (DQM) – The DQM is a Lachat Omnion Software specific term used within a Run Worksheet/Tray by defining properties of the samples DQM Tests, DQM Pass and Fail Messages, and DQM Pass and Fail Actions. DQM sets are defined within the Run Worksheet/Tray. After all customer samples have been entered into the Run Worksheet/Tray, the CCV/CCB (6.3) is defined as the DQM set which is then scheduled to run after 10 samples and at the end of the run. This ensures that all samples are bracketed by the method required CCBs and CCVs. This repeating DQM Set will start at the current row in the Run Worksheet/Tray, so it is important this first occurrence of the DQM Set is in the correct row before setting its schedule.

## 7.0 Interferences

- 7.1 Silica forms a pale blue complex, which also absorbs at 880nm. This interference is generally insignificant, as a silicate concentration of approximately 30mg SiO<sub>2</sub>/L would be required to produce a 0.005mg P/L positive error in orthophosphate.
- 7.2 Concentrations of ferric iron greater than 50mg Fe<sup>+3</sup>/l will cause a negative error due to competition with the complex for the reducing agent ascorbic acid and the subsequent loss of orthophosphate. Samples high in iron can be pretreated with sodium bisulfite to eliminate this interference. Treatment with bisulfite will also remove the interference due to arsenates.
- 7.3 Arsenates react with the molybdate reagent to produce a blue color similar to that formed with phosphate causing a negative error.
- 7.4 Glassware contamination is a problem in low level phosphorus determinations. Glassware should be washed with 10% HCl and rinsed with deionized water. Commercial detergents should rarely be needed but, if they are used, use special phosphate-free preparations for lab glassware.

## 8.0 Safety

- 8.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.
- 8.2 Material Safety Data Sheets (MSDS) are available to all personnel involved in the chemical analysis. The following chemicals have the potential to be highly toxic:
- 8.3 Personal Protective Equipment (PPE) should be used where appropriate.

- 8.4 Maintain working areas in a safe manner, which includes cleaning of bench tops, putting away chemicals and glassware after use, cleaning spills and keeping general clutter to a minimum.

## 9.0 Equipment and Supplies

- 9.1 Dedicated Class A glassware that has been acid soaked in 10% HCL and rinsed several times with D.I. H<sub>2</sub>O.
- 9.2 60mL pre-cleaned disposable vessels with PTFE lined screw caps (QEC Item # 2112-60mLC).
- 9.3 Autoclavable Test Tube Racks.
- 9.4 Balance - Analytical, capable of accurately weighing to the nearest 0.0001g.
- 9.5 Lachat QuickChem 8000 Flow Injection Analysis instrument.
- 9.6 Lachat Omnion 3.0 Software.
- 9.7 Automatic Pipettes ranging from 100µl to 10ml.
- 9.8 Autoclave.

## 10.0 Reagents and Standards

- 10.1 Reagent preparation must be recorded in the Nutrients Reagent Logbook located next to the analytical balance and must include the following:
- 10.1.1 Preparation date and chemist's initials (i.e. mmddyyDGM).
- 10.1.2 Manufacturer with lot number of chemical or prep date (i.e. mmddyyDGM) of chemical being used.
- 10.2 The prep dates of all reagents used for each sample analysis must be recorded on the TP/DP Standards/QC Spreadsheet found on the Phosphorus computer.
- 10.3 The preparation dates of all Calibration Standards, Spike Solutions and Quality Control Check Samples are recorded on the TP/DP Standards/QC Spreadsheet. A copy of this spreadsheet is printed and included with the final data package.
- 10.4 Reagents
- 10.4.1 Ammonium Persulfate – Sigma Aldrich Cat # 248614-500g
- 10.4.2 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>) – Fisher Cat # A300SI-212
- 10.4.3 Ammonium Molybdate Tetrahydrate – Sigma Aldrich Cat # A7302-500g
- 10.4.4 Antimony Potassium Tartrate Trihydrate – Fisher Cat # A867-250
- 10.4.5 Dodecyl Sulfate Sodium Salt, 99% (SDS) – Acros Cat # 23042-1000
- 10.4.6 Ascorbic Acid – Fisher Cat # A62-500
- 10.5 Digestion Reagents
- 10.5.1 Ammonium Persulfate Digestion Reagent – Prepared daily  
40g Ammonium Persulfate (10.4.1) → 100mL in DI H<sub>2</sub>O.  
Based on the above recipe, prepare enough of the reagent by adding reagent to a graduated cylinder and diluting to volume with DI H<sub>2</sub>O.  
Cover the cylinder with Parafilm and invert to mix. Reagent volume is 1mL per test tube.
- 10.5.2 11N H<sub>2</sub>SO<sub>4</sub> – Caution: Strong exothermic Reaction...Always add acid to water  
In a 1L volumetric flask, slowly and carefully add 310mL Concentrated

H<sub>2</sub>SO<sub>4</sub> (10.4.2) to 600mL DI H<sub>2</sub>O. Allow to cool. Dilute to 1L mark with DI H<sub>2</sub>O. Expiration date is 1 year from preparation date. Reagent volume is 1mL per 50mL sample.

## 10.6 Analytical Reagents

### 10.6.1 Carrier and Diluent Reagent (Acid Wash) – Expiry date of 1 year.

Fill a 2L volumetric flask with approximate 1.5 liters of DI H<sub>2</sub>O. Add 40mL 11N H<sub>2</sub>SO<sub>4</sub> (10.4.2) and 16g Ammonium Persulfate (10.4.1). Dilute to 2L mark with DI H<sub>2</sub>O. Pour into an autoclavable polycarbonate container. Digest in the autoclave the Acid Wash for 30 minutes at 121°C and 15psi exposure. Allow to cool before use.

### 10.6.2 Ascorbic Acid Reagent – Expiry date of 5 days

Fill a 1L volumetric flask with approximately 700mL of DI H<sub>2</sub>O. Add 60.0g Ascorbic Acid (10.4.6). Dilute to 1L mark with DI H<sub>2</sub>O and invert to mix. Pour into a 1L plastic container and add a stir bar. Add 1.0g of SDS (10.4.5). Place on stir plate and allow to mix for a few minutes. Discard solution if the solution becomes yellow.

### 10.6.3 Stock Ammonium Molybdate Reagent – Expiry date of 30 days

In a 500mL volumetric flask dissolve 20.0g Ammonium Molybdate Tetrahydrate (10.4.3) in approximately 300mL DI H<sub>2</sub>O. Dilute to mark with DI H<sub>2</sub>O, cover with parafilm and stir for a minimum of four hours (can be left stirring overnight). Store in plastic and refrigerate.

### 10.6.4 Stock Antimony Potassium Tartrate Reagent – Expiry date of 30 days

In a 100mL volumetric flask dissolve 0.3g Antimony Potassium Tartrate (10.4.4) in approximately 80mL DI H<sub>2</sub>O. Dilute to mark with DI H<sub>2</sub>O, cover with parafilm and invert to mix. Store in a dark bottle and refrigerate.

### 10.6.5 Molybdate Color Reagent – Expiry date of 5 days

Fill a 1L volumetric flask with approximately 500mL DI H<sub>2</sub>O. Add 21.0mL H<sub>2</sub>SO<sub>4</sub> (10.4.2). Swirl to mix. Add 72.0mL Stock Antimony Potassium Tartrate Reagent (10.4.4). Swirl to mix. Add 213mL Stock Ammonium Molybdate Reagent (10.6.3). Swirl to mix. Dilute to mark with DI H<sub>2</sub>O, cover with parafilm and invert to mix.

## 10.7 Standards and Spike Solutions

### 10.7.1 All calibration standards and ICVs must be digested as in section 14.0 in the same manner as unknown customer samples.

### 10.7.2 1000mg/L Phosphate-Phosphorus – Spex CertiPrep Cat # AS-PO4P9-2Y

### 10.7.3 100µg P/L ICV Standard – Expiry date of 30 days

Measure 50mL DI H<sub>2</sub>O in a pre-cleaned 60mL test tube with screw cap (9.2). Add 500µL of 1000mg/L Phosphate (10.6.2). Refer to section 14.0 for digestion.

### 10.7.4 Intermediate (Int) Calibration (Spex) Stock Standards – Expiry date of 28 days

#### a) 10mg P/L Int Cal Stock

1mL (10.7.2) → 100mL in DI H<sub>2</sub>O

#### b) 1mg P/L Int Cal Stock

100µL (10.7.2) → 100mL in DI H<sub>2</sub>O

**10.7.5 Working Calibration Standard Prep – Expiry date of 30 days**

- a) Prepare the calibration by using the following volumes of 10mg/L (10.7.4a) or 1mg/L (10.7.4b). Standards are prepared in DI H<sub>2</sub>O.

**Table 1**

Concentration (µg P/L)	Recipe
200µg P/L	4mL of 10mg/L (10.7.3a) → 200mL
100µg P/L	2.5mL of 10mg/L (10.7.3a) → 250mL
50µg P/L	1mL of 10mg/L (10.7.3a) → 200mL
10µg P/L	2mL of 1mg/L (10.7.3b) → 200mL
5µg P/L	1mL of 10mg/L (10.7.3b) → 200mL
0µg P/L	200mL DI H <sub>2</sub> O

- b) Using a graduated cylinder, measure 50mL aliquots of each standard and pour into pre-cleaned 60mL screw top test tubes (9.2). Refer to section 14.0 for digestion.

**10.7.6 1000mg/L Phosphate as P – ERA Cat # 061**

**10.7.7 Intermediate (ERA) LCS/MS Stock Standards – Expiry date of 28 days**

- a) **10mg P/L Int LCS/MS Stock**  
1mL (10.7.6) → 100mL in DI H<sub>2</sub>O
- b) **1mg P/L Int LCS/MS Stock**  
100µL (10.7.6) → 100mL in DI H<sub>2</sub>O

**10.7.8 LCS, LCS Low and MS Prep**

- a) Measure 50mL of DI H<sub>2</sub>O in pre-cleaned 60mL test tubes with screw caps (9.2) for the LCS and the LCS Low. Pre-measured samples are provided to the lab by field personnel to use for MS Prep.

**Table 2**

	Volume of ERA Stock	Volume Matrix	Concentration
LCS Low	250µL 1mg/L (10.7.7b)	50mL DI H <sub>2</sub> O	100µg P/L
LCS	500µL 10mg/L (10.7.7a)	50mL DI H <sub>2</sub> O	100µg P/L
MS	500µL 10mg/L (10.7.7a)	50mL Sample	100µg P/L

**11.0 Sample Collection, Preservation, Shipment and Storage**

- 11.1 Pre-cleaned 60mL test tubes with PTFE lined screw caps (9.2) are to be marked to show the 50mL fill-to line using a sharpie and 'jig' prior to sending the test tube out to samplers by lab personnel. All TP and DP samples are collected in these pre-marked/pre-cleaned 60mL test tubes.
- 11.2 Samples being analyzed for DP are filtered through a 0.45µm membrane filter by field personnel. Field personnel are to provide and login a filter blank sample for lab analysis.
- 11.3 Field personnel will provide field split samples which will be used for required

laboratory quality control purposes as duplicates and matrix spikes.

