

# Quality Assurance Project Plan (QAPP) for Water Quality Monitoring in the South Shore Estuary Reserve Western Bays: A Continuation and Expansion of the Town of Hempstead Bay Study

## Monitoring Organizations

Town of Hempstead Department of Conservation and Waterways  
&  
Hofstra University

## Coordinating Organizations

Town of Hempstead – Department of Conservation and Waterways

Funded By  
Long Island Regional Planning Council, Long Island Nitrogen Action Plan

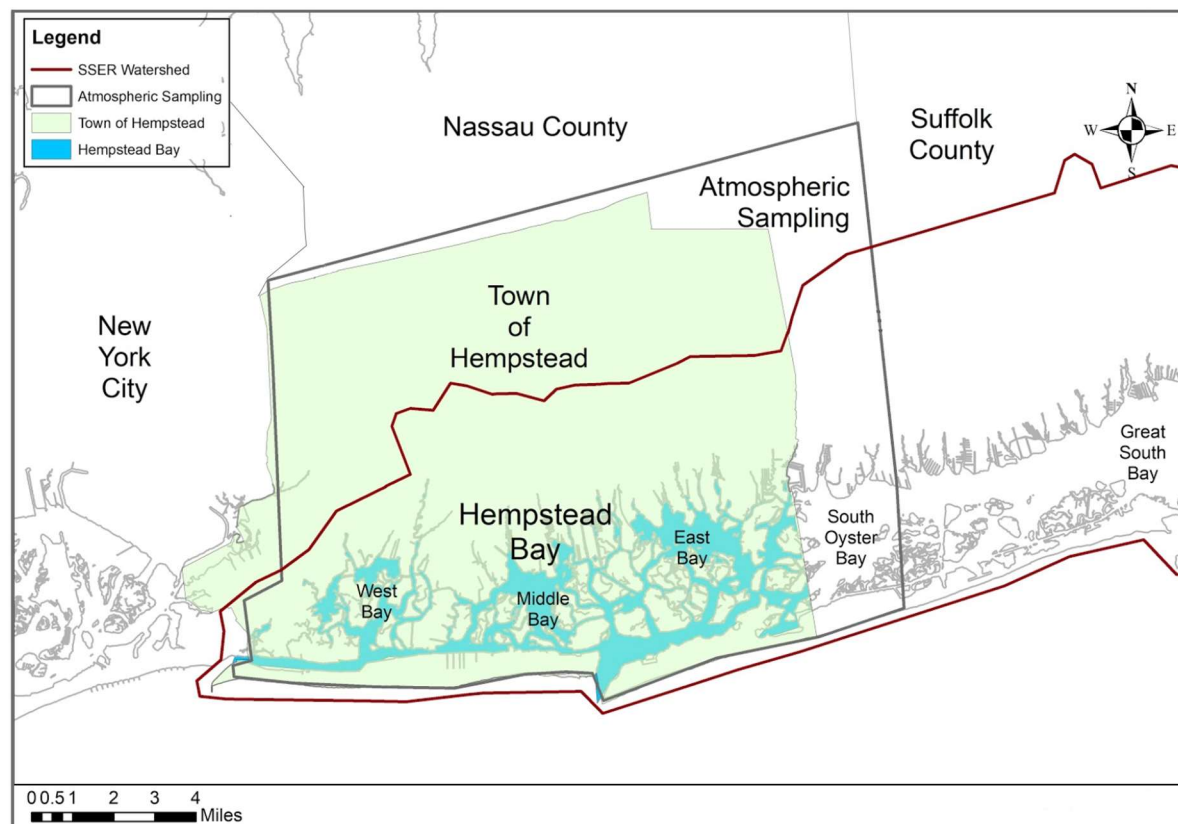
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None.

## Abstract

The goal of this QAPP is to document the partnership between TOH and Hofstra University to monitor nutrients and other water quality parameters in Hempstead Bay and contributing tributaries while also adding measurements of atmospheric nitrogen deposition. Many of the methods and sampling locations in this program build upon the fifty-year record of water quality monitoring conducted by TOH's Marine Laboratory (Udell 1968, Conservation & Waterways 2013, Fisher et al. 2018). By building upon this past work, we will extend the long-term record of water quality monitoring in the region. The monitoring program described in this QAPP includes: i) monthly one meter depth water sampling for nitrate, nitrite, ammonia, orthophosphate, dissolved oxygen (DO), salinity, temperature, chlorophyll a, and silica in Hempstead Bay and its tributaries; ii) monthly vertical profiles from the surface to maximum depth using YSI SONDEs to collect salinity, DO, temperature, fluorometric chlorophyll, turbidity, and pH at deep water locations throughout Hempstead Bay; iii) continuous water quality monitoring using in-situ instruments located in each of the three bays (West Bay, Middle Bay, and East Bay) within Hempstead Bay to provide a record of salinity, DO, temperature, fluorometric chlorophyll, turbidity, and tidal depth at 12 minute intervals, and iv) an atmospheric nitrogen deposition monitoring network within the southern half of Nassau County. The study area for activities under this QAPP includes Hempstead Bay, its major tributaries, and a network of atmospheric deposition monitoring stations located largely within the Nassau County portion of the South Shore Estuary Reserve (SSER) watershed (Map i).



**Map i.** The study area covered under this QAPP includes i) water quality monitoring in the tributaries and coastal waters of the South Shore Estuary Reserve (SSER) within Nassau County (red outline) and ii) land areas inside and just outside this boundary (dark gray line) to help us characterize sources of atmospheric nitrogen deposition. Please see Figures 2 and 3 for detailed maps that include the location of all monitoring stations.

## Project Management

### A.1 Approval Page

Prepared by: James P. Browne Date Dec 16, 2019  
James P. Browne, Ph. D., Conservation Biologist III  
Town of Hempstead, Department of Conservation and Waterways

Prepared by: Steve Raciti Date December 16, 2019  
Steve M. Raciti, Ph. D., Assistant Professor  
Hofstra University, Biology Department

Approved by: Rose Ann Garry Date 12/19/2019  
Rose Ann Garry, Quality Assurance Officer  
New York State Department of Environmental Conservation

Approved by: Kyle Rabin Date December 16, 2019  
Kyle Rabin, Representing  
Long Island Regional Planning Council &  
Long Island Nitrogen Action Plan

## Hempstead Bay Water Quality Monitoring QAPP Update Log

Prepared/Revised By:	Date:	Revision No.	Summary of changes and location in the document:

*‘No substantive changes’ may be listed to reflect updating of references, correcting typographical errors, and clarifying certain language to make the document more useful and effective.*

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### A.3. Distribution List

Name	Organization	Email	Address	Telephone
Rose Ann Garry	NYS DEC	roseann.garry@dec.ny.gov	NYS DEC Division of Water 625 Broadway Albany, NY	(518) 402-8233
Richard V. Guardino, Jr.	LIRPC	Rguardino@lirpc.org	1864 Muttontown Road, Syosset, NY 11791	(516) 671-7613
Kyle Rabin	LIRPC, LINAP	Krabin@lirpc.org	1864 Muttontown Road, Syosset, NY 11791	(516) 571-7613
James P. Browne, Ph. D	TOH C&W	jamebro@tohmail.org	PO Box 180, Point Lookout, NY 11569	(516) 897-4113
Lawrence Levy, Executive Dean	National Center for Suburban Studies, Hofstra University	Lawrence.Levy@hofstra.edu	101 Oak Street Center, Hofstra University, Hempstead, NY 11549	(516) 463-9770
Steve M. Raciti, Ph. D	Hofstra University, Biology Department	Steve.M.Raciti@hofstra.edu	227 Gittleson Hall, Hofstra University, Hempstead, NY 11549	(516) 463-6001
Nicolette Lovari	Pace Analytical Services, NYS ELAP Laboratory ID: 10478	Nicolette.Lovari@pacelabs.com	575 Broad Hollow Road, Melville, NY 11747	(516) 370-6044

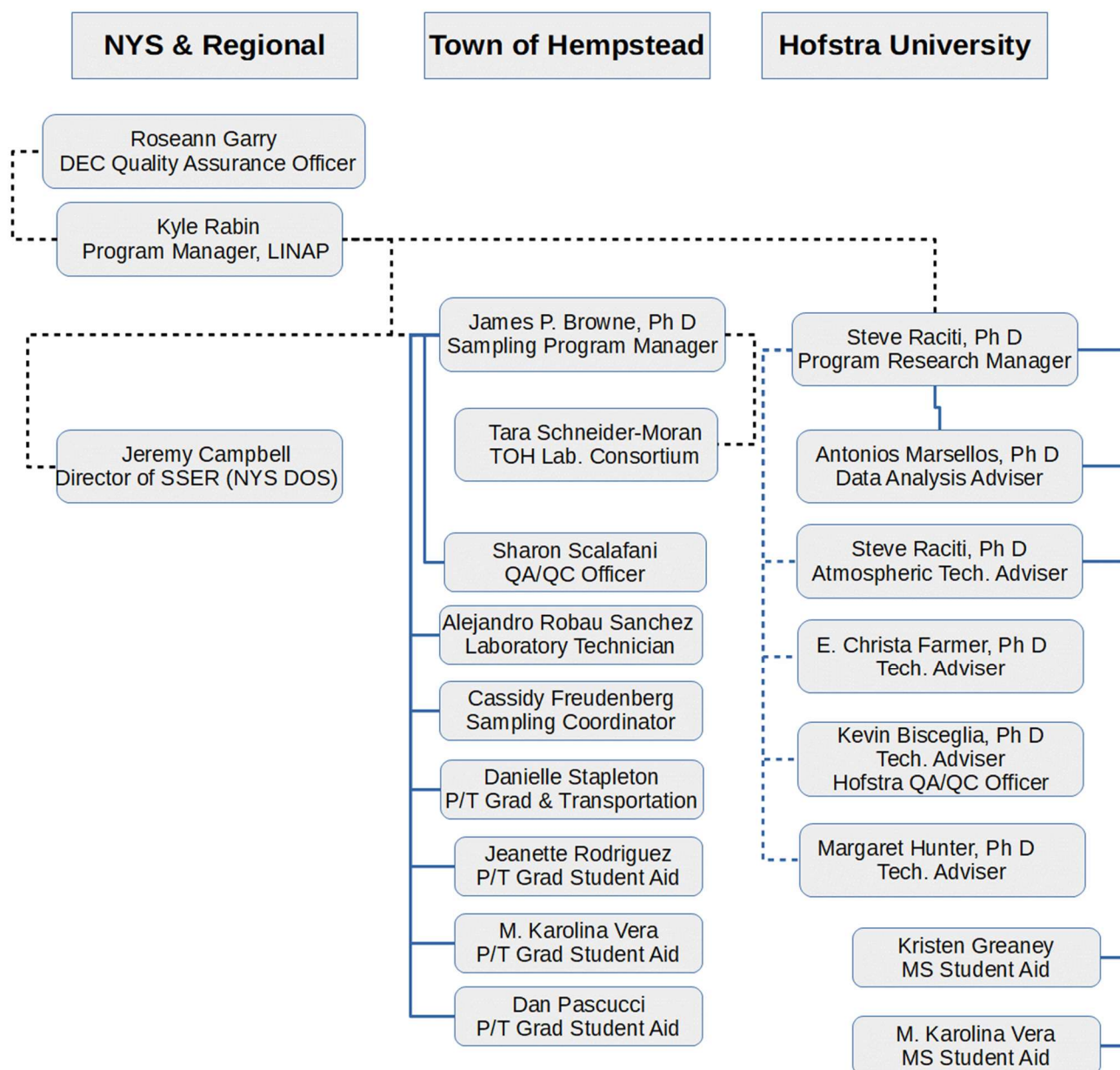
#### **A.4. Project / Task Organizations**

Project Organization (Table 1 and Fig. 1). The water quality monitoring program is planned, organized, and implemented by the Department of Conservation and Waterways, Town of Hempstead, in cooperation with Hofstra University with funding and oversight by Long Island Regional Planning Council. The Town's Conservation Biologist III, who works with water quality issues (Dr. James P. Browne, Ph. D.) and staff will be responsible for overall program supervision and QA review; conducting appropriate reviews of laboratory data; laboratory QC; ensuring that QA and reporting requirements are met; review and verification of data, including quality assurance data, for completeness and to document any obvious or suspected problems; accuracy and completeness of the Program database; and coordination with the appropriate Laboratory QA Officer to rectify any obvious or suspected problems. This will include responsibility for oversight of all field operations and data management of the Monitoring Program, including: scheduling and logistics; hiring and training seasonal assistants; overseeing and directing activities of field/office program staff; ensuring that field staff have reviewed Program QAPP and SOPs, received appropriate training in field and data entry/processing methods, and have shown competence in the performance of assigned duties; field data and sample chain-of-custody documentation; database development and maintenance; documentation, records, and reporting; and assisting with field operations logistics including scheduling and conducting field surveys, hiring and training of seasonal field staff, and data entry and processing.

The Town of Hempstead Water Quality Lab, or other ELAP Certified laboratory, will provide nutrient analyses to the appropriate Water Quality Laboratory's (WQL) Director and/or Quality Assurance Officer and ensure quality for the laboratory procedures. The Laboratory's Nutrient Lab Chemist or Technician will be responsible for nutrient lab sample handling, custody procedures, and sample analyses, as well as the provision of required supplies to the field crew. Field parameters and parameters not certified by NYS ELAP or otherwise covered under 40C.F.R. Part 135 will be collected by TOH C&W or Hofstra personnel.



**Figure 1. Organizational Chart**





**Table 1: Project organization**

Key project personnel and their corresponding responsibilities

<b>Name(s)</b>	<b>Organization</b>	<b>Project Title - Responsibilities</b>
Kyle Rabin	Long Island Regional Planning Council	Funding Agency Project Contact – Oversees grant administration and reporting through LIRPC and general project oversight
Rose Ann Garry	NYS DEC	NYS DEC Quality Assurance Officer – reviews, comments, approves QAPP
Jeremy Campbell	NYS DOS	Director of SSER (NYS DOS) – Oversees grant administration and reporting through NYS DOS
James P. Browne, Ph. D.	TOH C&W	Monitoring Program Coordinator
Tara Schneider-Moran, Ph. D.	TOH C&W	Town of Hempstead Laboratory Consortium Coordinator – Coordinating contact with consortium members that are conducting research in Hempstead Bay
Sharon Scalafani	TOH C&W	QA/QC Officer
Cassidy T. Freudenberg	TOH C&W	Sampling Coordinator
Alejandro Rabau Sanchez	TOH C&W	Laboratory Technician
Danielle Stapleton	TOH C&W	P/T (part time) Grad Student & Transportation (incl. boats)
Jeanette Rodriguez	TOH C&W	P/T Grad Student Aid
Dan Pascucci	TOH C&W	P/T Grad Student Aid
Steve M. Raciti, Ph. D.	Hofstra University	Monitoring Program Research Coordinator, Atmospheric Monitoring Technical Adviser
E. Christa Farmer, Ph. D.	Hofstra University	Technical Adviser
Kevin Bisceglia, Ph. D.	Hofstra University	Technical Adviser, Hofstra QA/QC Officer
Margaret Hunter, Ph. D.	Hofstra University	Technical Adviser for water contaminants
Kristen Greaney, Hofstra	Hofstra University	Hofstra MS Student & Student Aid
M. Karolina Vera	Hofstra University & TOH C&W	Hofstra MS Student, HU Student Aid & P/T C&W

## **A.5. Problem Definition**

### **Monitoring Criteria and Objectives:**

The overarching goal of this proposal is to provide a framework for monitoring, analysis, and reporting of water quality parameters within the surface waters of Nassau County's South Shore Estuary Reserve (i.e. Hempstead Bay and its major tributaries). To achieve this goal, Hofstra University and the Town of Hempstead Department of Conservation and Waterways (TOH C&W) will continue, and expand upon, the water quality monitoring that the TOH C&W has conducted in the south shore of Long Island in Nassau County, New York over the past 50 years (Udell 1968, Conservation & Waterways 2013, Fisher et al. 2018).

The primary focus of this work is to monitor and document basic water column characteristics (temperature, salinity, density, chlorophyll), nutrient concentrations, and rates of atmospheric nitrogen deposition, to detect and track changes over time and be able to estimate the rate of any such changes. Many of the parameters and monitoring locations within the current program are a direct continuation of past monitoring activities in the area (Udell 1968, Conservation & Waterways 2013). Therefore, this program, when combined with data from past efforts, will continue to serve as a long-term, consistent data source to support conservation goals in the Long Island South Shore Estuary Reserve (SSERC 2001, Fisher et al. 2018). Because the Program's focus is measurements, the goals for data quality outlined here focus on individual measurements, although some comprehensive analysis will also be conducted.

Most water sampling procedures are based on previous data collected by TOH C&W within this same area (Conservation & Waterways 2013). Measurements of atmospheric nitrogen deposition are based on past work by Dr. Raciti and colleagues (Rao et al. 2014). Consistent field and laboratory procedures, well documented with appropriate SOPs, help ensure consistent and reproducible data.

### **The goals of this project are:**

- To monitor water quality parameters and atmospheric nitrogen deposition (a contributor to water quality) year round
- To maintain a long-term database of the information collected
- To review the data periodically, in combination with available historical data, for trends
- To provide state and federal managers and policy-makers with information on existing conditions and trends that can be used in the development, implementation and assessment of strategies to control and improve water quality in the South Shore Estuary Reserve and meet the goals and actions described in the SSER CMP (SSERC 2001)
- To make the data available for related efforts such as water quality assessments, research, Total Maximum Daily Load (TMDL) development and evaluation, and water quality model development and calibration
- To make data available to other interested individuals/groups

This work involves sampling at numerous fixed stations on a regular basis (see locations in Figure 2, Figure 3, and Appendix B). **Hempstead Bay** sampling stations, **Tributary** sampling stations, and **Vertical Profile** sampling stations are sampled once per month. Three **Continuous Monitoring** stations, one each within the West Bay, Middle Bay, and East Bay sections of Hempstead Bay, measure a subset of water quality parameters *in situ* at 12-minute intervals. **Atmospheric Nitrogen Deposition** stations use passive samplers to continuously capture nitrate and ammonia from atmospheric deposition. The resultant samples are collected and measured every 1.5 months to provide seasonal trend information. Generally speaking, Hempstead Bay water chemistry and bacteriology are sampled during the first week of Ebb tides for the month with Vertical Profiles and Tributary stations sampled two weeks later. Weather, vessel/crew availability, and competing project constraints are expected to occasionally affect this schedule, resulting in samples taken earlier or later, or occasional missed samples.

### **Parameters:**

The monitoring program described in this QAPP includes: i) Tributary and Hempstead Bay sampling on a monthly basis at one meter water depth for nitrate, nitrite, ammonia, orthophosphate, dissolved oxygen (DO), salinity, temperature, chlorophyll a, and silica in Hempstead Bay and its tributaries; ii) monthly Vertical Profile sampling from the surface to maximum depth using YSI SONDES to collect salinity, DO, temperature, fluorometric chlorophyll, turbidity, and pH at deep water locations throughout Hempstead Bay; iii) Continuous Monitoring of water quality using in-situ instruments located in each of the three bays (West Bay, Middle Bay, and East Bay) within Hempstead Bay to provide a record of salinity, DO, temperature, fluorometric chlorophyll, turbidity, and tidal depth at 12 minute intervals, and iv) an Atmospheric Nitrogen Deposition monitoring network with 12 locations within the southern half of Nassau County which uses passive samplers to measure deposition of nitrate and ammonia. The study area for activities under this QAPP includes Hempstead Bay, its major tributaries, and a network of atmospheric deposition monitoring stations located largely within the Nassau County portion of the South Shore Estuary Reserve (SSER) watershed (Map i, Figure 2, and Figure 3).

### **Data Availability:**

All field data will be processed within one month of recovery, and then become available in the Program's databases. Analytical data from the analysis laboratory will be available in the Program's database as soon as practical, following receipt and review. Laboratory data and QC reports are expected to be available for inspection within 60 days of sample delivery.

### **Procedures for Assessing Accuracy and Precision:**

This QAPP is designed to ensure that accurate and precise data are being generated. Quality control (QC) measures include those actions which are taken in the laboratory to verify that the measurement system is in control (e.g. instrument calibration; the analysis of reference standards; the analysis of matrix spikes, replicates, and blanks). The QA program is designed to manage sample handling, documentation and custody; proper data generation; and quality

control actions. The QA program primarily tracks and monitors the fate of a sample from collection to data submission allowing the Project Manager and technical staff to assure proper sample analysis through appropriate methods, and that the necessary QC measures have been taken to ensure that representative data of definable quality have been produced. Analytical laboratory procedures, including the key elements of laboratory quality control are documented in laboratory-specific documentation (Appendices E & F). A number of routine quality control (QC) checks are analyzed with each batch of samples, including continuing calibration verification, calibration blanks, laboratory duplicates, and spike sample analyses. The goal for each sample batch is to run each QC check on 10% of samples. Field blanks (prepared randomly once each sampling day to evaluate contamination potential) and field duplicates (replicates taken in rapid succession to estimate field precision) are also provided to the laboratory, at a rate of at least one per ten samples (10%).

Determination of accuracy will be accomplished by evaluating a continuing series of spiked samples. Percent recovery in the range of 85 to 115% is considered to be acceptable providing, all other QC conditions are within acceptable limits. Accuracy of analysis will also be assessed by analyzing standard reference materials obtained commercially. The Continuing Calibration Verification (CCV), by analysis of standard reference materials (including, when available, EPA Quality Control Solutions) must fall within the control limits of 85-115% of the true value for instrument performance to be deemed acceptable.

Determination of precision will be accomplished by evaluating a continuing series of replicated samples. The Relative Percent Difference (RPD) is used to evaluate the long-term precision of the method for each parameter. A control limit of +/- 15% RPD shall be used to define acceptable precision.

Accuracy and precision goals for measured parameters are provided in Tables 3 and 4, along with quality assurance sample types. Accuracy and precision goals are based on instrument manufacturer or analytical laboratory specifications, or historical data or experience. Most variables have one or more QA/QC samples associated with them.

## **Institutions involved in this monitoring work**

### **Town of Hempstead (TOH) Department of Conservation and Waterways (C&W)**

The Town of Hempstead (TOH) Department of Conservation and Waterways (C&W) administers the wetlands management plan of the Town of Hempstead (§53 of Town Code). The quantitative analysis of the chemical and biological characteristics of the waters was specifically included in the Town Code and was the basis of establishing the Conservation Division and the Town Water Quality Laboratory (§53-3C1 of Town Code). The Town of Hempstead Department of Conservation and Waterways initiated a pilot water sampling program in 1968 (Udell 1968), and then initiated regular Bay Study sampling in the early 1970s, which consisted of surface water sampling within Hempstead Bay. A report on this program was published using support from the New York State Department of State, Environmental Protection Fund (NYS DOS EPF) in 2013 (TOH C&W 2013). New technologies were incorporated into sampling protocols during

the 1990s and into the early 2000s, including vertical profiles of water quality parameters at deeper locations and tributary sampling. Long term data sets are known to be extremely important for ecological and marine management work (Lindenmayer et al 2012, Addison et al. 2015, Hughes et al. 2017), therefore we will continue to use a subset of the existing water quality stations. This is similar to what has been done in the central waters of Long Island Sound and Chesapeake Bay (Connecticut DEEP 2017, Donat 2018). Data has been traditionally been available upon request to the Department of Conservation and Waterways, Town of Hempstead.

The Nassau County treatment plant discharges effluent into the bay, a consideration that was noted in the 1968 report and a focus of this continuing study. Added to this is the need and intent to understand the effects from non-point sources. These water quality efforts are in conjunction with the Department's other goals, including the successful management of local wildlife, fish, shellfish, marshlands, and other natural resources within the Town of Hempstead. Proposed changes to this system require the collection of data to track the resulting changes to the environment. The data provided by this program is considered essential to the continued evaluation and monitoring of this section of the South Shore Estuary Reserve and implements Outcomes 6-1 & 6-3 of the SSER Comprehensive Management Plan (SSERC 2001, Fisher et al. 2018). This management plan (SSER CMP) is currently the regional management plan of record in which the Town of Hempstead is a participant.

### **Hofstra University**

Hofstra University, founded in 1935, has been involved with the Town of Hempstead Department of Conservation and Waterways since the Department's inception and assisted with early water quality studies. This association has continued, with Hofstra alumnae on the Department's staff and continued scientific collaboration with Hofstra researchers.

Members of the Biology department, in cooperation with Hofstra University's National Center for Suburban Studies and other Hofstra departments, will undertake data analysis, assist the collection of water quality data, and initiate a study of atmospheric deposition. Previous work by Dr. Raciti and others indicates that atmospheric nitrogen deposition is likely to be underestimated as a source of direct and non-point source nitrogen to our waters because existing estimates are derived from national monitoring networks whose sites are purposely located to avoid the urban and suburban deposition sources that are likely to be important in this region (Rao et al. 2014).

## A.6. Project / Task Description

### Types of Monitoring Stations:

**Water Quality Stations** are locations at which water quality parameters are measured either directly (i.e. *in-situ*) or via the subsequent analysis of water samples collected at those locations. Among these Water Quality Stations, the **Hempstead Bay, Tributary, and Vertical Profile** monitoring stations are sampled on ebb tides for all 12 months of the year. Hempstead Bay sample stations (1 m depth) are collected once per month. Vertical Profile and Tributary stations are collected two weeks later to produce instrument readings twice per month. The **Continuous Monitoring** stations in this program consist of permanently located instruments that measure a range of water quality parameters in situ at 12-minute intervals. **Atmospheric Nitrogen Deposition** monitoring stations use passive samplers to continuously capture nitrate and ammonia from atmospheric deposition. The resultant samples are collected and measured every 1.5 months to provide seasonal trend information. The number and location of all Water Quality and Atmospheric Nitrogen Deposition stations are provided in Appendix B. The parameters measured at each station type are listed below.

#### For each Hempstead Bay monitoring station water quality run:

- Date, Personnel, High Tide at Jones Inlet prior to sampling, General weather conditions
- For each station:
  - Time
  - 1-meter water depth parameters using YSI SONDE:
    - temperature
    - salinity (conductivity)
    - dissolved oxygen (mg/L)
    - pH
- 1-meter water depth parameters for laboratory analysis (2-liter samples):
  - Nitrate
  - Nitrite
  - Ammonia
  - Kjeldahl N [Dissolved]
  - OrthoPhosphate
  - Chlorophyll a (specific colorimetric method)
  - Silicates
- Bacteria Water Sample (½ liter) at surface and bottom, plus salinity and Temperature (C) using YSI SONDE.

**For each Tributary water quality run:**

- Date, Personnel, High Tide at Jones Inlet prior to sampling, General weather conditions
- For each station:
  - Time
  - Full Downcast collecting parameters using YSI SONDE
  - Temperature
  - Salinity (conductivity)
  - Dissolved oxygen (mg/L)
  - Chlorophyll, “total” (fluorometer estimates)
  - Turbidity
  - Depth
  - pH
  - 1-meter depth water sample for laboratory analysis (½ liter samples):
    - Nitrate
    - Nitrite
    - Ammonia
    - Kjeldahl N [Dissolved]
    - orthoPhosphate
    - Chlorophyll a (specific colorimetric method)
    - Silicates
  - Bacteria Water Sample (½ liter) at surface and bottom, plus salinity and Temperature (C) using YSI SONDE.

**For each Vertical Profile water quality run:**

- Date, Personnel, High Tide at Jones Inlet prior to sampling, General weather conditions
- For each station
  - Time
  - Full Downcast collecting parameters using YSI SONDE
  - temperature
  - salinity (conductivity)
  - dissolved oxygen (mg/L)
  - Chlorophyll (fluorometer estimates)
  - Turbidity
  - Depth
  - pH



**For each Atmospheric Deposition Station run:**

- Date, Time, Personnel, General weather conditions, Damage to Collectors
- For each collector:
  - Nitrate (single, combined measurement)
  - Ammonia

**For each Continuous Monitoring Station:**

- Continuous *in-situ* measurements of the following parameters at 12-minute intervals:
  - salinity (conductivity)
  - Dissolved oxygen (mg/L)
  - temperature
  - Chlorophyll (fluorometer estimates)
  - turbidity
  - tidal depth

**DEC Shellfish Sanitary Stations (see map in Figure 2)**

These are stations that often overlap in location with the Hempstead Bay monitoring stations. These stations are included in the maps and tables of this QAPP (see Figure 2) for these reasons: i) as a helpful reference to additional water quality data that are being collected by TOH C&W under separate funding, and ii) because for overlapping sites, we will be using a common water sample for bacteriological data for both the program represented in this QAPP and for shellfish sanitary sampling. In other words, rather than duplicate effort (and cost) the same water sample, collected from these overlapping sites, will be analyzed and used to meet TOH C&W's obligations under this QAPP and for monitoring NYS DEC shellfishing areas.

See the section labelled "For each Tributary water quality run" (above) for the list of parameters that will be measured at the stations that overlap both this project and TOH C&W's Shellfish Sanitary Stations.

**Roles of Project Participants:**

The Town of Hempstead, Department of Conservation and Waterways will provide boat transportation and collect Bay, Vertical Profile, Tributary samples, the Laboratory analysis thereof, data entry, and data analysis. Hofstra University will maintain and collect samples from Atmospheric Deposition monitoring equipment, extract samples, deliver extracted samples to ToH C&W, provide hardware as agreed, and perform data analysis.

**How the Sampling Plan Supports Regional Objectives:**

Data Collected under this QAPP will be collected in a manner to allow the data to be used as part of the SSER CMP commitments by the Town of Hempstead (SSERC 2001, Fisher et al. 2018). This includes the continued sharing of these data with universities and researchers.

**Overview of data handling process:**

Field data will be collected on standardized field sheets. Examples are provided under the various sub-project categories in the Appendix D. Results from laboratory analysis will be handled in accordance with the procedures outlined in section B.10 of this QAPP.

### **Sample Custody Procedures:**

#### *Sample Collection*

The location of field monitoring activities and associated sample collections is determined using a Global Positioning System (GPS) device to achieve a more accurate positioning than by reference to land-based objects, except in confined channels or off bridges. Upon reaching the sampling site, the exact sampling location, time and other observations are recorded onto the field data sheet. Samples are then collected, subsampled, processed (to the extent possible depending on boat size, vehicle, and weather), and preserved in accordance with the field operations standard operating procedures (Appendix C). Once sample processing and preservation have been completed, the samples are immediately placed into the freezer (if available) or packed in ice, as appropriate. During the remainder of the sampling cruise, samples are considered to be in the custody of the Chief Scientist and field technicians. Upon completion of the cruise, all samples are transported to the analytical laboratory packed in ice or frozen samples are placed frozen in the cooler.

#### *Sample delivery and Laboratory procedures*

As soon as possible after arrival at the laboratory, samples are placed in either refrigerators, freezers or ovens, whichever is specified by the applicable SOPs (see Appendix sections) including submission of the appropriate field chain of custody (CoC) forms. The refrigerators, freezers and ovens are pre-numbered for identification. Appropriate entries are made onto the laboratory chain-of-custody logbook (Appendix D-6). Anytime a sample is handled for any reason, the chain-of-custody logbook page (Appendix D-6,) entries are performed, including the reason for sample handling. Samples are replaced into a refrigerator or freezer as soon as possible with chain-of-custody entries made. After the completion of all required analyses and data validation, sample disposal will occur according to QAPP specifications. Only the Laboratory may authorize disposal of samples. When this occurs, chain-of-custody logbook entry is made noting disposal, the date and time of disposal, and the initials of the individual who performed this function.

