A. Project Management and Information/Data Quality Objectives

A.1 Title Page

Unified Water Study Embayment Research for 2024 Season Quality Assurance Project Plan (QAPP)

This QAPP was created in accordance with the EPA S2 QAPP Standard.

Grant # LI 96217623 Award Date: 10/01/2023 End Date: 12/31/2025
EPA QAPP 2024-28 (this QAPP)

Monitoring Organizations

Ash Creek Conservation Association, Bronx River Alliance, Clean up Sound and Harbors (CUSH), Coalition to Save Hempstead Harbor, Connecticut River Conservancy, Cornell Cooperative Extension of Suffolk County Marine Program, East Basin Enterprises Friends of the Bay, Friends of the Farm River Estuary, Earthplace, Inc. (Harbor Watch), Interstate Environmental Commission, New England Science & Sailing Foundation, Salonga Wetland Advocates Network, Save the River –Save the Hills, Inc., Save the Sound, Setauket Harbor Task Force, SoundWaters, The Maritime Aquarium at Norwalk, Town of Darien, Town of Fairfield – Conservation Department, Town of Stratford – Conservation Department, River Advocates of South Central Connecticut, Guardians of Flushing Bay, East River Watershed Research Institute, SUNY Maritime, Project Oceanology, Fishers Island Seagrass Management Coalition

Coordinating Organization

Save the Sound

Funded By

The United States Environmental Protection Agency – Long Island Sound Study

Version Date (yyyy.mm.dd)
April 17, 2024

QAPP Effective Date (yyyy.mm.dd)
April 25, 2024

Prior Associated Approved QAPPs:

QAPP Title	EPA QAO Approver	Approval Date	Agreement Title, Agreement Number, with QAPP Identifier	Notes
Mamaroneck Harbor and Little Neck Bay, UWS Water Quality Monitoring QAPP	Kathryn Drisco, EPA Region 2 Quality Assurance Officer	8/3/2017	NFWF Grant 53526/ Water Quality Monitoring Initiative for Long Island Sound Embayments (NY), EPA Cooperative Agreement LI-00A00129-0 (FC.R278).	First UWS QAPP with two New York embayments piloting Tier II procedures
Long Island Sound Embayment Water Quality Monitoring QAPP. For monitoring activities conducted as part of the Long Island Sound Tier 1 Unified Water Study (UWS)	Esther Nelson, EPA Region 2 Quality Assurance Officer	6/5/2018	National Fish and Wildlife Foundation (NFWF), US EPA recipient via Cooperative Agreement LI 00A00382 (NFWF FC.R334)	UWS Tier I added to QAPP
Long Island Sound Embayment Water Quality Monitoring QAPP. For monitoring activities conducted as part of the Long Island Sound Tier 1 Unified Water Study (UWS)	Esther Nelson, EPA Region 2 Quality Assurance Officer	5/2/2019	Unified Water Study: Nitrogen Impacts on Long Island Sound, EPA Agreement No. LI96259818.	Additional sites and stations to QAPP
Long Island Sound Embayment Water Quality Monitoring QAPP. For monitoring activities conducted as part of the Long Island Sound Tier 1 Unified Water Study (UWS)	Esther Nelson, EPA Region 2 Quality Assurance Officer	3/16/2020	Unified Water Study: Nitrogen Impacts on Long Island Sound, EPA Agreement No. LI96259818	Additional sites and stations to QAPP and COVID-19 considerations for trainings and season start
Long Island Sound Embayment Water Quality Monitoring QAPP. For monitoring activities conducted as part of the Long Island Sound Tier 1 Unified Water Study (UWS)	Esther Nelson, EPA Region 2 Quality Assurance Officer	4/20/2021	Unified Water Study 2021, EPA Agreement No. LI96259818	Additional sites and stations to QAPP
Long Island Sound Embayment Water Quality Monitoring QAPP. For monitoring activities conducted as part of the Long Island Sound Tier 1 Unified Water Study (UWS)	Suriya Rao, EPA Region 2 Quality Assurance Officer	3/15/2022	Unified Water Study Embayment Research for 2022 Season + Chittenden Park Living Shoreline Restoration Design, EPA Agreement No. LI96244321	Additional sites and stations to QAPP
Long Island Sound Embayment Water Quality Monitoring QAPP. For monitoring activities conducted as part of the Long Island Sound Tier 1 Unified Water Study (UWS)	Suriya Rao, EPA Region 2 Quality Assurance Officer	4/5/2023	Unified Water Study Embayment Research for 2023 Season, EPA Agreement No. LI96239522 (EPA QAPP 2023-16)	Additional sites and stations to QAPP