11.4 Samples are not preserved prior to digestion. Samples have a hold time of 28 days once digested.

11.5 Samples are received via drop off by field personnel or the mail. 10.8.6 Samples are stored at room temperature. Undigested samples (samples as received into the lab) do not need to be stored in secondary containment. Digested samples, which contain oxidizers and have a pH < 2, must be stored in some form of secondary containment.

## 12.0 Quality Control

12.1 The laboratory operates a formal Quality Control (QC) program. The minimum requirements of this program consist of an initial demonstration of capability, the analysis of method blanks, LCS's, sample matrix spikes, duplicates, and ICV as checks on the analytical performance. The laboratory maintains records that monitor the quality of data.

12.2 Initial Demonstration of Capability (IDC) – The date and analyst's initials of the following are to be documented on the Demonstration of Capability Certification Statement sheet and filed appropriately in the trainee's training folder:

12.1.1 The review of relevant reference method(s)

12.1.2 The review of the laboratory SOP

12.1.3 Observation of analysis by current analyst

12.1.4 Analysis of samples with little to no supervision

12.1.5 Analysis of four LCS or ICV samples.

12.1.6 The completion date of training

12.1.7 Signatures of the trainee, trainer and the quality assurance officer.

## 12.3 Calibration

12.3.1 The Initial Calibration must use a minimum of five standards and a blank. All standards are run in replicates of 2 as an Indication of Instrument Precision. The lowest calibration standard should be at the reporting limit and the highest concentration at the upper end of the calibration range ensuring that the calibration range encompasses the expected concentration values of the samples or required dilutions.

a) Indication of Instrument Precision – comparison between replicates of each calibration standard. The acceptance criteria is  $\leq 10\%$  RSD between each standard.

12.3.2 Analyses of the CCB and the CCV Mid demonstrate the ongoing precision and recovery and are analyzed on an ongoing basis. They are analyzed at the beginning of the run, again every ten samples and at the end of the run.

a) CCB acceptance criteria is  $\leq \frac{1}{2}$  of the PQL.

b) CCV Mid acceptance criteria is  $\pm 10\%$  recovery of the target value.

12.3.3 Analysis of an ICV verifies the calibration curve through a secondary source. It is analyzed at the beginning of the run. ICV acceptance criteria is  $\pm 10\%$  recovery of the target value

12.3.4 Analysis of a CCV Low demonstrates the ongoing precision and recovery at the low end of the calibration curve. It is analyzed at the beginning of



the run. Acceptance criteria for the CCV Low  $\pm 10\%$  recovery of the target value.

#### **12.4 Laboratory Performance**

**12.4.1** Analyses of a Method Blanks are required to demonstrate freedom from contamination. One Method Blank is required per Digestion Prep Batch of 20 samples. Acceptance criteria for the Method Blank  $\leq \frac{1}{2}$  of the PQL.

**12.4.2** Analyses of LCS Mids are required to evaluate laboratory performance and analyte recovery in a blank matrix. One LCS Mid is required per Digestion Prep Batch of 20 samples. Acceptance criteria for the LCS Mid  $\pm 10\%$  recovery of the target value.

**12.4.3** Analyses of Matrix Spikes (MS) and Duplicate samples are required to demonstrate method accuracy and precision and to monitor matrix interferences caused by the sample. Field Split Samples are provided to the laboratory by field staff for the use of matrix spikes or duplicates. The yearly goal is for 10% of the total yearly samples to have been analyzed as duplicates and as matrix spikes.

a) MS acceptance criteria  $\pm 15\%$  recovery of the target value.

b) Duplicate acceptance criteria  $\leq 10\%$  RPD for samples  $\geq$  the PQL.

**12.4.4** Analysis of LCS Low is required to evaluate the laboratory performance of the method and analyte recovery at the reporting limit. One LCS Low is required per daily TP digestion and daily DP digestion. Acceptance criteria  $\pm 30\%$  recovery of the target value.

**12.4.5** Proficiency Evaluation – A sample with an unknown amount of analyte is analyzed to test whether the analyst/laboratory can produce analytical results within specified acceptance criteria. It is analyzed annually.

#### **13.0 Calibration and Standardization**

**13.1** Prepare reagents and standards as described in section 10.0.

**13.2** Set up manifold as shown in Appendix 1.

**13.3** Input data system parameters as shown in Appendix 1.

**13.4** Pump DI H<sub>2</sub>O through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

**13.5** Place standards in the sampler. Input the information required by the data system.

**13.6** Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with the peak area for each standard to determine the calibration curve. Acceptance criteria is  $\geq 0.995$ .

**13.7** Verify calibration using a CCV Low, CCV Mid and CCB as described in section

**13.8** If percent recovery exceeds acceptance criteria as described in section 18.0, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected and the analytical batch reanalyzed.

## **14.0 Procedure**

### **14.1 Digestion Procedure**

**Note:** Samples may be diluted prior to digest when high concentrations can be predicted.

**14.1.1** 60mL test tubes with a 'Collect sample for Duplicate or Spike' label are provided to the lab by field personnel for required laboratory duplicate or matrix spike quality control purposes. The analyst will decide at the time of analysis whether to use the sample as a Duplicate or as an MS by clearly marking the label. The samples designated as matrix spikes will be set aside for fortifying with spike solution as per section 10.6.8.

**14.1.2** Sample container should contain 50mL as indicated by the black mark on the 60mL test tube. Shake well and decant excess sample if required.

#### **14.1.3 TP Sample Digestion**

- a) Prepare 1 LCS Low (10.7.8) per daily digestion prep batch.
- b) Prepare 1 Method Blank and 1 LCS Mid (10.7.8) per digestion prep batch of 20 samples.

#### **14.1.4 DP Sample Digestion**

- a) Prepare 1 LCS Low (10.7.8) per daily sample digestion batch.
- b) Prepare 1 Method Blank and 1 LCS Mid (10.7.8) per sample digestion batch of 20 samples.

#### **14.1.5 TP/DP Calibration Standards and ICV**

- a) Prepare calibration standards as per 10.7.

**14.1.6** Calibration standards, QC and samples are digested using the following procedure:

- a) Set up samples in autoclaveable racks.
- b) Uncap all samples.
- c) Dispense 1mL Ammonium Persulfate Digestion Reagent to each sample.
- d) Dispense 1mL 11N H<sub>2</sub>SO<sub>4</sub> (10.5.2) to each sample.
- e) Replace caps securely.
- f) Label racks with Date of Digestion. Autoclave samples for 30 minutes at 15 psi and 121°C (use the pre-programmed autoclave method P6). Record the sample type (TP, DP, Standards or Acid Wash), digestion date, initials and autoclave program being used.
- g) After cycle is complete, remove racks from autoclave and allow to cool before analysis.

### **14.2 Creating a Run Worksheet and Sample Tray Setup Procedure**

**14.2.1** Open Omnion 3.0 Icon.

**14.2.2** Click on: Run → Open → ....Omnion → Data folder.

**14.2.3** Select Phosphorus Total for the TP worksheet template or select Dissolved Phosphorus for the DP worksheet template. Three windows will appear on the screen: the Run Worksheet, the Run Properties and one Channel Data Display.

#### **14.2.4 Calibration Standard Tray Setup**

- a) The Cup No.'s (1<sup>st</sup> column of the Run Worksheet) used for the standards are identified as S1, S2, S3, etc.

- b) The Calibration Standard/Sample Type (3<sup>rd</sup> column of the Run Worksheet) rows will be highlighted a blue color.
- c) The CCB, CCV Mid, CCV Low and ICV Mid Check Standards rows will be highlighted a green color.
- d) Uncap and place 60mL test tubes containing digested standards into standards tray that corresponds with the Cup No. on the Run Worksheet.

#### 14.2.5 Sample Tray Setup.

- a) The Cup No.'s (1<sup>st</sup> column of the Run Worksheet) are identified as 1, 2, 3, etc. in the Run Worksheet. The Cup No. refers to the labeled position number in the sample rack.
- b) Working with one digested sample at a time, begin scanning or manually entering the samples in the Sample ID column (the 2<sup>nd</sup> column in the Run Worksheet screen). Once entered, pour an aliquot of sample into a 7mL test tube and place into the tray position that corresponds with the Cup No. (1<sup>st</sup> column of the Run Worksheet).
  - 1. To delete extra rows, click and drag along the selected rows, then right-click and select Delete.
  - 2. To add new rows to the end of the spreadsheet, select any row, then right-click to get the edit menu. Click on the Append Row, to add one row, or on Append Many, to add more than one row.
  - 3. To insert a row or rows before or above a row, click on the row to select it, right-click, then click on Insert Row or Insert Many.
  - 4. To Auto Number Cups, click and drag on the rows in the spreadsheet in which the Cup No. sequence should appear. The right-click and click on Columns, Auto Number Cups. All Samples rack Cup Nos., those not in the Standards rack (S1, S2, etc.) will be renumbered sequentially, incrementing by 1, starting with the first non-Standards rack Cup No. of the selection.
- c) Place the sample tray in the auto-sampler. Make sure the tray is positioned properly in the auto-sampler tray. Sample trays are placed from left to right in the auto-sampler. Three racks of 90 samples can be placed in the auto-sampler.
- d) Place a rack of empty 7mL test tubes last space on the right of the auto-sampler. These are to be used for dilutions by auto-diluter.

#### 14.2.6 Defining DQM

Click and drag the CCB and CCV Mid green Check Standard rows. Right-click and select Define DQM Set. Select "After every N samples". Enter #: 10 in the empty field. Make sure the Close End of Run box is checked. Click OK. The DQM Set is now scheduled to appear at the beginning of the run, every 10 samples and at the end of the run.

### 14.3 Calibration and Sample Analysis

#### 14.3.1 Setup manifold and manifold pump tubing.

#### 14.3.2 Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate.

#### 14.3.3 From the main menu, select Configuration → Autosamplers to open the

Configure Autosamplers window.

- a) Click on Initialize Autosampler to initialize communication between the autosampler and the computer.
- b) Click on Prime Dilutor to prepare the autodilutor for samples needing dilution.
- c) Click Close to return to the Run Worksheet window.

**14.3.4** From the main menu, select the Start icon to begin instrument calibration and sample analysis. The data system will then associate the concentrations with the instrument responses for each standard.