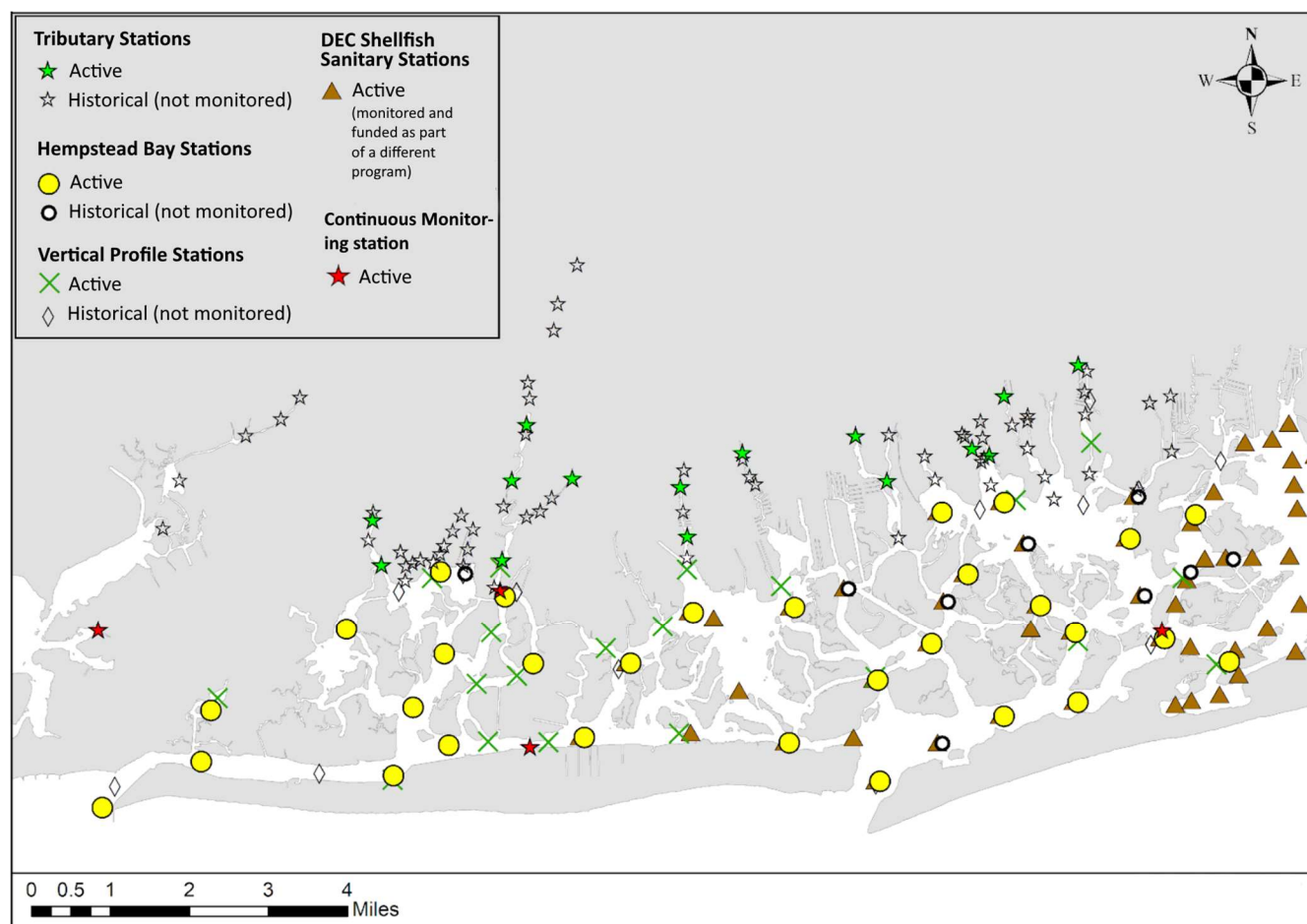
**A.6.a. Field sampling types covered by this general QAPP**

- Sampling location listed as WGS84 coordinates
- Temperature
- Salinity (conductivity)
- Dissolved Oxygen (DO)
- Chlorophyll a concentrations (filtered water samples colorimetric lab analysis)
- Chlorophyll a concentrations (in situ fluorescence)
- Turbidity
- Nitrogen forms, including nitrate (NO<sub>3</sub>), nitrite (NO<sub>2</sub>), ammonia (NH<sub>3</sub>), Total Kjeldahl Nitrogen (TKN) and measurement levels
- Phosphorus forms (orthoP) and measurement levels
- Atmospheric Nitrogen
- Total Coliforms (Bacteria) using NYS DEC Shellfisheries Laboratory procedure under USFDA National Shellfish Sanitation Program (NSSP)

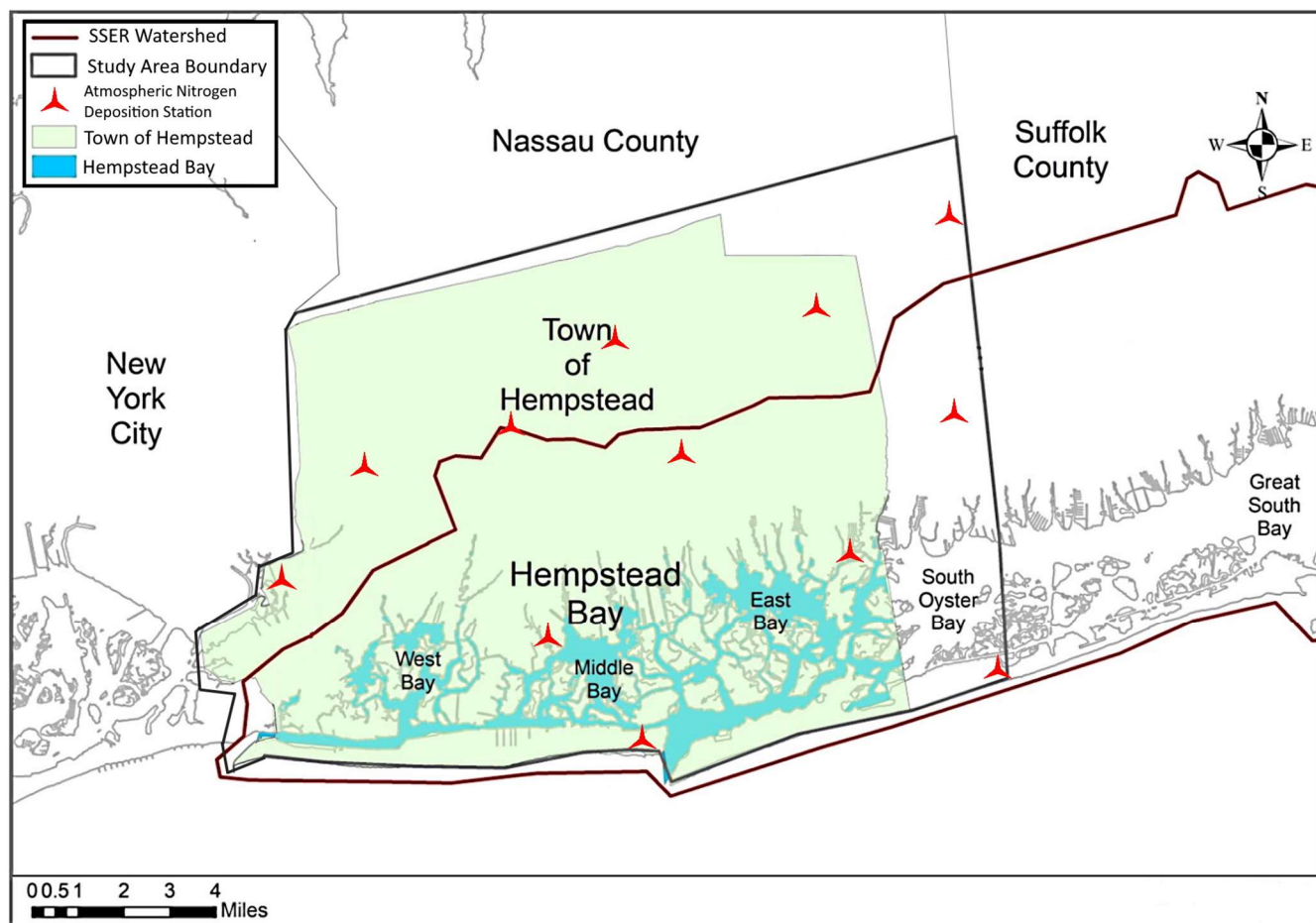
**A.6.b. Laboratory analysis parameters covered by this general QAPP**

- Nitrate
- Nitrite
- Ammonia
- Kjeldahl N (Dissolved)
- orthoPhosphate
- Chlorophyll a concentrations (filtered water samples colorimetric lab analysis)
- Silicates

### A.6.c. Maps of Study Area and Sampling Stations



**Figure 2.** Map of water sampling stations. Hempstead Bay sampling stations, Tributary sampling stations, and Vertical Profile sampling stations are sampled once per month for a wide range of water quality parameters. Three Continuous Monitoring stations, one each within the West Bay, Middle Bay, and East Bay sections of Hempstead Bay, measure a subset of water quality parameters *in situ* at 12-minute intervals. TOH C&W also operates a continuous monitoring station in Jamaica Bay (western side of the map). DEC Shellfish Sanitary Stations often overlap in location with the Hempstead Bay monitoring stations and are included in the maps and tables of this QAPP as i) a helpful reference to additional water quality data that are being collected by TOH C&W under separate funding, and ii) because for overlapping sites, we will be using a common water sample collection to measure bacteriological data for both the program represented in this QAPP and for shellfish sanitary sampling. See *A.6 Types of Monitoring Stations* for a complete list of parameters measured at each station type.



**Figure 3.** Map of Atmospheric Nitrogen Deposition Monitoring Stations. These monitoring stations use passive samplers to continuously capture nitrate and ammonia from atmospheric deposition. The resultant samples are collected and measured every 1.5 months to provide seasonal trend information.

### A.6.d. Annual Task Calendar

The annual task calendar describes when certain activities will occur.

### Table 2: Annual Task Calendar

These tasks are repeated annually.

[illegible]

## A.7. Data Quality Objectives

Summary of criteria are provided in Table 3.

**Table 3:** Measurement Performance Criteria

Data Quality Indicators	Measurement Performance Criteria	QC Activity
Precision – overall	$RPD \leq$ value indicated in Table 5.	field duplicates
Precision – Analytical	$RPD \leq$ value indicated in Table 5.	analytical duplicates
Accuracy / Bias	$85\% \leq \text{recovery} \leq 115\%$	certified reference material lab fortified matrix (spikes)
Comparability	standard methods followed	Appropriate methods are chosen
Completeness	data from surface and bottom at each station meet data quality objectives	data completeness check
Sensitivity	$\text{value} \geq \text{IDL}^*$	sample value check

\* IDL = instrument detection limit. This is a reporting limit based on the lowest standard accurately analyzed in the analysis.



**Table 4: Data Quality Objectives.**

NOTE: The samples listed as “yes” in the ELAP column will be analyzed at **Pace Analytical Services, NYS ELAP Laboratory ID: 10478**

Parameter	ELAP	Units	Accuracy	Precision (RPD)	Approx. Range	Sensitivity (Resolution, MDL, or IDL)
Depth (Ross960)	No	Meters (m)	0.20m	0.20m	.5-300m	0.10m
Depth (YSI 6600V2)	No	Meters (m)	+/- 0.12		0-60	0.001m
Depth (WetLabs WQM)	No	Meters (m)	+/- 0.1%		0-100	0.01%
GPS Coordinates	No	Dec. Deg	0.0002			0.0002
Temperature (YSI 6600V2)	No	°C	+/- 0.15		-5 - 50	0.01
Temperature (WetLabs WQM)	No	°C	0.002		-5 - 35	0.001
Conductivity (YSI 6600V2)	No	µS/cm	+/- 0.001	0.5%	0-100	0.1
Salinity (YSI 6600V2)	No	‰	+/- 0.1	1.0%	1 - 70	0.01
Conductivity (WetLabs WQM)	No	µS/cm	+/- 30		0-90,000	5.0
Salinity (WetLabs WQM)	No	‰	+/- 0.022		0-64	0.013
DO (ROX YSI 6600V2)	No	mg/L	0.1		0-20	1.01
DO (WetLabs WQM)	No	mg/L	0.1		120% Saturated	0.01
Chlorophyll a (Laboratory)	No	mg/L	1 mg/L	+/-15%	0-200 mg/L	0.08
Chlorophyll, Total (fluorometric YSI 6600V2)	No	mg/L	NA		1-100	0.1
Chlorophyll, Total (fluorometric WetLabs WQM)	No	mg/L	0.2% FS		0-60	0.04% FS
Turbidity (YSI 6600V2)	No	NTU	+/- 0.3		1-1000	0.1

Turbidity (WetLabs WQM)	No	NTU	+/- 0.1 FS		0-25 FS	0.04% FS
pH (YSI 6600V2)	No	pH	+/- 0.2		0-14	0.01
TDKN (filtered)	Yes	mg/L	+/- 10%	+/- 20%		0.10
Ammonia – NH3 (sum of NH3, NH4+)	Yes	mg/L	+/- 10%	+/- 20%		0.10
Nitrate - NO3	Yes	mg/L	+/- 10%	+/- 20%		0.05
Nitrite - NO2	Yes	mg/L	+/- 10%	+/- 20%		0.05
OrthoP (~DIP)	Yes	mg/L	+/- 10%	+/- 20%		0.05
Silica	Yes	mg/L	+/- 10%	+/- 20%		430
Atmospheric N (see rows for Nitrate and Ammonia, above)	Yes	see rows for Nitrate and Ammonia, above	see rows for Nitrate and Ammonia, above	see rows for Nitrate and Ammonia, above	see rows for Nitrate and Ammonia, above	see rows for Nitrate and Ammonia, above
Total Coliforms <sup>1</sup>	No	MPN cm <sup>3</sup>			3-1100	3 cells

<sup>1</sup> NYS DEC Shellfisheries Laboratory procedures under USFDA National Shellfish Sanitation Program.

## A.8. Special Training / Certification

This training will be based on the Field SOP. As the same personnel are not always available for every cruise. The Department personnel are cross-trained so that staff members will be proficient in the specific calibration and sample collection techniques required for this QAPP and associated SOPs.

**Table 5: Project specific Training**

Training: type & Description	Trainer(s)	Training Date(s)	Trainees	Location of Training Records
Boater safety and handling	TOH Bay Constables and Monitoring Coordinator	Approximately one year after hiring.	Experienced samplers that show interest and capability	TOH C&W, NYS Parks
Nutrient water sampling: Collection of samples, <b>filtering</b> , and preservation of samples.	Monitoring Coordinator	Typically, after hiring seasonals/ part timers in June.	Seasonal Staff, interns, volunteers	C&W
Atmospheric N sampling and extraction	Atmospheric Technical Advisor	Fall 2019	Graduate Students	Hofstra
Data logging: Cleaning of WQM loggers, data retrieval, and intercomparison of field readings between YSI SONDE and WetLabs WQM	Monitoring Coordinator	Typically, after hiring seasonals/ part timers in June.	Seasonal Staff, interns, volunteers	CW
Bacterial Sampling	Monitoring Coordinator	Typically, after hiring seasonals/ part timers in June.	Seasonal Staff, interns, volunteers	CW, DEC

## **A.9. Documents and Records**

**Calibration and Sample Event Datasheets and Field Datasheets** will be completed by Monitoring Personnel.

**Sample Labels** will be put on all containers prior to leaving for sampling. Extra containers and labels will be included to provide replacements in case of damage or loss.

**Chain of Custody (CoC)** Forms will accompany samples from collection sites to laboratories. The correct CoC forms from all laboratories expecting samples will be used and will be brought into the field, and each form will be filled out with the information matching events in the field.

**Training records and field audit information** will be kept in hard copy for a minimum of 10 years and recorded digitally for indefinite retention and archiving.

## **B. Data Generation and Acquisition**

### **B.1. Sampling Process Design (Experimental Design)**

Estuary water quality stations were selected to provide sufficient spatial coverage while also continuing historical records at sites with up to 50 years of monitoring history (see Udell 1968, Conservation & Waterways 2013, Fisher et al. 2018).

Tributary water quality stations were selected in tributary streams flowing into each embayment (West Bay, Middle Bay, and East Bay; Figure 2). The stations were selected as boat accessible locations following the salinity gradient from marine waters down to and below <1 ppt. Locations with long term monitoring history were prioritized among suitable sites.

Continuous sampling stations were selected from fixed structures in strategic locations that can support WetLabs WQM units such that there is one or more loggers per embayment (West Bay, Middle Bay, and East Bay) per considerations detailed in Wagner et al. (2006) and Schubert (2010). Three of the locations were pre-existing sites with a valuable long-term record of past monitoring.

**Sampling Safety.** Personal safety shall be a primary consideration, the field SOP (Appendix C) includes notes and a checklist outlining normal precautions when sampling.

**Design Considerations.** A summary of design considerations incorporated into this project are included in Table 6. Specifics in the design approaches to the number of stations, depth of sampling, frequency of sampling, and the timing of sampling are included in the Field SOP Appendix C.

Field instruments and equipment are exposed to salt spray and extreme conditions in the field. Recognizing the probability of failure in the field, TOH C&W has mandated redundancy in the field for all instruments and equipment critical to collecting field data and samples as much as feasible. Extra sampling bottles, batteries, and when possible a second SONDE or hand held DO/Temp/Salinity instrument (YSI Pro2030 or equivalent) will be included in field kit. Additional back-up equipment will be stationed within a short distance of docking facilities if all field instruments fail.

There are 30 Hempstead Bay Sampling stations, 15 Tributary stations, and 20 Vertical Profile stations that will be sampled monthly. There are 4 Continuous (12-minute interval) stations that will be visited monthly for maintenance, but will record data continuously. There are 12 Atmospheric stations, which will be continuously collect atmospheric nitrogen deposition via passive methods (ion exchange resin columns). The ion exchange resin columns will be collected every 1.5 months for analysis and replaced with fresh columns.

**Table 6. Sampling Approaches**

Assessment Type: Water Quality Stations.

Indicators	Number of Stations	Frequency, Duration, Special conditions	Field Survey QC
GPS	70	Start of project	
Station Depth	50	Hempstead Bay, Vertical Profile, and Continuous, Once at start of program	Ross 960 (Appendix C-9)
Sample Depth	40	Vertical Profile & Tributary, Monthly downcasts (@ 5 sec intervals),	Vertical Profile (App. C-2.2), Tributary (App. C-2.3),
Temperature	70	Hempstead Bay Monthly, Vertical Profile & Tributary, Monthly downcasts (@ 5 sec intervals), Continuous, (@ 12 min intervals)	Hempstead Bay (App. C-2.1), Vertical Profile (App. C-2.2), Tributary (App. C-2.3), Continuous (App. C-2.5)
Salinity (conductivity in FW)	70	Hempstead Bay Monthly, Vertical Profile & Tributary, Monthly downcasts (@ 5 sec intervals), Continuous, (@ 12 min intervals)	Hempstead Bay (App. C-2.1), Vertical Profile (App. C-2.2), Tributary (App. C-2.3), Continuous (App. C-2.5)
DO	70	Hempstead Bay Monthly, Vertical Profile & Tributary, Monthly downcasts (@ 5 sec intervals), Continuous, (@ 12 min intervals)	Hempstead Bay (App. C-2.1), Vertical Profile (App. C-2.2), Tributary (App. C-2.3), Continuous (App. C-2.5)
Turbidity	60	Vertical Profile & Tributary, Monthly downcasts (@ 5 sec intervals), Continuous, (@ 12 min intervals)	Vertical Profile (App. C-2.2), Tributary (App. C-2.3), Continuous (App. C-2.5)
Chlorophyll a (Lab)	46	Hempstead Bay & Tributary, Monthly	Hempstead Bay (App. C-2.1), Tributary (App. C-2.3),
Chlorophyll fluorometric (field)	60	Monthly, Vertical Profile & Tributary, Monthly downcasts (@ 5 sec intervals), Continuous, (@ 12 min intervals)	Vertical Profile (App. C-2.2), Tributary (App. C-2.3), Continuous (App. C-2.5)
Nutrients	46	Hempstead Bay & Tributary, Monthly	Hempstead Bay (App. C-2.1), Tributary (App. C-2.3), Continuous (App. C-2.5)
Atmospheric Nitrogen	12 stations (6 samplers per station)	Terrestrial Sites, every 1.5 months	Simkin et al 2003
Total Coliforms (using NYS DEC Shellfisheries Laboratory procedures under USFDA National Shellfish Sanitation Program)	28 initially, 39 later	Monthly (“random”) and after a subset after rain events according to DEC requests.	NYS DEC, Appendix C-3.2.3

Assessment Type: Atmospheric Nitrogen

Indicators	Number of Stations	Frequency, Duration, Special conditions	Field Survey QC
GPS	12 stations (6 samplers per station)	1.5 months	N/A
nitrate (NO <sub>3</sub> <sup>-</sup> ) and ammonia (sum of NH <sub>3</sub> , NH <sub>4</sub> <sup>+</sup> )	12 stations (6 samplers per station)	1.5 months	Simkin et al 2003, ELAP certified laboratory analysis

## B.2. Sampling Methods

Pre-coordination shall occur with the laboratory being used, both the TOH Lab and external lab(s) as appropriate for the sampling being conducted.

1. Pace Labs (**ELAP Laboratory ID: 10478**), contracts are in place for most parameters other than MPN Total Coliforms (DEC Shellfish protocol under USFDA National Shellfish Sanitation Program) and Chlorophyll a (not ELAP regulated and labs have not bid on contracts offered for Chlorophyll a).

2. Town of Hempstead, Conservation and Waterways, Water Quality Laboratory. Laboratory is being renovated and NYS ELAP certification reinstatement is being pursued. Chlorophyll a does not have an ELAP certification available or require one. Chlorophyll a also lacks a specification in 40 C.F.R. Part 136. We will use the same sources for methods listed in 40 C.F.R Part 136 and these samples will be analyzed at TOH C&W using EPA Method 446.0 or Standard Methods 10200H as listed in Table 9 and described in Appendix F-2. The Town of Hempstead's Department of Conservation and Waterways has performed Chlorophyll a analysis for over 50 years.

3. NYS DEC Shellfisheries Laboratory, Leonora Porter. Sanitary Shellfish samples are being collected for MPN Total Coliforms and these data will be used when stations overlap. These data have already been used by other divisions of the NYS DEC for TMDL development. The certification of this laboratory, and all Shellfish laboratories within the USA is, by law, regulated under Federal Department of Agriculture (FDA) due to the consumption of shellfish as a food. The strict guidelines for testing the bacterial presence in the waters, including total coliforms used here, is determined by the National Shellfish Sanitation Program (NSSP), and specified in the Guide for the Control of Molluscan Shellfish (FDA 2017) The Town of Hempstead has received additional funding from New York State with the specific goal of reestablishing this FDA certification for the bacteriology section of the TOH Marine Laboratory.

4. Hofstra, Raciti Lab. Field samples collected from the atmospheric deposition throughfall collectors will be transported back to Hofstra University. Chromatography columns, containing mixed-ion exchange resin beads, will be transported to the lab in marked containers.



**Table 7. Overview of Sample Collection Methods**

Assessment type: Water Quality Parameters

Parameter	Container and Preparation	Minimum Quality	Sample Preservation	Maximum Holding Time
GPS	NA		Digital	NA
Station Depth	NA		Digital	NA
Sample Depth	Digital		Digital	NA
Multiparameter SONDE: - Depth - Temperature - Salinity - DO - Turbidity - Chlorophyll (Fluorometric)	Digital		Digital	NA
Nutrient samples	2L Nalgene® Container		On ice 0-5 °C	Max 3 months (1 year frozen)
Chlorophyll a (extracted)	2L Nalgene® Container		On ice 0-5 °C	28 days
Bacterial Sample	SCL/SPEC 100ml (pre-sterilized)		On ice 0-5 °C	<<30 Hr before lab incubation, <6 hr preferred.

Assessment type: Atmospheric Nitrogen.

Parameter	Container and Preparation	Minimum Quality	Sample Preservation	Maximum Holding Time
GPS	NA		Digital	NA
Reactive N	Resin column	Amberlite IRN150 H/OH Ion Exchange resin, which is nuclear grade and pretreated to remove ionic and non-ionic contamination.	On ice 0-5 °C after extraction	Max 3 months after extraction (1 year if frozen).

**Table 8: Overview of Field Considerations**

Sample Type	Parameter(s)	Sampling Considerations
<i>In-situ</i> sampling	Depth at Bay Sampling stations	Ross 960, with R8 RTK GPS
<i>In-situ</i> sampling, GPS	Lat Long WGS84	Weather and tide conditions can make station keeping difficult.
<i>In-situ</i> sampling, multiparameter SONDE	Temperature, salinity, conductivity, DO, pH, Chl (fluorimetric)	Probe readings that are unstable and out of normal range may indicate damage. DO probe should remain wet, and keeping SONDE in a container of sea water between stations increases probe life and reduces stabilization time.
Grab samples (Water samples)	Inorganic, organic, and total nutrients. Chlorophyll a.	These should be from 1-meter depth, avoid introducing contaminants during collection, and keep in cooler with sufficient ice <5°C.
Grab samples (Surface Water samples)	Total coliforms <sup>1</sup>	Handling collection bottles using sterile technique to avoid contamination is critical. Must be kept on ice <5°C.
Atmospheric N collection	N	Deposition collectors must be protected from potential interference from humans and animals; careful site selection should help with this. Extractions will be performed with clean equipment and kept at < 5°C until analysis.

<sup>1</sup> NYS DEC Shellfisheries Laboratory procedures under USFDA National Shellfish Sanitation Program.

### B.3. Sample Handling and Custody

Sample handling and labeling:

1. Pace Labs (ELAP 10478) handling specifications and supplied containers:

Pace labs supplies their own containers that are chosen for each parameter. Each location has an Ammonia container with H2SO4 (for sample preservation), an orthoPhosphate container, and another container for the rest of the parameters. Pace supplies their own labels that are filled with the project, date, time, and the sampling station name. These samples are kept at a temperature <5° C and delivered to Pace in less than 48 hours from the time of collection. Pace Chain of Custody forms are used that include the name of the persons collecting the samples for a given day, the person delivering the samples, and the Pace employee receiving the samples. At this time, the NO3, NO2, NH4, TKN, Silicates, and orthophosphate results from these samples are the results of record for this QAPP.

2. Town of Hempstead Department of Conservation and Waterways, Water Quality Laboratory: Qualified TOH C&W personnel fill a 2-liter Nalgene HDPE bottle from 1-meter depth at each water quality monitoring station. Samples are kept at a temperature  $<5^{\circ}\text{C}$  until analysis. The water is thoroughly mixed and then one liter is filtered for Chlorophyll extraction and the remaining water is used for analysis at TOH C&W laboratory. A TOH C&W Chain of Custody form is filled out reflecting the person or persons collecting a given set of samples and the person recording the delivery. The Chlorophyll a results are the results of record for this QAPP while the other parameters may be measured for comparison (i.e. with Pace Analytical results) and training purposes as TOH C&W works toward reinstating their ELAP certification.

3. NYS DEC Shellfisheries Laboratory, standard procedures under the USFDA National Shellfish Sanitation Program (NSSP): Guide for the Control of Molluscan Shellfish: Qualified TOH C&W personnel collect water samples under the instructions from Lee Porter of the NYS DEC, who is in charge of all NSSP sample analysis. These samples are recorded on NYS DEC Chain of Custody forms and are kept at a temperature  $<5^{\circ}\text{C}$  until delivered to the USFDA certified laboratory.

4. Hofstra University, Raciti Lab atmospheric nitrogen deposition monitoring samples: All samples will be uniquely identified by the site name and the sampling date. All samples will be further identified by the collector number (1-6) at each site (there are six deposition collectors per site). Once the sampling columns are removed from the field and are extracted, the extracts are stored in containers supplied by Pace Labs (ELAP 10478), including ammonia sample bottles that include a small amount of  $\text{H}_2\text{SO}_4$  and separate containers for  $\text{NO}_3$ . Samples are then kept at a temperature  $<5^{\circ}\text{C}$  and delivered to Pace within 48 hours accompanied By Pace Chain of Custody forms that reflect the person doing the extractions, the person making the delivery, and the Pace employee receiving the delivery.

**The following steps shall be taken to avoid sample mislabeling.**

Labels will be prepared prior to departure on the previous business day.

1. Pace Labs.
2. Town of Hempstead, Conservation and Waterways, Water Quality Laboratory.
3. NYS DEC Shellfisheries Laboratory, Lee Porter.
4. Hofstra, Raciti Lab. Sample containers to be used to store and deliver samples to the nutrient analytical lab will be pre-labeled with Site Name, Sampling Date, and Collector # 1-3.

#### **B.4. Analytical Methods**

Analytical methods will be chosen to comply with the methods approved by the EPA, FDA, or listed in Standard Methods for the Examination of Water and Wastewater. See Appendix E and

Appendix F.

**Table 9:** Overview of Analytical Methods, both listed methods may be used and confirmed in respective project laboratory SOP in Appendix E or Appendix F.

Parameter	ELAP	Method #	Source of Method	Typical MDL	Alternative Applications, Special Provisions
Chlorophyll a	No	EPA 446.0 <sup>1</sup> , SM 10200 H	EPA, Standard Methods	1 mg/L	Done at TOH C&W
Total Chlorophyll (Fluorescence)	No	EPA 445.0	EPA	0.1 mg/L	(Field Samples; See YSI and WQM)
TKN	Yes	Hach Method 10242, SM 4500-Norg	EPA-CRF;136	1 mg/L	Hach Kjeldahl (EPA approved, Appendix D3.5)
TKN	Yes	EPA 351.2 <sup>1</sup>	EPA	0.1 mg/L	(@ Pace)
Ammonia (NH3)	Yes	SM 4500-NH3	Standard Methods	0.1 mg/L (7.14 µm)	Synthetic ocean water (SOW) as standard in sea water DI in FW (@ Pace)
Ammonia (NH3)	Yes	A026 (EPA 350.1 <sup>1</sup> , 350.2,350.3)	Astoria-Pacific (EPA)	0.0007 mg/L (0.05 µm)	Based on EPA 350.1; STORET NO Total 00610 Dissolved 00608 (@TOH)
Nitrate + Nitrite (dissolved)	Yes	EPA 353.2, 352.1, 353.4	EPA	0.050 mg/L (3.57 µm)	Synthetic ocean water (SOW) as standard in sea water, DI in FW (@Pace)
Nitrate + Nitrite (dissolved)	Yes	A117 <sup>2</sup> (based on SM 4500-NO3 Nitrates)	Astoria Pacific; Standard methods	0.0007 mg/L (0.05 µm)	Synthetic ocean water (SOW) as standard in sea water, DI in FW @ TOH C&W
Nitrite (Without Cd reduction)	Yes	A117 <sup>2</sup> ; EPA 353.2, 352.1, 353.4; SM 4500-NO3 Nitrates	Astoria Pacific, EPA, Standard methods	0.00028 mg/L (0.02 µm)	Synthetic ocean water (SOW) as standard in sea water, DI in FW, @TOH
Nitrite (dissolved)	Yes	EPA 353.2,	EPA	0.050 mg/L (3.57 µm)	@ Pace
Ortho Phosphate	Yes	SM 4500-P-E <sup>1</sup>	Standard Methods	0.050 mg/L (1.614 µm)	@ Pace
Ortho Phosphate	Yes	A204 <sup>2</sup> Based on EPA Method 365.1	Astoria Pacific, EPA	0.0005 mg/L (0.001 µm)	@ TOH C&W
Silicate (dissolved)	Yes	A221 <sup>2</sup>	Astoria Pacific	0.126 mg/L (0.0045 µm)	Filtration & analysis @ TOH C&W
Silicate (dissolved)	Yes	EPA 200.7 <sup>1</sup>	EPA	430 mg/L (15.1 µm)	Filtration & analysis @ Pace
Total Coliforms <sup>4</sup>	No	USFDA <sup>4</sup>	USDA	3 cells/ml	Most Probable Number

1. Methods used in Pace Contracts (**Laboratory ID:** 10478); 2. Methods used at TOH C&W Laboratory; 3. Hofstra, Raciti Laboratory; 4. NYS DEC Shellfisheries Laboratory under USFDA National Shellfish Sanitation Program

(NSSP)

## B.5. Quality Control

Lab Quality Control (QC) protocols and appropriate sample containers and holding times have been coordinated with Pace Labs, with Nicolette Lovari as the project manager.