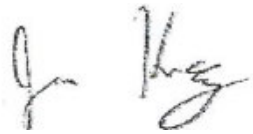
A.2. APPROVAL PAGE

date: 4/25/2024

Peter Linderoth, Monitoring Program Project Manager
and Quality Assurance Officer
Save the Sound

date: 4/25/2024

Jamie Vaudrey, UWS Science Advisor
University of Connecticut



date: 4/25/2024

Jason Krumholz, UWS Science Advisor
University of Connecticut

See U.S. EPA Region 2 -Quality Assurance Project Plan Approval Form for Signature

date:

Elizabeth Tanzi, EPA Region 2 Project Officer
US Environmental Protection Agency, Region 2

date:

Erwin Smieszek, EPA Region 2 Quality Assurance Officer
US Environmental Protection Agency, Region 2

U.S. EPA REGION 2 - QUALITY ASSURANCE PROJECT PLAN APPROVAL FORM

PROJECT INFORMATION

Quality Assurance Officer:	Erwin J. Smieszek (LSASD/MAB)
Project Officer or Project Mgr.:	Elizabeth Tanzi (WD/WMB/LISO)
Title of Quality Assurance Project Plan:	Unified Water Study Embayment Research for 2024 Season
Assistance Agreement or Contract #:	LI 96217623
QA File Number:	2024-28

REGIONAL QA MANAGER OR DELEGATED APPROVER

Approved ☑ Conditionally Approved* ☐

*** Conditional Approval may be provided when there are unresolved comments that do not impact the data collection or the quality of the data and where the project has a small window of opportunity to collect such data. Conditional Approval expires 30 days from the signature date. If updated quality documentation (QD) is not provided by the expiration date or another due date is not agreed upon by EPA, then the QD will be considered delinquent.**

Comments:

Signature EPA QA Officer ERWIN SMIESZEK Digitally signed by ERWIN SMIESZEK Date: 2024.04.25 07:51:02 -04'00'

Signature EPA PO or PM ELIZABETH TANZI Digitally signed by ELIZABETH TANZI Date: 2024.04.25 08:40:45 -04'00'

REVIEW SUMMARY:
A review was conducted on the above referenced Quality Assurance Project Plan. The subject QAPP was reviewed for conformance with Directive (2105-S-02.0) dated July 18, 2023; the USEPA Region 2 Guidance for the Development of QAPPs for Environmental Monitoring Projects, April 2004 and other EPA QAPP guidance documents as appropriate.

This approval form documents EPA's decision of approval or conditional approval* for the aforementioned QAPP. After the QAPP is approved by EPA via this approval form, obtain the required signatures from your organization on the QAPP Title/Signature page. Send the signed QAPP to the EPA Project Officer and others on the QAPP distribution list within the timeframe stipulated in the AA terms and conditions.

A.3. TABLE OF CONTENTS

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A.4. PROJECT PURPOSE, PROBLEM DEFINITION, AND BACKGROUND

Despite three decades of effort to improve water quality, Long Island Sound (LIS) remains a severely stressed environment. In the western Sound, from Greenwich to Nassau County, dissolved oxygen concentrations—a key measure of the Sound's health—consistently fall to levels too low to sustain aquatic wildlife. Low levels of dissolved oxygen, or hypoxia, are worsened by excess nitrogen (N) from outdated sewage collection systems, failing septic systems, contaminated stormwater runoff, and fertilizers. Moreover, there are serious eutrophication-related impacts in throughout the Sound[1]. According to the EPA's Nitrogen Reduction Strategy, "Impairments linked to excess discharges of N include harmful algal blooms, low DO, poor water clarity, loss of submerged aquatic vegetation and tidal wetlands, and coastal acidification."