#### **14.4 End of Sample Analysis**

**14.4.1** Remove the TP Color Reagent manifold line from the reagent. Place the line a 0.1N – 0.3N NaOH solution and allow 1-3 inches of the solution to pump through the line. Remove the line out of the NaOH solution and place into a flask containing DI H<sub>2</sub>O and allow to pump for a few minutes.

**14.4.2** Remove all other manifold lines from their reagents and place into the flask containing DI H<sub>2</sub>O and allow to pump for a few minutes.

**14.4.3** Remove all manifold lines from the DI H<sub>2</sub>O and allow air to pump through the manifold lines for a few minutes.

**14.4.4** Turn off the manifold pump and unclamp the manifold pump lines.

**14.4.5** Re-cap calibration standards, reagents and waste container. Refer to section 21.0 for sample waste disposal.

#### **14.5 Data Acquisition and Reduction**

##### **14.5.1 Export Data to File**

- a) Once the analysis is complete, insert a thumb drive into the computer's USB port. In the Runs Properties window (upper right of the screen), click on the Run tab. Click on *Export Data to File*. This action will copy the data to a USB thumb drive.

##### **14.5.2 Format and Print Run Report**

- a) Use the cursor to highlight the Calibration peaks in the Channel Data Display window.
- b) In tool bar, click on Report, and Open Format. Choose TP for Phosphorus-Digested or DP for Phosphorus Filtered/Digested format.
- c) Click on the Custom Report Format icon (which is the 8<sup>th</sup> icon (yellow) from the left in the toolbar) to display the Custom Report Format window. Click on the Layout Tab to adjust the look of the report which includes the analyst's name and analysis date. Click Apply once all changes have been made and then click Close. Refer to the Omnion 3.0 Software User Guide if other adjustments to the report need to be made.
- d) Print analytical run report. Click on Print icon, 7<sup>th</sup> from the left. Select *Print*.
- e) Save report format. Go to tool bar, click on Report, and Save Format. Choose TP for Phosphorus-Digested or DP for Phosphorus Filtered/Digested and click OK. Close window

**14.5.3** Print a copy of the TP/DP Standards/QC spreadsheet to include with the

analytical run report.

- 14.5.4 Save an electronic copy of the TP/DP Standards/QC spreadsheet by clicking on the 'Save' radio button located on the spreadsheet.
- 14.5.5 Use the cursor to highlight the Calibration peaks in the Channel Data Display window.

#### 14.6 Parse the Data

- 14.6.1 Insert the thumb drive into USB port on a DEC Sample Master LIM System networked computer.
- 14.6.2 Open Windows Explorer. Open the following: Y Drive > LIMS > Instrument Parsers Folder > Lachat Omnion 3 folder > Lachat Omnion 3 Parser.
- 14.6.3 Enter analyst initials, confirm analysis date and OK. At the prompt, go to the E: / drive and choose the file to be parsed. Parsing will commence. Data will be displayed in a color coded format. Review data, QC numbers, recovery calculations and formulas. Highlight and set the Print Area to be printed. Print a copy. Click on the Save icon. Minimize this screen.
- 14.6.4 Enter the QC Batch ID (refer to 12.7 for creating a QC Batch) in the window and click OK. Parsing will finish and data will be configured for import into the DEC Sample Master LIM System. Review one last time. Click the Save Icon and close the screen.

#### 14.7 Create a QC Batch

- 14.7.1 Log in to the DEC Sample Master LIM System. Click on the 'Data Entry' icon in the Main Menu window. Highlight the 'Create QC batch' then click on the 'Select' option.
- 14.7.2 In the 'Matrix' drop down box select 'water'.
- 14.7.3 In the 'Test' drop down box select 'Phosphorus-Digested', or 'Phosphorus-Filtered/Digested'. Make sure that the 'Unassigned Samples' box is checked. Select 'Retrieve'.
- 14.7.4 In the 'QC Batch' window, check the boxes of the sample numbers to be included in the QC batch.
- 14.7.5 Click the 'New' button. A QC Batch ID numbered is automatically generated by the Sample Master LIM System to all the checked samples. This QC Batch ID number is required to complete the parsing process (refer to section 14.6.4). The date of sample digestion is considered the date of analysis. If the date of digestion is different from the date of the QC Batch ID, change it to reflect the date of digestion. Write this QC batch number on the front page of the colored parsed data report.
- 14.7.6 The 'New QC batch' window will appear. Click the 'Advanced' button. The 'New QC batch - Sequence' window will appear. Move desired type and frequency of QC from left side of window into the run sequence section on the right. After this is done, click 'Close'. This will return you to the 'QC Batch' window.

**14.7.7** In the '*QC Batch*' window, use the drop down boxes to assign order and sample numbers for each Duplicate(s) and Matrix Spike(s). After this is done, click the '*Add Samples*' button. The check marks in sample boxes will disappear. Click '*Close*'.

**14.7 Import Data**

**14.7.1** In the Sample Master LIM System, click on the red/green icon 2nd from the bottom. Highlight the phrase *Import All Files in One Directory* and click *Select*.

**14.7.2** In the dropdown box choose Lachat as the directory to import data from. Click *Import Immediately*. Sample Master will display *Do you wish to delete the completed task?* Click *No*. Close import window. Click on the 2nd icon from top and select Result Entry. Review the imported data.

**14.7.3** Forward the analytical run report to another analyst for review and validation. Validated data is then authorized for reporting by the lab supervisor.

**15.0 Calculations**

**15.1 Duplicate Sample – Relative Percent Difference (RPD)**

$$RPD = \left( \frac{|\text{Sample Result} - \text{Duplicate Result}|}{((\text{Sample Result} + \text{Duplicate Result})/2)} \right) 100\%$$

**15.2 Matrix Spike (MS) Sample – Percent Recovery**

$$\% \text{ Recovery} = \left( \frac{(\text{MS Sample Result} - \text{Sample Result})}{\text{Known MS added Concentration}} \right) 100\%$$

**15.3 LCS, CCV, ICV Samples – Percent Recovery**

$$\% \text{ Recovery} = \left( \frac{\text{Found Value}}{\text{True Value}} \right) 100\%$$

**16.0 Method Performance (See section 18.0)**

**16.1 Method Detection Limit (MDL)**

**16.1.1** To determine MDL values, seven aliquots of reagent water fortified at approximately half the PQL are processed through the entire analytical method.

**16.1.2** Perform all calculations defined in the method and report the concentration values in the appropriate units (µg P/L).

a)  $MDL = (t) \times (s)$

(t) = 3.14 Student (t) value for 7 replicates

(s) = standard deviation of the 7 replicates

**16.1.3** The MDL is determined annually, when there is a new operator, or when there is a significant change in the background or instrument response.

- 16.2** Practical Quantitation Limit (PQL) – The PQL is the lowest concentration level achievable within specified limits during routine laboratory operations. It is typically 2 – 5 times the calculated MDL. The PQL for this method is 5.0 ppb.
- 16.3** Performance Evaluation (PE) Tests – Participation in periodic PE Tests, such as USGS studies, are analyzed semi-annually. If failures occur, corrective action is taken until acceptable performance is achieved.

### 17.0 Pollution Prevention

- 17.1** Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation.
- 17.2** Laboratory policy is to purchase reagents and standards on an as needed basis and log them into the chemical inventory database and assigning an expiration date, eliminating the need for a stockroom. The database is reviewed on an ongoing basis for expired reagents that can be updated and used for another year

### 18.0 Table 3 - Data Assessment and Acceptance Criteria for Quality Control Measures

Assessment	QC Procedure	Frequency	Limits	Corrective Action
Calibration Curve Linearity	Correlation coefficient	Each calibration	$\geq 0.995$	Re-calibrate.
Indication of Instrument Precision	Duplicate measurements of Calibration Standards	All standards	$\leq 10\%$ RSD	Re-calibrate.
Assessment of Method Performance against second source standard	ICV Mid	Beginning of analysis	$\pm 10\%$	Re-analyze. If still out of control, find and correct source of problem. Re-calibrate the instrument if the problem is instrument related. Re-prepare a new ICV Mid if the problem is sample prep related.
Calibration Curve Stability	CCB	Beginning of analysis, every 10 samples and at end of run analysis	$\leq 1/2$ PQL	Re-analyze. If still out of control, find and correct source of problem. Re-calibrate the instrument if the problem is instrument related. Re-prepare a new CCB if the problem is sample prep related.
Calibration Curve Stability	CCV Mid	Beginning of analysis, every 10 samples and at end of run analysis	$\pm 10\%$	Re-analyze. If still out of control, find and correct source of problem. Re-calibrate the instrument if the problem is instrument related. Re-analyze any and all samples that are not bracketed by passing CCV Mids. However, if a high CCV is recorded and the samples are non-detects, results may be reported with no remark codes if necessary.
Calibration Curve Stability	CCV Low	Beginning of analysis	$\pm 10\%$	Re-analyze. If still out of control, find and correct source of problem. Re-calibrate the instrument if the problem is instrument related. Note that the CCV Low is 1-2 times the PQL which is $\approx$ LOQ
Lab Contamination Monitor	Method Blank	1 per 20 samples	$\leq 1/2$ PQL	Re-analyze. If still out of control, find and correct source of problem. The PQL for samples not bracketed by two passing Method Blanks will be adjusted to reflect a potential high bias due to lab contamination.

Assessment	QC Procedure	Frequency	Limits	Corrective Action
Assessment of Method Performance	LCS	1 per 20 samples	$\pm 10\%$	Re-analyze. If still out of control, remark code and comment in sample master.
Sample Matrix Effect on Accuracy of Results	MS	Varies per digestion batch	$\pm 15\%$	Remark code and comment in sample master.
Assessment of Method Performance at the PQL level	LCS Low	1 per digestion batch	$\pm 30\%$	Re-analyze. If still out of control, remark code and comment in sample master.
Sample Matrix Effect on Precision of Results	Duplicate	Varies per digestion batch	$\pm 15\%$	Remark code and comment in sample master.

## 19.0 Corrective Actions for Out of Control Data (See section-18.0)

- 19.1 Performing routine instrument maintenance such as changing manifold pump tubing, manifold tubing, and other fittings prior to analysis may correct for baseline issues, flow issues, etc. The Lachat Analyzer used primarily for chlorides, nitrates, etc. can also be used as a backup analytical system.
- 19.2 Contact the lab supervisor, nutrients technical director, QC officer with any questions and/or concerns.
- 19.3 For technical assistance, contact Lachat Instruments at 1-800-247-7613, account # 119791.
- 19.4 Lachat Auto Analyzer Data Backup Procedure – Use CDRW on the instrument computer to back up data. This should be done annually, and noted in the instrument maintenance logbook and the data spreadsheet.