**Table 10:** Quality Control Measures

Note that 5% of field samples equates to one station per field day sampled as replicate for water quality sampling.

Sample Type	Instrument / Parameter	Accuracy Checks	Precision Checks	% Field QC Samples (blanks & field duplicates)
GPS	GPS/WGS84 Lat/Long	Initiate with GIS base map	Readings at a Nassau Co. survey monument or Federal Monument	1/ year or field day?
Station Depth	Ross Bathymetry	Ball Check	Replicate readings/ Ball Check	5%
Multiparameter YSI SONDE	Depth, temperature, conductivity, salinity, DO, turbidity, Chlorophyll (fluorescence)	Pre-survey calibration and post-survey checks	Duplicate profiles at one station per field day and readings are only recorded when values are stable (3-5 min at 1 m, 2-3 minutes per meter downcast)	5%
Multiparameter WetLab WQM	Depth, temperature, conductivity, salinity, DO, turbidity, Chlorophyll (fluorescence)	Pre-survey calibration and post-survey checks	Duplicate profiles at least once per month with YSI SONDE at same depth	5%
Water samples - grab	TKN, TDKN, NH3, NO3, NO2, orthoP, Silica, Chlorophyll a,	Field: blanks Lab: Spiked Samples or lab QC standards	Field replicates, Lab Duplicates	5%
Bacterial samples - grab	MPN Total Coliforms <sup>1</sup>	Field: blanks Duplicates	Field replicates, Lab Duplicates	Field: blanks Duplicates
Atmospheric Resin Column	NO3 & NH3	Capped field blanks, lab resin column blanks	6 resin columns per site for analysis Lab duplicates	7%

<sup>1</sup> NYS DEC Shellfisheries Laboratory procedures under USFDA National Shellfish Sanitation Program

## B.6. Instrument / Equipment Testing

Maintenance of instruments and equipment shall occur as needed during the field season. Annual maintenance and inter-calibration...

**Table 11:** Instrument / Equipment Inspection and Testing Procedures,

Equipment Type	Inspection Frequency	Type Inspection	Maintenance, Corrective Action
GPS unit	Before use	Check batteries	Change/charge batteries, swap unit
Depth sounder, Ross 960	Annually or if suspected problem	Check against Ball standard	Calibration or factory repairs
Multiparameter SONDE	Before use	Check batteries	Calibrate, replace defective probes with spares, periodically calibrate DO against Winkler titration
Multiparameter WQM	Before and after use	Check batteries, clean, repaint	Calibrate before and after deployment, interpolate to correct for drift
Nutrient sample bottles	Before use	Clean, undamaged	Acid washed
Bacterial sample bottles	Before use	Clean, undamaged	Sealed sterile
Filtering apparatus (Chl a)	Every week	Clean, functioning	Spare filters

## B.7. Instrument / Equipment Calibration and Frequency

Calibration shall occur within a day prior to a sampling trip.

Records of calibration shall be kept in a logbook (hard copy or digital with backups).

A summary of calibration procedures for instruments and equipment is provided in Table 12.

Detailed calibration procedures are described in SOP's contained in Appendix C.

**Table 12.** Instrument / Equipment Calibration Procedures

Instrument	Inspection and Calibration Frequency	Standard of calibration and Instrument use	Corrective Action
Ross 960 (Depth)	Annually	Speed of sound from YSI SONDE downcast	Correct records of bottom conditions and submit data to NOAA.
Multiparameter SONDE	Before each sampling run	Standard solutions, periodically calibrate DO against Winkler titration	According to manufacturer's instructions, spare probe
Multiparameter WQM	Before each sampling run	DO bath, pump function	According to manufacturer's instructions

## B.8. Inspection / Acceptance of Supplies and Consumables

Procedures for inspection and acceptance of supplies and consumables listed in Table 13 shall be followed by the Monitoring Groups.

**Table 13:** Supplies Inspection and Acceptance Procedures

Supplies	Inspection Frequency	Type of Inspection	Available Parts	Maintenance
Calibration Standards	Before each sampling date	Visual inspection of quantity and expiration date	Spare fresh solutions	Storage according to manufacturer's recommendations, annual replacement at beginning of sampling season
SONDE sensors, batteries	Before each sampling date	Visual inspection of quantity, integrity	Spares	Storage according to manufacturer's recommendations
WQM cage, chain, batteries	Before each sampling date	Visual inspection of quantity, integrity	Spares	Storage according to manufacturer's recommendations
Atmospheric N deposition collectors: resin beads, columns, funnels	Before each sampling date	Visual inspection of quantity, integrity	Spares	Storage according to manufacturer's recommendations
Field and lab sample sheets	Before sampling date	visual	Additional copies	Print or copy as needed
Waders and life preservers	Before sampling date	Visual inspection	Patch kit	As needed
Sample bottles	Before sampling date	Visual, clean	One set of spare bottles	Clean after use, acid wash nutrient bottles (HCl), New bacterial bottles
Cooler	Before each sampling date	Cleanness, ice / ice packs	Spare coolers & ice	Annually as needed



## B.9. Non-direct Measurements

To provide high-quality data to enhance the interpretation of data collected as part of this Monitoring program, data may be acquired from sources approved by Monitoring Program Coordinator. The USGS tide gauges will be used for tide information. Precipitation will be acquired from TOH Bay Constables, USGS Reynolds Channel station, and/or SoMAS Merrick tide station. Details of the external data sources are described in Table 14.

**Table 14:** Non-Project Data Validity

The following data will be used as part of the Monitoring Program. This is secondary use of data.

Title or descriptive name of data document	Source of data	QAPP Written Y/N	Notes on quality of data	Planned restrictions to use of the data due to questions about data quality.
Time of low and high tide, heights of tides	USGS station #01310740 at Point Lookout, NY	Y <sup>1</sup>	USGS quality control methods.	Displayed data is classified by USGS as temporary until checked and calibrated. <sup>2</sup>
Heights of tides, USGS 6 minutes	USGS stations #01310521, #01310740, #01311143, #01311145	Y <sup>1</sup>	USGS quality control methods.	Displayed data is classified by USGS as temporary until checked and calibrated. <sup>2</sup>
High and low temperature and precipitation within 24 hours prior to the field trip, other weather and WQ data	USGS station #01310740	Y <sup>1</sup>	USGS	Displayed data is classified by USGS as temporary until checked and calibrated.
Precipitation within 24 hours	TOH Bay Constables	N <sup>3</sup>	Rain gauge supplied by DEC as part of shellfish sanitation procedures	Procedures prescribed by the DEC Shellfish division in inches to 2 decimal places at 8:00 AM each morning.
SoMAS rain gauge at Merrick	SoMAS	N	SoMAS quality control methods	Based on determination by SoMAS using their own quality control methods
Heights of tides, SoMAS	Bay Park, Merrick, Seaford	N	SoMAS quality control methods	Based on determination by SoMAS using their own quality control methods

1. Identical methods as described in the QAPP for Long Island Sound tide stations. (Schubert et al. 2010)

2. The USGS temporary classification means that documented routine inspections and other quality assurance measures are not performed that would make the data acceptable for archival, retrieval, or future use in general scientific or interpretive studies

3. DEC Shellfish Division SOP used

## B.10 Data Management

Field teams shall record data on field sheets, review them, and them, and sign them if they are in the chain of custody (CoC) documents and turn over to Monitoring Coordinator.

### *Field QC Checks*

In the field, the following QC checks are made:

- ☐ field blank - taken at or near the end of each cruise day and carried through the handling and analytical processes to evaluate contamination potential. These samples should be below the lowest standard analyzed for the parameter. Troubleshooting occurs if field blanks are above this threshold.
- ☐ collocated replicates - replicates taken in rapid succession to estimate field precision as a contrast to laboratory precision. field splits - samples collected in the same sample container but filtered separately to estimate filtration precision
- ☐ Field accuracy (apparent bias) and field and laboratory precision are evaluated quarterly for quadruplicate samples taken from a Hempstead Bay station and *triplicate samples taken from a tributary station*

Each person who handles or transports samples shall also sign the custody form upon receipt of the samples. Chain of custody forms will accompany each delivery of samples to the analytical laboratory and then be returned back to Monitoring Coordinator by mail or pickup after each analysis run is completed. Alternatively, scanned copies may be emailed or faxed.

Once laboratory analyses are complete, the laboratory personnel shall deliver (digital or hard copy) lab results to the Monitoring Coordinator or arrange for pickup.

The Monitoring Coordinator will enter, or supervise, the entry of raw field and lab data into the project database. Monitoring Coordinator shall also review sheets and confer with field teams on any needed corrective action. Documentation of data recording and handling, including all problems and corrective actions, shall be included in all preliminary and final reports.

Computer-entered data shall be compared with field sheets for accuracy. This task will be conducted by someone on the sampling team other than the individual that entered the data. Data sheets will be signed and dated after this QA process is complete. This task will be supervised by the Monitoring Coordinator.

Original data sheets will be stored by the Monitoring Coordinator for at least 10 years. Digital back-ups and copies of the non-digitized data will be made and stored in one or more separate locations designated by the Monitoring Coordinator, including Hofstra University at least once per month.

Examples of data forms are provided in the Appendix D. Table 15 in this document accurately represents the procedures utilized by this Monitoring Program for data management, review,

validation, and verification.

**Data Management Systems** – Spreadsheets, instrument controller software, data conversion software tools, databases, statistical, and graphical software packages location of data records (paper and electronic), are described here:

All data will be entered from field data sheets to an Access Database for storage and retrieval. Field data sheets will be kept on file in Conservation and Waterways office for at least 10 years. Digital scans of paper records will be generated from scans and stored on the Conservation and Waterways server, that is backed up weekly. The Project database is intended to be continued into the future and maintained indefinitely and shared with research partners at Hofstra.

**Table 15:** Data Management, Review, Validation, Verification Process Summary  
 The term “Field Sampler” refers to the person conducting the sampling in the field.

Activity	By Whom	Corrective action, if needed
Conduct field audits...	Monitoring program field coordinator	Correct any discrepancies with this QAPP or SOPs
Check labels just prior to sampling...	Field sampler	Correct label
At time of sampling, record data, sign field sheets.	Field sampler	Remind sampler of proper procedures, retrain if needed
Fill out, sign chain of custody (CoC) forms prior to going to lab	Field sampler or supervisor	Resample if possible, or flag suspect data. Remind sampler of proper procedures, retrain if needed
Before turning in field sheets, sanity check and check for completeness	Field sampler	Resample if possible, or flag suspect data
Upon receipt of field sheets, recheck and sanity checks of data	Monitoring group leader	Confer with field sampler(s) within 24 hours. Resample if feasible, otherwise flag suspect data
Check all sheets, sign CoC, forms, copies for archive ... etc.	Monitoring group leader	Contact field samplers, locate missing data, etc...
Upon receipt of samples, field sheets, and CoC forms, check to see the sheets match number of samples, sign CoC, make copies...	Lab coordinator(s) Lab Director if internal	Discrepancies reviewed with the responsible personnel, corrected as possible, and procedures reviewed to prevent future problems. Continued problems can result in replacement of personnel.

Upon completion of laboratory analysis, fill out lab sheets including QC tests	External Lab	Reanalyze if possible or otherwise flag on forms and in database
Upon receipt of lab data, review for completeness and legibility	Monitoring group leader	Confer with Monitoring Program Laboratory Coordinator
Upon completion of data entry, compare with field/lab sheets for accuracy	Monitoring group leader or designated employee	Re-enter correct data
Translate data into preliminary data reports; run statistical analysis and/or prepare graphical summaries of data. Check for agreement with QC objectives for completeness.	Monitoring program coordinator	Confer with QA officers, FLAG OR DISCARD SUSPECT DATA
In-season (at least once) and end of season review of data sets...	Monitoring group lead or designated appointee	Flag suspect data. Confer with Monitoring Program Quality Assurance Officer

## **C. Assessment and Oversight**

### **C.1. Assessment and Response Actions**

The Monitoring Coordinator and Laboratory QA Officer (and others as applicable) will identify and effectively address any issues that affect data quality, personal safety, and other important project

components. The progress and quality of the monitoring program shall be assessed to ensure the objectives are being accomplished. The Monitoring Coordinator will check on a monthly basis as needed to confirm the following:

- a. Monitoring is occurring as planned.
- b. Sufficient written commentary and supporting photographs exist.
- c. Sufficient field members are available for all sampling groups.
- d. Samplers are collecting in accordance with project schedules
- e. Datasheets and custody control sheets are being properly completed and signed.
- f. Data are properly interpreted.
- g. Plans for dealing with adverse weather are in place.
- h. Retraining or other corrective action is implemented at the first hint of non-compliance with QAPP or SOPs. These actions will be documented in a Word document with the final report and field data sheet for the following events.
- i. Labs are adhering to the requirements of this QAPP in terms of work performed, accuracy, acceptable holding times, timely and understandable results and delivery process.
- j. Data management is being handled properly, i.e. data are entered on a timely basis, is properly backed up, is easily accessible, and raw data are stored in a safe place.
- k. Procedure for developing and reporting the results exists.

The Monitoring Coordinator shall confer with the Laboratory QA Officer as necessary to discuss any problems that occur and what corrective actions are needed to maintain program integrity. In addition, the Monitoring Coordinator and Laboratory QA Officer shall meet at the end of the sampling season, to review the draft report and discuss all aspects of the program and identify necessary program modifications for future sampling activities. All problems discovered and program modifications made shall be documented in the final version of the project report.

If modifications require changes in the Quality Assurance Project Plan, these changes shall be submitted to the QAPP distribution list for review. If data are found to be consistently outside the Data Quality Objectives as defined in section A.7. of this document, the Monitoring Coordinator (and others as applicable) shall review the program and correct problems as needed. Corrections may include retraining staff; rewriting sampling instructions; replacement of staff; alteration of sampling schedules, stations, or methods; or other actions deemed necessary.

## C.2. Reports to Stakeholders

Data that have passed preliminary QC analysis as described in Table 16 may be shared with stakeholders, including the New York State Department of Environmental Conservation, the Long Island Nitrogen Action Plan, and/or the Long Island Regional Planning Council. A caveat will accompany these or any data released on a preliminary basis, explaining that they are for review purposes only and subject to correction after completion of a full data review occurring at the end of the year.

The Monitoring Coordinator will write a final report. This will be sent to the distribution list. The final report will include (updated as necessary) any tables and graphs that were developed for initial data distribution efforts, and it will describe the program's goals, methods, quality control results, data interpretation, and recommendations. This report may also be used in public presentations. All reports, preliminary or final, will include discussion of steps taken to assure data quality, findings on data quality, and decisions made on use, censorship, or flagging of questionable data. Any data that are censored in reports will be either referred to in this discussion or presented but noted as censored.

In short, the final report will include:

- Raw data
- QC data
- Associated metadata
- Questionable data, flagged
- Identification of status as “preliminary” or “final” report

**Table 16: Report Mechanisms, Responsibilities, and Distribution**

Reporting Mechanism	Person Responsible for writing report	Distribution list
Monitoring Group Master Data Entry Template	Monitoring Group Leader or designated appointee	Monitoring Program Coordinator
Final Monitoring Data	Monitoring Program Coordinator	Signatories of this QAPP, NYS DEC, SSER, and other management groups.
Final Monitoring Report, Website, other public communication	Monitoring Program Coordinator	All signatories of this QAPP

## **D. Data Validation and Usability**

### **D.1. Data Review, Verification, and Validation**

All project data, metadata, and quality control data shall be critically reviewed to look for problems that may compromise data usability.

The Monitoring Coordinator will review field and laboratory data after each sampling run and take corrective actions as described in Table 12 of this document. At least once during the season, at the end of the season and if questions arise, the Monitoring Coordinator will share the data with the Quality Assurance Officer to determine if the data appear to meet the objectives of the QAPP. Together, they will decide on any actions to take if problems are found.

### **D.2. Verification and Validation Methods**

All project data and metadata are reviewed and approved as usable data, or as unusable when the data are questionable for any reason.

Data verification and validation will occur as described in Table 15, and will include checks on:

- Completion of all fields on data sheets; missing data
- Completeness of sampling runs (e.g. number of stations visited / samples taken vs number proposed, when all parameters sampled / analyzed).
- Completeness of QC checks (e.g. number and types of QC checks performed vs. number or type proposed).
- Number of samples exceeding QC limits for accuracy and precision and how far limits were exceeded.

### **D.3. Reconciliation with User Requirements.**

At the conclusion of the sampling season, after all in-season quality control checks, assessment actions, validation and verification checks and corrective actions have been taken, the resulting data set will be compared with the program's data quality objectives (DQOs) as defined in section A.7. This review will include, for each parameter, calculation of the following:

- Completeness goals: overall % of samples passing QC tests vs. number proposed.
- Percent of samples exceeding accuracy and precision limits.
- Average departure from accuracy and precision targets.

After reviewing these calculations, and taking into consideration such factors as clusters of unacceptable data (e.g. whether certain parameters, stations, dates, field teams, etc. produced poor results), the Monitoring Coordinator and Laboratory QA Officer ( and others as applicable) will evaluate overall program attainment of DQOs and determine what limitations to place on the use of the data, or if a revision of the DQOs is allowable.

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## **Appendices**

### **Appendix A. Supplemental Distribution List**

### **Appendix B. List of sampling stations, Table A2**

### **Appendix C. Standard Field Operating Procedures**

#### C-1 Introduction

#### C-2 Station Selection Criterion

##### C-2.1 Bay Samples

##### C-2.2 Vertical Profiles

##### C-2.3 Tributary Sampling

##### C-2.4 Atmospheric Deposition Stations

##### C-2.5 Continuous Monitoring Stations

#### C-3 Field Safety and Sampling routines

##### C-3.1 General field activity procedures

##### C-3.2 Hempstead Bay sampling supplementary procedures & Considerations

###### C-3.2.1 Nutrient Samples – Van Dorn

###### C-3.2.2 Water Clarity Samples – Secchi Disk

###### C-3.2.3 Bacterial Samples – See C-4 for DEC procedures

###### C-3.2.4 YSI 6600-V2 or handheld for single readings at one meter and 10-15 ft cable.

##### C-3.3 Vertical Profile supplementary procedures & Considerations

###### C-3.3.1 Downcasts using YSI 6600-V2 with continuous data recording and 100 ft cable.

##### C-3.4 Tributary Sampling supplementary procedures & Considerations

###### C-3.4.1 Nutrient Samples – Van Dorn from boat, bridge, bulkhead, etc.

###### C-3.4.2 Downcasts using YSI 6600-V2 with continuous data recording and 100 ft cable.

#### C-4 Sampling Procedure for Total Coliforms, NYS DEC Protocol for Assessing Suitability for Shellfish Harvesting in Marine Waters

#### C-5 Wet Labs WQM Maintenance and Calibration

#### C-6 Wet Labs WQM Data Transfer

#### C-7 YSI 6600-V2 Maintenance and Calibration

#### C-8 SONDE Vertical Profile Data Transfer

#### C-9 Ross 960 Bathymetry

#### C-10 Atmospheric Sample Collection – resin column field procedures

### **Appendix D. Data Forms, Checklists, and Chain of Custody Forms**

#### D-1 Calibration Datasheets

##### D-1.1. YSI 6600 Calibration Formation

##### D-1.2 WQM Calibration Form

#### D-2 Field Datasheets and Checklists

##### D-2.1. TOH Hempstead Bay Form

##### D-2.2. TOH Tributary Form

###### D-2.2.a Old Tributary Form

###### D-2.2.b New Tributary Form

D-2.3. DEC Sanitary Study Field Sheet  
D-3 Vertical Profile Datasheet  
D-4 Chlorophyll Chain of Custody (CoC) Forms  
D-5 External Lab CoC form – Pace 2018  
D-6 C0C Log Book page  
D-7 Field Equipment Checklist

## **Appendix E. External Labs – Analytical Methods**

E-1 Pace Labs SOP – Nutrients

## **Appendix F. In-House Analysis and In-Lab Calibrations and Data Transfers**

F-1 Hofstra SOP – extraction of Nitrogen samples from atmospheric samplers

F-2 TOH C&W WQ Lab SOP – Chlorophyll

F-3 TOH C&W WQ Lab SOP – Nutrient analysis SOP procedures

F-3.1 Astoria-Pacific Ammonia

F-3.2 Astoria-Pacific Nitrates and Nitrites

F-3.3 Astoria-Pacific orthoPhosphates

F-3.4 Astoria-Pacific Silicates

F-3.5 Hatch simplified Kjeldahl N

F-4 Quality Controls

## **Appendix G. Background**

## **Appendix H. Glossary of Terms and Abbreviations**

## Appendix A. Supplemental Distribution List

Name	Organization	Email	Address	Telephone
Donald X. Clavin, Jr., Supervisor	Town of Hempstead	dxcalvin@tohmail.org	1 Washington Street, Hempstead, 11550	(516) 812-3260
Christopher Carini, Town Board, 5th District	Town of Hempstead	chricari@tohmail.org	1 Washington Street, Hempstead, 11550	(516) 812-3285
Thomas E Doheny, Commissioner	TOH C&W	thomdoh@tohmail.org	PO Box 180, Point Lookout, NY 11569	(516) 431-9200
Thomas Dauscher, Deputy Commissioner,	TOH C&W	thomdau@tohmail.org	PO Box 180, Point Lookout, NY 11569	(516) 431-9200
Tara Schneider-Moran	TOH, C&W	tschneider@tohmail.org	PO Box 180, Point Lookout, NY 11569	(516) 897-4109
Jeremy Campbell	NYS DOS, SSER	Jeremy.Campbell@dos.ny.gov	One Commerce Plaza, 99 Washington Ave Albany, NY 12231-0001	(518) 474-6000
Lane Smith	NYS Sea Grant	lane.smith@stonybrook.edu	125 Nassau Hall Stony Brook University Stony Brook, NY 11794-5001	(631) 632-9780
Susan Van Patten	NYS, DEC	Susan.vanpatten@dec.ny.gov	NYS DEC Division of Water 625 Broadway Albany, NY	(518) 402-8233
Michele Golden	NYS, DEC	michele.golden@dec.ny.gov	NYS DEC Division of Water 625 Broadway Albany, NY	(518) 402-8233
Julia Socrates	NYS DEC	julia.socrates@dec.ny.gov	NYSDEC Region 3 Offices, 21 S Putt Corners Road, New Paltz, NY 12561	(845) 256-3000
Sean E. Sallie, Deputy Commissioner	Nassau County Department of Public Works	ssallie@nassaucountyny.gov	1194 Prospect Avenue Westbury, NY 11590-2723	(516)-571-9342

Brian Schneider, Deputy County Executive for Parks and Public Works	Nassau County Department of Public Works	bschneider@nas saucountyny.gov	1550 Franklin Avenue County Executive Suite, Rm 223 Mineola, New York 11550	(516) 571- 6725
Don Irwin, Commissioner of Health	Nassau County Department of Health	dirwin@nassauc ountyny.gov	200 County Seat Dr Mineola 11501	(516) 227- 9697
Rob Weltner	Operation SPLASH	operationsplash @optonline.net	202 Woodcleft Ave, Freeport, NY 11520	(516) 378- 4770
Adrienne Esposito	Citizens Campaign for the Environment	aesposito@citize nscampaign.org	225A Main Street, Farmingdale, NY 11735	(516) 390- 7150
Christopher Clapp	The Nature Conservancy	cclapp@tnc.org	322 8th Ave, New York, NY 10001	(631) 329- 3981 ext 218
Chris Schubert	USGS	schubert@usgs.g ov	New York Water Science Center 2045 Route 112, Building 4   Coram, NY 11727-3085	(631) 736- 0783 x109

## Appendix B. Sampling Stations

**Table 2:** Station coordinates in WGS 1984 for all Hempstead Water Quality Stations, including Bay Water Quality Stations (B), Vertical Profiles (V), DEC Shellfish Sanitary Stations (S), Continuous Monitoring stations (C), and for Atmospheric Nitrogen deposition monitoring stations (A).

### Stations: Hempstead Bay Water Quality

Station ID	Embayment	Longitude	Latitude	Type
1	West Bay	-73.75765	40.58465	B
2	West Bay	-73.73370	40.59287	B
2A	West Bay	-73.73115	40.60222	B
3	West Bay	-73.68745	40.58977	B
4	West Bay	-73.67403	40.59517	B
6	West Bay	-73.68249	40.60224	B
5	West Bay	-73.69821	40.61684	B
8	West Bay	-73.67531	40.62719	B
10	West Bay	-73.65989	40.62246	B
7	West Bay	-73.65339	40.60996	B
6A	West Bay	-73.67478	40.61202	B
11	Middle Bay	-73.64137	40.59626	B
12	Middle Bay	-73.62994	40.60971	B
13A	Middle Bay	-73.59018	40.61965	B
15	Middle Bay	-73.59204	40.59468	B
14	Middle Bay	-73.57714	40.62291	B
16	Middle Bay	-73.57042	40.60592	B
18	Middle Bay	-73.57030	40.58736	B
19	East Bay	-73.54016	40.59890	B
20	East Bay	-73.52232	40.60125	B
17	East Bay	-73.55728	40.61244	B
33	East Bay	-73.50117	40.61267	B
30	East Bay	-73.50907	40.63128	B
31	East Bay	-73.54830	40.62524	B
21	East Bay	-73.52264	40.61414	B
25	East Bay	-73.53922	40.63835	B
147	East Bay	-73.53088	40.61924	B
24	East Bay	-73.55431	40.63669	B
26	East Bay	-73.49325	40.63549	B
28	East Bay	-73.48567	40.60822	B

**Stations: Tributaries**

<b>Station ID</b>	<b>Embayment</b>	<b>Longitude</b>	<b>Latitude</b>	<b>Type</b>
205	West Bay	-73.66049	40.62949	B
203	West Bay	-73.65787	40.64411	B
206	West Bay	-73.65409	40.65429	B
212	Middle Bay	-73.60053	40.64415	B
214	Middle Bay	-73.60220	40.64854	B
241	West Bay	-73.68963	40.62889	B
243	West Bay	-73.69159	40.63719	B
314	East Bay	-73.53711	40.65283	B
325	East Bay	-73.51885	40.66252	B
333	Middle Bay	-73.56749	40.64290	B
334	Middle Bay	-73.57491	40.65130	B
284	West Bay	-73.64331	40.64428	B
224	Middle Bay	-73.61732	40.64242	B
222	Middle Bay	-73.61584	40.63327	B
304	East Bay	-73.54685	40.64861	B
310	East Bay	-73.54272	40.64732	B

**Stations: Shellfish Sanitary (Total Coliform Bacteria using NYS DEC Shellfisheries Laboratory procedures under USFDA National Shellfish Sanitation Program)**

Station ID	Embayment	Longitude	Latitude	Type
11	Middle Bay	-73.64137	40.59626	S
11A	Middle Bay	-73.61578	40.59699	S
12	Middle Bay	-73.62994	40.60971	S
13	Middle Bay	-73.61462	40.61898	S
13A	Middle Bay	-73.59018	40.61965	S
15	Middle Bay	-73.59204	40.59468	S
15A	Middle Bay	-73.60981	40.61813	S
15B	Middle Bay	-73.60393	40.60456	S
14	Middle Bay	-73.57714	40.62291	S
16	Middle Bay	-73.57042	40.60592	S
18	Middle Bay	-73.57030	40.58736	S
18A	Middle Bay	-73.55632	40.59447	S
18D	Middle Bay	-73.57660	40.59566	S
19	East Bay	-73.54016	40.59890	S
20	East Bay	-73.52232	40.60125	S
17	East Bay	-73.55728	40.61244	S
33	East Bay	-73.50117	40.61267	S
22	East Bay	-73.50581	40.62075	S
30	East Bay	-73.50907	40.63128	S
34	East Bay	-73.50694	40.63895	S
32	East Bay	-73.55321	40.62026	S
31	East Bay	-73.54830	40.62524	S
21	East Bay	-73.52264	40.61414	S
25	East Bay	-73.53922	40.63835	S
146	East Bay	-73.53369	40.63066	S
147	East Bay	-73.53088	40.61924	S
17.1	East Bay	-73.53346	40.61517	S
24	East Bay	-73.55431	40.63669	S
26	East Bay	-73.49325	40.63549	S

**Stations: Continuous (12 min) Monitoring Logging Devices (WQM)**

Station ID	Embayment	Longitude	Latitude	Type
110	Middle Bay	-73.65449	40.59491	C
106	West Bay	-73.66115	40.62389	C
111	East Bay	-73.50153	40.61484	C
236	Jamaica Bay	-73.75809	40.61755	C

## Stations: Vertical Profiles

Station ID	Embayment	Longitude	Latitude	Type
2	West Bay	-73.687678	40.589183	V
4	West Bay	-73.677495	40.626317	V
6	West Bay	-73.660945	40.628050	V
8	West Bay	-73.667112	40.606533	V
9	West Bay	-73.664545	40.595917	V
10	Middle Bay	-73.650062	40.595650	V
12	Middle Bay	-73.618528	40.596900	V
13	Middle Bay	-73.622078	40.616667	V
14	Middle Bay	-73.615995	40.627150	V
15	Middle Bay	-73.571012	40.606667	V
17	East Bay	-73.488795	40.607900	V
18	Middle Bay	-73.593412	40.623817	V
20	East Bay	-73.536478	40.638917	V
22	East Bay	-73.518128	40.649233	V
24	West Bay	-73.663412	40.616017	V
25	East Bay	-73.496662	40.624050	V
30	West Bay	-73.729529	40.604645	V
31	East Bay	-73.522078	40.612659	V
32	West Bay	-73.657385	40.607962	V
33	Middle Bay	-73.635873	40.612741	V



**Stations: Atmospheric Nitrogen Deposition Stations**

Station ID	Latitude	Longitude	Type
1	40.6450166	-73.596118	A
2	40.677553	-73.696678	A
3	40.648162	-73.502942	A
4	40.592461	-73.596118	A
5	40.685887	-73.575103	A
6	40.716727	-73.596010	A
7	40.690275	-73.643285	A
8	40.725906	-73.508077	A
9	40.752201	-73.454444	A
10	40.699696	-73.452295	A
11	40.612171	-73.430570	A
12	40.623168	-73.624770	A

## Appendix C. Standard Field Operating Procedures

### C-1. Introduction

This document is intended for the Standard Operating Procedure (SOP) for the collection of:

1. Samples for the Town of Hempstead, Department of Conservation and Waterways (TOH, C&W).
2. Hempstead Bay sampling, including; East Bay Sanitary samples from stations for Department of Environmental Conservation (DEC) shellfish sanitary program.
3. It is critical to have an understanding of the effects of urban environment on the nutrient gradient in local estuaries. To do so, detailed data must be kept over the long term and require careful collection and attentive field sampling procedure. The procedure used is also important to ensure the safety of shellfish collection, which is used for human consumption. This document serves as a guideline for the correct procedure for field sampling.
4. Field sampling can be time consuming and strenuous work. It is important to collect samples efficiently and cautiously so that laboratory analysis can produce accurate results. Sampling should be done meticulously to avoid unstable samples that would then require repetition of the collection. Careful field work is the first step to accurate data generation. Demand for professional procedure and data has increased with the availability of modern field instrumentation. The use of professional instrumentation has made it possible to move work previously done in laboratories into the field, allowing information to be gathered quickly and accurately. For instance, the YSI SONDE uses electronic probes that are carefully designed to detect specific chemical properties in the complex medium of seawater, which is a difficult environment for analysis. These probes require frequent maintenance and careful use to maximize effectiveness.
5. Electronic probes have their limitations. For example, Dissolved Oxygen (DO) in sea water must cross a membrane barrier before it can react with a medium within the probe and change electric potentials that can be measured. This takes time to stabilize to the same concentrations on both sides of the membrane. Obtaining accurate readings takes some patience, so timing and weather should be taken into account prior to collecting. Other probes have their own characteristics, including pH, conductivity/salinity, temperature, turbidity, and other probes that can be installed on instrumentation.
6. Another source of error is that sensor probes drift or change how they react to a given concentration. This requires a calibration prior to use, at a schedule that varies between probes.
7. Water samples that are collected for analysis using laboratory methods must also be collected, handled, and transported in ways that minimize any changes in the final measurements from actual field conditions. Typical methods include
  - minimized contamination using specially cleaned containers,
  - avoiding adding contaminants during collection (do not touch rims or caps)
  - keeping samples on ice in coolers (2-4 degrees Celsius)
  - minimizing the time before laboratory analysis (preferably well under 28 hours)

8. Samples taken for the analysis of different parameters have different requirements that are detailed in the methods described in the QAPP document, but briefly outlined below. Biological samples that can react within the sample container, including bacterial samples and Chlorophyll a, are among the most sensitive. Quality Control (QC) checks should be done for each batch of samples, which will include calibration verification, calibration blanks, laboratory duplicates, and spike sample analyses. The goal for each batch is to run the QC on 10% of the samples. Field blanks and field duplicates are provided to the laboratory at a rate of at least **ONE** per ten samples (10%). **Field Blanks** are prepared randomly once each sample day to evaluate contamination potential, and **Field Duplicates** are replicates taken in rapid succession to estimate field precision.