Main-stem Long Island Sound water quality data are abundant and readily available from Connecticut Department of Energy and Environmental Protection, New York City Department of Environmental Protection, and the Interstate Environmental Commission for analyses. However, there are limited environmental health data being collected in LIS embayments. The Unified Water Study (UWS) will fill in many of the data gaps that exist amongst LIS embayments. These data sets will have myriad of uses including comparing embayment environmental health, informing water quality management decisions, and conveying the information to the public so they can be better informed about the environmental health of LIS embayments.

The groups selected to participate in the 2018 UWS season went through an application process administered by the Monitoring Program Project Manager, Monitoring Program Coordinator, and the Monitoring Program Field Coordinator. A standardized application form was distributed and the administrators used a metric to select groups. In 2018, there were 19 monitoring groups monitoring a total of 33 embayments. In 2019, three new groups were

[1] Vaudrey, J. M., Yarish, C., Kim, J. K., Pickerell, C., Brousseau, L., Eddings, J., & Sautkulis, M. (2016). Comparative analysis and model development for determining the susceptibility to eutrophication of Long Island Sound embayments. Connecticut Sea Grant Final Project Report, 38.

added to the UWS. The 2019 group and embayment total is 22 groups in 37 embayments. 12 of the 37 embayments in the UWS will also receive Tier II monitoring. In 2020, one new group is being added to the UWS. The 2020 group and embayment total is 23 groups in 38 embayments. 13 of the embayments will receive Tier II monitoring. The 2021 group and embayment total is 24 groups monitoring 41 embayments. 13 of the embayments will receive Tier II monitoring. The 2022 group and embayment total is 26 groups monitoring 44 embayments. 12 of the 44 embayments will receive Tier II monitoring. The 2023 group and embayment total is 26 groups in 44 embayments. 14 of the 48 embayments will receive Tier II monitoring. The 2024 group and embayment total is 28 monitoring groups and 48 embayments. 14 of the 48 embayments will receive Tier II monitoring.

The final locations of the Tier I embayments in the UWS are dependent on the applications and respective monitoring group's interests. Tier II embayments are selected referencing priority embayment plans put forth by Connecticut Department of Energy and Environmental Protection, New York State Department of Environmental Conservation, and Long Island Sound Study. Monitoring group experience is also a factor in the decision.

Organizational History and Mission

The mission of Save the Sound (STS) is to protect and improve the land, air and water of Connecticut and Long Island Sound. Founded in 1978, STS merged in 2004 with Save the Sound, a respected voice for the protection of Long Island Sound's shoreline, marine habitat and water quality with a track record of more than 40 years. The proposed project is in line with one of Save the Sound's strategic goals: "Our Long Island Sound, rivers and lakes are safe for people and wildlife."

Data collected under this QAPP will be collected in a manner to allow the data to be used as part of the Unified Water Study. The UWS is a coordinated effort among groups monitoring Long Island Sound with the goal of comparing water quality parameters associated with eutrophication within and among embayments. The UWS is comprised of two tiers, Tier I and Tier II. Tier I data is required for entry into the study. The parameters monitored in Tier I of the study are dissolved oxygen, conductivity (salinity), chlorophyll a, temperature, turbidity, and qualitative macrophyte assessments. Tier II parameters monitored as part of the UWS are nutrient concentrations, logged dissolved oxygen and conductivity (salinity) data, and underwater camera quantitative assessments of macrophytes. Tier I and Tier II parameters are covered in this QAPP.

Monitoring History and Status

The New York Office of Save the Sound initiated a pathogen-indicator and water quality monitoring program in 2013 and has since expanded the spatial and temporal scale of the water quality monitoring program. Save the Sound was the lead facilitator in the development of the UWS and participated in the 2016 UWS pilot season. Save the Sound continues to

participate in the UWS as the coordinating organization as well as a monitoring group. Measuring the eutrophic conditions in the bays and harbors of Long Island Sound directly relates to Save the Sound's overarching goal of reducing nitrogen and other pollutants in the Sound.

The UWS conducted a pilot season for the Tier I parameters with four existing monitoring groups in 2016. The goal of the 2016 season was to develop protocols that followed standard methods for embayment monitoring. All groups involved with the 2016 season had previous experience monitoring their embayments and were involved in ongoing monitoring programs. Groups involved with the 2016 pilot season, and other advisory participants such as academics and federal and municipal agencies, assisted with developing and finalizing the UWS Tier I SOPs.