## 20.0 Contingencies for Handling Out of Control or Unacceptable Data

- 20.1 Remark Code and Comments – Data and/or samples that do not meet acceptance criteria upon receipt or during analysis need to be either Remark Coded and/or Commented on in the Sample Master LIMS system.
  - 20.1.1 Remark Codes – Remark codes are entered after all data has been parced into Sample Master. To enter a remark code, go to Results Entry. Select QC Batch ID of the data and click Retrieve. In the upper left corner of the View Results window, click on Results to Validate option. Click the “+” box of the sample/QC data needing the remark code and place the appropriate code in the Remark Column. Click the “Close” button on the bottom left of the window (do not click the Validate button) to close the window. All remark codes will be saved. The following codes are to be entered in the appropriate field in Sample Master when necessary:

**Table 4**

SRM Code ID	Description
B	Reported value is associated with a blank contamination
BH	Reported value may be biased high



BL	Reported value may be biased low
D	Dilution resulted in instrument concentration below PQL
E	Estimated Value
H	Hold time exceeded
I	Matrix Interference
N	Not processed
O	Outside calibration range, estimated value
OL	Outside Limit

**20.1.2** Comments – Additional analyst comments can be entered when more detail information is needed. To enter a comment, go to Results Entry. Select QC Batch ID of the data and click Retrieve. In the upper left corner of the View Results window, click on Results to Validate option. Click the “C” box of the sample/QC data needing the comment to open the Comment window. Enter the comment into the field and click OK when finished. Click the “Close” button on the bottom left of the window (do not click the Validate button) to close the window. All comments will be saved.

**20.2** Method Blank contamination – Acceptance criteria for Method Blanks  $\leq \frac{1}{2}$  the PQL. Samples must be bracketed by passing Method Blanks to report samples at the PQL. If a Method Blank fails  $> \frac{1}{2}$  the PQL, the PQL will be adjusted and remark coded “BH” (section 20.1.1) for samples with results between the 5 – 10ppb. Samples with results  $> 10$ ppb within the same bracket will not need a remark code.

**20.3** Duplicate – RPD acceptance criteria for Duplicate analysis  $\leq 15\%$  for samples  $> \frac{1}{2}$  the PQL. The sample result for the Duplicate sample is remark coded “OL” (section 20.1.1) if the Duplicate RPD is  $\geq 15\%$ . If a Duplicate RPD fails, the sample result of the Duplicate is remark coded “OL” (section 20.1.1). If the sample result  $\leq \frac{1}{2}$  the PQL, the Duplicate RPD does not need to be remark coded.

**20.4** MS – MS recovery acceptance criteria  $\pm 15\%$ . The MS result is remark coded “OL” (section 20.1.1) if the MS recovery is  $\geq 15\%$ .

## **21.0 Waste Management**

**21.1** Phosphorus and Dissolved Phosphorus are first digested in individual sample collection vessels using Ammonium Persulfate and Sulfuric Acid. The automated analysis system utilizes several reagents containing toxics and corrosives such as Ammonium Molybdate, Ammonium Persulfate, and Sulfuric Acid. Because of their toxic and corrosive characteristics, sample analysis waste is collected into a 20 liter waste container and disposed through ESF. A “waste tag” is filled out by the employee generating waste, and submitted to the LSO who then enters tag information on line, for pickup.

**21.2** Because the sample is digested in each individual sample collection vessel, the unused sample (in this case, digestate) is poured into analysis waste container and disposed through ESF in the manner stated above.

- 21.2 See Appendix II of Department of Environmental Conservation Laboratory Final Laboratory Waste Management Plan, September 3, 2012.

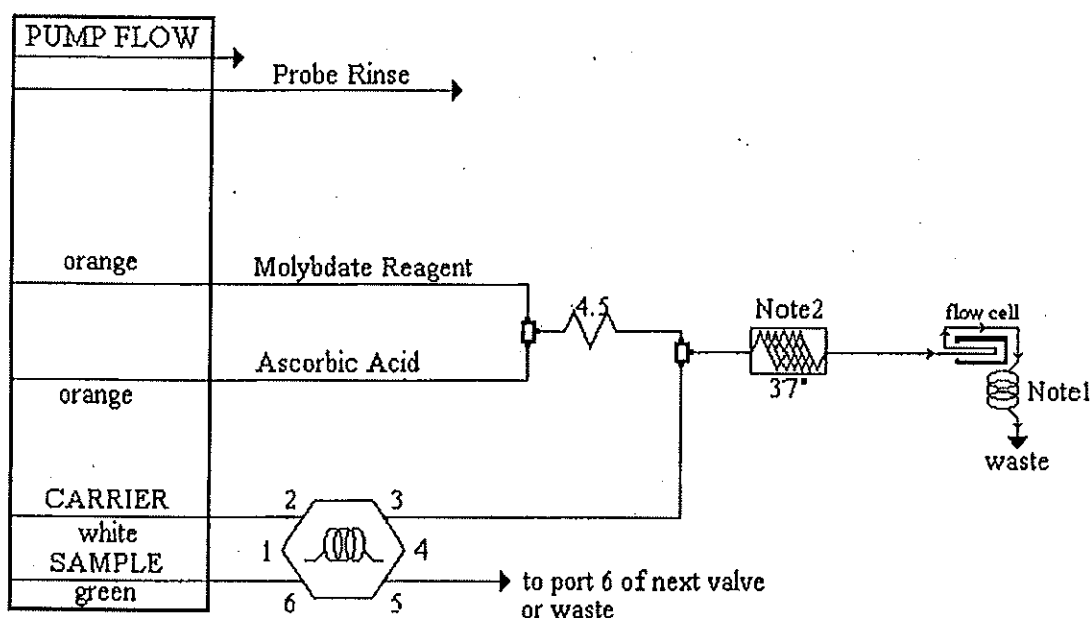
**22.0 References**

- 22.1 Standard Methods for the Examination of Water and Wastewater, 21<sup>th</sup> Ed. APHA-AWNA/WPCF Method 4500-P H Manual Digestion and Flow Injection Analysis for Total Phosphorus.
- 22.2 Determination of Total Phosphorus by Flow Injection Analysis Colorimetry, QuikChem Method 10-115-01-1-F, 27Aug03/csv.
- 22.3 QuikChem FIA+ Automated Ion Analyzer User Manual, Lachat Instruments, Hach Company, 2003.
- 22.4 Omnion 3.0 Software User Guide, Lachat Instruments, Hach Company, 2003.


## 23.0 Tables, Diagrams, Flowcharts and Validation Data

### APPENDIX 1

Total Phosphorus Manifold Diagram



Carrier: 0.13 M sulfuric acid  
 Manifold Tubing: 0.8 mm (0.032 in) i.d. This is 5.2  $\mu$ L/cm.  
 AE Sample Loop: 100 cm  
 QC8000 Sample Loop: 100 cm  
 Interference Filter: 880 nm

**Apparatus:** An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  shows 175 cm of tubing wrapped around the heater block at the specified temperature.

**4.5:** 70 cm of tubing on a 4.5 cm coil support

**Note 1:** 200 cm back pressure loop, 0.52 mm (0.022 in.) i.d.

**Note 2:** 175 cm of 0.8 mm i.d. tubing on the heater.

## Appendix 2

### 23.1 Data System Parameters for Quikchem 8000

Under **Analyte** tab, Channel 1

Property	Value
Description	Phosphorus-Digested
Channel OFF	(box not checked)
Method	FIA

Under **Analyte** tab, Channel 1, Phosphorus-Digested

Property	Value
Analyte Name	Phosphorus-Digested
Concentration Units	ug/l
Calibration Fit Type	Second Order
Clear Calibration	Yes
Force Through Zero	No
Calibration Weighting	None
Auto Dilution Trigger	Yes
% of High Standard	100
Quick Chem Method	10-115-01-1-F
Chemistry:	Direct/Bipolar
Calibration by Height	No

Under **Timing** tab, Run

Property	Value
Method Cycle Period(s)	60
Sample Period (s)	23
Min. Probe in Wash Period	10
Pump standby active	Yes
Use minutes	No
Channel in minutes	No
Analyte in minutes	No
Pump idle before standby	0
Pump at speed before analysis	0

Under **Timing** tab, Run, Channel 1

Property	Value
Load period (s)	18
Inject period (s)	42
Time to valve (s)	26
Use retention time	No

Under **Timing** tab, Run, Channel 1, Phosphorus-Digested

Property	Value
Expected inject to peak start (s)	6
Expected peak base width (s)	65

Under **Rack** tab, choose 3x60 rack configuration

Under **Run** tab, the drop down boxes should show the following

**Instrument:** Instrument 1 (Flow Injection Analysis)  
**Autosampler:** Autosampler 1 (ASX 500 / DRD)

Data configuration for export are set from tool bar. Go to *Configuration* and open *Options*. Choose **Data Export** tab. Under *File Export*, the following boxes should be checked

Export to CSV File Enabled

Include Column Headers

Export in Omnion 2.0 Format

Click on *Data Items*. This will open *Export Data* window. The following items should be entered in the following order. The order is important.

**Location** (to export) F:\ drive

For Channel Independent Data, the Selected Items are (in order shown)

Sample ID  
Sample Type  
Replicate Number  
Detection Date  
User Name  
Detection Time  
Manual Dilution Factor  
Auto Dilution Factor

For Channel Dependent Data, the Selected Items are (in order shown)

Channel Number  
Analyte Name  
Peak Concentration  
Concentration Units

**24.0 Additional Notes:**

<b>Date:</b>	<b>Revision #:</b>	<b>Summary of Changes:</b>	<b>Submitted By/Date:</b>	<b>Approved By:</b>	<b>Effective Date:</b>
1/28/2015	7	This SOP was rewritten to include NELAC required format and informational points. Where guidance is not applicable or would be redundant, an N/A, or another section within the SOP is referenced.	DGM/CMB 1/28/2015		

## Standard Operating Procedure Signature Page

The signatures below indicate the analyst has read, understands, and will follow the SOP.

X	Date:
X	Date:
X	Date:
X	Date:
X	Date:
X	Date:
X	Date:
X	Date:
X	Date:
X	Date:

**APPENDIX C:**  
**Determination of Total Nitrogen by Flow Injection Analysis 24 7 1-2015**  
**(Persulfate Digestion Method)**



**Standard Operating Procedure (SOP) for**  
**Standard Operating Procedure (SOP) For Total Nitrogen**

Reviewed by: Daniel McAvinney Date: 3/26/15  
Daniel McAvinney, Environmental Scientist\*

Revised by: Daniel McAvinney Date: 3/26/15  
Daniel McAvinney, Environmental Scientist \*\*

Reviewed and Approved by:

Dan Needham Date: 03-26-2015  
Dan Needham Interim Quality Assurance Officer\*

Dan Needham Date: 03-26-2015  
Dan Needham, DEC Laboratory Supervisor\*\*

Vermont Department of Environmental Conservation Laboratory

\*Signature implies that the individual has read, understands and agrees to follow this Standard Operating Procedure.