## **C-2. Sampling Station Location Choice**

### **C-2.1 Hempstead Bay Samples**

These stations were chosen circa 1970 to determine conditions at larger bays and the confluence of channels. Some additional sample stations were added when data gaps were observed and at the request of NYS DEC for the purpose of bacterial samples for the determination of safely harvesting Shellfish for human consumption. We intend to continue the Hempstead Bay stations to retain continuity of the data set. In addition, many of these stations fulfill regulatory requirements of the NYS DEC Shellfisheries Division.

### **C-2.2 Vertical Profiles**

These stations were chosen to provide the deepest possible downcasts within a given section of estuary to obtain the most complete and representative data record possible. The bathymetric patterns of these bays were often determined by the dredging of borrow pits that so that there is an uneven bottom with locally deep holes surrounded by shallower water. Some channels contain scours caused by tidal currents that also represent locally deep points. These locally deep points caused by various events represent the best opportunities for the representative data collection of data on the water column conditions.

### **C-2.3 Tributary Sampling**

The tributary sample stations proposed in this QAPP represent a subset of the stations that TOH C&W had original chosen to help locate illicit discharge events. The subset was chosen to provide the one or two most representative stations for each tributary.

### **C-2.4 Atmospheric Deposition Sites**

12 sites were chosen from greater than 100 potential properties owned by the Town of Hempstead. Sites determined to have potential, via examination using Google Maps imagery,

were visited for further inspection. Site visits assessed canopy cover and protection from anthropogenic damage to the atmospheric nitrogen deposition collectors. Each site required both relatively protected areas that possessed sufficient tree canopy cover and an open area (i.e. open to the sky) so we could locate three collectors under each of those conditions (for a total of six per site). Tree canopy cover was considered sufficient if all three under-canopy collectors fit under the canopy and the target canopy cover possessed similar leaf area index or LAI across sites. Minimization of risk of anthropogenic damage to collectors was protection from fences and isolation from main pathways in locations such as a park or school. Final site selection also accounted for parameters that correlate with atmospheric N deposition including on-road CO<sub>2</sub> emissions, proximity to major urban areas, and proximity to major point sources. Spatial distribution of sites was designed to capture both background deposition and trends related to on-road emissions, point sources, impervious surface land coverage, and proximity to New York City.

### **C-2.5 Continuous Monitoring Stations**

Continuous water quality monitoring using in-situ instruments were located in each of the three bays (West Bay, Middle Bay, and East Bay) within Hempstead Bay to provide a record of salinity, DO, temperature, fluorometric chlorophyll, turbidity, and tidal depth at 12 minute intervals. Under NYS DOS EPF funding, continuous water quality recording was initiated in 2014, but also mostly discontinued after June of 2017. Long term data sets are known to be extremely important for ecological and marine management work (Lindenmayer et al 2012, Addison et al. 2015, Hughes et al. 2017), therefore we will be using these carefully chosen sampling locations to continue to use these station locations. Continuous sampling stations were selected from potential locations with fixed structures in strategic places that could support WetLabs WQM units and per considerations detailed in Wagner et al. (2006) and Schubert (2010).

## C-3 Field Sample Collection and Safety Procedures

Field safety precautions are taken to ensure the safety of staff and crew, as well as to protect equipment and samples from damage. **All TOH C&W personnel and Hofstra University personnel will be required to complete field, laboratory, and boater safety training (for water sampling, only) prior to performing any work under this QAPP. This training will be administered by qualified personnel at each respective institution per that institution's procedures and protocols.** The information contained below represents a basic set of reminders and checklists to help guide these trained personnel as they perform their duties. No individuals may take part in the sampling activities described in this QAPP prior to completing the required safety training.

### C-3.1 General field activity procedures

#### *Safety Protocols*

**Personal Protective Equipment:** Crew members are responsible for wearing field appropriate clothing and footwear while in the field. A list of recommended personal equipment is provided in C-3.1.2.

**Motor Vehicles.** Crew members are responsible for inspecting their vehicles before every use to ensure the vehicles are in safe working condition. This includes visually checking tire pressure, ensuring visibility through all windows, adjusting mirrors, and securing all equipment. Rules that must be followed when operating a town vehicle include:

- All passengers in a government vehicle (or any field vehicle) are required to wear a seat belt.

- Use of cell phones (both talking and texting) is strictly prohibited while driving.

- Only town employees or authorized cooperators and contractors are allowed to operate a government vehicle.

- Passengers who are not town employees or authorized cooperators and contractors are forbidden from riding in a government vehicle.

- Drivers must adhere to all federal and state vehicle regulations, including all posted speed limits.

**Radios:** Boat crew should carry walkie talkies or boat radios for emergency use.

Radios should be tuned into the Bay Constable channel 16 in case of distress or emergencies.

#### *C-3.1.2. Recommended Field Gear*

- Rain gear (waterproof coats, windbreakers, gloves, shoes).

- Warm Winter clothing (during the winter months: multiple layers, gloves, thick socks, warm hats, coats, waterproof gear).

- Protective shoes, all shoes must grip the wearer's heel (boots recommended)

- Sunglasses (polarized recommended)

Sunscreen and bug spray (summer months).  
Lightweight clothing during summer. Layering recommended for summer for temperature changes and sun exposure.  
Brimmed hats (summer)  
Waders  
Water canteen

## **C-3.2 Bay Study supplementary procedures & Considerations**

### **C-3.2.1 Nutrient Samples – Van Dorn**

The Van Dorn bottles provide a means of obtaining water samples at selected depths below the surface. It consists of an open ended clear plastic cylinder that can be attached to the hydrographic wire (the steel wire wound on the winch) and lowered to any desired depth. A deckhand operates the winch. The bottles also provide a platform to which thermometers can be attached to record the temperature of the water at the location of each Van Dorn bottle.

Each end of the cylinder is fitted with a rubber cover. The Van Dorn bottle is attached to the line with the covers pulled out and twisted back and around to the side. The bottle is lowered to a pre-selected depth. The Van Dorn has a temperature range of to determine the in-situ temperature, the water sampler has a standard thermometer mounted. Temperature range between  $-10$  and  $+60$  C°. A metal weight called a "messenger" is attached below the upper bottle. The water sample is taken by dropping a "messenger" down the wire. When the weight hits the catch on the upper Van Dorn bottle, the catch releases the rubber end covers. The two ends snap around and seal off the ends. The other "messenger" then travels down the winch line to the lower Van Dorn bottle causing it to be sealed. When both bottles have been tripped, they are retrieved and returned to their storage rack. Water samples from each bottle can then be taken for analysis and the temperature read from the attached thermometers. You may be able to see organisms in the water samples through the clear walls of the Van Dorn bottles.

*Special Request Procedures:* Two Van Dorn bottles are attached to the same line and lowered to two different pre-selected depths. When it is time to lower the Van Dorn bottles into the water (this is called making a "cast"), a decision is made about the depth to which to send the bottles. This decision is based upon the depth of the water at the station and the number of samples needed. Normally only two water samples (surface and bottom) are taken. In shallow areas, typically only take one water sample is taken. If a third sample is required, three Van Dorn bottles are stacked on the hydrographic cable.

Procedure:

1. Open the Van Dorn water sampler by pulling the elastic bands and lids back and secure the hooks. Make sure that the mechanism is locked so that it will be released by the releasers weight, and that the valve is closed.
2. Attach the free end of the messenger line to the boat.

3. Lower the sampler to the desired depth.
4. Trigger the sample by releasing the messenger weight so that it slides down the line.

Emptying Van Dorn:

1. Raise the full sampler out of the water. Set in on a clean, flat surface in an upright position.
2. To avoid any contamination, do not set the sampler in the bottom of the boat.
3. Empty the water sampler by releasing the tap at the bottom of the tube.
4. When emptying the sampler, the amount of water through the tap, can be adjusted by the upper air valve.
5. For 2 and 3 liters models you must allow a slightly opening of the valve to empty the bottle.
6. For the 5 liters model we recommend to keep the valve closed at the beginning to avoid a heavy flow at the tap.

### **C-3.2.2 Water Clarity Samples – Secchi Disk**

Excessive waves, wind, or sunlight may jeopardize Secchi Disk readings. To minimize these effects, take readings during calm days that are partly cloudy to sunny. Anchor the boat at the sampling station to avoid boat drift and lower the Secchi disk off the shady side of the boat. If the Secchi disk drifts too fast for an accurate reading – that is, the line is not vertical in the water – try weighting the bottom of the disk to make it sink faster or taking the measurement on the downwind side of the boat. If none of these techniques work, and you do not think you can obtain an accurate reading, DO NOT make the measurement because it will not be a good representation of lake conditions on that day. Be sure to note weather conditions along with the Secchi disk reading.

**NOTE:** Secchi depth readings are rarely taken in streams because of the inaccuracies associated with flowing water, disk movement, and shallow depths.

#### **Measurement Methods**

Slowly lower the disk into the water to the point where it just disappears.

Place a clothespin on the line where it meets the water surface or mark the point on the line in some other way.

Continue lowering the disk a few more inches, and then slowly raise it until it just becomes visible again. Mark this spot with another clothespin or hold the rope here between your fingers.

The spot halfway between the two marks represents the average Secchi disk reading. Mark the spot by moving the clothespin or other marker to the spot.

Carefully measure or count the distance from the disk to the marked spot. Record the distance to the nearest tenth of a foot or meter.

### C-3.2.3 Bacterial Samples – See C-4 at this time

Each month, Town of Hempstead collects water samples from east bay and middle bay for the Department of Environmental Conservation to analyze bacteria presence. The sampling is usually performed at the beginning of the month, but will vary with the tidal cycle. Samples are taken on an ebb tide at an hour after the highest peak of high tide. Samples are taken at with 28 100mL bottles at Stations listed as Priority S in Table 2. If possible, samples are immediately taken to the Department of Environmental Conservation (DEC) Shellfish Laboratory while kept on ice in the large cooler immediately after disembarking from the boat. Samples can be delivered to the DEC directly after completing sampling route and should be delivered no later than 15:00 hours (3:00 pm) on a given day. Samples must be delivered to the lab for analysis within 5 to 23 hours. For details, please see section C-4 for procedures, equipment, and quality controls.

Bacteriology for DEC requires the working knowledge of tidal times and cycles as well as proper sample procedure and boat handling. *Refer to C-2.1. for field sheets and checklists.*

#### Equipment:

- 28, 100mL bottles
- YSI SONDE, plus backup sonde, batteries, and cables.
- Pole (for attaching bottles)

#### Pre-Sampling Procedure:

- Prepare the 28 100mL bottles for sampling by ensuring the bottles are labeled properly and have a black meniscus line.
- Fill out field sheet for sampling day. Include the names of crew and recorders, tide, rainfall data, and fill out stations and bottle numbers.
- Calibrate YSI to ensure it is working properly.
- Assemble necessary equipment.
- Check weather to prepare for conditions in the field.
- Ensure boat is fueled properly for the trip.
- Perform field blank.
- Add ice to coolers.
- Load the boat with appropriate materials.

#### Field Procedure:

- Place 28 bottles, 1 field blank, and one temperature control in the large cooler. Add extra bottles in case of contamination or breakage.
- Fill sides of bottle rack with ice. Do not leave ice cubes on top or near the lid of the bottles.
- Take the field blank before disembarking.
- Once in the field, take temperature control.



Use the pole to attach the sample bottle and secure well enough so it does not fall out.

Remove the plastic wrap carefully and avoid touching the lip of the bottle.

Remove lid and take the sample from the surface of the water, using the pole.

Fill the bottle to 100mL (black line on bottle).

The meniscus should be at or as close as possible to the black line.

Recap the bottle without touching lip or inside of cap and remove from pole.

Place the bottle in the cooler.

Write time on field sheets

Take samples directly to the DEC after sampling or as soon as possible. Keep on ice until at the DEC to maintain temperature control.

*Please refer to Section D-2.1. for the DEC Bacteria Field Sheets and Checklists.*

Please Note:

Sample temperatures for chemistry should be kept below 5.0 degree Celsius.

Deliver Bacteria samples from East Bay to DEC within **5 to 23** hours (or ASAP), kept on ice.

Fill water to where the surface in the center of the bottle matches the meniscus line without touching or otherwise contaminating any of the inside surfaces such as the inside of the cap.

Sample temperatures for bacteriology should be kept < 5.0 °C.

**C-3.2.4** YSI 6600-V2 or handheld for single readings at one meter and 10-15 ft cable.

For one-meter readings while visiting the monthly Hempstead Bay and Sanitary Sampling stations, the parameters are read from the hand held controller and entered onto field sheets.

**C-3.3** Vertical Profile supplementary procedures & Considerations

Vertical profiles are taken as slow downcasts. The speed of the SONDE decent should be sufficiently timed to allow probes to equilibrate at the sampling depths.

**C-3.3.1** Downcasts using YSI 6600-V2 with continuous data recording and 100 ft cable.

The data are labeled by station and recorded digitally on the handheld to be downloaded after returning to the office. Data is discarded after the time that the SONDE reaches the bottom and a turbidity spike from disturbing the sediments is seen.

**C-3.4** Tributary Sampling supplementary procedures & Considerations

Tributary sampling consists of Nutrient samples at one meter or ½ the water depth if the depth is less than 1 ½ meter. Full downcasts are also taken with the YSI6600-V2 SONDES in a manner similar to Vertical Profiling.

**C-3.4.1** Nutrient Samples – Van Dorn from boat, bridge, bulkhead, etc.

Van Dorn samplers will be used to capture water samples for laboratory analysis of Nutrients, Chlorophyll a, and any other laboratory analysis of water. Van Dorn samplers are suspended from a cable to the desired depth and triggered to close with a messenger weight once water has had time to circulate to represent the desired depth of sampling.

## **C-4. Sampling Procedure for Total Coliforms, NYS DEC Protocol for Assessing Suitability for Shellfish Harvesting in Marine Waters**

**STATE OF NEW YORK  
DEPARTMENT OF ENVIRONMENTAL CONSERVATION  
SHELLFISHERIES SECTION  
205 NORTH BELLE MEAD ROAD, SUITE 1  
EAST SETAUKET, NEW YORK 11733**

### **Procedures for the Collection of Water Samples in Shellfish Growing Areas by Local Government Personnel**

1. Sample collection must be done by local government personnel according to the attached "PROTOCOL FOR THE COLLECTION OF BAY SURVEY WATER SAMPLES FOR SANITARY BACTERIOLOGICAL EXAMINATION." Local government personnel must be instructed in the proper use of the PROTOCOL prior to collecting samples. A Laboratory Quality Assurance Record of your training will be maintained in the laboratory. **Samples collected by untrained personnel or non-government personnel cannot be accepted by DEC.**
2. Unless otherwise arranged, samples for DEC (i.e., Conditional Area Sampling) must be collected under the following conditions:
  - ▶ **During ebbing tide**, sample collection may begin no sooner than 1.5 hours following high tide or later than 1 hour after low tide. It is important that accurate tide tables be used.
  - ▶ Samples are to be collected at stations designated by or acceptable to DEC's shellfish program biologists (growing area sampling charts will be prepared and provided by DEC and must be taken into the field).
  - ▶ Prior to establishing conditional harvesting programs: within 0-96 hours following a rainfall in a range specified by a DEC Shellfish Program Biologist.
3. **Prior to sampling**, field blanks (FB bottles) must be filled from a potable (reliable) source of drinking water. Samples collected without the proper field blanks and temperature controls (TC bottles) will be deemed invalid and discarded upon arrival at the DEC laboratory. **A FB and TC must accompany each ice chest/cooler used in the collection and transport of samples.**
4. Sample bottles must be used in numerical order. **DO NOT** try to match bottle numbers with station numbers. Samples in bottles not in numerical order in racks will be discarded.
5. **DO NOT place anything in the ice chest with the sample bottles**, including lunches and beverages. Ice must be made with water of drinking water quality, commercially sold ice is acceptable. Flaked ice is preferable, but cubes can be used. Cubes can make it very difficult to replace bottles back in the rack after the sample is taken because the cubes fall into the bottle rack holes. Cold packs are permitted if samples can be maintained between 0°C and 10°C.

## **C-5. WetLabs WQM pre- and post-deployment SOP**

Note that WetLabs/SeaBird had recommended discontinuing the use of the bleach dispenser pending better solutions for the precipitants forming from stabilizers in the bleach that clog pump tubing.

## **WQM Pre/Post-Deployment Outline**

### ***Pre-Deployment:***

Remove WQM from cage prior to pre-deployment  
Internal Uninterruptible Power Supply  
BLIS Prep: Check for BLIS Operation, then fill BLIS reservoir, then install BLIS reservoir.  
Anti-Fouling Maintenance: electrical tape and anti-fouling paint  
Calibrate the WQM against the SONDE  
Deploy

### ***Post-Deployment:***

Clean conductivity and O2 sensors  
Clean the FLNTU (Biowiper/Copper Components)  
Add date of completion for each step on the “WQM Schedule” found in  
“J:\BayStudy\WQM” on the server.

### **Detailed Steps:**

1. Checking BLIS Operation: Remove the BLIS end cap: Use a 7/64-in. hex key to remove the two screws.
2. Twist and pull to remove the cap and expose the bleach reservoir.
3. Grasp the bleach reservoir by the rim of the bottle and pull gently. You may feel the resistance of a slight suction as the nipple pulls free of the intake.
4. Remove the BLIS–CTD clamp. Use a 5/32-in. hex key to loosen the clamp. Slide it up and off the BLIS and CTD.
5. Use a 7/64-in. hex key to remove the two screws at the base of the outer BLIS sleeve (copper tube).
6. Remove the outer BLIS sleeve by pulling straight up with a minimum of twisting.
7. Clean the BLIS module (black plastic housing attached to WQM) with fresh water and a rag to remove all sediment and loose material. Inspect the intake and rinse it gently with fresh water if you see debris in the intake.
8. Clean the BLIS cap and outer sleeve with fresh water and a rag to remove all sediment and loose material. These parts must be clean to protect the BLIS intake during reassembly. Firmly attached corrosion (i.e. patina) is ok. Flaking corrosion must be removed with Scotch-Brite.
9. Connect the WQM to the host PC and establish communication with the host software. Supply

power to the WQM: it will automatically begin collecting data. Select “Stop WQM Sample” and enter Standby Mode.

10. In WQMHost program select “Troubleshooting” from the Help Menu and then “BLIS Testing” to display the tab below.

11. Fill the bleach intake port with water. Command the pump to inject 300 squirts (150 seconds at 2 Hz). The intake should be emptied before the pump stops.

12. Reassemble the outer sleeve to the base of the BLIS. The slot in the sleeve must line up with the little tube between the BLIS and the CT-DO sensor head. Secure the outer sleeve to the BLIS base. Install the two 6-32 x 3/8-in. screws using the 7/64-in. hex key.

13. Slide the clamp over the CT guard and the BLIS sleeve into position, approximately as shown. Use the 5/32” hex key to snug up the screw. Do not overtighten. Install the BLIS end cap: Install the BLIS end cap to keep the parts together and to keep the BLIS intake clean.

**COMPLETE THIS STEP (ABOVE) IF THE WQM WILL NOT IMMEDIATELY BE RETURNED TO SERVICE.**

## C-6 WQM data transfer SOP

Allows real-time viewing of selected parameters from the WQM Data area (left side of window) or the View Data Setup (see Fig C-6-1 below). Plotted parameters can be changed on-the fly.

Figure C-6-1 WQM Data Transfer screen.



Select **Advanced** menu, then **Show Output Controls** (right). With the meter in Standby, select or deselect parameters, then select **Send Output Configuration** to the WQM. The new parameters will be displayed in the WQM Data area and the legend. Either or both can be hidden or displayed. Both show current output values for each parameter. **Scroll Data** allows you to view real-time raw data according to the parameters selected in the Output Controls tab of the host program.

Options in this tab allow you to select the data files to be uploaded from the WQM to the host PC.

Get WQM Directory Displays a list of files saved on the WQM.

Select one or more and allows you to manage data files.

Opens a window to allow you to select the location on the host PC to which the WQM's internal files will be saved.

Cancels any download in progress.

**Select Download Folder:** Brings up a window for you to select or create a folder in which the .raw WQM files will be stored.

**Download WQM Files:** Saves the selected .raw files to the previously selected download folder.

**Erase WQM Files:** Selected files will be deleted from the WQM memory.

**Cancel Download:** Halts the process of saving .raw files. The host will save all of any file being saved when “cancel” is selected and any remaining, unsaved files will remain selected but will not be saved.

**Advanced File Processing:** After downloading (saving) files to the host PC in the WQM Files tab, you can select various derived parameters for the WQM Host program to calculate as part of the processed file.

## C-7 YSI SONDE maintenance SOP

### Sonde Calibration

Water Saturated Air



- ☐ Completely unscrew plastic cover.
- ☐ Remove sponge and add a small amount of de-ionized water. (Always Available @ the lab)
- ☐ Make sure water is fresh and clean.
- ☐ Remove any H<sub>2</sub>O droplets by gently shaking probe before calibration.
- ☐ Rest SONDE on top of the plastic cover threading allowing air to vent.
- ☐ Wait 5-10 minutes to allow saturation.
- ☐ Run SONDE. Allow temperature and Dissolved Oxygen readings to stabilize.
- ☐ Go to SONDE Menu
- ☐ Select Calibrate
- ☐ Select Calibrate Dissolved O<sub>2</sub> %
- ☐ Barometric pressure is calculated automatically. Press Enter
- ☐ Wait for DO% to stabilize at 100.0%, then press calibrate.
- ☐ Select continue.
- ☐ SONDE should be calibrated every day before using.
- ☐ Does **not** need to be calibrated in between readings or after power is shut off.
- ☐ When finished using the SONDE, fill clear plastic cover halfway with de-ionized water and attach SONDE. Gently shake the unit to rinse off all the sensors.
- ☐ DO membrane should be replaced every two weeks.

The YSI 6600-V2 requires proper storage and handling to continue to function and prevent damage. Store the YSI Sonde in its protective case when not in use and when transporting. Cables should not be wrapped tightly or against the wires natural bend, and should be wrapped up according to its natural bend around the wire hook found in the case. The YSI while in use should have a bucket of water used to leave probes in while not being used.

SONDE Calibration Requirements:

pH  
Conductivity  
DO  
Water Saturated Air  
O2  
Turbidity

O2 Sonde Calibration: Water Saturated Air

Completely unscrew plastic cover (Calibration Cup) and inspect gasket.  
Remove sponge and add a small amount of deionized water. (Always Available at the lab).  
Make sure water is fresh and clean.  
Remove any H2O droplets by gently shaking probe before calibration.  
Rest SONDE on top of the plastic cover threading allowing air to vent.  
Wait 5-10 minutes to allow saturation.  
Run SONDE. Allow temperature and Dissolved Oxygen readings to stabilize.  
Go to SONDE Menu.  
Select Calibrate.  
Select Calibrate Dissolved O2 %.  
Barometric pressure is calculated automatically. Press Enter.  
Wait for DO% to stabilize at 100.0% Then press calibrate.  
Select continue.  
SONDE should be calibrated every day before using.  
Does not need to be calibrated in between readings or after power is shut off.  
When finished using the SONDE, fill clear plastic cover halfway with deionized water and attach SONDE. Gently shake the unit to rinse off all the sensors.  
DO membrane should be replaced every two weeks.

pH Sonde Calibration

Two point pH value (7 & 10) Standards.  
Completely unscrew plastic cover (Calibration Cup) and inspect gasket.  
Remove sponge and add a small amount of deionized water. (Always Available at the lab).  
Make sure water is fresh and clean.  
Clamp upright – use 300 ml of standards  
Remove any H2O droplets by gently shaking probe before calibration.



### Turbidity Sonde Calibration

YSI 6073 Turbidity Standard.

Use only a plastic cover (Calibration Cup) with a black end.

Remove sponge and add a small amount of deionized water. (Always Available at the lab).

Clamp upright – use 180 ml of 6073 Turbidity Standard.

Replace Calibration Cup until only one thread is engaged

Run SONDE. Allow temperature and Dissolved Oxygen readings to stabilize.

Go to SONDE Menu

Select Calibrate. Then; next menu: 8-Optic T-Turbidity

Wait for Turbidity to stabilize at 126 NTU. Then press calibrate.

Select continue.

SONDE should be calibrated every day before using.

### Conductivity (Salinity) Sonde Calibration

LaMatte 58640  $\mu\text{S/cm}$  Standard

Completely unscrew plastic cover (Calibration Cup) and inspect gasket.

Remove sponge and rinse with a small amount of deionized water. (Always available at the lab).

Make sure water is fresh and clean.

Clamp upright – use 425 ml of standards.

Run SONDE. Allow temperature and Dissolved Oxygen readings to stabilize.

Go to SONDE Menu.

Select Calibrate 1-Conductivity.

From next menu, choose 1-Sp Cond.

Enter the value **58640**.

Wait for Conductivity to stabilize, then press calibrate.

Select continue.

SONDE should be calibrated every day before using.

Remove any H<sub>2</sub>O droplets by gently shaking probe before calibration.

### Chlorophyll Sonde Calibration

LaMatte 58640  $\mu\text{S/cm}$  Standard.

Completely unscrew plastic cover (Calibration Cup) and inspect gasket.

Remove sponge and add a small amount of deionized water. (Always Available at the lab).

Make sure water is fresh and clean.

Clamp upright – use 180 ml of standards.

Remove any H<sub>2</sub>O droplets by gently shaking probe before calibration.

### Depth Sonde Calibration

Relative to ambient air pressure

SONDE should be calibrated every day before using.

Equipment:

In addition, each meter “setup” should be equipped with the following items so that field repairs can be undertaken as necessary:

Extra O2 solution and membrane caps for probe

Extra batteries

Field data sheet

Screwdriver for removing back of meter to replace batteries

Pencil with eraser

### General Sampling Protocol

Record site location on data sheet.

Remove probe from calibration cup or sleeve.

Submerge probe in the water at the site where you are monitoring, as described in your group’s approved SAP. Give the probe a quick shake to release any air bubbles.

For either parameter (DO or temperature), allow the temperature reading to stabilize (at least 15 seconds) before recording the value on the field sheet.

Follow the instructions below measuring specific parameters.

The meter should remain turned on between stations, unless time between samplings exceeds 30-60 minutes. If meter is turned off, the field probe should be stored inside the calibration chamber during transport, sufficient time (5-15 min) should be allowed for warm-up, and the meter should be recalibrated.

## C-8 YSI SONDE Data transfer Vertical Profile SOP

### *Downloading Data:*

YSI data can be uploaded from the YSI SONDE to a PC using EcoWatch.

Turn on handheld, connect to computer with USB cable once powered up.

Open EcoWatch software is on the computer, wait for software to recognize handheld

In Options (gears):

- choose sync with handheld

- In the File Sync section, choose Data Files

**NOTE:** Units of enabled parameters may be changed. Select Options, then Units; select desired units and choose Apply. Currently selected units can now be viewed and exported.

In Data (file folder):

- choose View/Export

- select the desired file to view

- choose the Export Data button (2nd to the right of the file name), data will export to excel

- choose File, Save as, name file CBP#### where #### is the cruise number

- Transfer to the network 6 K:\sci\sci cbp water quality

- lab\FIELD\_YSI\YSI\_DATA\

- Refer to Database Instructions binder, alter and save file as .csv (do not import to database).

Download Data from Sonde to EcoWatch:

Plug Sonde into PC:

On Sonde: Enter Sonde-->file-->upload to PC

On Ecowatch--> Comm--> Click on Sonde -->make sure com1 is selected.

## **C-9- Bathymetry – Ross 960 Running HyPack Software**

### Start Up

- Turn on the converter, the small black box running from the generator to the Ross 960 computer
- Turn on the toggle switch on the side of the Ross 960 computer
- Turn on the secondary monitor

### Wireless Internet Setup

- Turn on the phone, go to settings, tethering and portable hotspot, select “portable wifi hotspot”
- Using the Ross 960 Unit, go to network connections and connect to the WiFi hotspot, the name of the network is foxFi08

### Set Up Second Monitor

- Right click on the desktop, click properties, settings, display, digital
- MONITOR 1- select flat panel option
  - Check box: use this device as primary monitor
  - Check box: extend my windows desktop onto this monitor
- MONITOR 2- Default monitor option
  - Do Not check box: use this device as primary monitor
  - Check Box: Extend my windows desktop

### Running HYPACK

- Desktop, select HYPACK 2012 icon (most recent version)
- Select hardware icon on the toolbar (next to globe and whale icons)
- Check hardware settings:
- Select the globe in the toolbar (Geodesy, for horizontal datum configuration)
- Check to make sure settings are correct:

### GPS Configuration

- From Desktop, select the GPS Configurator icon (responsible for internet GPS Corrections)
- Select the Trimble R8
- Under “Port Settings” select Port 2. we will always be in Port 2 on the R8.
- Under NMEA, select “ADD”, select GGA (lat and long), Port 2, and leave at 1 Hz
- Under NMEA, select “ADD”, select HDT (heading), Port 2, and leave at 1 Hz

### To Begin Measurements

- Open Hypack 2012
- for reference purposes, the folders on the left-hand side of the screen contain the following:
  - raw data files=measurements already taken
  - Edited Data files= processed data which has been corrected
  - Sorted data files = exported files

Line Editor: in HYPACK, click the paper and pencil icon on the toolbar. Select line editor

## Processing Data in HYPACK:

In order for HYPACK to recognize the profile data taken with the Sonde, it must be converted from a *.DAT* file to *.VEL* file. In order to do this you must first export the Sonde data as a *.CDF* in the program EcoWatch. You can then find the *.CDF* file on the server under Cwproj\BayBotm\YSI\_Prof

The next conversion is made using the program CDF 2 VEL which can be found on the HYPACK desktop. Open CDF 2VEL program and open the CDF you want to convert. Click “Process”. The end Result is a *.VEL* file which will allow the HYPACK software to know the density of the water that the survey was conducted in.