2017 marked the inaugural season of the UWS with twelve groups participating in the study. Eleven of these groups monitored in Long Island Sound and one monitored off the south shore of Long Island, NY. These groups maintained their own QAPPs based on a template. These QAPPs provided integrity to the Study but monitoring groups in the UWS now operate under a collective EPA-approved QAPP, this document. The groups are responsible for adhering to the QAPP and Save the Sound will ensure that quality objectives are met for each embayment in the study as outlined in this document. The collective QAPP will be updated upon changes to embayments, participating groups, or procedures in the study.

Monitoring and Data Use Objectives

Data collected under this QAPP will be collected in a manner to allow the data to be used as part of the UWS. The UWS is designed to facilitate equitable water quality comparisons across Long Island Sound embayments. All data will be available to the public via request or download from Save the Sound's website. Data will also be uploaded to the Environmental Protection Agency Water Quality Portal. Save the Sound has met, and continues to meet and discuss, UWS data usage by Connecticut Department of Energy and Environmental Protection, New York State Department of Environmental Conservation, and UWS monitoring groups are welcome and encouraged to share their data on a local level to potentially elicit changes that could improve water quality in their respective embayments. There is also an overarching primary project goal to include the UWS data sets in the Long Island Sound Report Card which is issued by Save the Sound. The report card compares water quality indicators (dissolved oxygen, nutrients, chlorophyll a, and water clarity) to scientifically derived thresholds or goals. These indicators are combined into an overarching Water Quality Index, which is presented as a subregion percent score. The report card provides a geographically specific assessment of annual Long Island Sound ecosystem health.

Additionally, the activities covered under this QAPP will provide quality-controlled data that can support secondary goals such as the assessment and restoration of coastal embayments and watersheds through the implementation of programs such as but not limited to:

- EPA's 305(b) water body health assessments and 303(d) TMDL development for impaired waters
- Clean Water Act Section 319 projects
- Connecticut Department of Energy and Environmental Protection and New York Department of Environmental Conservation Watershed Management Plans
- Long Island Sound Study's Comprehensive Conservation and Management Plan
- Long Island Sound Study Environmental Indicators Project
- New York State Department of Environmental Conservation Long Island Nitrogen Action Plan

A.5. PROJECT / TASK DESCRIPTION

A.5.a. Sampling Types Covered by this QAPP

Five types of monitoring stations are included in the UWS

1) *Tier I water quality* stations are sampled within three hours of sunrise between the months of May through October using a multiparameter sonde. A minimum of four stations per embayment are required. If multiple regions of the embayment are delineated, a minimum of three stations are required per region. Monitoring groups will plan to sample Tier I water quality stations at a minimum every two weeks from May to October. However, if unforeseeable circumstances make this plan not possible, a minimum of six sample events between May and October are required for inclusion in the UWS; including at least one sample event in each of the months of June, July, August, and September. The number and location of Tier I water quality stations for embayments in the UWS are provided in Section A.5.b.

Tier I Water Quality – Water quality parameters are selected to facilitate comparisons between embayments. Monitoring groups must collect the following data to be included in the UWS:

- for each station
    - GPS coordinates of stations, recorded each sample date
    - Date and time
    - Total water depth
  - 0.5 m below the surface, 0.5 m above bottom, mid-depth if total depth >10 m; if total depth is less than 1.5 m, only a mid-depth reading will be collected
    - Temperature
    - Conductivity (salinity)
    - Dissolved oxygen
    - Chlorophyll a
    - Turbidity
  - Once per field day undertake a replicate profile including all parameters
- Obtain from an online NOAA tide table and weather station approved by Monitoring Program Coordinator:
  - Time of high and low tide nearest time of sampling
  - High and low air temperature for 24 hours preceding field sampling
  - Precipitation out a week preceding sampling event
- Within 1 day of the field sampling day, read the GPS of a land-based reference station

Monitoring groups will collect water quality data for the Unified Water Study according to procedures provided in the UWS SOP Depth and GPS, UWS SOP Sonde Profile, and UWS SOP Filtered Chlorophyll in Appendix A.

2) *Qualitative Tier I Macrophyte* stations are land-based or boat-based. They are sampled only mid-summer and may be sampled on different days from the water quality stations. Sampling occurs on three separate days between July 15 and August 7. Two sample days or a date slightly outside of the date criteria may be sufficient in the event of unforeseen complications. This decision will be made by the Monitoring Program Quality Assurance Officer and UWS Science Advisor(s).