\*\*Signature indicates SOP has been revised.

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**1.0 Identification of Test Method:**

- 1.1 This SOP for VTDEC is based on Hach/Lachat method 10-107-04-1-C for the analysis of nitrate/nitrite as nitrogen in water, with reference to Standard Method SM 4500-N C Modified.

**2.0 Applicable matrix or matrices:**

- 2.1 This method determines the amount of total nitrogen in drinking, ground, and surface water and in saline, domestic and industrial wastewater, and soil extracts.

**3.0 Method detection limit (MDL) / Limit of quantitation (LOQ):**

- 3.1 Method Detection Limit (MDL) is approximately equal to the LOQ, and is used to calculate the Practical Quantitation Limit (PQL). This information is summarized in section 23.0
- 3.2 The PQL for is Total Nitrogen 0.10 mg/l.

**4.0 Scope and application, including components to be analyzed:**

- 4.1 This method determines nitrate/nitrite as nitrogen in water in liquid matrices by automated flow injection analysis.
- 4.2 The applicable range is 0.05 to 2.0 mg N/l.

**5.0 Summary of test method:**

- 5.1 A small sample volume is combined with an alkaline persulfate solution, and digested at 121 C / 15 psi. This process digests ammonia, nitrite and nitrogenous organic materials, oxidizing them to form nitrate.
- 5.2 Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520nm. Nitrite alone also can be determined by removing the cadmium column.

**6.0 Definitions:**

- 6.1 Calibration Blank (CB) - A volume of reagent (0.2 % sulfuric acid) in the same matrix as the calibration standards, but without the analyte.
- 6.2 Calibration Standard (CAL) - A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument.
- 6.3 Method Blank (MB) - A laboratory reagent (0.2 % sulfuric acid) blank that is treated exactly as a sample, and is used to monitor lab contamination. Digested sample and QC results are corrected for blank contamination using the averaged Method Blank results from an analytical run.
- 6.4 Filter Blank (FB) - A laboratory reagent (0.2 % sulfuric acid wash) blank that is treated exactly as a sample, and is used to monitor lab contamination. A filter blank is analyzed only when sample filtration is required at the bench.

- 6.5 Laboratory Duplicate (LD) - Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. The lab duplicates are treated exactly as the samples. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation or storage procedures.
- 6.6 Matrix Spike (MS) - A routine environmental sample with a known concentration of analyte added. The added analyte should have the same concentration as the Laboratory Control Sample (LCS), and be treated exactly as the samples.
- 6.7 Laboratory Control Sample (LCS) - A laboratory reagent blank with a known amount of analyte added. The added analyte should have the same concentration used for the Matrix Spike (MS), and be treated exactly as the samples.
- 6.8 Laboratory Control Sample – Low (LCS-Low) - A laboratory reagent blank with a known amount of analyte added. The added analyte should have a concentration at or near the PQL, and be treated exactly as the samples.
- 6.9 Initial Calibration Verification (ICV) - The ICV is obtained from a source other than the calibration standards, and treated exactly as the calibration standards.
- 6.10 Method Detection Limit (MDL) - The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.
- 6.11 Limit of Detection (LOD) – The LOD is the lowest concentration level that can be statistically different from a blank. The LOD is approximately equal to MDL.
- 6.12 Limit of Quantitation (LOQ) – The LOQ is approximately equal to the PQL. A CCV Low is included in each analysis at 1-2 times the PQL.
- 6.13 Practical Quantitation Limit (PQL) - The laboratory's reporting limit, which is 2 to 5 times the minimum detection limit.
- 6.14 Continuing Calibration Verification Solution (CCV) - A calibration standard used to monitor instrument performance.
- 6.15 Continuing Calibration Blank (CCB) - A calibration blank standard used to monitor instrument performance.
- 6.16 Proficiency Evaluation (PE) – Certified solution of method analyte that is unknown to the analyst.
- 6.17 Data Quality Management (DQM) – Defines various quality control samples or sample sets within a tray protocol. These can be CCB/CCV Mid after a calibration curve and every ten samples, at the end of an analytical run; a Method Blank/LCS, a sample and its duplicate / MS.

**7.0 Interferences:**

- 7.1 Sulfide can rapidly and significantly reduce cadmium column efficiency.
- 7.2 Residual chlorine can oxidize the cadmium column.
- 7.3 High concentrations of iron, copper or other metals can give low results. EDTA is added to the buffer to reduce this interference.

- 7.4 Turbidity / sediment can interfere, and can be removed by filtration through a 0.45  $\mu\text{m}$  pore diameter membrane filter prior to analysis.
- 7.5 Oil and grease in high concentrations can coat the surface of the cadmium. Eliminate this by pre-extracting the sample with an organic solvent.

## 8.0 Safety:

- 8.1 Material Safety Data Sheets (MSDS) or Safety Data Sheets (SDS) are stored online at [www.thermofisher.com](http://www.thermofisher.com), and with the Lab Safety Officer (LSO).
- 8.2 The Laboratory Safety Plan is available for review as a hardcopy, and on the State of Vermont intranet (Y drive) and used by personnel involved in the analysis.
- 8.3 The following reagents are known to be toxic or hazardous. For more detailed explanations consult the MSDS/SDS information, and Lab Safety Plan.
  - 8.3.1 Sulfuric acid
  - 8.3.2 Ammonium hydroxide
  - 8.4.3 Sodium hydroxide
  - 8.4.4 Phosphoric acid
  - 8.4.5 Ammonium chloride
  - 8.4.6 Cadmium
  - 8.4.7 Sulfanilamide
  - 8.4.8 Potassium persulfate

## 9.0 Equipment and Supplies:

- 9.1 Balance(s) - Analytical, capable of accurately weighing to the nearest 0.001g
- 9.2 Class 'A' volumetric flasks and lab ware as needed.
- 9.3 Rainin EDP pipette w/ disposable tips.
- 9.4 Flow injection analysis instrumentation designed to deliver and react sample and reagents in required order and proportion.
  - 9.4.1 Auto sampler.
  - 9.4.2 Auto dilutor.
  - 9.4.3 Multi-channel peristaltic pump with at least 4 channels.
  - 9.4.4 Reaction unit or mixing manifold.
  - 9.4.5 Colorimetric detector, including 80 $\mu\text{l}$  flow cell with 10mm path length.
  - 9.4.6 Interference filter 480nm  $\pm$  10nm band pass.
  - 9.4.7 Cadmium reduction column
  - 9.4.8 Data handling system
- 9.5 50ml polyethylene screw-top centrifuge tubes as needed
- 9.6 16 x 125 mm glass screw top tubes with marking spot, threaded polypropylene (liner less) caps.
- 9.7 16 x 100 mm glass test tubes as needed
- 9.8 Filters as needed.

**10.0 Reagents and standards:**

- 10.1 Carrier/Diluent 0.2 % Sulfuric acid. In a 2L volumetric flask with 1800 ml D.I. water, add 4ml low nitrogen sulfuric acid (Fluka #84727) and dilute to volume. Prepare daily.
- 10.2 Digestion Reagent-Each sample needs 5ml digestion reagent. Prepare volume according to Table A.

Volume	Potassium Persulfate ( $K_2S_2O_8$ )	Sodium Hydroxide (NaOH)
1 L	20.0 g	6.0 g
500 ml	10.0 g	3.0 g
250 ml	5.0 g	1.5 g
100 ml	2.0 g	0.6 g

- 10.3 Ammonium Chloride Buffer-In a 2 L volumetric flask dissolve 170.0g ammonium chloride ( $NH_4Cl$ ) and 2.0g disodium EDTA ( $Na_2-EDTA \cdot 2H_2O$ ) in approximately 1800ml D.I. water. Add 16.0ml ammonium hydroxide ( $NH_4OH$ ). Dilute to 1L with D.I. water and mix on magnetic stir plate until dissolved. Adjust pH to  $8.50 \pm 0.05$  with ammonium hydroxide. Hold time is one month.
- 10.4 Sulfanilamide Color Reagent-To a 1L volumetric flask add 40.0g sulfanilamide, and enough D.I. water to wet. Then add 100ml of 85% phosphoric acid ( $H_3PO_4$ ) and swirl to mix, add 500 ml D.I. water and mix until dissolved. Add 1.0g N-(1-naphthyl) ethylenediamine dihydrochloride (NED). Dilute to volume and mix on magnetic stir plate until dissolved. Store in a dark bottle. Hold time is 1 month.
- 10.5 Primary standard, Nitrate as N 1000mg/l (Spex #AS-NH3N9-2Y). Expiration date is given by the manufacturer or one year from date opened.
- 10.6 Secondary standard, Nitrate as N 1000 mg/l (ERA #052), Expiration date is one year from ship date.
- 10.7 Reduction efficiency standard, Nitrite as N 1000 mg/l, either of the following can be used: Spex #AS-NO2N9-2Y or ERA #053.

**11.0 Sample collection, preservation, shipment and storage:**

- 11.1 Samples are collected in pre-cleaned, disposable 50ml polyethylene screw top centrifuge tubes.
- 11.2 Samples are delivered to the lab by field personnel or courier.
- 11.3 Samples are acidified w/ low nitrogen sulfuric acid and stored at  $\leq 6$  C.
- 11.4 Sample hold time is 28 days.