Using this file as corrective data, you choose the drop down “Processing” and click the “Single Beam Editor” Click “file and Open to find the raw data files you wish to plot on the map. Choose the “Select All” option. From this menu you can see the category “Sound Velocity Corrections” where you click on the “Choose File” tab. The *.VEL* file you have created will be on the server located in Cwproj\BayBotm\YSIProfiles

Editing- Once the single beam editor is opened, the raw files can be edited. Once the raw file is opened, click “view” and open the “profile window”. This shows the course the boat took as well as a profile view of the information recorded. On the profile view, you can use an eraser and a line editing tool to delete any outliers in the data recorded. Once you are done with editing of the raw data, it can then be saved and is ready for export.

## Exporting From HYPACK

Select “Final Products” and choose the Export function

- Choose the log file you wish to export from the “Edited Files”
- Select “User Defined File”
- Choose Parameters: -Date
- Time
- Sound Velocity Corrected
- Tide Corrected
- Depth Corrected
- X
- Y

Bring File Into ARC

Open a new file in ARC

Select charts from: cw\_proj\baybotm\charts\charts utm

-of these charts, 12352(4), 12352(5), 12352(6), and 12352(7) are relevant to our bays.

In ARC select Tools and click “Add X Y Data”

Select the file you wish to work with.

Set coordinate system

Projected→UTM→WGS84→UTM Zone18N;

Click Add

## **C-10 – Atmospheric Nitrogen Deposition Monitoring: Deposition Collector Construction and Pre-Sampling Procedure**

### **Deposition Collector Construction**

Deposition collectors will be constructed in the lab before deployment in the field. Each collector will consist of a 20 cm diameter funnel attached sequentially to a foam collar, tygon tubing, an HDPE barbed connector, and a tygon ‘O-ring’ seal, and a disposable chromatography column. The foam collar will provide friction between the funnel and the PVC pipe, holding the column apparatus in place. The tygon tubing and HDPE barbed connector provide a transition between the wider diameter of the funnel spout and the column, with the tygon ‘O-ring’ seal preventing leakage of captured rainwater before it reaches the resin column. Poly wool will be placed at the neck of the funnel to prevent debris from entering the resin column. Each disposable column will house 10g of mixed ion exchange resin. Resin will capture ions from the solution that passes through the column. Plastic pieces of this apparatus will be rinsed with double deionized (DDI) water, assembled and placed in reclosable plastic bags for transport to the field. Disposable columns will be packed with a 30 µm pore-size filter at the bottom of each resin column. Six collectors per site will be prepared, in addition to three blanks every 1.5 months, totaling 75 IER columns.

### **Pre-Sampling Procedure**

The resin used for the ion exchange resin collector is a mixed bed anion and cation exchange resin. The cation exchange resin is highly basic with a hydroxy ionogenic group and  $H^+$  as counterion. The anion exchange resin is highly acidic with a quaternary amine ionogenic group with  $OH^-$  as counterion. The resins will be prepared by rinsing 1 L batches of resin with three bed volumes (approximately 3 L) to remove both excess NaOH and ‘fines’ (broken resin beads). 10g of resin will then be poured into each disposable column. Columns will be filled to 20 mL with a slurry of ion resin in DDI water, and air pockets will be eliminated from the resin bed. Resin columns will be protected from heat and light exposure by storing them in a cool, dark location before deployment to the field.

A total of six throughfall collectors will be placed at twelve field sites located across the study area. Three throughfall collectors which will be placed under canopy at least 1 m apart to provide replication and to capture spatial heterogeneity beneath the canopy at each site. Another set of three throughfall collectors will be placed in an open area (i.e. no canopy) at least 1 m apart at each site. In the field, a 1m section of PVC pipe (1.5 inch outer diameter) will be driven into the ground and a hole will be drilled just above ground level to allow for adequate drainage of precipitation from the pipe. Each collector will be set on top of the pipe so that funnel portion of

the collectors are each 1 m above ground. Resin columns, prepared in advance, will be lowered into the pipe with the funnel seated on top of the pipe. To prevent saturation of the resin beads with captured ions, we will replace the resin columns at least once every three months for one year (planned replacement ins every 1.5 months). The resin columns will be transported back to Hofstra University for extraction.

## **C-11 – Atmospheric Nitrogen Deposition Monitoring: Lab Protocols for Preparing Columns and Extractions**

Adapted from Templer Lab Protocol, 2007 (used by Raciti and colleagues in Rao et al. 2014)

### **Phase 1: Prepare Resin Columns**

#### **Materials:**

Dowex Monosphere MR-3 UPW Mixed Ion Exchange Resin BioRad Econo-Pac disposable chromatography columns (20mL capacity) Plexi-glass column holder Millipore (aka double de-ionized water [DDIW]) Filter replacement tools (unbent paperclip, forceps, plunger small enough to fit in columns – all \ wiped with a Kimwipe and 70% ethanol)

#### **A. Load columns with resin**

1. Rinse 1 L batches of resin with 5 bed volumes (5 L) of double de-ionized (DDI) water (minimum 18.1 mega-Ohm resistance) to remove 'fines' (broken beads of resin). The mixed resin we get is considered non-hazardous and so, the water it gets rinsed with can be poured down the drain as long as it is within the correct pH limits that the NYS DEC stipulates. DO NOT POUR RESIN BEADS DOWN THE DRAIN!!
2. Set up the columns in the plexi-glass column holder with the buckets underneath.
  - a. Make sure that all tools have been cleaned with ethanol.
3. Replace 0.125”-thick, 30 micron pore-size filter at bottom of column (as comes with at purchase) with the 0.250”-thick, 30 micron pore-size filter that ships with the column. Use an unbent paper clip (wiped with 70% ethanol) to poke the original filter out. With forceps, place new filter on top of column and then use the plunger to push it all the way to the bottom of the column. It is thought that the thick filter plugs less easily. Preferably, the filters would have a pore-size of 200-350 microns.
4. Fill columns just past 20 mL (the resin will settle during washing) with a slurry of the mixed resin in DDI, taking care to eliminate air pockets from the resin bed.
  - a. The mixed resin is more difficult to work with than resin that is either just anion or just cation. You must make sure that the slurry entering each column has an even mixture of anion beads and cation beads. The anion beads tend to be lighter than the cation ones, so they will float to the top of the slurry.



b. Use a one-liter beaker and fill it with your washed mixed resin. Use a utensil to stir the resin and get a homogenous mixture of resin types (preferably a plastic utensil so you do not scratch the glass beaker).

c. Once you have a homogenous mixture you can start pouring the resin columns

d. Keep mixing while you are pouring to ensure that what you are pouring remains as homogenous as possible

e. You want to fill column up to bottom of bell without any air bubbles. If you have bubbles you can shake back and forth with top and bottom cap on to release it. Resin settles out of water fairly quickly so you can see your bed volume easily after you let it settle. It is best to fill a bunch and then pour out as needed. If you need to pour resin out of the column, you must make sure to mix it around a bit so that you are not just pouring out the lighter anion beads.

5. Fill to top of bell with DDI and cap the top and bottom of the column.

6. Prepped and capped columns should be stored in the fridge (4C) in a closed container (horizontally in a Tupperware container is fine) and should also be protected from light exposure.

## **Phase 2: Washing collector components**

### **A) Wash funnels**

\*\*\* ALWAYS handle the funnels using clean latex/nitrile gloves\*\*\*

1. If funnel is dirty from the field, give it a pre-wash by wetting it, brushing off gunk (a new toothbrush or bottlebrush works well), and rinsing it three times with DI water. If funnel is new or otherwise reasonably clean skip to step 2.

2. Soak (submerge) the funnels in DI water overnight. Use a large Rubbermaid or other plastic container with a lid that has been washed and rinsed thoroughly and is dedicated to soaking clean equipment. It's best to fill the container with water first to avoid getting air bubbles inside the funnels so all surfaces are actually being soaked.

3. Rinse the funnels with DI water. For each funnel, rinse the inside of the funnel 3X, and rinse the outside 3X, being sure to contact all of the surface area.

4. Air-dry the funnels on paper towels in a clean (non-dusty) area. 5. Stack the funnels inside of new clear garbage bag and inside a heavy-duty garbage bags, for transport to the field.

## B) Wash other collector components

1. Procedure for connector pieces (sections of Tygon tubing, HDPE connector, Tygon “donut”) is essentially the same as for funnels, but much less cumbersome since these pieces are more compact

2. Soak new Poly-wool (a.k.a. polyester fiberfill) in double de-ionized water (DDIW) overnight and then rinse a couple times with DDIW. Form poly-wool into small balls (~3/4 in. diam.) and place in a small, clean recloseable plastic bag. Resin Column Lab Protocol; Templar Lab, last updated August 3, 2007

## **Phase 3: Assemble collector components and pack gear for the field**

A) Pre-assemble funnels and connector pieces (see figure C-11-1 showing collector design) Do as much pre-assembly of the collectors as possible, to help reduce contamination of clean parts and speed things along in the field. Remember to use clean latex/nitrile gloves and take great care to avoid contamination whenever touching inner surfaces of the sampler.

1) At one end of the black HDPE connector, connect the ~3 in. long Tygon tubing so that it covers all four barbs (i.e., provides a good seal). At the other end, slip-on the thicker-walled Tygon ‘donut’.

2) Soak poly-wool (a.k.a. non-cotton pillow fiberfill) overnight in DDI water (to leach out any contamination). NOTE: This step was mentioned in an above section as well.

3) Squeeze out excess water using gloved hands, rinse the polywool in DDI a few times, squeeze out the excess water once more, and form poly-wool into small (~3/4 in. diam.), loose balls that are just big enough to avoid slipping down the neck of the funnel. IF THE POLY-WOOL PLUG IS TOO LARGE OR DENSE IT MAY PLUG UP THE FUNNEL NECK, CAUSING THE FUNNEL TO OVERFLOW AND RUINING THE SAMPLE.

4) Put a supply of poly-wool balls into a clean reclosable plastic bag, making sure to take lots of extras.

## B) Prepare resin columns

1) Load plastic columns with ion exchange resin, as described in lab protocol.

2) Label columns with site, collector number, period number and dates of field exposure.

C) Prepare components that support funnel and resin column

- 1) Cut plastic pipe to 1m lengths and drill a small hole about 1/4 to 1/3 of way up the pipe to allow water fluid to drain out in the event that it can't escape out bottom of pipe
- 2) Cut foam pipe insulation into ~ 2" lengths for use as "collar" to stabilize funnel on pipe

D) Pack gear

- 1) tools for pounding pipes into ground:
  - a) engineer's hammer (aka mini-sledge)
  - b) pipe pounder (metal plumbing flange that goes over the pipe, so it isn't destroyed when being pounded into the ground)
- 2) tools for measuring landscape features at throughfall collector location
  - a) compass
  - b) GPS
  - c) clipboard, pens, data sheets
  - d) dbh tape
- 3) funnel assemblies constructed above
- 4) resin columns loaded above
- 5) plastic pipe, rebar, and foam collars used to support funnel
- 6) DDI water squirt bottles to rinse funnel assemblies, etc. if necessary
- 7) carboy of DDIW for emergency cleaning needs
- 8) first aid kit and cell phone

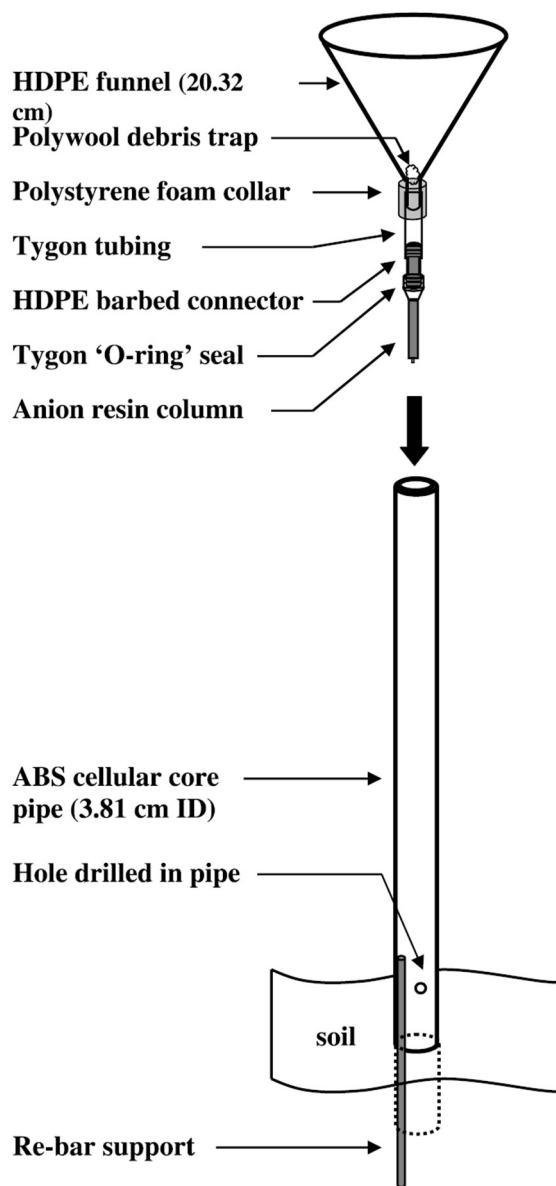


Figure C-11-1. Design view of mixed ion exchange resin sampler (adapted from Simkin et al. 2004)

#### **Phase 4: Sample throughfall**

##### **A) Installing bagged collectors in the field.**

- 1) The clean funnels should be transported to field sites inside of a heavy-duty resealable bag inside a back-pack. Take care not to squash the funnels, and do not let twigs puncture the reclosable bags inside.
  - 2) If you have not done so already, connect the funnel to the long Tygon end of HDPE connector assembly. If you can't get a good grip on the funnel neck, you may have to resort to pressing against the funnel rim (but only with your hand outside the plastic bag or using a gloved hand).
  - 3) Use clean plastic tweezers to place a poly-wool ball in the top of the funnel neck (keep tweezers in clean plastic bag when not in use).
  - 4) The new resin columns should be transported using a protective container (e.g. Tupperware containers). The column tip and cap seal the column; so individual bagging is not necessary.
  - 5) Remove the cap from the new resin column.
  - 6) REMOVE THE YELLOW TIP from the bottom of the resin column and let excess water drain. THIS STEP IS EASY TO FORGET AND WILL RESULT IN A RUINED SAMPLE.
  - 7) Connect Tygon donut end of HDPE connector assembly to resin column. It provides a better seal if you first push ONLY the Tygon 'donut' in, until it butts against the constriction in the column. THEN push the HDPE connector in, until at least three barbs of the connector are covered.
  - 8) Slip a foam collar around the funnel neck and then push the resin column and connector components into the pipe until the funnel bumps against the top of the pipe. Make sure the foam collar is snug, which keeps the funnel upright and stable.

##### **B) Collector deployment/unveiling.**

- 1) So far the collector deployment and collection processes have never been spoiled by a pattern destroying rain event. If a rain event occurs during the initial collector deployment, continue deploying collectors quickly. A dry canopy will take a little

while before it becomes rain saturated enough to begin throughfall. Be very careful not to contaminate a sample by letting rain drip from you, your hat, or your hands when you are working over the funnel! If there is heavy rain, which usually does not last very long, hang out a bit and hope it's over soon. C)

C) Sample collection / resin column change-out.

1) Remove funnel assembly from pipe and gently disconnect resin column from Tygon donut, **TAKING CARE NOT TO SPILL RESIN BEADS FROM THE COLUMN.**

2) Inspect Tygon donut, HDPE connector, long Tygon tube, and poly wool ball for stray resin beads and rinse back into resin column with DI squirt bottle if necessary.

3) Also rinse beads from the upper bell of the resin column down into the column itself to ensure that the column cap will have a good seal.

4) Push on a column cap, ejecting the majority of the column's fluid **OUT THE BOTTOM OF THE COLUMN** (This will help avoid bacterial/microbial growth as well as push your sample through the column). The cap can be removed and replaced several times to eject more fluid if the first does not eject the majority of it.

5) Push on a yellow column tip. (A spare column cap and tip from a clean, empty resin column can be used here, and then replaced with the column cap and tip from the new resin column)

1) Remove funnel, tygon tubing and column as a single unit by disengaging it from the PVC/foam collar grip. Replace this combination with a new apparatus.

2)6) Make sure that the label on the old column is clearly legible, attached, and correct, and then place in protective container. (Although columns should be clearly labeled with the appropriate sample period, the just-collected columns with sample should be kept separate from the new columns about to be installed to avoid confusion).

3)7) Visually inspect the inside of the funnel for crud. Spot-wipe using a kimwipe and tweezers, rinse the tweezers with DI squirt bottle, and then install a new poly wool ball.

8) Replace the upper Tygon tubing, the HDPE connector, and/or the Tygon 'donut' if they have microbial growth on them, or if they have worn-out such that they will no longer provide a good seal. In our previous experience, this is necessary every 3 months.

9) Install new columns using the same procedure used in the initial deployment

10) Exchanging old columns for new columns will be more challenging to complete within the necessary rain-free window of opportunity.

## **Phase 5: Extract resin samples with 2 M KCl in the lab**

### **Materials**

Mixed ion-exchange resin columns (samples and blanks)

2.0 M KCl (150mL for each sample)

Bottle-top dispenser for 2 M KCl (set to 50mL)

Reservoir bottle for KCl solution (fitted with bottle-top dispenser)

Millipore (aka double de-ionized water [DDIW] – minimum 18.1 megaOhm resistance)

150 ml Extraction cups and lids

Extraction composite bottles- 250mL Nalgene

Shaker table (with capacity for at least 24 extraction cups)

Plexi-glass column holder and 2 Fischer catalogs

Small rectangular buckets to capture the DDIW from hydration

### **A. Extraction Prep**

1. Generate an extraction worksheet listing all of the resin column samples to be extracted that day. On this sheet, you should indicate the date, the start and stop times for each extraction, and make note of any problems encountered.
2. Pre-label extraction cups and composite bottles with the sample names from the extraction worksheet.
3. Clean work surface with DDIW.
4. Verify that the sample names on the extraction worksheet match those on the resin column samples. Place the resin columns on the plexi-glass rack in order from low to high sample number. Place a Fischer catalog or other thick and sturdy support, under each end of the rack and tape in place to achieve the correct height. Place the rectangular buckets under the rack to capture drainage from the columns.

5. Remove the top cap and saturate resins in resin column with DDIW for at least 15 min before extraction. Use a squirt bottle to fill the columns with DDIW. This 'hydration' step 'flexes' the resin polymer into a regular shape, thereby making all exchange sites on resin beads accessible to the KCl solution during the following steps. The bottom yellow cap of the column may need to be loosened in order for the DDIW to reach the bottom of the column; tighten the cap when DDIW fills the entire column.
6. Fill labeled extraction cups with ~50 mL of Nanopure water. Rinse the resin from its column into the matching extraction cup by pouring small amounts of the Nanopure water back and forth between the extraction cup and the resin column. Make sure that all of resin beads and Nanopure water end up in the extraction cup. After resin transfer is complete, remove yellow tip from column so that it can gravity drain and air dry. Later, tap column to remove any drops that have collected at bottom of column.
7. Rinse the resin with Nanopure to remove organic debris. First, decant the ~50 mL of Nanopure used in step # 6. Add ~50 mL more Nanopure to the resin in the extraction cup, then decant the liquid. Do Not allow any resin beads to float out with the rinse water. If you have floating resin beads, decant the rinse water through the original resin column, such that any beads will be trapped and can be recovered. If necessary, repeat the rinsing process. Although you don't want to spill resin beads, you do want to pour off as much of the water as possible in the last rinse, and keep the amount of residual water left in each extraction cup as consistent as possible.
8. Fill the reservoir bottle with 2.0 M KCl solution. Attach the bottle-top dispenser and set the dispense volume to 50ml. 'Prime' the unit by switching the lever to 'recycle mode' and pumping until all air is purged from the unit. Turn the lever back to 'deliver mode'. Pump about 10ml KCl through the delivery tube to get rid of any air bubbles in the tubes. If the dispenser has not been used recently, confirm that the delivery volume is 50 mL by dispensing into a dry 50 mL volumetric flask.

## B. Extraction Procedure

1. Extract the resin columns in batches of 20 (or whatever number of samples you can process within the 30min required for each extraction).
2. Draw 50mL of KCl into the bottle-top dispenser chamber by raising the pump using a single, even motion. Then depress the pump all the way to the bottom using a single, even motion, thereby dispensing 50 mL of 2.0 M KCl into labeled extraction cup.
3. Transfer the extraction cup containing resin and 50 ml KCl to the shaker table (set to ~120



RPM the solution should swirl in the cups, not slosh)

4. Shake for 30min (on the extraction sheet write down the time that you placed the first extraction cup on the shaker table). The shaking helps to break up any clumps of resin and promotes desorption of analyte ions. For 20 samples, if you spend about a minute dispensing each 50 mL of KCl, then all 20 extraction cups will be on the shaker table in about 20 minutes, giving you 10 minutes to do other stuff such as add labels to bottles. If you dispense much faster than this, then you may fall behind during the 2nd and 3rd extractions.
5. After 30 min., begin removing extraction cups from the shaker table in the same order that you put them on, keeping an eye on the clock to make sure that you are maintaining an even pace so that all cups are shaken as nearly precisely to the desired 30 minutes as possible. Decant the 1st resin extract through the matching filter/funnel setup and into the matching 250 mL extraction composite bottle. Try to prevent resin bead transfer from the extraction cup to the filter as much as possible.
6. Repeat this extraction process 2 more times (Three 50 mL extractions in total).
7. Cap and vigorously shake each 250 mL extraction composite bottle to insure full mixing and then store bottles in clearly labeled flats in a dark, refrigerated place (4° C).
8. Make sure to keep a KCl blank to be run with samples.

### C. Cleaning Procedure

1. Using DDIW, rinse out all resin from extraction cups into a hazardous waste container.
2. Rinse out all resin from columns into a hazardous waste container and clean columns.
3. Wash extraction cups (following lab washing procedures) and clean off all areas that may have come into contact with resin. Be careful to clean up all resin as soon as possible since it spreads easily if it is not cleaned up quickly.

## Appendix D. Data Forms, Checklists, and Chain of Custody Forms

### D-1 Calibration Datasheets

#### D-1.1 Calibration Documentation Form – YSI SONDE

Calibration Log Sheet for YSI SONDE					
Date	Who calibrated?	Parameter	Calibration Settings	Calibration Status (Success/Failure)	Notes

**D-1.2. WQM Calibration Documentation Form**

Calibration Log Sheet for SeaBird & WetLabs Long Term deployment instruments							
Date	Ser #	Who calibrated?	Pre or Post deployment	Parameter	Calibration expectation	Calibration result	Notes



### D-2.2.a. Tributary Data Form (Old Version – for hand-held YSI only)

### Tributaries: YSI Meter Readings

Air Temp(c):

Location:

Tide:

Documenter:

[illegible]

Marine Biological Laboratory  
Tributary Data Sheet[illegible]


Samples Examined By (Name not initials):	Date Examined:	Time Examined: (lab processing began)
Chemistry by (initials):	Process Controls (initial):	PASS: FAIL:
Data entry by (Name not initials):	Temperature Controls (Chem):	Date/Time/Initials: (°C)
Data for analysis (Circle)	UNACCEPTABLE	Date/Time/Initials: (°C)

## **Field Data Sheet**

- Calibrate Sonde for pH and % oxygen saturation
- Make sure previous data files were uploaded to ensure sufficient memory use
- Record field data before beginning data collection
- Upload YSI data after each use.
- Rinse Sonde with Deionized water after each use.

<b>Date:</b>	<b>Time In/Time Out:</b>
<b>Biologists:</b>	<b>Vessel:</b>
<b>Weather:</b>	<b>Air Temp:</b>
<b>High Tide Jones Inlet:</b>	<b>Location:</b>
<b>Project:</b>	
<b>Comment:</b>	
<b>File Name:</b>	
<b>File Export Location:</b>	
<b>Raw Data Location:</b>	
<b>Back-Up Location:</b>	
<b>Microsoft Access Day ID #:</b>	

Rev. 8/16



NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION  
BUREAU OF FISH, WILDLIFE & MARINE RESOURCES  
BAY SURVEY

AREA NO.      BAY      DATE COLLECTED      BY (Name, not initials)

LAB NO.

BTL NO.

STA NO.

TIME

FC MPN/100mL

SALINITY(000)  
SURFACE      BOTTOM

WATER TEMP °C  
SURFACE      BOTTOM

WATER DEPTH (FEET)

REMARKS

70743 Certified  
70747 Emergency  
70745 Cond/Seas

TIDE

0 24 48 72  
/ / / /

SAMPLES EXAMINED BY (Name, not initials)

DATE EXAMINED

TIME EXAMINED  
(Incubation begun)

READINGS BY (Initials)

PROCESS CONTROLS  
(Circle & Initials)

PASS

FAIL

COMPUTATIONS BY (Initials)

TEMPERATURE CONTROL

DATA USABLE FOR ANALYSIS: (Circle)

ACCEPTABLE

UNACCEPTABLE

COLD ROOM TEMPERATURE (Include d.

°C



### D-3. Vertical profiles Field Sheet

## Field Data Sheet

- Calibrate Sonde for pH and % oxygen saturation
- Make sure previous data files were uploaded to ensure sufficient memory use
- Record field data before beginning data collection
- Upload YSI data after each use.
- Rinse Sonde with Deionized water after each use.

<b>Date:</b>	<b>Time In/Time Out:</b>
<b>Biologists:</b>	<b>Vessel:</b>
<b>Weather:</b>	<b>Air Temp:</b>
<b>High Tide Jones Inlet:</b>	<b>Location:</b>
<b>Project:</b>	
<b>Comment:</b>	
<b>File Name:</b>	
<b>File Export Location:</b>	
<b>Raw Data Location:</b>	
<b>Back-Up Location:</b>	
<b>Microsoft Access Day ID #:</b>	


# D-4 Chain of Custody Form – Chlorophyll, In-House Lab (Generic EPA example)

## CHAIN OF CUSTODY RECORD

WORK ORDER #:  
 CUSTODY No:  
 PROJECT:  
 SAMPLED BY:  
 LOCATION:

SAMPLE NUMBER	DATE	TIME	SAMPLE LOCATION	MATRIX	COMPOSITE OR GRAB	FIELD MEASUREMENT	No. OF CONTAINERS	ANALYSIS REQUIRED				REMARKS (PRESERVATION, ETC.)
RELINQUISHED BY: (Signature)	DATE:	TIME:	RECEIVED BY: (Signature)	DATE:	TIME:	RELINQUISHED BY: (Signature)	DATE:	TIME:	RECEIVED BY: (Signature)	DATE:	TIME:	
RELINQUISHED BY: (Signature)	DATE:	TIME:	RECEIVED BY: (Signature)	DATE:	TIME:	RELINQUISHED BY: (Signature)	DATE:	TIME:	RECEIVED BY: (Signature)	DATE:	TIME:	
RELINQUISHED BY: (Signature)	DATE:	TIME:	RECEIVED BY: (Signature)	DATE:	TIME:	RELINQUISHED BY: (Signature)	DATE:	TIME:	RECEIVED BY: (Signature)	DATE:	TIME:	
RELINQUISHED BY: (Signature)	DATE:	TIME:	RECEIVED BY: (Signature)	DATE:	TIME:	RELINQUISHED BY: (Signature)	DATE:	TIME:	RECEIVED BY: (Signature)	DATE:	TIME:	
RELINQUISHED BY: (Signature)	DATE:	TIME:	RECEIVED BY: (Signature)	DATE:	TIME:	RELINQUISHED BY: (Signature)	DATE:	TIME:	RECEIVED BY: (Signature)	DATE:	TIME:	

## D-5 Chain of Custody Forms – External Lab: Pace Analytical CoC 2018

 <b>CHAIN-OF-CUSTODY Analytical Request Document</b> Chain-of-Custody is a LEGAL DOCUMENT - Complete all relevant fields Billing Information:		LAB USE ONLY - Affix Workorder/Login Label Here or List Pace Workorder Number or MTL Log-in Number Here <b>ALL SHADED AREAS are for LAB USE ONLY</b>											
Company:		Container Preservative Type **											
Address:		Lab Project Manager:											
Report To:		** Preservative Types: (1) nitric acid, (2) sulfuric acid, (3) hydrochloric acid, (4) sodium hydroxide, (5) zinc acetate, (6) methanol, (7) sodium bisulfate, (8) sodium thiosulfate, (9) hexane, (A) ascorbic acid, (B) ammonium sulfate, (C) ammonium hydroxide, (D) TSP, (U) Unpreserved, (O) Other											
Copy To:		(C) ammonium hydroxide, (D) TSP, (U) Unpreserved, (O) Other											
Customer Project Name/Number:		Lab Profile/Line: Lab Sample Receipt Checklist: Custody Seals Present/Intact Y N NA Custody Signatures Present Y N NA Collector Signatures Present Y N NA Bottles Intact Y N NA Correct Bottles Y N NA Samples Received on Ice Y N NA VOA - Headspace Acceptable Y N NA USDA Regulated Soils Y N NA Samples in Holding Time Y N NA Residual Chlorine Present Y N NA Cl Strips: Y N NA Sample pH Acceptable Y N NA pH Strips Present Y N NA Sulfide Present Y N NA Lead Acetate Strips: Y N NA LAB USE ONLY: Lab Sample # / Comments:											
State: / County/City:		Time Zone Collected: <input type="checkbox"/> PT <input type="checkbox"/> MT <input type="checkbox"/> CT <input type="checkbox"/> ET											
Email To:		Compliance Monitoring? <input type="checkbox"/> Yes <input type="checkbox"/> No											
Site Collection Info/Address:		DW PWS ID #: DW Location Code: Immediately Packed on Ice: <input type="checkbox"/> Yes <input type="checkbox"/> No											
Turnaround Date Required:		Rush: <input type="checkbox"/> Same Day <input type="checkbox"/> Next Day <input type="checkbox"/> 3 Day <input type="checkbox"/> 4 Day <input type="checkbox"/> 5 Day (expedited charges apply) Field Filtered (if applicable): <input type="checkbox"/> Yes <input type="checkbox"/> No Analysis:											
Sample Disposal:		* Matrix Codes (Insert in Matrix box below): Drinking Water (DW), Ground Water (GW), Wastewater (WW), Product (P), Soil/Solid (SU), Oil (OL), Wipe (WI), Tissue (TS), Bioassay (B), Vapor (V), Other (OT)											
( ) Dispose as appropriate ( ) Return ( ) Archive: ( ) Hold:		Customer Sample ID Matrix * Comp / Grab Collected (or Composite Start) Date Time Date Time Composite End Res Cl Cms											
Customer Remarks / Special Conditions / Possible Hazards:		Type of Ice Used: Wet Blue Dry None Packing Material Used:											
Relinquished by/Company: (Signature)		SHORT HOLDS PRESENT (<72 hours): Y N N/A Lab Tracking #:											
Relinquished by/Company: (Signature)		Lab Sample Temperature Info: Temp Blank Received: Y N NA Therm ID#: Cooler 1 Temp Upon Receipt: oC Cooler 1 Therm Corr. Factor: oC Cooler 1 Corrected Temp: oC Comments:											
Relinquished by/Company: (Signature)		Samples received via: FEDEX UPS Client Courier Pace Courier Date/Time: Date/Time: Date/Time: Date/Time:											
Relinquished by/Company: (Signature)		Table #: Actnum: Template: Prelimin: PM: PB:											
Relinquished by/Company: (Signature)		Trip Blank Received: Y N NA HCL MeOH TSP Other Non Conformance(s): YES / NO Page: of:											

[illegible]

## D-7. Atmospheric Nitrogen Field Data Sheet

Date \_\_\_\_\_ Time \_\_\_\_\_ Field Note Taker Initials \_\_\_\_\_

Site Name \_\_\_\_\_ Site Code \_\_\_\_\_

Notes	Collector 1	Collector 2	Collector 3
Signs of Disturbance to the collectors (if any)			
Densiometer Reading			
Other notes, comments, or concerns			

## **D-8. Field Work Checklists**

### **Water and Atmospheric Deposition Sampling Checklist**

#### **Personal Gear** *(Summer/Winter)*

Drinking water and food/snacks

Sunblock

Sunglasses

Weather Appropriate Clothing (rain gear, warm clothes in winter, waders, raincoats, windbreakers)

Radio

Non Slip Shoes (Boots, Sneakers, etc)

Bug spray

PFD for all crew (for sampling on the boat)

#### **Instrumentation for Water Sampling**

{ } YSI Sonde (Should be calibrated)

{ } Sonde Case (Includes: YSI handheld, extra batteries, extra cables, screw driver)

{ } Cooler(s)

{ } Field Blank

{ } Clipboard (Maps/Field Sheet/Pens/Sharpie)

{ } Radio(s)

{ } Ice (In Coolers)

{ } Pole with Clamps/Grips

{ } Secchi Disk

{ } Keys (Boat/Car)

{ } Bucket (to be filled with water on bay)

{ } Extra bottles (In case of breakage/loss/contamination)

{ } 2 liter Nalgene/Kremmeren Bottles

{ } Van Dorn

#### **Disembarking Procedure for Water Sampling:**

{ } Load boat with supplies

{ } Unlock and secure cabin door

{ } Check oil gauge

{ } Check Gas Tank (Minimum  $\frac{3}{4}$  tank before sampling, check the day before)

{ } Turn back switch (starboard, back battery) to **ALL** (8 Boat)

- { } Turn on the console switch in cabin to **ON** (8 Boat &32)
- { } Lower Engine
- { } Turn on the engine
- { } After engine is **ON**, and in water, untie lines
- { } Untie **BOW** and **STERN** lines at Captain's discretion (will change based on day/slip/weather)
- { } Secure lines to cleats on boat (do not leave loose lines on boat floor)
- { } Take in fenders
- { } Disembark to **Station 15**

### **Docking Procedure for Water Sampling:**

- { } Untie lines from boat cleat
- { } Put out fenders
- { } Use lines to loop onto the **dock cleat**
- { } Tie cleats with cleat hitch and lock, NOTE, one half turn around base. (see Fig. D-8-1)
- { } Turn the engine **OFF**, and remove key
- { } Once tied to dock securely, **RAISE** engine
- { } Switch cabin battery to **OFF**
- { } Switch battery on starboard and stern to **OFF**
- { } Remove all equipment and instrumentation
- { } Lock cabin door
- { } Load up car
- { } DONE

### **Ready to Sample? **First ask yourself/crew:****

- Is the YSI Calibrated?
- Does the boat have enough gas?
- Does everyone have food/water/protection?
- Is there enough **ICE** in the coolers?
- Have you taken all the necessary equipment?
- Did you take the **FIELD BLANK**?
- Is the field sheet properly filled out?
- Is the **TIDE** at the right time/heights?
- What is today's **WEATHER**?