## 12.0 Quality control:

- 12.1 The laboratory operates a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, determination of minimum detection limit, periodic analysis of laboratory reagent blanks (method blanks), laboratory control samples, sample (matrix) spikes and duplicates, initial calibration verification solutions as checks on analytical performance and meeting a minimum correlation coefficient for the calibration curve. The laboratory maintains and monitors the data in the Lab Information Management System (LIMS). Definitions below may refer to a Data Quality Management (DQM) set, defined as one or more QC samples analyzed concurrently to monitor instrument performance.
- 12.2 Method Detection Limit (MDL) - MDLs are determined/verified annually, when a new operator begins work, or whenever there is a significant change in the method procedure. The MDL is determined by analyzing 7 samples at 0.1 mg/L, yielding a PQL of 0.1 mg/L.
- 12.3 Linear Dynamic Range (LDR) - The LDR must be determined initially or whenever a significant change in instrument response is observed or expected.
- 12.4 Initial demonstration of Ability (IDA) – An IDA is required by new analysts before reporting results. The reference method and lab SOP must be reviewed. The new analyst must observe the current analyst running at least one analytical batch, then analyze an analytical batch under current analysts supervision, and finally analyze and meet QC criteria for four replicates of LCS or ICV.
- 12.5 Proficiency Evaluation (PE) – Successful analysis of a PE sample at a minimum of one concentration must be completed prior to reporting results. Results should be within the test limits established by USEPA for the category of sample being tested.
- 12.6 Lab Reagent Blank aka Method Blank (MB) – are analyzed to determine if reagents contribute contamination to the process. An MB is paired with an LCS and referred to as a DQM set. This DQM set is analyzed with each analytical batch of 20 or fewer samples. Results should be less than ½ the PQL. If the result is greater than ½ the PQL, sample results in the corresponding analytical batch that are between the PQL and 2x the value of the Method Blank are given a remark code 'BH' (result may be Biased High).
- 12.7 Laboratory Control Samples (LCS) – A laboratory reagent blank with a known amount of analyte added. The added analyte should have the same concentration used for the Matrix Spike (MS), and be treated exactly as the samples. An LCS is paired with an MB and referred to as a DQM set. This DQM set is analyzed with each analytical batch of 20 or fewer samples. LCS recovery of 90 – 110 % is expected. Minimum frequency is 5%, or 1 LCS per analytical batch, whichever is greater.

- 12.8 Laboratory Control Sample - Low (LCS Low) – A laboratory reagent blank with a known amount of analyte added at or near the PQL. The added analyte should be treated exactly as the samples. An LCS Low is run once during the analysis with an expected recovery of 75 – 125 %.
- 12.9 Matrix Spike (MS) - A routine environmental sample with a known concentration of analyte added, and is paired with an unspiked sample. The added analyte should have the same concentration as the Laboratory Control Sample (LCS), and be treated exactly as unspiked samples. Recovery of 85 – 115% is expected. Minimum frequency is 5%, or 1 LCS per analytical batch, whichever is greater.
- 12.10 Lab Duplicate - Two portions of the same environmental sample treated identically throughout the analytical procedure, and treated exactly as the samples. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation or storage procedures.
- 12.11 Initial Calibration Verification (ICV) - The ICV is obtained from a source other than the calibration standards, and treated exactly as the calibration standards. The frequency is once per analysis, immediately after the calibration is acquired. Expected recovery is within 10 % of the true value. Re-prepare and rerun if the ICV recovery is outside expected limits.
- 12.12 Continuing Calibration Verification (CCV) – are calibration standards used to monitor instrument precision and performance. Data is kept in LIMS and monitored by the QC Officer.
  - 12.12.1 CCB - Continuing Calibration Blank is analyzed after the calibration and every ten samples thereafter. It is paired with the CCV Mid and referred to as a Data Quality Management (DQM) set. CCB results should be less than  $\frac{1}{2}$  the PQL. If the CCB fails, the analysis must be stopped, the cause determined and the instrument recalibrated. The CCB data must be kept on file with the sample analysis data.
  - 12.12.1 CCV Low - is a low level calibration standard near or at the PQL, and is analyzed once during the run after the calibration. The expected recovery for the CCV Low is within 70 -130% of the true value. If the CCV Low fails, re-run once. If still unacceptable, the analysis must be stopped, the cause determined and the instrument recalibrated. The CCV Low data must be kept on file with the sample analysis data.
  - 12.12.2 CCV Mid - is a midlevel calibration standard analyzed after the calibration is complete and every ten samples thereafter. It is paired with the CCB and referred to as a DQM set. The expected recovery for the CCV Mid is  $\pm 10\%$  of its true value. If the CCV Mid fails, the analysis must be stopped, the cause determined and the instrument recalibrated. The CCV Mid data must be kept on file with the sample analysis data.



- 12.13 Correlation Coefficient – The minimum correlation coefficient for Chloride is 0.995 or greater.
- 12.14 % Residual for Calibration Standards – The expected % residual for duplicate calibration standards is  $\leq 10\%$ .

### 13.0 Calibration and standardization:

- 13.1 Intermediate standard –Nitrate as N 10 mgN/l. Dilute 1.0 ml of 1000 mg/l primary stock to 100 ml with DI water.
- 13.2 Working standards - Use intermediate nitrate standard to prepare 100 ml volumes of working standards as noted in table below. Bring to volume with D.I. water then acidify with 200 $\mu$ l low nitrogen sulfuric acid. Dispense into 50 ml plastic screw top centrifuge tubes. Hold time is 28 days.

Volume (ml) of 10 mg/l Nitrate Stock	Concentration mg/l
20	2.0
10	1.0
5	0.5
1	0.10
0.5	0.05
0.0 (100 ml D.I. water)	0.0

- 13.3 Prepare (NO<sub>3</sub>-N) Nitrate as N ICV at a mid-calibration level using other than primary stock solution. Bring to 100 ml volume with D.I. water then acidify 200 $\mu$ l low nitrogen sulfuric acid. Dispense into 50 ml plastic screw top centrifuge tube. Hold time is 28 days.
- 13.4 Prepare (NO<sub>2</sub>-N) Nitrite as N reduction efficiency standard. Dispense 100 $\mu$ l nitrite stock 1000 mg/l to 100 ml volumetric flask. Dilute to volume. Do not acidify.
- 13.5 Prepare (NO<sub>3</sub>-N) lab control sample (LCS and MS) standard, 100 mg/l NO<sub>3</sub>. Use Rainin pipet to make a 1:10 dilution of the primary stock solution into a test tube. The lab uses 100 $\mu$ l of 100mg/l stock + 10 ml volume to yield a concentration of 1 mg/l.
- 13.6 Prepare TN lab control sample (LCS and MS) stock standard, 100 mgN/l. Dissolve 0.2627 mg of L-Glutamic acid in 250 ml volumetric flask with D.I. water. The lab uses 25  $\mu$ l of 100mg/l stock + 5 ml volume to yield a concentration of 0.5 mg/l TN.
- 13.7 Prepare TN LCS Low stock. Dilute an aliquot of ERA Simple Nutrient QC (Item #505) to create an intermediate spiking solution. The final concentration of a blank spiked with this solution should be at or near the PQL of 0.1 mg/l.

- 13.8 Record the following information on the TN QC spreadsheet: Standards and QC prep, instrument model, Standard Method reference, test, analyst, test date, color reagent lot number and expiration date, primary and secondary standards with their respective concentrations, lot numbers, expiration dates. Information is updated with each date of analysis and saved in a folder on the instrument computer by clicking on the 'Save' radio button.

**14.0 Procedure:**

- 14.1 Sample Digestion-Prepare digestion reagent according to Section 10.2, Table A.
- 14.1.1 Remove samples from the refrigerator and bring them to room temperature. Check each sample to ensure that the pH is  $\leq 2$ .  
Note: If sample pH is greater than 2 and the sample is within 24 hours of receipt then add 0.1 ml per 50 ml of sample. If after 24 hours, acidify and analyze sample including the proper remark code.
- 14.1.2 Write sample number on glass test tubes with a permanent marker. There are 2 method blanks, an LCS, and an LCS Low at the beginning of the digestion run. A digestion run can contain many batches (a batch consists of 20 samples) with each batch containing a method blank and an LCS. End the digestion run with 2 method blanks.
- 14.1.3 Add the following to each test tube:  
Method Blank. Use 5 ml of acid wash for method blanks.  
LCS. Add 25  $\mu$ l of the 100 mgN/l spike standard to 5 ml of the 0.2% acid wash to the tubes marked LCS.  
LCS Low. Dispense a small volume of a second source QC standard to 5 ml of 0.2% acid wash to achieve a concentration at or near the PQL. Include 1 LCS Low per digestion batch.  
Matrix Spike. Dispense 25  $\mu$ l of the 100 mgN/l spike standard to empty marked tube, then add 5 ml of well-mixed sample.
- 14.1.4 Use 'dilution' function on 10 ml Rainin pipet to draw / mix 5 ml digestion reagent and 5 ml of 'WELL shaken' sample. Dispense this mixed volume into a labelled glass tube and **cap immediately** and firmly. Ammonia can be lost if sample is not capped immediately upon addition of digestion reagent. Include a minimum of 5% spikes and duplicates.
- 14.1.5 Place racks in the autoclave and digest for 30 minutes at 121°C and 15 psi. Record digestion in autoclave log book. After cycle is complete, remove samples from autoclave, and let the samples cool to room temperature before analysis.
- 14.2 Prepare standards (Section 10.0) and reagents for analysis (Section 13.0). Install manifold, sample loop and filter. Turn on power to instrument via power strip. Turn on computer and log onto instrument. Double click on the Omnion icon.

- 14.3 Click on Run, Open and open Data folder. Select Total Nitrogen method and choose TN template.omn.
- 14.4 0.2 % sulfuric acid (Section 10.1) is used as carrier in 1 liter Erlenmeyer flask. Place auto dilutor tubing into this container. Begin pumping carrier and reagents through manifold. Tubing should be clearly labeled. Waste stream is saved and disposed of according to the Laboratory hazardous waste plan.
- 14.5 Initialize the auto sampler by clicking on *Configuration* and *Auto samplers*. Choose *Autosampler 1* tab and click *Initialize Autosampler*. After this is done, click on *Prime Auto dilutor*. Close dialog box.
- 14.6 Calibration standards. Place each prepared standard in its respective standard rack slot. Each standard is run in duplicate.
  - 14.6.1 The method timing and acquisition parameters should already be entered and optimized in the tray template. The calibration standards and QC elements and reduction efficiency standard should have been entered with their assigned values, acceptance limits and failure actions. See Lachat method #10-107-04-1-C for guidance.
- 14.7 Enter sample ID numbers via bar code scanner into the empty slots in the tray template. Place samples and QC into corresponding tray locations. Press 'Enter' to save entry and advance cursor.
  - 14.7.1 For samples diluted prior to digestion, check box in MDF column and enter dilution factor. It's helpful to include the dilution factor with the sample ID in the tray template.

As sample ID numbers are being scanned in, use the QC menu sheet on the bench to scan MB/LCS/MS into the tray template. Sample batches of  $\leq 20$  samples are bracketed by a method blank (MB), and lab control sample (LCS). Highlight and delete the remaining empty tray slots.
- 14.8 Enter DQM sets within the tray template. Move cursor into the gray *Sample No* column to the left of the *Cup No* column. Left click and drag cursor so that the rows with the CCB and CCV Mid are highlighted. Right click and select *Define DQM Set*. In the 'User Defined DQM Set' box under 'Scheduling Options' select 'After every N samples'. The DQM set is run after every 10 samples, (enter 10), and uncheck 'Close end of run' box. Click OK.
- 14.9 Press the 'Start' icon to begin the run.
- 14.10 Once analysis is complete, export data. Insert a thumb drive into the USB port. In top right corner of screen, go to *Run Properties* window and click on the *Run* tab. Click on *Export Data to file* to copy run data to thumb drive. Use cursor to highlight the Calibration curve peaks on the screen.  
 See section 14.3 for parsing instructions.  
 See section 14.4 for creating a QC batch.  
 See section 14.5 for data importing instructions.