### **Things to Remember while **Driving Boat:****

Which way is the wind blowing?  
Is the tide FLOOD or EBB?  
Monitor BUOYS and other traffic

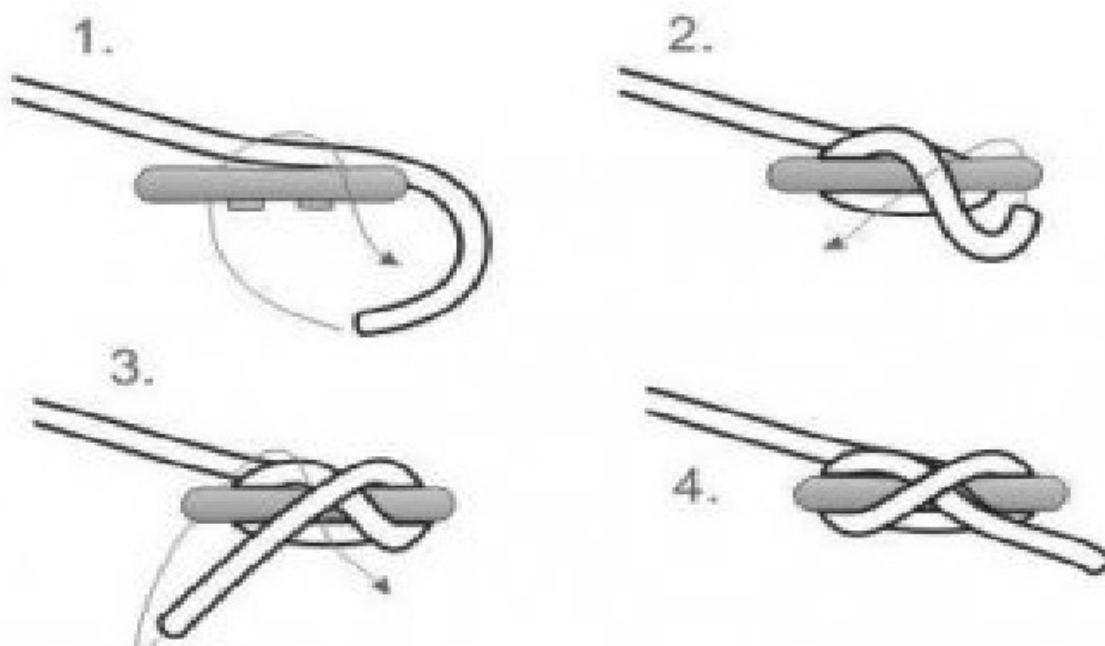
Things to Remember When **Sampling**:

Always write the time of sample  
Do **NOT** touch the rim/inside/or edge of sample bottles  
Open only **ONE** bottle at a time  
Take Temperature Control  
Check that the bottle matches the station assignment  
Water level must be as close to meniscus as possible

**Nitrogen Deposition Field Checklist**

Replacement resin column (and filter paper)  
Cooler with ice  
Clipboard with data sheets and pens  
Polywool  
Densimeter

**Figure D-8-1.** The cleat hitch with lead from left, if lead is from the right then start wraps ½ turn later after going around base as if this image was rotated 180 degrees.





## Appendix E. External Labs – Analytical Methods

### Pace Analytical Laboratories, Long Island, New York DOH - ELAP 10478

575 Broad Hollow Road  
Melville, NY 11747-5076

The Long Island laboratory has been providing full-service analytical testing services to environmental markets for more than 50 years and is a leading testing source for water quality and waste characterization in Long Island and in the metropolitan New York area. Formerly operating as H2M Labs, Inc., Pace acquired the laboratory in December 2013 and is certified under the NYS ELAP program as **Laboratory ID: 10478**.

The Long Island laboratory has specific experience supporting municipal customers and utilities, with unique value-added services such as 24/7 availability for emergency situations, around-the-clock coliform sampling and analysis for municipalities, and a comprehensive database to monitor sample collection frequency to ensure water districts are in compliance with local and state regulations.

Phone: 631.694.3040

Fax: 631.420.8436

**Sr. General Manager:** [Colin Walters](#)

**Quality Manager:** [Diana Losito](#)

#### Major Instrumentation:

- 7 Gas Chromatographs
- 11 GC/MS Systems
- 2 Mercury Analyzer
- ICP/MS Total Organic Carbon Analyzer
- 2 ICP
- 2 HPLC
- Ion Chromatograph
- 2 Autoanalyzer

## Appendix F: In-House Laboratory SOP Documents

### F1. Extraction of Nitrogen from Atmospheric Sample

The extraction of resin columns releases the anions and cations adsorbed to the resin beads back into solution. These extracts can then be analyzed by ion-chromatography (IC) to determine the flux of ions over the period of resin column exposure. Resin extraction will be completed within 24 hours of collecting each batch of resin columns from 15 sites. For resin extraction, we will add 50 ml of 2 M KCl to the 10 g resin beads three times sequentially (a total of 150 ml), shaking the samples gently on an oscillating shaker table for 30 minutes between each 50 ml extraction. KCl is a commonly used resin extractant for N compounds ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ). KCl has been shown to have a nearly complete (98–104%) ion recovery in the first KCl extraction in laboratory tests performed with resin columns that were preloaded with a simulated throughfall solution (Fenn et al. 2002). At the end of each extraction period, the supernatant from the KCl solution will be decanted through the plastic column into a high-density polyethylene bottle, leaving the resin at the bottom of the extraction cup. The second and third extractions will be performed similarly with 50 mL of KCl; all three extractions will be decanted, producing a composite sample of KCl extract solution with a total volume of 150 mL. The final 150ml extractant solution will be gravity filtered with Whatman #1 filter paper through a Nalgene filter housing (Thermo Scientific 300-4000, Nalgene Filter holder with Receiver, PSF, 47mm, 250ml) and stored in a 250ml Nalgene high-density polyethylene bottle.  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations will be determined via ion chromatography.

Three blanks per sampling interval (i.e. every 1.5 months) will be analyzed to determine background contamination levels, if any, within all containers, filters, IER resin material, or extractant solutions. Mixed ion exchange resins and KCl solution can contain trace levels of ions, so blanks will be deployed in the field. Three field blanks, in the form of capped IER columns, will be deployed to a “random” selection of field sites. These columns will remain in the field for the same length of time as the other IER columns. These columns will be transported to the lab and undergo the extraction process of the experimental columns. This is in addition to three blanks that will be generated in the laboratory using all of the same methods, but without field exposure. Finally, three IER columns will be exposed to “simulated rainfall” (i.e. “spiked” DI water with known concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) in order to determine ion capture and extraction efficiency of the collectors. This test of capture and extraction efficiency will be done before the start of the sampling campaign and repeated on an annual basis thereafter and whenever any substantial change is made to methods or materials.

## F-2. Chlorophyll, using EPA Method 446.0

TOH C&W lab SOP includes the use of 0.8 um AAWP Mixed Cellulose Esters Membrane filters (Strickland and Parsons, 1972) and a Perki Elmer Lambda 25 UV/VIS Spectrometer for this analysis.

### Preparing Samples:

- Connect manifold, flasks and vacuum pump with tubing.
- Place one 0.8 um AAWP Mixed Cellulose Esters Membrane filter (Strickland and Parsons, 1972) onto each filter holder, and then tighten funnel
- 1000 mL of sample will be used in total.
- Pour 500 mL of the sample into the funnel (can run three samples at a time, each in its own funnel)
- Turn vacuum pump on, as water begins to filter through add the rest of the sample.
  - NOTE: If water stops filtering through the filter, turn off the vacuum pump and switch the filter. Multiple filters used will be placed into a single falcon tube for a sample.
- Once the sample is done filtering, turn the pump off and remove the filter.
- Fold the filter into eighths, and cut off the white border where no chlorophyll is located.
- Place into 15 mL falcon tube with 5 mL of 90% acetone.
- Shake falcon tube to dissolve filter, and place into fridge (0-4°C). Make sure the test tube rack the falcon tube is placed in the fridge is covered with aluminum foil.
- Leave sample overnight, and prepare it for use with the spectrometer at least a day after filtration.
- Before being used with the spectrometer samples should be spun for at least 20 minutes at 3500 rpm in the centrifuge. The supernatant will be used in the cuvettes.

### Using Spectrometer:

- the Perki Elmer Lambda 25 UV/VIS Spectrometer needs to be warmed up for at least 30 minutes to an hour before use
- Turn off and restart the spectrometer to allow internal recalibration while warm.
- Open program Lambda 25
- Use method titled as the EPA template for 8 spectra. Create copy of method with date in the title (Ex. ep8Nv19).
  - Edit the copy version of the method by deleting stations that are not needed. Include stations that were used as QC points by including Q in the title.
- Place a cuvette of 90% acetone in the spectrometer in the back spot; this will act as a reference.

- NOTE: Wipe sides of cuvette down with kimwipe to make sure the sides are absolutely clean and clear. Replace any scratched or otherwise damaged cuvettes.

#### Determining Chlorophyll a:

- Convert the spectrometer output file into \*.CSV format
- Bring the new data into Chlorophyll\_Calc.R script and run the calculations. This script calculates Chlorophyll a using the Jeffery and Humphrey tri-chromatic equations recommended in the EPA Method 446.0 (Erar 1997) and confirmed as accurate in a UNESCO study (Lorenzen and Jeffery 1980). As a quality check, the absorbance for 750 nm should also be below 0.05 as a QC check for sufficient separation when using the centrifuge and sufficiently clean and clear cuvettes as also recommended by Erer (1997).

#### References:

Erar, Elizabeth J., 1997. EPA Method 446.0; In Vitro determination of Chlorophyll a, b, + c, and phaeopigments in marine and freshwater algae by visible spectrophotometry. National Exposure Research Laboratory, Cincinnati, Ohio 45268. 26pp.

Available at:

[https://cfpub.epa.gov/si/si\\_public\\_record\\_report.cfm?Lab=NERL&dirEntryId=309415](https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NERL&dirEntryId=309415)

Lorenzen, C.J. and S.W. Jeffery, 1980. Determination of chlorophyll in seawater; Report of intercalibration tests sponsored by SCOR and carried out in September-October 1978. UNESCO technical papers in marine science # 35. UNESCO, Place de Fontenoy, Paris, 21pp.

Strickland, J.D.H. and T.R. Parsons, 1972. IV.3 Pigment analysis. p185-192. *in* A practical guide of seawater analysis. Bulletin of Fisheries Research Board of Canada, No 167.

## **F-3.1. Ammonia in Seawater (Astoria-Pacific A026)**

### **Determination of Ammonia in Water Using the Astoria Pacific Segmented Flow Analyzer**

#### 1. SCOPE AND APPLICATION

1.1. Concentrations of ammonia from the method detection limit (MDL), 0.05 ppm to 2.0 ppm in drinking, well and waste waters are determined using an Astoria Pacific Segmented Flow Analyzer. The range may be extended by dilution.

1.2. This SOP is based on Astoria Pacific Method Number A303-S023-A01, ammonia analysis. The EPA Method number is 350.1 (Automated Phenate), the March 1983 revision, as approved at 40 CFR part 136. The tests covered by this SOP are W-NH3 and W-NH3-F.

#### 2. SUMMARY OF THE METHOD

2.1. Samples are analyzed for ammonia using a segmented flow analyzer equipped with an autosampler. The sample is mixed with a complexing agent. Ammonia reacts with alkali phenol, hypochlorite, nitroferrocyanide to form indophenol blue. The analytical stream is debubbled just before it enters the flow cell. The absorbance of indophenol blue at 660 nm is directly proportional to the concentration of ammonia in the sample.

2.2. Interferences: Precipitation of calcium and magnesium hydroxides is eliminated by the addition of a combined potassium sodium tartrate/sodium citrate complexing reagent. Samples that are turbid must be filtered prior to analysis. Also, samples with a background absorbance at the analytical wavelength may interfere.

2.3. Sample preservation and holding time: Samples are preserved with H2SO4 to a pH <2 and kept at four deg C, and must be analyzed within 28 days of collection.

#### 3. APPARATUS AND EQUIPMENT

##### 3.1. Astoria Pacific computer controlled segmented flow analysis system

3.1.1. 301 autosampler: pecking off; sample/wash 30/55 (set from within the sample table using software)

3.1.2. 302 pump: speed 42

3.1.3. 313 analytical cartridge, heater temp. 50 deg. C

3.1.4. 305D detector: range 0.2 AUFS, rise time 3 sec, wavelength 660 nm. The 305D detector contains a 10 mm flow cell. The flow cell size cannot be changed.

##### 3.1.5. pump tubing:

orn/orn: debubbler line

blk/blk: debubbler line

orn/grn: nitroferricyanide

orn/grn: hypochlorite

orn/grn: phenolate

red/red: sample

orn/wht: nitrogen

blk/blk: complexing agent

grn/grn: sample wash

### 3.2. Glassware, bottles and pipettes

Note: All flasks listed are volumetric.

3.2.1. 7-100 mL flasks for working standards

3.2.2. Volumetric pipettes 10.0, 5.0, 2.0, 1.0

3.2.4. 1-200 mL flask for phenolate

3.2.5. 1 amber glass 250 mL reagent bottle

3.2.6. 1-1 L flask for sodium nitroferricyanide

3.2.7. 1-1 L amber Nalgene bottle

3.2.8. 3-500 mL Nalgene bottles for carrier, complexing agent and startup

3.2.9. 2-1 L Nalgene bottles with NaOH solution fume traps for waste

### 3.3. Miscellaneous

3.3.1. spatulas for weighing out reagents

3.3.2. 25 mL graduated cylinder

3.3.3. 100 mL flask

3.3.4. Oxford pipettes 0 - 5 mL, 0 - 10 mL

3.3.5. amber 250 mL glass phenolate reagent bottle

3.3.6. pH paper, 0 - 3.0

## 4. CHEMICALS AND REAGENTS

Note: Before preparing reagents or standards or running samples, please read the safety notes in the safety/hazardous waste section of this SOP and the MSDS about the chemicals used in this analysis.

Note: All reagent preparations should be documented in the Reagent Preparation Logbook.  
Archive the preparation of the standard solution in the Standard Preparation Tracker in the LIMS (Laboratory Information Management System).

4.1. Ammonium Sulfate,  $(\text{NH}_4)_2\text{SO}_4$

4.2. Brij-35, 30% w/v

4.3. Deionized Water, ammonia-free

4.4. Chloroform,  $\text{CHCl}_3$

4.5. Liquefied Phenol, 88%  $\text{C}_6\text{H}_5\text{OH}$

4.6. Potassium Sodium Tartrate,  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$

4.7. Sodium Citrate, Dihydrate,  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$

4.8. Sodium Hydroxide,  $\text{NaOH}$

4.9. Sodium Hypochlorite,  $\text{NaOCl}$  (Household Bleach)

4.10. Sodium Nitroferricyanide (sodium nitroprusside),  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$

4.11. Alkaline Phenol solution:

4.11.1. Place ~700 mL DI water and stir bar in a beaker. While stirring on magnetic stir plate in an ice bath, add 85 mL 10N  $\text{NaOH}$ . When cool add 12mL liquid phenol (phenol is harmful if inhaled or if it

contacts the skin). Allow to stir until thoroughly mixed, approx. 1 min.

4.11.2. Transfer mixture to a 1L flask and QS to mark with DI water. Invert flask 3 times. Transfer immediately to a dark bottle and store at 4 deg. C. This reagent is filtered. A batch of phenolate is used no longer than 1 week and turns darker over time. Before running, check the color of the phenolate. If dark amber it must not be used, if medium or light amber, it may be used. Store in refrigerator. Good ~1 month.

4.12. Hypochlorite

4.12.1. Add 2.5mL Household bleach ( $\text{NaOCl}$ ) to a 100-mL flask. Bring to volume with DI water.

This reagent is made daily and not filtered.

4.13. Sodium Nitroferricyanide

4.13.1. Dissolve 0.5 g sodium nitroferricyanide in ~800mL DI water in a 1 L volumetric flask. Dissolve and then dilute to volume. Filter. Store in amber bottle and stable at least 1 month.

4.13.2. Store in a dark bottle. This reagent is stable for at least one month. Do not filter.

4.14. Stock Complexing Reagent

4.14.1. Dissolve 33g Potassium Sodium Tartrate ( $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ) and 24g Sodium Citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) ~800mL DI water. Using a magnetic stirring bar and pH meter to adjust the pH of the solution to pH5.0 with Conc. Sulfuric Acid.

4.14.2. Transfer to a 1L flask and QS to volume, then filter. Store in refrigerator.

4.15. Working complexing agent: Add 4 drops Brij to every 100 mL of the stock complexing agent. Prepare daily.

4.16. Startup solution: Add 20 drops Brij to approx. 500 mL DI water and stir thoroughly.

4.17. Sample Wash: DI water

4.18. Stock 10 N NaOH: While stirring slowly, add 400 g NaOH to approx. 800 mL DI. Bring to volume in a 1 L flask.

**Caution:** the solution will become hot as sodium hydroxide is added to water. Use a glass lasagne dish containing ice and water to cool the NaOH solution.

#### 4.20. Calibration Standards and Quality Control (QC) Standards:

4.20.1. Stock 1000 ppm  $\text{NH}_3$  as N for the prep of a 100 ppm working stock standard:

Dissolve 4.7168g dried  $(\text{NH}_4)_2\text{SO}_4$  in 800 mL DI water contained in a 1 L flask. Dry ammonium chloride for 1 hour at 110 degrees C., cool in a desiccator. Add 2 drops Chloroform ( $\text{CHCl}_3$ ) and mix well. Store in refrigerator. Holding time is ~1 month.

4.20.2. Working stock and spiking solution, 100 ppm:

To a 100 mL flask containing about 50 mL DI water, add 10 mL of the 1000 ppm stock listed in 4.20.1. QS to volume. Refrigerate. Holding time is 2 weeks.

4.20.3. Fresh working standards of 2.0, 1.0, 0.50, 0.10 mg/L if /L when analyzing ammonia:

Prepare standards by pipetting specific amounts of the concentrated stock standards into 100mL flasks containing ~50mL DI water. Bring to volume with DI water, mix well and store in the refrigerator. Holding time is 2 weeks.

4.20.4. QC standards are prepared from stock standards. The supplier for the QC stock standards (usually SPEX) differs from the supplier of the calibration standards.

Table 1: Standard Concentration (mg/l); Final Volume (mL); Volume of 20 ppm stock (mL);

0.01	250	0.125
0.02	250	0.25
0.04	250	0.50
0.10	250	1.25
0.20	250	2.5
0.40	250	5.0
1.0	100	5.0



## 5. SAMPLE PREPARATION PROCEDURE

5.1. Choose two samples from each job to check for any necessary adjustment. If both samples require the same adjustment, use that adjustment for all the samples in that job. If the adjustments are different, check each sample independently from that job for adjustment.

5.1.1. Place two drops of 10 N NaOH in a 20 mL cup and add 20 mL of sample, mix well.

Check the pH on 0.0-3.0 pH paper. If pH > 3.0 (pH paper stays blue), the adjustment for the sample is 2 drops of 1:1 H<sub>2</sub>SO<sub>4</sub> into 20 mL of sample.

5.1.2. If pH < 3.0 (pH paper turns green), add three more drops of 10 N NaOH, mix and check the pH

5.1.2.1. If pH > 3.0, the sample needs no adjustment.

5.1.2.2. If pH < 3.0, add three drops of 10 N NaOH, mix and check the pH. If pH > 3.0, the adjustment will be 3 drops of 10 N NaOH into 20 mL of sample.

5.1.2.3. If pH still < 3.0, repeat step 5.1.2.2 until pH < 3.0. The adjustment will be equal to the total number of drops of NaOH minus 5 into 20 mL of sample.

5.2. Prepare an adjusted 20 mL aliquot of carrier solution (4.17) to check for contamination in stock 10 N NaOH (4.18) and stock 1:1 H<sub>2</sub>SO<sub>4</sub> (4.19). Add 108 uL of 10 N NaOH (4.18) and 60 uL of 1:1 H<sub>2</sub>SO<sub>4</sub> (4.19) to 20 mL of carrier solution (4.17). Stir well and analyze.

5.3. Run all blanks (trip, field, equipment, etc.) without adjustment first. If they are over the MDL, check each blank for adjustment. If they need no adjustment, run the blank again to confirm the high result. If the blank needs adjustment, re-run with the correct adjustment. If the adjusted result is below the MDL, the result is acceptable. If the result is still above the MDL, rerun with the correct adjustment to confirm the high result.

## 6. SAMPLE ANALYSIS/QUANTITATION (SEE SOP NU-033)

6.1. Alpkem with SFA Detector and Pump Start-Up Procedure (Refer to Start-Up Procedure SOP NU-034-1.)

6.1.1. Place all reagent tubes and the sample line in containers of freshly prepared startup solution. Connect the sampler wash line to the carrier.

6.1.2. Turn on the 313 analytical cartridge power switch, 313 analytical cartridge heater switch and detector. The heater will take approximately 15 minutes to come to temperature. Turn on the pump and secure the platens for the tubing being used. Raise the tension levers to optimize the pumping action.

6.1.3. Set the appropriate parameters on the detector to the settings listed in 3.1.5 and press the front panel zero button to set the baseline to zero. After the flow has stabilized, place the complexing agent on the line. After 10 minutes place the other reagents on the line. Check the heater temperature display to ensure that the temperature has stabilized at the correct

operating temperature. Wait 10 minutes and observe the reagent baseline. If the baseline is stable, the system is ready to run.

## 6.2. Faspac Start-Up

6.2.1. Boot up the computer if necessary and initiate data logger by double clicking on the “data logger” icon. Launch the Faspac program by double clicking the Faspac icon. Choose the appropriate configuration from the list in the left box of the screen and enter a run name at the prompt. Enter the run data in the template.

6.2.2. Click on peak screen and view the baseline by choosing options -> display signal. When the baseline is stable with reagents running through the system, start the run by choosing Run -> Begin at the table screen or pressing the F5 key. When the last peak has been recorded, choose Run -> End or press the F5 key while holding down the shift key. Refer to the user’s software manual for report printing instructions

## 6.3. Color Correction:

6.3.1. The presence of organic matter and other colored material in the samples may result in false readings. If the sample is dark, color correction is to be carried out at the end of the analysis after the drift correction standard has been analyzed. Color correction is performed by pulling the tubing out of the hypochlorite and placing it in a Brij and water mixture (approx. 5 mL Brij to 500 mL DI water).

6.3.2. The timing of this switch is important and must take place no earlier than 4 sample cups after the Dn sample (Drift Correction sample, n= the calibrant number) has been injected by the autosampler. The system should be allowed to rinse with this reagent for at least 10 cups prior to injection of the first sample to be analyzed for color-correction. The baseline will shift when the reagents are changed, therefore, it is necessary to use baseline corrections (B) for the cups directly preceding and following the baseline shift.

6.3.3. If the color results are less than the MDL do not subtract the color corrected value. If the result is greater than or equal to the MDL, subtract the color corrected value from the initial sample result to obtain the reportable result. Note: Some of the converters in the QC calculator already perform this function.

## 6.4. Data and Results

6.4.1. After completion of the analysis print a summarized report containing the peaks, calibration graph and values. Archive the data onto a floppy disc.

6.4.2. Load the result file into the QC Manager and convert the file. Calculate the percent recoveries of the quality controls and samples.

6.4.3. See the Nutrients Quality Assurance and Quality Control Standard Operation Procedure (SOP NU-038) for QC limits and protocols. When the percent recovery of a QC sample or standards are not within the accepted limits the sample results are rejected or qualified. This also applies to the percent difference of sample duplicates. When sample results have been approved, the results must be entered into the Laboratory Information Management System (LIMS).

## 7. DATA ARCHIVAL

Archive analysis data onto a floppy disk. After the data has been archived, delete the analysis file from the hard drive.

## 8. QUALITY CONTROL

8.1. Refer to Nutrient QA/QC SOP NU-038 for detailed information about QC.

8.2. Linear Calibration Range: See QA Manual Section 9.0, 'Protocol for Determining the Test Method Range of Applicability'.

## 9. SAFETY/HAZARDOUS WASTE MANAGEMENT

9.1. Refer to the MSDS notebook for information on the safe handling of reagents and samples. Use caution and appropriate safety gear when working with acids and bases. Wear gloves to avoid contacting samples.

9.2. Phenol is harmful if inhaled or if it contacts the skin. The phenolate reagent is to be prepared under a hood while wearing gloves. Use the following bottles designed to minimize escape of phenolate fumes into the air: phenolate reagent bottle; debubbler waste bottle; and sample waste bottle with waste traps containing 2M NaOH. Check the manifold for leaks before flushing with reagents.

9.3. Avoid breathing NaOCl fumes.

9.4. Hazardous Waste Management

9.4.1. Excess sample, buffer, nitroprusside and hypochlorite may be poured down the sink, flushing with water during and after pouring.

9.4.2. After running, phenolate waste from the flow cell and from the debubbler should be transferred to a 2.5 or 4 L bottle labeled phenolate waste.

9.4.3. The waste produced from the manifold while running contains approximately 1 L of phenolate reagent per 6.5 L of waste. This waste, along with excess phenolate reagent, is poured into the phenolate waste drum immediately after the 2.5 or 4 L collection bottle has been filled. Excess phenolate reagent must be diluted before or during transfer into the drum as follows: 1 L phenolate: 5.5 L H<sub>2</sub>O. Rinse from glassware, which contained phenol, is combined with the manifold waste and poured into the drum.

## 10. MANIFOLD CLEANING, MAINTENANCE

Observe routine maintenance as recommended by the instrument manufacturer and enter any maintenance performed in the maintenance logbook. The manifold is to be cleaned with 1 M NaOH every 2 weeks to remove any phenolate buildup. Change the pump tubing as needed.

## 11. REFERENCES

- 11.1. EPA Method #350.1 (4-79-020) Automated Phenate, 3/79
- 11.2. Astoria-Pacific Astoria Analyzer manual
- 11.3. Astoria Pacific method for ammonia nitrogen analysis A303-A023-01 – Rev. B  
11/2000
- 11.4. Astoria-Pacific FaspacII Manual

## **F-3.2.**

### **Determination of Nitrate and Nitrite in Water Using the Astoria-Pacific Analyzer (Astoria A117)**

#### 1. SCOPE AND APPLICATION

This method is based on SM18-20 4500-NO<sub>3</sub> F and Lachat method 10-107-04-1-C. It can be used for the determination of nitrate and nitrite in drinking, well and waste waters. Tests covered by this SOP are NO<sub>2</sub>&NO<sub>3</sub> Drinking and Waste waters.

#### 2. SUMMARY OF THE METHOD

Nitrate is reduced quantitatively to nitrite by cadmium metal in the form of an open tubular cadmium reactor (OTCR). The nitrite originally present plus the reduced nitrate can then be determined by colorimetry. The nitrite is diazotized with sulfanilamide and coupled with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye, which is measured at a wavelength of 520nm. This method is also used to analyze Nitrite, minus the OTCR.

##### 2.1. Interferences

2.2.1 Build up of suspended matter in the reduction column will restrict sample flow sample may be filtered prior to analysis.

2.2.2 Low results may be obtained for samples containing high concentrations of iron, copper and other metals. EDTA is added to the buffer solution to eliminate these interferences.

#### 3. APPARATUS AND EQUIPMENT

Astoria Pacific computer controlled segmented flow analysis system

3.1.1. 301 autosampler: pecking off; sample/wash 30/55 (set from within the sample table using software)

3.1.2. 302 pump: speed 42

3.1.3. 313 analytical cartridge, heater temp. 50 deg. C

3.1.4. 305D detector

3.1.5. pump tubing

orn/orn: debubbler line

blk/blk: debubbler line

orn/grn: color reagent

orn/grn: stock ammonium chloride-edta buffer

orn/wht: nitrogen

orn/ylw: sample

orn/wht: nitrogen

grn/grn: sample wash

3.2. Glassware, bottles and pipettes

3.5.1. 10ml, 5ml, 3ml, 1ml volumetric Pipettes

3.5.2. 100ml Volumetric Flasks

3.5.3. 4mL Sampling Cups

3.5.4. 1 L Volumetric Flask

3.5.5. 2 L Beaker

3.5.6. 500mL Volumetric Flask

4. REAGENTS AND CHEMICALS

4.1. Stock Ammonium Chloride-EDTA Buffer Solution, purchase: Labchem LC11020-4

4.1.1. Dissolve 85g of ammonium chloride and 0.1g of disodium EDTA in ~900ml of diH<sub>2</sub>O contained in 1L beaker. Adjust to pH 8.5 with conc. Ammonium hydroxide. Transfer solution to 1L volumetric flask and dilute to the mark with diH<sub>2</sub>O. Record each new batch in the reagent log.

4.2. Color Reagent

4.2.1. Add 50mL of 85% phosphoric acid to ~300 mL of dI water in a 500mL volumetric flask. Mix and add 20g of sulfanilamide and 2.0g of N-(1-naphthyl)ethylenediamine dihydrochloride (NED). Stir for twenty minute and dilute to the mark. Filter reagent using an aspirator with a 0.45 µm filter. The color reagent is stable for several months and refrigerate in a dark container. Discard if it turns pink.

4.3. 1000ppm Nitrate Nitrogen Stock Solution, purchase pre-made Labchem LC179007

4.3.1. Dissolve 7.218 g potassium nitrate (KNO<sub>3</sub>) in a 1000mL volumetric flask containing ~800mL DI water. Add 2 drops of chloroform and dilute to the mark with DI water. Mix thoroughly and store in refrigerator. Stock should be made a minimum of every six months or as needed.

#### 4.4. 100mg/L Nitrate Working Stock Standard

Pipette 10mL of 1000 ppm nitrate stock standard (4.4.) into a 100mL volumetric flask containing 50 mL of dI H<sub>2</sub>O. Dilute to the mark with dIH<sub>2</sub>O and mix well. Store in refrigerator. The maximum holding time for this standard is ~1 month.

#### 4.3. 1000ppm Nitrite Nitrogen Stock Solution, purchase pre-made Labchem LC17007 or prepared 1000ppm Nitrite Nitrogen Stock Standard

4.3.1. Preparation of 100mg/L Std. Dissolve 0.6076g potassium nitrite (KNO<sub>2</sub>) in a 1000mL volumetric flask containing ~800mL DI water. Add 2 drops of chloroform and dilute to the mark with DI water. Invert flask 12 times to mix thoroughly and store cold. Stock should be made a minimum of every six months or as needed.

#### 4.6. 100mg/L Nitrite Working Stock Standard

Pipette 10mL of 1000 ppm nitrite stock standard (4.4.) into a 100mL volumetric flask containing 50 mL of dI H<sub>2</sub>O. Dilute to the mark with dIH<sub>2</sub>O and mix well. Store in refrigerator. The maximum holding time for this standard is ~1 month.

#### 4.7. Working Standards

Concentration (mg/L), Volume of Stock Standard , Added (mL) Final Volume in dI H <sub>2</sub> O (mL)					
NO <sub>2</sub> Std			NO <sub>3</sub> Std		
Mg/l	ml(volume of inter. Std)	Final Volume	Mg/l	ml(volume of inter. Std)	Final Volume
5.0	5(100)	100	5.0	5(100)	100
3.0	3(100)	100	3.0	3(100)	100
1.0	1(100)	100	1.0	1(100)	100
0.5	5(10)	100	0.5	5(10)	100
0.1	1(10)	100	0.05	5(1)	100
0.05	5(1)	100			
0.01	1(1)	100			

#### 4.6. QCSPEX-NUT1

Prepare working SPEX by diluting the stock solution (QCSPEX-NUT1) to 0.10 ppm using 0.2% H<sub>2</sub>SO<sub>4</sub> (4.3.). The following formula can be used to determine the correct dilution:

$$M1V1=M2V2$$

M1= Concentration of QCSPEX-NUT1 used, V1= Volume being prepared, M2= Concentration of working standard, V2= Amount of stock required.

#### 4.7. CATCHCK

Prepare CATCHCK by diluting the stock solution (1000 mg N/L NO<sub>2</sub> standard purchased

from Fisher, referred to as ALTQC) to 0.50 ppm using DI water. **Do not acidify the NO<sub>2</sub> standard. The presence of acid will oxidize the NO<sub>2</sub> to NO<sub>3</sub>.**

The following formula can be used to determine the correct dilution:

$$M_1V_1=M_2V_2$$

M<sub>1</sub>= Concentration of ALTQC used, V<sub>1</sub>= Volume being prepared, M<sub>2</sub>= Concentration of working standard, V<sub>2</sub>= Amount of stock required.

### 5. SAMPLE ANALYSIS AND QUANTITATION

#### 5.1. Sample Selection

5.1.1. See SOP NU-033 for sample selection and check out procedures.

5.1.2. Reagents should be removed from refrigeration while checking out samples and allowed to warm with samples.

#### 5.2. Instrument Setup

5.2.1. Turn on surge protector located behind the analyzer and all three instrument components and computer.

5.2.2. Locate manifold for NO<sub>2</sub>NO<sub>3</sub> and check the condition of the tubing and column. Make sure all connections are made as shown in the Astoria-Pacific method manual located on the counter behind the instrument.

5.2.3. Lock down all tubing in the peristaltic pump and flush with Startup/Shutdown Solution for at least 15 minutes.

5.2.4. While tubing is flushing select the FASPAC II icon on the computer desktop to open the instrument program. Enter User Initials at the log on screen, then select OK

5.2.5. Select *Nitrite or Nitrate* from the current configuration menu on the main screen. Then the software will prompt you to choose a run name.

5.2.6. Modify the sample run sequence of the template.

5.2.7. Remove intake lines from water bath, set pump to 35 rpm, and place in appropriate buffer or color reagent, and allow to flush while continuing with setup.

5.2.8. Load samples.

5.2.9. Select *Start* button on the toolbar to begin analysis. If the analysis needs to be

paused or stopped select the *Stop* button on the toolbar. The instrument is now in pause mode. If you want to resume analysis select *Resume* or select *Stop Now* to end current sequence.

5.2.10. After completing the run save the data by selecting *Run --> Save As YYYYMMDDn#* (Using YY for the year, MM for the month, DD for the day, and # for the number of the run).

5.3.2. Repeat steps 5.2.5. – 5.2.10.

## 6. Data Archival

### 6.1. Printing Data

6.1.1. Select the *Tools ? Custom Report*

6.1.2. Select *Print* button. (Font size may be changed)

6.1.3. Calibration info will print along with data.

### 6.2. Exporting Files

6.2.1. Select the Run tab in the Run Properties window.

6.2.2. Select *Export Data to File* button.

6.2.3. Convert file in QC Manager, and save as raw file.

6.2.4. Format data file, select uploadable samples, and place in folder for further review by supervisor.

## 7. Quality Control

7.1. For method performance and acceptance criteria for QC measures and corrective action for out-of-control data refer to Nutrients Quality Assurance and Control SOP NU-038.

7.2. The sample spikes (1mg/l) are prepared from the 100mg/l intermediate nitrate standard solution.

7.3. Check the column efficiency for the OTCR, by measuring 5mg/l NO<sub>2</sub> standard vs. 5mg/l NO<sub>3</sub> side by side, these samples are run right after the Carryover and Wash. If the recovery is less than 90% or greater than 110% the run is invalid and the column needs to be “cleaned” by rinse with buffer and CUSO<sub>4</sub> solution and rinsing with buffer again. If the recovery falls between 110 and 115% the column will need to be replaced as soon as possible. If recovery is less than 85% then an analytical error has occurred and the analyst should discontinue analysis and report the failure to a supervisor.

7.4. Linear Calibration Range: See QA Manual Section 9.0, ‘Protocol for Determining the



Test Method Range of Applicability’.

#### 8. Safety/Hazardous Waste Management

8.1. Read the MSDS information for safe reagent and sample handling. Note: Cadmium is a hazardous substance. Read MSDS regarding the handling and disposal of cadmium.

8.2. Proper safety equipment such as gloves, lab coats, and safety glasses should be worn at all times during analysis.

#### 9. References

9.1. SM 18-20 4500-NO3 F

9.2. Astoria Pacific method for Nitrate + Nitrite Nitrogen analysis A303-A173-A00–  
Rev. B 11/2000

## F-3.3. Ortho-Phosphate (Astoria-Pacific A204)

### ORTHO-PHOSPHATE

#### A204

#### A. Scope and Application

This method is used for the determination of ortho-phosphate in seawater and is applicable to many ranges.

#### B. Summary of Method

Ortho-phosphate reacts with molybdic acid to form phosphomolybdic acid. This complex is subsequently reduced with hydrazine to phosphomolybdous acid. (1) Absorbance is measured at 820 nm.

#### C. Interferences

Turbid samples must be filtered before determination. Samples with background absorbance at the analytical wavelength may interfere.

#### D. Sample Handling and Preservation

Analyze samples as soon as possible. Refrigerate samples at 2-8°C if immediate analysis is not possible.

#### E. Raw Materials Required

**NOTE: Chemicals should be of ACS grade or equivalent.**

Ammonium Molybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (FW 1235.86)

Chloroform  $\text{CHCl}_3$  (FW 119.38)

Deionized Water (ASTM Type I or II)

Hydrazine Sulfate  $(\text{NH}_2)_2\text{H}_2\text{SO}_4$  (FW 130.12)

Low Nutrient Seawater (LNSW) \*

Magnesium Sulfate  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (FW 246.48) \*

Potassium Dihydrogen Phosphate  $\text{KH}_2\text{PO}_4$  (FW 136.09)

Sodium Bicarbonate  $\text{NaHCO}_3$  (FW 84.01) \*

Sodium Chloride  $\text{NaCl}$  (FW 58.44) \*

Sodium Lauryl Sulfate (SLS),  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$  (FW 288.38)

Sulfuric Acid, concentrated  $\text{H}_2\text{SO}_4$  (FW 98.08)

\* See Operating Notes for information on matrix choices.

#### F. Reagent Preparation

##### 1. Sodium Lauryl Sulfate (SLS), 15% w/w

Deionized Water.....85 ml

Sodium Lauryl Sulfate (SLS) .....15 g

$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$  (FW 288.38)

Dissolve 15g of SLS in 85 ml of deionized water contained in a 250 ml erlenmeyer flask. Gentle warming may be needed for complete dissolution.

## 2. Stock Ammonium Molybdate (500 ml)

Ammonium Molybdate.....54.5 g

(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O (FW 1235.86)

Deionized Water

Dissolve 54.5 g of ammonium molybdate in approximately 400 ml of deionized water contained in a 500 ml volumetric flask. Dilute the solution to the mark with deionized water and mix it well.

## 3. Sulfuric Acid Solution (Approx. 1450 ml)

**CAUTION: Mixing sulfuric acid with water releases a great amount of heat.**

Sulfuric Acid .....640 ml

H<sub>2</sub>SO<sub>4</sub>, concentrated

Deionized Water .....810 ml

Slowly and carefully add 640 ml of sulfuric acid to 810 ml of deionized water contained in a 2 liter flask. Allow to cool between partial additions. Cool to room temperature.

## 4. Molybdic Acid Reagent

Stock Ammonium Molybdate.....500 ml

Sulfuric Acid Solution ..... Approx. 1450 ml

Mix together the entire amounts of both solutions and allow to cool. If the reagent has a bluish tinge or develops a precipitate, discard it. Store in a dark polyethylene bottle at room temperature. Stable for 3 months.

## 5. Working Molybdic Acid Reagent

Molybdic Acid Reagent .....30 ml

Deionized Water.....30 ml

SLS, 15% .....6 drops

Mix together 30 ml of molybdic acid reagent and 30 ml of deionized water. Filter to 0.45 µm with a syringe and add 6 drops of 15% SLS.

## 6. Stock Hydrazine Sulfate (500 ml)

Hydrazine Sulfate .....2.5 g

(NH<sub>2</sub>)<sub>2</sub> H<sub>2</sub>SO<sub>4</sub> (FW 130.12)

Deionized Water

Dissolve 2.5 g of hydrazine sulfate in about 400 ml of deionized water. Dilute to 500 ml with deionized water. Filter to 0.45 µm. Generally stable until consumed. Store in refrigerator at 2-8°C.

## 7. Working Hydrazine Sulfate Reagent (60 ml)

Stock Hydrazine Sulfate .....60 ml

SLS, 15% .....3 drops

Warm 60 ml of stock hydrazine sulfate to room temperature. Add 3 drops 15% SLS.

## 8. Startup/Shutdown Solution (100 ml)

Deionized Water.....100 ml

SLS, 15% .....2 ml  
 Add 2 ml of 15% SLS per 100 ml of deionized water.

## 9. Artificial Seawater (ASW) (4 L) (See Operating Notes)

Sodium Chloride.....128.5 g  
 NaCl (FW 58.44)  
 Magnesium Sulfate.....28.5 g  
 MgSO<sub>4</sub>•7H<sub>2</sub>O (FW 246.48)  
 Sodium Bicarbonate .....0.672 g  
 NaHCO<sub>3</sub> (FW 84.01)

Deionized Water

Dissolve 128.5 g of sodium chloride, 28.5 g of magnesium sulfate and 0.672 g of sodium bicarbonate in about 3 liters of deionized water. Dilute to 4 liters with deionized water. These reagents must be high quality, reagent grade to avoid excessive nutrient or trace metal contamination.

## 10. Sampler Wash

See Operating Notes.

## G. Calibrants

Specific Stock and Working Calibrant preparation instructions can be found on the back of the flow diagram. Be sure to use the flow diagram which covers the concentration range you wish to analyze.

Working calibrants may be prepared to cover alternate ranges by adding the appropriate volumes of stock or intermediate calibrant to 100 ml volumetric flasks that contain approximately 80 ml of sampler wash solution. Dilute the solution to 100 ml with sampler wash solution and mix well.

The following formula can be used to calculate the amount of stock (or intermediate) calibrant to be used.

$$C_1V_1 = C_2V_2$$

Where:

C<sub>1</sub> = desired concentration (in mg/L) of working calibrant to be prepared

V<sub>1</sub> = final volume (in ml) of working calibrant to be prepared (generally 100 ml)

C<sub>2</sub> = concentration (in mg/L) of stock (or intermediate) calibrant

V<sub>2</sub> = volume (in ml) of stock (or intermediate) calibrant to be used

Rearranging the equation to solve for V<sub>2</sub> yields:

$$V_2 = C_1V_1$$

For example, to prepare a 1.0 mg/L working calibrant from a 1000 mg/L stock calibrant, use 0.1 ml (100 µl) of the stock calibrant in 100 ml final volume.

$$V_2 = (1.0 \text{ mg/L}) (100 \text{ ml})$$

$$1000 \text{ mg/L}$$

$$V_2 = 0.1 \text{ ml}$$

Add this amount of stock calibrant to the volumetric flask and then dilute to volume with the sampler wash solution.

## H. Operation Procedure

1. Set up the cartridge as shown in the flow diagram. Check all tubing and connections. Replace if necessary.
2. Place reagent lines in startup solution.
3. Turn on power to all units including heat bath and latch pump platens to begin liquid flow.
4. Verify that the bubble size and spacing is consistent throughout the cartridge. If bubbles are splitting up as they enter or exit a coil or heat bath, check and replace fittings if necessary. The bubbles should flow smoothly without dragging. If dragging occurs, add more SLS to the startup solution.
5. Check all reagent containers on the instrument for particulate matter. Reagents should be filtered. Be sure all containers are properly labeled and filled before pumping reagents.
6. After the heat bath has reached the desired temperature and a stable baseline has been verified on the startup solution, place reagent lines in reagent bottles. Due to the lower amount of SLS in the reagents, the flow and bubble pattern may drag slightly.
7. Set up the appropriate sample table in FASpac.
8. Allow reagents to run for 5 to 10 minutes and verify a stable baseline.
9. Load the sampler tray with calibrants, blanks, samples, and QC or monitor samples.
10. Select the appropriate parameters for the detector and sampler. (See Flow Diagram.)
11. Begin analysis.
12. At the end of analysis place all reagent lines in startup solution and turn off the heat bath. Pump startup solution for 20 to 30 minutes to flush all of the reagents out of the cartridge and to allow the heat bath to cool.
13. Turn off the power to all units and release pump platens.

## I. Operating Notes

1. Acid washed glassware should be used for all reagents and calibrants. Commercial detergents containing phosphorus should never be used to clean glassware used in phosphorus determination. Wash the glassware with 1:1 hydrochloric acid and rinse it thoroughly with deionized water. Store the glassware filled with deionized water. If the glassware is reserved for use only in phosphorus determination, treatment with hydrochloric acid is necessary only occasionally.
2. A common cause of low sensitivity and noise in the baseline is debris in the flowcell. Particulate matter from the reagents and samples become lodged in the flowcell restricting the amount of light that is passed through the flowcell. Flushing the flowcell with approximately 10 ml of sampler wash solution with a syringe will dislodge any debris in the flowcell. Following proper filtration procedures for the reagents and samples will reduce the frequency of this occurring.
3. Poly Flow tubing (API p/n 303-2674-01) is used for transmission tubing on this

cartridge to help achieve smooth flow and reduce carryover.

4. High quality SLS is important. Fisher catalog numbers 02674-25, BP166-100 or BP166-500 are acceptable.

5. Clean the cartridge regularly with CHEMWASH (API p/n 80-0005-250). Over several weeks the flowcell may become coated with hydrazine. It may be cleaned by pumping or syringing a 5-10% sulfuric acid solution through it.

6. There are special considerations when running seawater samples on any flow system.

#### A. Standards

Primary standards should be prepared from the best grade of chemicals available. Certificates of Analysis are available from the chemical manufacturer. These should be consulted to identify impurities.

Standard material should be oven dried for two hours at 110°C before weighing. It is advisable to periodically verify the concentrations of the working standards. This can be done by running standards against standards from an outside source.

The matrix of the standards should be consistent with that of the samples. If deionized water standards are used it becomes important to determine the salt effects of each individual test (see number 7 under Operating Notes.).

#### B. Matrix

Optimal system performance can be expected if the sample matrix is carried over into the sampler wash solution and the standards. Care should be taken when using deionized water wash solution with seawater standards. Many investigators recommend segregating the samples by salinity and running as a group to make corrections easier.

There are many options with respect to the matrix of the calibrant and sampler wash solutions. The relative merits of several types of material are presented here.(2)

#### Deionized Water

##### **Advantages:**

1. The quality of the water is usually well known.
2. The quality of the water is usually not highly variable.
3. The prepared standards are relatively stable with time.
4. Large volumes of water are easily available.

##### **Disadvantages:**

1. The chemical factors may be different than in salt solution (salt effect).

#### Artificial Seawater Solution (and/or Deionized Water-Sodium Chloride Solution)

##### **Advantages:**

1. Salt effects on the chemical factors are minimized.
2. Sodium chloride solution is easy to prepare and is not expensive.

**Disadvantages:**

1. Ammonium impurity is quite large in sodium chloride.
2. Large quantities of sodium chloride are sometimes required.

Low Nutrient Seawater

**Advantages:**

1. Salt effects are eliminated.
2. In certain regions of the ocean it is easily obtained.

**Disadvantages:**

1. It always contains some nutrients.
2. If not used immediately, it must be filtered to remove any particulate matter.
3. Often it is difficult to obtain when working in eutrophic waters.
4. Storage is difficult, so large quantities are not easily obtained.

7. As stated above, the system is optimal when the sample matrix is carried over into the sampler wash solution and the standards. If this is not possible (i.e. if deionized water is used for the sampler wash and/or calibrants), it is advisable to check for refractive index disturbance effects. This can be accomplished by running without the hydrazine present. After the initial sample run is finished, place the data collection in pause, replace the hydrazine reagent with SLS water, wait for a stable baseline, autozero the detector and run the samples again. The peaks that are seen are due to the refractive index disturbance.

8. If bubbles are sticking in a debubbler, cleaning the debubbler will allow bubbles to escape smoothly out the debubble line. Bubbles sticking in the debubbler can cause a loss in the overall precision of the peak height. To clean, soak the debubbler for 2-3 hours in a mixture of 20-30% Contrad®NF (API p/n 80-0007-04) and hot tap water. Rinse thoroughly.

9. If the flowrate of the sample pump tube is  $\leq 226 \mu\text{l/minute}$  (a blk/blk pump tube) a helper line must be added when the cartridge is run alone. See Section 9 of the Astoria Analyzer Operation Manual for information on how to add a helper line.

**NOTE: If the sample line is debubbled, a helper line is not necessary.**

10. Cover all reagents and other solutions to avoid interference due to dust and other particulates. This will also help prevent contamination of the solutions from absorbance of analytes in the air.

**J. References**

1. Bernhardt, H. and A. Wilhelms. "The continuous determination of low level iron, soluble phosphate and total phosphate with the AutoAnalyzer." Technicon Symp., 1967, Vol. I, p. 386.
2. Automated Nutrient Analysis in Seawater, Technical Report, Brookhaven

National Laboratory, Whitledge, Veidt, et. al., May 1986.

## **ACKNOWLEDGMENTS**

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Pennsylvania



## F-3.4 Silicate (Astoria Pacific A221)

### SILICATE

#### A221

#### A. Scope and Application

This method is used for the determination of silicate in seawater and is applicable to many ranges.

#### B. Summary of Method

Silicomolybdic acid is formed by the reaction of silicate with molybdic acid. The silicomolybdic acid is reduced by stannous chloride to form molybdenum blue with an absorbance maximum at 820 nm.(1-4)

#### C. Interferences

Interference from orthophosphate and tannin is eliminated by the use of tartaric acid. Filter turbid samples before determination. Color absorbing at the analytical wavelength will interfere.

#### D. Sample Handling and Preservation

Collect samples in plastic containers. Analyze samples as soon as possible. Refrigerate samples at 2-8°C if immediate analysis is not possible.

#### E. Raw Materials Required

**NOTE: Chemicals should be of ACS grade or equivalent.**

Ammonium Molybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (FW 1235.95)

Chloroform  $\text{CHCl}_3$  (FW 119.38)

Deionized Water (ASTM Type I or II)

Hydrochloric Acid, concentrated,  $\text{HCl}$ , (FW 36.46)

Low Nutrient Seawater (LNSW)\*

Magnesium Sulfate  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (FW 246.48)\*

Sodium Bicarbonate  $\text{NaHCO}_3$  (FW 84.01)\*

Sodium Chloride  $\text{NaCl}$  (FW 58.44)\*

Sodium Hexafluorosilicate  $\text{Na}_2\text{SiF}_6$  (FW 188.06)

Sodium Lauryl Sulfate (SLS)  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3\text{Na}$  (FW 288.38)

Stannous Chloride  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (FW 225.65)

Sulfuric Acid, concentrated  $\text{H}_2\text{SO}_4$  (FW 98.08)

Tartaric Acid  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  (FW 150.09)

\*See Operating Notes for information on matrix choices.

#### F. Reagent Preparation

##### 1. Sodium Lauryl Sulfate (SLS) 15% w/w

Sodium Lauryl Sulfate ..... 15 g

$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3\text{Na}$  (FW 288.38)

Deionized Water ..... 85 ml

Dissolve 15 g of sodium lauryl sulfate in 85 ml of deionized water contained in a 250 ml Erlenmeyer flask. It may be necessary to warm the mixture in a water bath to dissolve.

## 2. Stock Molybdic Acid (1 L)

Ammonium Molybdate..... 10.8 g  
 (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O (FW 1235.95)

Sulfuric Acid..... 2.8 ml

H<sub>2</sub>SO<sub>4</sub>, concentrated (FW 98.08)

Deionized Water

While stirring, cautiously add 2.8 ml of sulfuric acid to approximately 900 ml of deionized water contained in a 1 L volumetric flask. Dissolve 10.8 g of ammonium molybdate in the acidic solution. Dilute the solution to the mark with deionized water and mix it well. Filter to 0.45 µm. Store the reagent in a plastic container. Do not refrigerate this reagent. Discard the solution if it becomes blue.

## 3. Working Molybdic Acid Reagent (100 ml)

Stock Molybdic Acid ..... 100 ml

SLS, 15 % w/w ..... 4 drops

Mix together 100 ml of ammonium molybdate and 4 drops of SLS. Prepare daily the quantity sufficient for the day's run.

## 4. Tartaric Acid, 20% w/v (1 L)

Tartaric Acid ..... 200 g

H<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> (FW 150.09)

Deionized Water

Chloroform..... 2 drops

CHCl<sub>3</sub>

Dissolve 200 g of tartaric acid in approximately 700 ml of deionized water contained in a 1 L volumetric flask. Dilute the solution to the mark with deionized water and mix it well. Filter to 0.45 µm. Add 2 drops of chloroform. Store the reagent in a plastic container and refrigerate it at 2-8°C. Filter every 10 days.

## 5. Stock Stannous Chloride (100 ml)

**CAUTION: Mixing hydrochloric acid with water releases a great amount of heat.**

Stannous Chloride..... 50.0 g

SnCl<sub>2</sub>•2H<sub>2</sub>O (FW 225.65)

Hydrochloric Acid..... 50 ml

HCl, concentrated, (FW 36.46)

Deionized Water

While stirring, cautiously add 50 ml of hydrochloric acid to 30 ml of deionized water contained in a plastic volumetric flask. Dissolve 50 g of stannous chloride in the acidic solution. Heating may be necessary to obtain complete dissolution. Dilute to 100 ml with deionized water and mix well. Store the stock solution in a tightly closed plastic container and freeze it at less than -10°C.

## 6. Hydrochloric Acid 1.2 N (1 L)

**CAUTION: Mixing hydrochloric acid with water releases a great amount of heat.**

Hydrochloric Acid..... 100 ml

HCl, concentrated, (FW 36.46)

Deionized Water

Cautiously, while stirring, add 100 ml of hydrochloric acid to approximately 800 ml of deionized water contained in a 1 L volumetric flask. Dilute the solution to the mark with deionized water and mix it well. Filter to 0.45 µm. Store the solution in a plastic container.

## 7. Working Stannous Chloride Reagent

Stock Stannous Chloride ..... 2.0 ml

Hydrochloric Acid, 1.2 N..... 100 ml

Mix together 2.0 ml of stock stannous chloride and 100 ml of 1.2 N hydrochloric acid in a plastic container. Prepare the reagent fresh daily.

**NOTE: This reagent is not stable for more than 8 hours.**

## 8. Startup/Shutdown Solution

Add 2 ml of 15% SLS per 100 ml of deionized water.

## 9. Artificial Seawater (ASW) (4 L)

Sodium Chloride.....128.5 g

NaCl (FW 58.44)

Magnesium Sulfate..... 28.5 g

MgSO<sub>4</sub>•7H<sub>2</sub>O (FW 246.48)

Sodium Bicarbonate ..... 0.672 g

NaHCO<sub>3</sub> (FW 84.01)

Deionized Water

Dissolve 128.5 g of sodium chloride, 28.5 g of magnesium sulfate and 0.672 g of sodium bicarbonate in about 3 liters of deionized water. Dilute to 4 liters with deionized water. These reagents must be high quality, reagent grade to avoid excessive nutrient or trace metal contamination.

## 10. Sampler Wash

See Operating Notes.

## G. Calibrants

Specific Stock and Working Calibrant preparation instructions can be found on the back of the flow diagram. Be sure to use the flow diagram which covers the concentration range you wish to analyze.

Working calibrants may be prepared to cover alternate ranges by adding the appropriate volumes of stock or intermediate calibrant to 100 ml volumetric flasks that contain approximately 80 ml of sampler wash solution. Dilute the solution to 100 ml with sampler wash solution and mix well.

The following formula can be used to calculate the amount of stock (or intermediate) calibrant to be used.

$$C1V1 = C2V2$$

Where:

C1 = desired concentration (in mg/L) of working calibrant to be prepared

V1 = final volume (in ml) of working calibrant to be prepared (generally 100 ml)

C2 = concentration (in mg/L) of stock (or intermediate) calibrant

V2 = volume (in ml) of stock (or intermediate) calibrant to be used

Rearranging the equation to solve for V2 yields:

$$V2 = C1V1$$

For example, to prepare a 1.0 mg/L working calibrant from a 1000 mg/L stock calibrant, use 0.1 ml (100 µl) of the stock calibrant in 100 ml final volume.

$$V2 = (1.0 \text{ mg/L}) (100 \text{ ml})$$

$$1000 \text{ mg/L}$$

$$V2 = 0.1 \text{ ml}$$

Add this amount of stock calibrant to the volumetric flask and then dilute to volume with the sampler wash solution.

## H. Operation Procedure

1. Set up the cartridge as shown in the flow diagram. Check all tubing and connections. Replace if necessary.
2. Place reagent lines in startup solution.
3. Turn on power to all units and latch pump platens to begin liquid flow.
4. Verify that the bubble size and spacing is consistent throughout the cartridge. If bubbles are splitting up as they enter or exit a coil, check and replace fittings if necessary. The bubbles should flow smoothly without dragging. If dragging occurs, add more SLS to the startup solution.
5. Check all reagent containers on the instrument for particulate matter. Reagents should be filtered. Be sure all containers are properly labeled and filled before pumping reagents.
6. After a stable baseline has been verified on the startup solution, place reagent lines in reagent bottles. Due to the lower amount of SLS in the reagents, the flow and bubble pattern may drag slightly.

**NOTE: Leave the stannous chloride reagent line in the startup solution for 5 minutes after adding the other reagents. This will allow the tartaric acid to reach the cartridge first.**

7. If using data collection software, set up the appropriate sample table.
8. Allow reagents to run for 5 to 10 minutes and verify a stable baseline.
9. Load the sampler tray with calibrants, blanks, samples, and QC or monitor samples.
10. Select the appropriate parameters for the detector and sampler. (See Flow Diagram.)
11. Begin analysis.
12. At the end of analysis place all reagent lines in startup solution. Pump startup solution for 10 to 15 minutes to flush all of the reagents out of the cartridge.

**NOTE: First move the stannous chloride reagent line to startup solution for 5 minutes before moving the other reagent lines. This will allow the stannous chloride line to rinse out before the tartaric acid is removed.**

13. Turn off the power to all units and release pump platens.

## **I. Operating Notes**

1. The use of glass containers should be avoided. Prepare all reagents and calibrants in plastic containers, or transfer all reagents and calibrants to plastic containers immediately following preparation.
2. The powdered stannous chloride,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , should be stored frozen at less than  $-10^\circ\text{C}$ . Allow to come to room temperature before opening.
3. Prepare fresh working stannous chloride if unstable baselines, poor peak shapes or reduced sensitivity are experienced.
4. Poly Flow tubing (API p/n 303-2674-01) is used for transmission tubing on this cartridge to help achieve smooth flow and reduce carryover.
5. High quality SLS is important. Fisher catalog numbers 02674-25, BP166-100 or BP166-500 are acceptable.
6. There are special considerations when running seawater samples on any flow system.

### **A. Standards**

Primary standards should be prepared from the best grade of chemicals available. Certificates of Analysis are available from the chemical manufacturer. These should be consulted to identify impurities. Standard material should be oven dried for two hours at  $110^\circ\text{C}$  before weighing. It is advisable to periodically verify the concentrations of the working standards. This can be done by running standards against standards from an outside source. The matrix of the standards should be consistent with that of the samples. If deionized water standards are used it becomes important to determine the salt effects of each individual test. (See number 2 under Operating Notes.)

### **B. Matrix**

Optimal system performance can be expected if the sample matrix is carried over into the sampler wash solution and the standards. Care should be taken when using deionized water wash solution with seawater standards. Many investigators recommend segregating the samples by salinity and running as a group to make corrections easier. There are many options with respect to the matrix of the calibrant and sampler wash solutions. The relative merits of several types of material are presented here. (1)

#### **Deionized Water**

##### **Advantages:**

1. The quality of the water is usually well known.

2. The quality of the water is usually not highly variable.
3. The prepared standards are relatively stable with time.
4. Large volumes of water are easily available.