- 14.11 Format and print the run report. Go to the tool bar and click on *Tools* and *Custom Report*. In tool bar, click on *Report*, and *Open Format*. Choose TN report format. Click to open the 8<sup>th</sup> icon (yellow) from the left. There are five tabs used to format the report.
- 14.11.1 Click on the *Sample* tab. Uncheck the *calibration standards* boxes. Click *Apply* in lower right of window.
  - 14.11.2 Click on *Table* tab. Check the *cup number* box. If the run included any instrument duplicates, auto or manual dilutions, check the boxes that pertain. Click *Apply* in lower right of window.
  - 14.11.3 Click on *Layout* tab. Check header information, change date of analysis. Click *Apply* in lower right of window.
  - 14.11.4 Click on *Calculations* tab. Under *Sample Preparation* check the boxes that apply so that results are multiplied by the auto or manual dilution factor. Click *Apply* in lower right of window.
  - 14.11.5 Click on the *Charts* tab. In the *Options* section, check *Calibration* and *Channel Data Display* boxes. In the *Channel Data Display* section, under *Select Channel(s) for Report*, #1 should be checked. Under *Display Options*, click on *Show \_\_\_ Peaks per Chart for All Peaks*. Enter 10. Click *Apply* then *Close* in lower right of window.
  - 14.11.6 Print analytical run report. On top of the screen, Click on *Print* icon, 7<sup>th</sup> from the left. Select *Print*. Save report format. Go to tool bar, click on *Report*, and *Save Format*. Choose TN, and OK. Close window. Print a copy of the *Standards/QC spreadsheet* to include with the analytical run report.
  - 14.11.7 Save an electronic copy of the *Standards/QC spreadsheet* to the folder by clicking on the '*Save*' radio button located on the spreadsheet. Save the desktop copy by clicking the '*Save*' icon at top left of screen.
- 14.12 Calculate TN results on instrument computer
- 14.12.1 Click on Icon '*Calculate TN results*' on lower toolbar to open macro. Enable macro, click on '*Calculate*' radio button.
  - 14.12.2 Navigate to thumb drive and open TN file to be calculated. Calculating will commence.
  - 14.12.3 Type in header info, and any sample dilution factors from the tray template. Check all formulas and cell references for accuracy.
  - 14.12.4 Set '*Print Area*' and print. Close this window without saving and remove thumb drive.

14.13 Create a QC Batch on LIMS networked computer

- 14.13.1 Log in to Sample Master. Click on the '*Data Entry*' icon in the Main Menu window. Highlight the '*Create QC batch*' then click on the '*Select*' option.
- 14.13.2 In the '*Matrix*' drop down box select '*Water*'.
- 14.13.3 In the '*Test*' drop down box select '*Nitrogen-Total Persulfate*'. Make sure that the '*Unassigned Samples*' box is checked. Select '*Retrieve*'.
- 14.13.4 In the '*QC Batch*' window, check the boxes of the sample numbers to be included in the QC batch, by referencing the TN (Calculated) Data sheet.
- 14.13.5 Click the '*New*' button to assign a QC batch ID to the checked samples. If the date of analysis is different from the date of the QC Batch ID, change it to reflect the date of analysis. Write this QC batch number on the front page of the TN data sheet.
- 14.13.6 The '*New QC batch*' window will appear. Click the '*Advanced*' button. The '*New QC batch – Sequence*' window will appear. Move desired type and frequency of QC from left side of window into the run sequence section on the right. After this is done, click '*Close*'. This will return you to the '*QC Batch*' window.
- 14.13.7 In the '*QC Batch*' window, use the drop down boxes to assign order and sample ID to the Duplicate(s) and Matrix Spike(s). After this is done, click the '*Add Samples*' button. The check marks in sample boxes will disappear. Click '*Close*'. Minimize Sample Master.

14.14 Parse the data on LIMS networked computer

- 14.14.1 Insert the thumb drive into a USB port on LIMS networked computer.
- 14.14.2 Open Windows Explorer. Open the following. Y drive, LIMS folder, Instrument Parsers Folder, Lachat Omnion 3 folder, TN Parser.xls.
- 14.14.3 Enter QC Batch, analyst initials, analysis date and OK. At the prompt, find and choose the file to be parsed. Click OK to commence parsing. Data will be displayed in Excel. Review results and QC numbers.
- 14.14.4 Delete any spaces or typed characters associated with sample ID's.
- 14.14.5 Data outside of calibration range cannot be reported. This should be deleted by row so as not to import it into the LIMS.
- 14.14.6 'Save' this spreadsheet, and close. Data will be saved in the '*Data2import*' folder.

14.15 Import Data into LIMS

- 14.15.1 Maximize Sample Master. Click on the Electronic Data Transfer (Green arrow) icon, second from the bottom. Highlight the phrase *Import All Files in One Directory* and click *Select*.
- 14.15.2 In the dropdown box choose TN as the directory to import data from. Click *Import Immediately*. Sample Master will display *Do you wish to delete the completed task?* Click *No*. Close import window. Click on second icon from top, choose Result Entry, and select. Review the imported data.
- 14.15.3 Forward imported data to another analyst for review and validation.

14.16 Data Validation - Data is peer reviewed for errors or omissions by a chemist familiar with the method.

- 14.16.1 The calibration curve correlation, MS, LCS, CCV, ICV recoveries and RPD values should all be within control limits. The interval of the DQM set(s) is checked.
- 14.16.2 Sample Master is opened and the QC batch is retrieved by clicking on the second icon from the top. Select *Result Entry*. Select the desired QC batch from the QC batch drop down box.
- 14.16.3 Select the *Data to be validated* radio button. Data in Sample Master and the analytical report should agree. All relevant data should be included and should be within acceptable limits. Any out of control values should be properly flagged and/or commented.
- 14.16.4 Values to be validated should have their respective boxes checked. Once this has been done, click *Validate* then *Close*.
- 14.16.5 The analyst will initial and note the date that the data was validated on the front page of the analytical run report. The report is filed.

15.0 Calculations:

- 15.1 Total Nitrogen sample results are calculated using a macro on the instrument computer (Section 14.12). To calculate manually, subtract the average method blank value from the obtained result and multiply by 2. This accounts for the known contamination added to each sample by the digestion reagent, as well as the dilution of the sample.

$$[\text{Raw Result} - \text{Avg. MB}] \times 2$$

- 15.1 Calculate the MS percent recovery using the following equation:

$$[(C_s - C_u) / C] * 100$$

C = spike (stock) concentration (mg/l)  
 C<sub>u</sub> = unspiked concentration (mg/l)  
 C<sub>s</sub> = spiked concentration (mg/l)

If the recovery of the analyte falls outside the designated MS recovery range and the laboratory performance for that analyte is shown to be in control, the recovery problem with the MS is judged to be either matrix or solution related, not system related.

- 15.2 Calculate Relative Percent Difference (RPD). Analytical duplicate results are used to calculate a Relative Percent Difference (RPD). If the determined RPD values are not within established control limits, the source of the problem is identified and corrected before results can be submitted.

$$\frac{|(D_1 - D_2)|}{(D_1 + D_2)/2} * 100 = \text{RPD}$$

D<sub>1</sub> = larger duplicate value      D<sub>2</sub> = smaller duplicate value

- 15.3 Laboratory Control Sample (LCS) – The Laboratory analyzes at least one LCS with each batch of 20 samples. Accuracy is calculated as percent recovery.  
 15.4 Laboratory Control Sample - Low (LCS Low) – The Laboratory analyzes at least one LCS Low with each digested batch of samples. Accuracy is calculated as percent recovery.

#### 16.0 Method performance:

- 16.1 Continuing Calibration Verification (Mid-level) - For all determinations the laboratory must analyze a mid-range continuing calibration verification standard (CCV Mid) and a continuing calibration blank (CCB) following daily calibration, after every tenth sample, and at the end of the analytical run. The result of the CCV Mid must be within 10% of its true value. If the calibration cannot be verified within the specified limits, reanalyze the CCV Mid solution. If the second analysis of the CCV Mid confirms the calibration to be outside control limits, sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable CCV Mid result must be reanalyzed. The results of the calibration blank and CCV Mid solution must be kept on file with sample analyses data.

- 16.2 Continuing Calibration Verification (Low level) – the CCV Low is a low range calibration standard with a value 1 to 2 times the Practical Quantitation Limit (PQL). The PQL is approximately equal to the Limit of Quantitation (LOQ). A CCV Low must be run once during the analytical run, and its recovery must be within 30% of its true value.
  - 16.3 Initial Calibration Verification (ICV) - A mid-range ICV is prepared from a source other than the calibration standards, and run after the calibration standards and before any samples are analyzed. The value must be within 10% of the true value or the run is stopped, and the cause determined before analyzing any samples.
  - 16.4 Matrix Spike (MS) - The analyst must add a known amount of analyte to a minimum of 5 % of routine samples. In each case the MS aliquot must be a duplicate of the aliquot used for sample analysis. The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL. The added analyte concentration and source should be the same as that used in the laboratory-control sample. If the recovery of the analyte falls outside the control limits of 85-115%, the MS is judged out of control, and the source of the problem is identified and resolved before continuing analysis.
- 17.0 Pollution prevention:**
- 17.1 Laboratory policy is to purchase reagents and standards on an as needed basis. Reagents and standards are logged into the chemical inventory database with an associated expiration date, eliminating the need for a stockroom. The database is reviewed on an ongoing basis for expired reagents, which are disposed of through UVM Environmental Safety Facility.



## 18.0 Data assessment and acceptance criteria for quality control measures

Summary Table of Quality Control Procedures, Limits and Corrective Actions

Assessment	QC Procedure	Frequency	Limits	Corrective Action
Linearity of Calibration Curve	Correlation coefficient	Each calibration	$\geq 0.995$	Recalibrate
Indication of instrument precision.	Duplicate measurements	All standards	$< 10\%$ residual	Re-analyze. If still out of control, find source of problem then re-calibrate.
Verification of calibration curve against second source standard	ICV Mid	After each calibration	90 – 110%	Prepare again and recalibrate
Stability of the low end of the calibration	CCB	After ICV , every 10 samples and at end of run	$< \frac{1}{2}$ the PQL	Identify and correct problem
Stability of Calibration Curve	CCV Mid	After ICV , every 10 samples and at end of run	90 – 110%	Rerun CCV. If still out, recalibrate and rerun all samples not bracketed by an acceptable CCV
Stability of Calibration Curve	CCV Low	Once during the run	90 – 110%	Identify and correct the problem. Note that the CCV Low is 1-2 times the PQL which is $\cong$ LOQ
Determine if methodology is In control	LCS	1 per batch	85 – 115%	Identify problem and correct, or prepare again and rerun sample
Indication of the effect of the sample matrix on the accuracy of the results	MS	5 % of all samples or 1 per batch, whichever is greater	85 – 115%	Prepare again and rerun
Indication of the effect of the sample matrix on the precision of the results	LD	5 % of all samples or 1 per batch, whichever is greater	10% RPD	Prepare again and rerun
Efficiency of column	Reduction/Efficiency standard	At the beginning and end of analytical run	$\pm 10\%$	Re-analyze. If still out of control replace cadmium column
Reagent water contamination	MB	1 per batch	$< \frac{1}{2}$ the PQL	Identify problem and correct.

**Note:** If sample values are reported from an analysis where any of the above limit criteria are exceeded, an appropriate remark code or sample note should be entered to justify reporting the results.

**19.0 Corrective actions for out of control data:**

19.1 See section 18.0

**20.0 Contingencies for handling out of control data:**

20.1 If a quality control measure is found to be out-of-control, and the data is to be reported, all samples associated with the failed quality control measure are reported with the appropriate data qualifying remark code found in Section 5.0 of laboratory QA Plan. In addition, final reports may include Order Comment written by analyst and/or supervisor, further qualifying data.

**Sample Remark Codes \***

Remark Code	Description
B	Reported value is associated with a lab blank contamination.
BH	Reported value may be biased high.
BL	Reported value may be biased low.
E	Estimated Value
D	Dilution resulted in instrument concentration below PQL.
H	Hold time exceeded.
I	Matrix Interference
O	Outside calibration range, estimated value.
OL	Outside Limit
P	Preservation of sample inappropriate, value may be in error.
S	Surrogate recovery outside acceptance limits.
T	Time not provided
W	Sample warm on arrival, no evidence cooling has begun.

**21.0 Waste Management:**

21.1 Waste generated from this analysis is disposed through ESF. A "waste tag" is filled out by the employee generating waste, which is then entered online for pickup. See Appendix II of Department of Environmental Conservation Laboratory, Final Laboratory Waste Management Plan.

**22.0 References:**

22.1 Standard Methods for Examination of Water and Wastewater, AWWA, APHA, 21<sup>th</sup> Ed. SM 4500-N C Modified.

## 23.0 Tables, diagrams, flowcharts and validation data:

### 23.1 Instrument Parameters

Under **Analyte** tab, Channel 1

Property	Value
Description	(none)
Channel OFF	(box not checked)
Method	FIA

Under **Analyte** tab, Channel 1,

Property	Value
Analyte Name	Nitrate- Nitrite Nitrogen
Concentration Units	mg/l
Calibration Fit Type	First Order
Clear Calibration	Yes
Force Through Zero	No
Calibration Weighting	None
Auto Dilution Trigger	Yes
% of High Standard	100
QuickChem Method	10-107-04-1-C
Chemistry:	Direct/Bipolar
Calibration by Height	No

Under **Timing** tab, Run

Property	Value
Method Cycle Period(s)	45
Sample Period (s)	15
Min. Probe in Wash Period	5
Pump standby active	No
Use minutes	No
Channel in minutes	No
Analyte in minutes	No
Pump idle before standby	0
Pump at speed before analysis	0

Under **Timing** tab, Run, Channel 1

Property	Value
Load period (s)	10
Inject period (s)	35
Time to valve (s)	24
Use retention time	No

Under **Timing** tab, Run, Channel 1, Nitrate-Nitrite Nitrogen

Property	Value
Expected inject to peak start (s)	26
Expected peak base width (s)	40

Under **Rack** tab, choose 3x60 rack configuration

Under **Run** tab, the drop down boxes should show the following

**Instrument:** Instrument 1 (Flow Injection Analysis)

**Autosampler:** Autosampler 1 (ASX 500 / DRD)

Data configuration for export are set from tool bar. Go to *Configuration* and open *Options*.  
Choose **Data Export** tab. Under *File Export*, the following boxes should be checked

Export to CSV File Enabled  
Include Column Headers  
Export in Omnion 2.0 Format

Click on *Data Items*. This will open *Export Data* window. The following items should be entered in the following order. The order is important.

**Location** (to export)      F: / drive

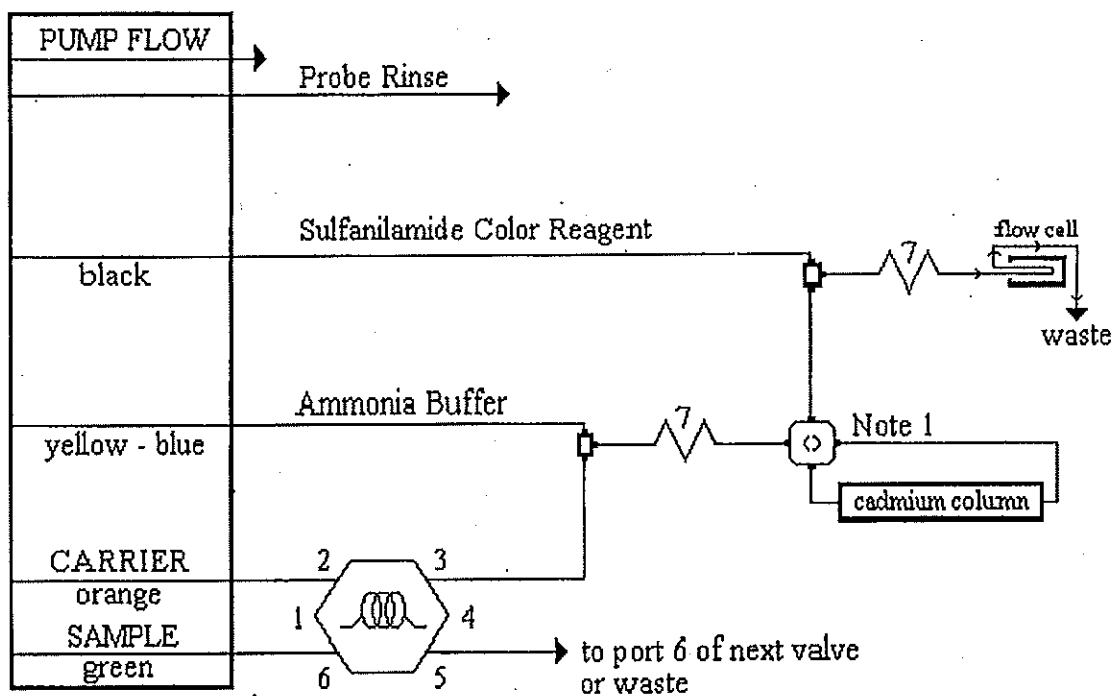
For Channel Independent Data, the Selected Items are (in order shown)

Sample ID  
Sample Type  
Replicate Number  
Detection Date  
User Name  
Detection Time  
Manual Dilution Factor  
Auto Dilution Factor

For Channel Dependent Data, the Selected Items are (in order shown)

Channel Number  
Analyte Name  
Peak Concentration  
Concentration Units

Nitrate Manifold Diagram

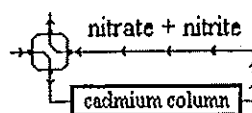
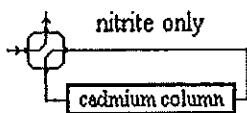


**Carrier:** Helium Degassed DI water  
**Manifold Tubing:** 0.8 mm (0.032 in) i.d. This is 5.2  $\mu\text{L}/\text{cm}$ .  
**AE Sample Loop:** 17 cm x 0.8 mm i.d.  
**QC8000 Sample Loop:** 22.5 cm x 0.8 mm i.d.  
**Interference Filter:** 520 nm

**Apparatus:** An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required.

**7:** 135 cm of tubing on a 7 cm coil support

**Note 1:** This is a 2 state switching valve used to place the cadmium column in-line with the manifold



## 24.0 Additional notes:

### Troubleshooting

- 24.1 Trouble is often traced to either mechanical or chemical sources. The following are suggestions to help prevent problems. For more detailed troubleshooting guidance, consult the Lachat training manual or call Lachat tech support at 800-247-7613
- 24.2 Mechanical problems can show up as air spikes, misshapen peaks or an unstable or noisy baseline. To minimize these potential problems, prior to beginning a test, do the following.
- 24.3 Reagents should be at room temperature prior to the run. Sparging reagents with helium is not needed.
- 24.4 Make sure all mixing manifold tubing connections are snug, but not tight enough to impede reagent flow.
- 24.5 While reagents are pumping through the manifold make sure there are no air bubbles in the flow cell. Remove the cell from the colorimeter and tap gently with finger to dislodge any bubbles.
- 24.6 Confirm that timing parameters are correct.
- 24.7 Chemical problems can show up as poorly shaped peaks, lower than expected peak areas or as an elevated baseline. Properly made and stored reagents can minimize these potential problems, and using reagents before the recommended expiration date.
- 24.8 Rainin EDP pipette is used to make standards, QC check samples and sample spikes. This pipette and attachments are serviced and calibrated annually. Calibration is verified quarterly.
- 24.9 Septic samples may have hydrogen sulfide present as well as high  $\text{NH}_3$  and low  $\text{NO}_3$ . If a strong rotten egg odor is noticed, dilute with acid wash 1:10. Hydrogen Sulfide will rapidly degrade column efficiency.
- 24.10 Nitrate/Nitrite samples without previous data or site history should be screened using EM QUANT Nitrate test strips (VWR Scientific 1-800-932-5000) and diluted prior to analysis.
- 24.11 ACS grade ammonium chloride can occasionally contain a small concentration of nitrate. Check the reagent assay prior to purchase. An alternative buffer recipe is provided in the Lachat Nitrate/Nitrite method.
- 24.12 Lachat Technical Support 1-800-247-7613.
- 24.13 Data backup to CD should be done annually, and noted in the instrument maintenance logbook and the data spreadsheet.

Rev. Date:	Revision #:	Summary of Changes:	Submitted By/Date:	Approved By:	Effective Date:
1/15/2015	7	This SOP was rewritten to include NELAC required format and informational points. Where guidance is not applicable or would be redundant, an N/A, or another section within the SOP is referenced.	DGM 1/15/2015		

## Standard Operating Procedure Signature Page

The signatures below indicate the analyst has read, understands, and will follow the SOP.

X	_____	Date: _____
X	_____	Date: _____
X	_____	Date: _____
X	_____	Date: _____
X	_____	Date: _____
X	_____	Date: _____
X	_____	Date: _____
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