**Disadvantages:**

1. The chemical factors may be different than in salt solution (salt effect).

Artificial Seawater Solutions ( and/or Deionized Water - Sodium Chloride Solution)

**Advantages:**

1. Salt effects on the chemical factors are minimized.
2. Sodium chloride solution is easy to prepare and is not expensive.

**Disadvantages:**

1. Ammonium impurity is quite large in sodium chloride.
2. Large quantities of sodium chloride are sometimes required.

Low Nutrient Seawater

**Advantages:**

1. Salt effects are eliminated.
2. In certain regions of the ocean it is easily obtained.

**Disadvantages:**

1. It always contains some nutrients.
2. If not used immediately it must be filtered to remove any particulate matter.
3. Often it is difficult to obtain when working in eutrophic waters.
4. Storage is difficult, so large quantities are not easily obtained.
2. As stated above, the system is optimal when the sample matrix is carried over into the sampler wash solution and the standards. If this is not possible (i.e. if deionized water is used for the sampler wash and/or calibrants), it is advisable to check for refractive index disturbance effects. This can be accomplished by removing the sodium hypochlorite reagent. After the initial sample run is finished, place the data collection in pause, replace the hypochlorite reagent with deionized water, wait for a stable baseline, autozero the detector and run the samples again. The peaks seen are due to the refractive index disturbance.

8. If bubbles are sticking in a debubbler, cleaning the debubbler will allow bubbles to escape smoothly out the debubble line. Bubbles sticking in the debubbler can cause a loss in the overall precision of the peak height. To clean, soak the debubbler for 2-3 hours in a mixture of 20-30% Contrad®NF (API p/n 80-0007-04) and hot tap water. Rinse thoroughly.

9. If the flowrate of the sample pump tube is  $\leq 226 \mu\text{l}/\text{minute}$  (a blk/blk pump tube) a helper line must be added when the cartridge is run alone. See Section 9 of the Astoria Analyzer Operation Manual for information on how to add a helper line.

**NOTE: If the sample line is debubbled, a helper line is not necessary.**

10. Cover all reagents and other solutions to avoid interference due to dust and other

particulates. This will also help prevent contamination of the solutions from absorbance of analytes in the air.

## J. References

1. Truesdale, V.W., C.J. Smith, "The Formation of Molybdosilicic Acids from Mixed Solutions of Molybdosilicic Acids from Mixed Solutions of Molybdate and Silicate", Analyst, March 1975, vol. 100, Pg. 203-212.
2. Armstrong, F.A.J., C.R. Stearns, and J.D. Stickland. 1967. The measurement of upwelling and subsequent biological processes by means of the Technicon™ AutoAnalyzer™ and associated equipment. Deep-Sea Res. 14(3): 381-389.
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4. Gordon, L.I., J.M. Krest and A.A. Ross. in preparation. Continuous Flow Analysis of silicic acid in seawater: Reducing sensitivity to laboratory temperature fluctuations.
5. Automated Nutrient Analysis in Seawater, Technical Report, Brookhaven National Laboratory, Whitledge, Veidt, et. al., May 1986.

## ACKNOWLEDGMENTS

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### F-3.5. Filtered Nutrients for Hach simplified TKN, and TON

Hach Company Method 10242 “Simplified Spectrophotometric Measurement of Total Kjeldahl Nitrogen in Water and Waste Water.

Digestion with peroxodisulfate, followed by Spectrophotometric (2,6-dimethyl phenol)

Listed in code of Federal Regulations, Title 40, vol 25. 2018-07-01

<https://www.govinfo.gov/content/pkg/CFR-2018-title40-vol25/xml/CFR-2018-title40-vol25-part136.xml>

## Nitrogen, Simplified TKN (s-TKN™)

DOC316.53.01258

**s-TKN™ Method**  
**0 to 16 mg/L TKN**

**Method 10242<sup>1</sup>**  
**TNTplus® 880**

**Scope and application:** For water and wastewater. Digestion is required.

<sup>1</sup> USEPA approved for water and wastewater analysis, 40 CFR part 136.

### Test preparation

#### Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows the adapter and light shield requirements for the applicable instruments that can use TNTplus vials.

To use the table, select an instrument, then read across to find the applicable information for this test.

**Table 1 Instrument-specific information for TNTplus vials**

Instrument	Adapters	Light shield
DR6000, DR5000	—	—
DR3900	—	LZV849
DR3800, DR2800	—	LZV646
DR1900	9609900 or 9609800 (A)	—

#### Before starting

DR3900, DR3800, DR2800: Install the light shield in Cell Compartment #2 before this test is started.
Review the safety information and the expiration date on the package.
The sample temperature must be 15–25 °C (59–77 °F) for accurate results.
The recommended temperature for reagent storage is 15–25 °C (59–77 °F).
Samples must be preserved with acid as specified in <a href="#">Sample collection and storage</a> on page 2. Make sure to adjust the pH and temperature before the analysis.
Important: Make sure to close each reagent bottle immediately after each use.
The 20-mm reaction tube can be used for 13 tests. After each use, clean the tube thoroughly with a brush and water, then rinse well with high-quality distilled water and let dry.
If a large amount of turbidity forms after the addition of MicroCap C, let the turbidity settle, then go to the next step. A small amount of turbidity does not interfere.
The nitrite concentration can be determined with nitrite reagents on samples that have not been preserved. The nitrite concentration must then be subtracted from the s-TKN result.
The total nitrogen concentration must be between 1 and 16 mg/L N. The combined nitrate/nitrite concentration must be between 0.23 and 13.5 mg/L N. Dilute the sample if necessary.
DR1900: Go to All Programs>LCK or TNTplus Methods>Options to select the TNTplus number for the test. Other instruments automatically select the method from the barcode on the vial.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.



### Items to collect

Description	Quantity
s-TKN TNTplus® Reagent Set	1
DRB200 reactor with 20-mm wells	1
Pipet, adjustable volume, 1.0–5.0 mL	1
Pipet, adjustable volume, 0.2–1.0 mL	1
Pipet tips	1
Test tube rack	1

Refer to [Consumables and replacement items](#) on page 5 for order information.

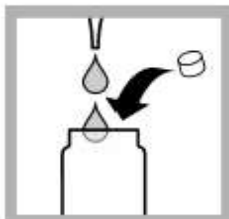
### Sample collection and storage

- Collect samples in clean glass or plastic bottles.
- Adjust the sample pH to less than 2 with concentrated sulfuric acid (approximately 2 mL per liter).
- Keep the preserved samples at or below 6 °C (43 °F) for a maximum of 28 days.
- Let the sample temperature increase to room temperature before analysis.
- Before analysis, adjust the pH to 7 with 5 N sodium hydroxide solution.
- Correct the test result for the dilution caused by the volume additions.

### Test procedure



1. Set the DRB200 reactor power to on. Set the temperature to 100 °C.



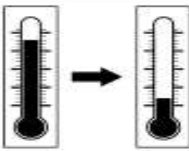

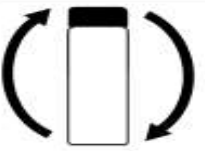
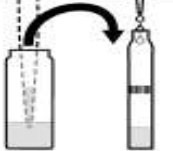
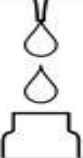

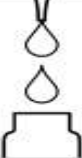
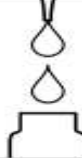




2. Add 1.3 mL of sample, 1.3 mL of Solution A and 1 Reagent B tablet in quick succession to a dry 20-mm reaction tube. Close the reaction tube immediately. Do not invert.



3. Insert the reaction tube in the preheated DRB200 reactor. Close the lid.



4. Keep the reaction tube in the reactor for 1 hour.

			
<p>5. When the timer expires, carefully remove the reaction tube from the reactor. Let the temperature of the reaction tube decrease to room temperature.</p>	<p>6. When cool, add 1 Micro Cap C to the reaction tube.</p>	<p>7. Tighten the cap on the reaction tube and invert until completely mixed.</p>	<p>8. Use a pipet to add 0.5 mL of the digested sample from the 20-mm reaction tube into a test vial 1 (red label).</p>
			
<p>9. Use a pipet to add 0.2 mL of Solution D to the test vial.</p>	<p>10. Quickly tighten the cap on the vial and invert until completely mixed. Immediately continue to the next step.</p>	<p>11. Use a pipet to add 1.0 mL of undigested sample to a test vial 2 (green label).</p>	<p>12. Use a pipet to add 0.2 mL of Solution D to the test vial.</p>
			
<p>13. Quickly tighten the cap on the vial and invert until completely mixed.</p>	<p>14. Start the reaction time of 15 minutes.</p>	<p>15. When the timer expires, clean the vials.</p>	<p>16. DR1900 only: Select program 880. Refer to <a href="#">Before starting</a> on page 1.</p>



17. Insert the test vial 1 (red label) into the cell holder. DR1900 only: Push **READ1**. Immediately continue to the next step.



18. Insert the test vial 2 (green label) into the cell holder. DR1900 only: Push **READ2**. Results show in mg/L Total N, mg/L  $\text{NO}_3\text{-N} + \text{NO}_2\text{-N}$  and mg/L TKN.

### Interferences

High levels of oxidizable organic substances (COD) have an effect on the reagent color and give high results. Use this test procedure for wastewater only when the COD level is less than 500 mg/L COD.

Table 2 shows that the ions were individually examined to the given concentrations and do not cause interference. No cumulative effects or influences of other ions were found.

**Table 2 Non-interfering substances**

Interfering substance	Interference level
$\text{Cd}^{2+}$	50 mg/L
$\text{Ca}^{2+}$	50 mg/L
$\text{Cl}^-$	500 mg/L
$\text{Cr}^{6+}$	5 mg/L
$\text{Co}^{2+}$	10 mg/L
$\text{Cu}^{2+}$	50 mg/L
$\text{Fe}^{2+}$	10 mg/L
$\text{Fe}^{3+}$	50 mg/L
$\text{Pb}^{2+}$	50 mg/L
$\text{Ni}^{2+}$	50 mg/L
$\text{NO}_2^-$	2 mg/L
$\text{K}^+$	500 mg/L
$\text{Ag}^+$	100 mg/L
$\text{Na}^+$	500 mg/L
$\text{Sn}^{2+}$	50 mg/L
$\text{Zn}^{2+}$	50 mg/L

### Accuracy check

#### Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:

- Wastewater Effluent Standard Solution, Mixed Parameter (expected result: 7.56 mg/L Total N, 4 mg/L  $\text{NO}_3\text{-N}$  +  $\text{NO}_2\text{-N}$ , 3.56 mg/L TKN)
1. Use the test procedure to measure the concentration of the standard solution.
  2. Compare the expected result to the actual result. The Wastewater Effluent Standard Solution contains a component that adds 1.56 mg/L N to the Total N and TKN values. This is in addition to the 2 mg/L  $\text{NH}_3\text{-N}$  and 4 mg/L  $\text{NO}_3\text{-N}$  shown on the label.

### Summary of Method

Total Kjeldahl Nitrogen (TKN) is the sum of organic nitrogen and ammonia. In the simplified TKN method, inorganic and organic nitrogen are oxidized to nitrate by digestion with peroxodisulfate. The nitrate ions react with 2,6-dimethylphenol in a solution of sulfuric and phosphoric acid to form a nitrophenol. Oxidized forms of nitrogen in the original sample (nitrite + nitrate due to sample preservation) are determined in the second test vial and then subtracted, which results in TKN.

### Consumables and replacement items

#### Required reagents

Description	Quantity/Test	Unit	Item no.
Simplified TKN (s-TKN) TNTplus® reagent set	1	25/pkg	TNT880

#### Required apparatus

Description	Quantity/test	Unit	Item no.
DRB200 Reactor, 115 VAC option, 9 x 13 mm + 2 x 20 mm, 1 block	1	each	DRB200-01
DRB200 Reactor, 230 VAC option, 9 x 13 mm + 2 x 20 mm, 1 block	1	each	DRB200-05
Pipet, adjustable volume, 1.0–5.0 mL	1	each	BBP065
Pipet tips, for 1.0–5.0 mL pipet	1	75/pkg	BBP068
Pipet, adjustable volume, 0.2–1.0 mL	1	each	BBP078
Pipet tips, for 0.2–1.0 mL pipet	2	100/pkg	BBP079
Test tube rack for 20-mm vials, 20 holes	1	each	2497912
Test tube rack for 20-mm vials, 40 holes	1	each	2497902
Light shield, DR3800, DR2800, DR2700	1	each	LZV646
Light shield, DR3900	1	each	LZV849

#### Recommended standards

Description	Unit	Item no.
Wastewater Effluent Standard Solution, Mixed Parameter, for $\text{NH}_3\text{-N}$ , $\text{NO}_3\text{-N}$ , $\text{PO}_4^{3-}$ , COD, $\text{SO}_4^{2-}$ , TOC	500 mL	2833249

#### Optional reagents and apparatus

Description	Unit	Item no.
Filter membrane, 0.45-micron, 25-mm	100/pkg	2514101
Filter holder, 25-mm, for Luer-type syringe	each	246800
Sampling bottle with cap, low density polyethylene, 500-mL	12/pkg	2087079
Sodium Hydroxide Standard Solution, 5.0 N	1 L	245053

Optional reagents and apparatus (continued)		
Description	Unit	Item no.
Sulfuric Acid, concentrated, ACS	500 mL	97949
Syringe, 10-cc, Luer-Lock tip	each	2202400
Digestion vials, 20 mm	5/pkg	LZP065



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 FAX: (970) 669-5077

#### F-4. Quality Controls

***Quality Control and Assessment Measures: Internal Checks*** Internal checks are performed by the project field volunteers, staff, and lab. Quality Assessment will

*Grabs.* Chlorophyll samples collected from the fluorometer for underway fluorometer calibration. One 1L brown HDPE bottle is used per day, and rinsed between uses. Samples are filtered and duplicate grab samples are not collected. Typically 5 grab samples are collected per field day within a minimum of 3 and collected at a range of voltage values from the fluorometer (if possible).

*Field Blanks.* A field blank is deionized water which is treated as a sample. It is used to identify errors or contamination in sample collection and analysis.

*Negative and Positive Plates (for bacteria).* A negative plate results when the buffered rinse water (the water used to rinse down the sides of the filter funnel during filtration) has been filtered the same way as a sample. This is different from a field blank in that it contains reagents used in the rinse water. There should be no bacteria growth on the filter after incubation. It is used to detect laboratory bacteria contamination of the sample. Positive plates result when water known to contain bacteria (such as wastewater treatment plant influent) is filtered the same way as a sample. There should be plenty of bacteria growth on the filter after incubation. It is used to detect procedural errors or the presence of contaminants in the laboratory analysis that might inhibit bacterial growth.

*Field Duplicates.* A field duplicate is a duplicate sample collected by the same team or by another sampler or team at the same place, at the same time. It is used to estimate sampling and laboratory analysis precision.

*Lab Replicates.* A lab replicate is a sample that is split into subsamples at the lab. Each subsample is then analyzed and the results compared. They are used to test the precision of the laboratory measurements. For bacteria, they are used to obtain an optimal number of bacteria colonies on filters for counting purposes.

*Calibration Blank.* A calibration blank is deionized water processed like any of the samples and used to "zero" the instrument. It is the first "sample" analyzed and used to set the meter to zero. This is different from the field blank in that it is "sampled" in the lab. It is used to check the measuring instrument periodically for "drift" (the instrument should always read "0" when this blank is measured). It can also be compared to the field blank to pinpoint where contamination might have occurred.

*Calibration Standards.* Calibration standards are used to calibrate a meter. They consist of one or more "standard concentrations" (made up in the lab to specified concentrations) of the indicator being measured, one of which is the calibration blank. Calibration standards can be used to calibrate the meter before running the test, or they can be used to convert the units read on the meter to the reporting units (for example, absorbance to milligrams per liter).

Duplicate: Filter one randomly chosen sample for every 10 to 20 samples. Using a



forceps, transfer 4.25 cm Whatman GF/F glass fiber filter, wrinkles side up, to the filtration tower. 12.2.1.13 in SOP paper (06/17/2019).

Identify QC activities needed for each sampling, analysis, or measurement technique. For each required QC activity, list the associated method or procedure, acceptance criteria, and corrective action. Because standard methods are often vague or incomplete in specifying QC requirements, simply relying on the cited method to provide this information is usually insufficient. QC activities for the field and the laboratory include, but are not limited to, the use of blanks, duplicates, matrix spikes, laboratory control samples, surrogates, or second column confirmation. State the frequency of analysis for each type of QC activity, and the spike compounds sources and levels. State or reference the required control limits for each QC activity and corrective action required when control limits are exceeded and how the effectiveness of the corrective action shall be determined and documented. Describe or reference the procedures to be used to calculate applicable statistics (e.g., precision and bias). Copies of the formulas are acceptable as long as the accompanying narrative or explanation specifies clearly how the calculations will address potentially difficult situations such as missing data values, “less than” or “greater than” values, and other common data qualifiers.

**Instrument/Equipment Testing, Inspection, and Maintenance.** Describe how inspections and acceptance testing of instruments, equipment, and their components affecting quality will be performed and documented to assure their intended use as specified. Identify and discuss the procedure by which final acceptance will be performed by independent personnel (e.g., personnel other than those performing the work) and/or by the EPA project manager. Describe how deficiencies are to be resolved, when re-inspection will be performed, and how the effectiveness of the corrective action shall be determined and documented. Describe or reference how periodic preventive and corrective maintenance of measurement or test equipment or other systems and their components affecting quality shall be performed to ensure availability and satisfactory performance of the systems. Identify the equipment and/or systems requiring periodic maintenance. Discuss how the availability of critical spare parts, identified in the operating guidance and/or design specifications of the systems, will be assured and maintained.

**Instrument/Equipment Calibration and Frequency.** Identify all tools, gauges, instruments, and other sampling, measuring, and test equipment used for data generation or collection activities affecting quality that must be controlled and, at Final EPA QA/R-5 19 March 2001 specified periods, calibrated to maintain performance within specified limits. Describe or reference how calibration will be conducted using certified equipment and/or standards with known valid relationships to nationally recognized performance standards. If no such nationally recognized standards exist, document the basis for the calibration. Identify the certified equipment and/or standards used for calibration. Indicate how records of calibration shall be maintained and be traceable to the instrument.

**Inspection/Acceptance of Supplies and Consumables.** Describe how and by whom supplies and consumables (e.g., standard materials and solutions, sample bottles, calibration gases, reagents, hoses, deionized water, potable water, electronic data storage media) shall be inspected and accepted for use in the project. State acceptance criteria for such supplies and

consumables.

**Non-direct Measurements.** Identify any types of data needed for project implementation or decision making that are obtained from non-measurement sources such as computer databases, programs, literature files, and historical data bases. Describe the intended use of the data. Define the acceptance criteria for the use of such data in the project and specify any limitations on the use of the data.

**Data Management.** Describe the project data management process, tracing the path of the data from their generation to their final use or storage (e.g., the field, the office, the laboratory). Describe or reference the standard record-keeping procedures, document control system, and the approach used for data storage and retrieval on electronic media. Discuss the control mechanism for detecting and correcting errors and for preventing loss of data during data reduction, data reporting, and data entry to forms, reports, and databases. Provide examples of any forms or checklists to be used. Identify and describe all data handling equipment and procedures to process, compile, and analyze the data. This includes procedures for addressing data generated as part of the project as well as data from other sources. Include any required computer hardware and software and address any specific performance requirements for the hardware/software configuration used. Describe the procedures that will be followed to demonstrate acceptability of the hardware/software configuration required. Describe the process for assuring that applicable information resource management requirements are satisfied. Describe the process for assuring that applicable Agency information resource management requirements (EPA Directive 2100) are satisfied (EPA QA Project Plans only). If other Agency data management requirements are applicable, such as the Chemical Abstract Service Registry Number Data Standard (EPA Order 2180.1), Data Standards for the Electronic Final EPA QA/R-5 20 March 2001 Transmission of Laboratory Measurement Results (EPA Order 2180.2), the Minimum Set of Data Elements for Ground-Water Quality (EPA Order 7500.1A), or new data standards as they are issued by EPA, discuss how these requirements are addressed.



## **Appendix G. Background**

The Town of Hempstead (TOH) was given jurisdiction over the Town Wetlands when the Town was originally chartered, first under the Dutch Kieft Patten of 1644, then reaffirmed under the British Dongan Patten of 1685, and finally by the New York State Legislature subsequent to the Treaty of Paris. By the 1960s the importance of the wetlands was realized and steps were taken to protect them, including the formation of the present form of the Department of Conservation and Waterways (C&W). The Town water quality sampling program that is addressed in this QAPP is a continuation of the data set that started with an original survey in 1968 (Udell 1968).

### **Organizational History and Mission:**

The Department is established for the purpose of implementing the policies of the Town of Hempstead that are intended to conserve and maintain its wetlands and waterways for the benefit of the residents of the town and to exclusively administer the wetlands management plan of the Town of Hempstead (§53 of Town Code). The Department of Conservation and Waterways shall, under the general supervision of the Commissioner, have charge of the administration and enforcement of all local laws and Town Board resolutions pertaining to the preservation, conservation, management and maintenance of the town wetlands and waterways, including leasing of underwater and marginal lands; structures in waterways; erosion protection; marinas, piers, moorings and docks; shellfishing, operation of boats and seaplanes, dredging and other designated uses of the wetlands and waterways; and such other matters as may from time to time be referred to the Department (§53-3 of Town Code).

The Conservation Division was created; to have general administration of the conservation, protection and management of the Town of Hempstead underwater lands and marshlands and the marine life and natural resources therein and thereon: to conduct continuing ecological studies and investigations and determine both in the laboratory and in the field, factors influencing population of marine life in the waterways, chemical and biological characteristics of the waters, circulation patterns of Hempstead Bay estuary, qualitative analysis of bottom sediments, productivity and carrying capacity of marshlands within the bay area to determine approximate populations of wildlife which may be supported within the bay complex; to establish and maintain shellfish and wildlife sanctuaries and to improve the ecological balance within the wetlands for desirable species of marine life that can contribute to the recreational enjoyment and economy of the Town of Hempstead (§53-3C1 of Town Code).

The Nassau County treatment plant discharges effluent into the bay, a consideration that was noted in the 1968 report and a focus of this continuing study. Added to this is the need and intent to understand the effects from non-point sources. These water quality efforts are in conjunction with the Department's other goals, including the successful management of local wildlife, fish, shellfish, marshlands, and other natural resources within the Town of Hempstead.

### **Monitoring History and Status:**

The Town of Hempstead Department of Conservation and Waterways initiated a pilot water

sampling program in 1968 (Udell 1968), and then initiated regular Bay Study (i.e. Hempstead Bay) sampling in the early 1970s. A report on this program was published using support from the New York State Department of State, Environmental Protection Fund (NYS DOS EPF) in 2013 (TOH C&W 2013). This sampling protocol was continued until June of 2016 when funding was discontinued and the TOH C&W Water Quality Laboratory was closed in June 2017 pending future support. The funding provided by NYS DEC through the Long Island Regional Planning Council (LIRPC) and Long Island Nitrogen Action Plan (LINAP) will contribute to the reopening and recertification of the C&W Water Quality Laboratory in 2019.

The goal of the Town in implementing the project described in this QAPP is to document the revival, continuation, and expansion of water quality studies within Hempstead Bay and its watersheds, that have yielded valuable long-term data sets originally developed at the Town of Hempstead (TOH) Marine Laboratory (Udell 1968, Conservation & Waterways 2013, Fisher et al. 2018). The current monitoring program represents a partnership between TOH and Hofstra University to continue many of the efforts carried out under TOH's past monitoring programs while also adding measurements of atmospheric nitrogen deposition. The monitoring program described in this QAPP includes: i) monthly one meter depth water sampling for nitrate, nitrite, ammonia, orthophosphate, dissolved oxygen (DO), salinity, temperature, chlorophyll a, and silica in Hempstead Bay and its tributaries; ii) monthly vertical profiles from the surface to maximum depth using YSI SONDEs to collect salinity, DO, temperature, fluorometric chlorophyll, turbidity, and pH at deep water locations throughout Hempstead Bay; iii) continuous water quality monitoring using in-situ instruments located in each of the three bays (West Bay, Middle Bay, and East Bay) within Hempstead Bay to provide a record of salinity, DO, temperature, fluorometric chlorophyll, turbidity, and tidal depth at 12 minute intervals, and iv) an atmospheric nitrogen deposition monitoring network within the southern half of Nassau County. The study area for activities under this QAPP includes Hempstead Bay, its major tributaries, and a network of atmospheric deposition monitoring stations located largely within the Nassau County portion of the South Shore Estuary Reserve (SSER) watershed (Map i).

At the time of writing, Hempstead Bay and the rest of the South Shore Estuary Reserve (SSER) are not covered under the EPA National Estuaries Program and are therefore not eligible for funding under that program (<https://www.epa.gov/nep/local-estuary-programs>). Therefore the EPA is not directly involved in this QAPP and the prime source of historical funding support has been NYS DOS, with additional funding through LIRPC/LINAP, NYS GIGP, NYS DEC, NOAA, NYS Sea Grant, Nassau County Soil and Water Commission, and other sources. This jurisdictional distinction is reflected in this document.

Additional Sampling protocols were developed and expanded during the 1990s and into the early 2000s, including Vertical Profiles at deeper locations that are more conducive to complete downcasts, and tributary sampling that was piloted using YSI water quality instruments but expanded to include chemical and bacterial work during the 2000s into the 2010s. Under NYS DOS EPF funding, continuous water quality recording was initiated in 2014, but also mostly

discontinued after June of 2017. Long term data sets are known to be extremely important for ecological and marine management work (Lindenmayer et al 2012, Addison et al. 2015, Hughes et al. 2017), therefore we are intending to continue to use a subset of the existing water quality stations rather than start a new study. This is similar to what has been done in the central waters of Long Island Sound and Chesapeake Bay (Connecticut DEEP 2017, Donat 2018).

Tidal data recording was also initiated at 6 locations within Hempstead Bay and one in Jamaica Bay during the 1970s using nitrogen gas pressure recorders (Bristol Inc), and transitioned to electronic data collection by USGS (TOH C&W, Freeport Village, and NYS DEC funding) and Stony Brook SoMAS (NYS DOS EPF and TOH C&W funded), with the addition of water quality and weather parameters at the USGS station at Point Lookout with matching funds from TOH C&W. USGS later added an additional station at Hog Island Channel under NYS DEC local match that includes nitrate and other water quality parameters, with calibration support from TOH C&W.

Trend studies and sediment characteristic studies of the salt marshes and bays were performed in collaboration with researchers from various organizations, including USGS, Stony Brook Ecology and Evolution, Stony Brook SoMAS, Hofstra University Geology and Sustainability, CUNY Baruch College, Adelphi University Environmental Studies, and others. Research on wildlife in the estuary and associated Barrier Beaches is continuing in cooperation with NYS DEC Wildlife Division, US FWS, NYS Audubon Association, Hofstra Biology Department, Adelphi Biology and Environmental Studies Departments, and many others. Citizen Science efforts have been made by SPLASH that include beach plantings, marsh clean-ups, some water quality sampling funded by the LI Sound Study, and volunteer assistance with shell bagging in support of the TOH C&W oyster reestablishment efforts. Local schools have also participated in estuarine research work and volunteer assistance, notably Long Beach High School. The Town of Hempstead also maintains estuarine educational facilities at the Oceanside Marine Nature Study Area since 1970 and the more recent Lido Nature Preserve, Levy Preserve.

The data provided by this program is considered essential to the continued evaluation and monitoring this section of the South Shore Estuary Preserve and implements Outcomes 6-1 & 6-3 of the SSER Comprehensive Management Plan (SSERC 2001, Fisher et al. 2018). This management plan (SSER CMP) is currently the regional management plan of record in which the Town of Hempstead is a participant. Data from the Town's programs have been traditionally been available upon request to the Department of Conservation and Waterways, Town of Hempstead.

### **Partnership with Hofstra University History:**

Hofstra university was founded as a branch of New York University in 1935, and subsequently granted an independent charter as Hofstra College and accreditation in 1940. Hofstra was therefore the first private university on Long Island. Hofstra has been involved with the Town of Hempstead, Department of Conservation and Waterways since the Department's inception and assisted with early water quality studies. This association has continued, with Hofstra alumnae on the Department's staff and continued scientific collaboration with Hofstra researchers.

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## Appendix H. Glossary of Terms and Abbreviations

BLIS- Bleach Injection System

CCV- Continuing Calibration Verification

CoC- Chain of Custody

COV - Coefficient of Variation. another index of precision if a sample is analyzed in triplicate to show it is # 20%. The calculation is as follows:

$$CV = 100 * \sigma / \bar{x}$$

Where:

$\sigma$  = Standard deviation,

$\bar{x}$  = mean

CTD- Conductivity Temperature Depth

C&W- Department of Conservation and Waterways

DDI- double deionized

DI- de-ionized

DIN- Dissolved Inorganic Nitrogen

DIP- Dissolved Inorganic Phosphorus

DON- Dissolved Organic Nitrogen

DQO- Data Quality Objectives

ELAP- Environmental Laboratory Approval Program, NYS Department of Health under EPA program

EPA - United States Environmental Protection Administration

FB- Field Blank

FLNTU- Combination Fluorometer and Turbidity Sensor

FS- Fluorescence Units (percent full scale)

FW - Formula Weight

FWS- Fish and Wildlife Service

Hach Simplified Kjeldahl - A manufacturer's modification by Hach that has been approved by the EPA

HDPE- high-density polyethylene resin

IDL- Instrument Detection Limit

IER- ion exchange resin

orthoP- orthoPhosphate

LAI- Leaf Area Index

LINAP - Long Island Nitrogen Action Plan

LIRPC - Long Island Regional Planning Council

MDL- Method Detection Limit

MPN- Most Probable Number

MSDS - Material Safety Data Sheet, these must be available to employees.

NTU- Nephelometric Turbidity Units

NSSP- National Shellfish Sanitation Program

NYS DEC - New York State Department of Environmental Conservation

NYS GIGP - New York State Green Innovation Grant Program

PFD- Personal Flotation Device

QA- Quality Assurance

QC- Quality Control

RPD- Relative Percent Difference. The system of overall precision assessments is determined for the combined sampling and analytical process through replicate analysis of samples. A relative percent difference (RPD) of 20% or less is generally considered acceptable for dissolved parameters and an (RPD) of 30% or less is generally considered acceptable for particulate parameters if all other QC conditions are within acceptable limits.

Relative Percent Difference (RPD)

$$RPD (\%) = [X1 - X2] / ((X1+X2) / 2) * 100$$

Where X1 and X2 represent results from different samples being compared, such as field duplicates.

Alternatively the coefficient of variance (CV) can be calculated

SCL/SPEC - Sterile Coliform 120ml screw cap bottles produced by Scientific Specialties Services Inc.

SOP- Standard Operating Procedure

SOW- Synthetic Ocean Water

SSER- South Shore Estuary Reserve

SoMAS- Stony Brook School of Marine and Atmospheric Sciences

SPLASH- Stop Polluting, Littering and Save Harbors Organization

SSER CMP- South Shore Estuary Reserve Comprehensive Management Plan

TC- Temperature Control

TOH- Town of Hempstead

TKN- Total Kjeldahl Nitrogen

TDN- Total Dissolved Nitrogen

TDKN- Total Dissolved Kjeldahl Nitrogen

TP- Total Phosphorus

TMDL- Total Maximum Daily Load

Vertical Profiles - the profiling of a water column at incremental depths in regards to water quality parameters

WQL - Water Quality Laboratory

WQM- Water Quality Monitor (Sea-Bird -Scientific long-deployment data logging instrument)

WGS 1984- global reference system, World Geodetic System 1984

YSI Sonde- multiparameter instrument for water quality by YSI, a Xylem Corp. brand name..