   The goal of this part of the UWS is to identify potential problem areas, versus characterizing the overall condition of the embayment; field teams will look for areas with the highest macrophyte abundance they can find. Groups will also look for and note the presence of eelgrass (a beneficial condition). This is not intended to be a quantitative assessment. Macrophyte surveys will complement chlorophyll a concentrations to better understand the dominant primary producer in the system.

Qualitative Tier I Macrophytes - Monitoring groups must collect the following data to be included in the UWS:

- for each macrophyte station
  - GPS coordinates of stations, recorded each sampling date
  - Date and time

    - Photos of macrophytes
- Within 1 day of the field sampling day, read the GPS of a land-based reference station

Groups will submit data and photos to the Unified Water Study according to methods provided in the UWS SOP Qualitative Macrophytes in Appendix A.

3) *Quantitative Tier II Macrophyte* stations are boat-based. They are sampled only mid-summer and are typically sampled on different days from the water quality stations. Sampling occurs on one day between July 15 and August 7.

Quantitative Tier II Macrophytes - Monitoring groups must collect the following data to be included in the UWS:

- For each macrophyte station
    - GPS coordinates
    - Date and time interval
    - Video of macrophyte abundance
- Within 1 day of the field sampling day, read the GPS of a land-based reference station

Groups will submit data and photos to the Unified Water Study according to methods provided in the UWS SOP Macrophyte Percent Coverage Via Camera in Appendix A.

4) *Tier II nutrients* stations are sampled a minimum every two weeks from May to October. However, if unforeseeable circumstances make this plan not possible, a minimum of six sample events between May and October are required for inclusion in the UWS; including at least one sample event in each of the months of June, July, August, and September. At a minimum, there will be two stations per embayment. In embayments with multiple regions, there will be a minimum of two stations per region. The number and location of Tier II nutrients stations for embayments in the UWS are provided in Section A.5.b. Stations in tributaries are sampled for nutrients on the same day as the embayment they flow into is sampled. These stations are chosen with respect to access and salinity value <1 ppt. A Long Island Sound reference station will also be sampled for nutrients on the same day the embayment stations are sampled.

Tier II Nutrients - Monitoring groups must collect the following data to be included in the UWS:

- For each water quality station
        - GPS coordinates of stations, recorded each sample date
        - Date and time
    - 0.5 m below the surface
        - Total Nitrogen
        - Total Dissolved Nitrogen
        - Dissolved Inorganic Nitrogen Species (nitrate, nitrite, ammonia)
        - Total Phosphorous

- Orthophosphate (also known as dissolved inorganic phosphorus)
- Salinity

Groups will submit data to the Unified Water Study according to methods provided in the UWS SOP Filtered Nutrients and UWS SOP Total Nitrogen and Total Phosphorous in Appendix A.

5) *Continuous dissolved oxygen* stations will be selected with consideration to representativeness and where access is granted for maintenance of the equipment. A minimum of one continuous dissolved oxygen station is required per embayment region. Logging will commence from May to October 31.

Continuous Dissolved Oxygen - Monitoring groups must collect the following data to be included in the UWS:

- for each continuous dissolved oxygen station
  - GPS coordinates of stations, recorded each sampling date
  - Date and time
  - Dissolved Oxygen
  - Conductivity (Salinity)
  - Barometric Pressure
  - Temperature
  - Light

Groups will submit data to the Unified Water Study according to methods provided in the UWS SOP Continuous Dissolved Oxygen in Appendix A.

Roles of Project Participants

The Monitoring Program Coordinator and Monitoring Program Field Coordinator or designee will provide guidance and advisement to the groups participating in the UWS, conferring with the UWS Science Advisors as needed. They will conduct trainings, field audits, station selection guidance, ongoing technical support, and lab coordination among other activities. The full set of participants and their respective roles can be referenced in Table 1 of this document. Figure 2 outlines the lines of communications between project participants.

UWS Project Laboratory Manager has agreed to the UWS SOP Filtered Chlorophyll, UWS SOP Total Nitrogen and Total Phosphorous, and UWS SOP Filtered Nutrients for sample collection in the field. The project laboratory has provided their laboratory method SOPs which can be reviewed in Appendix C of this QAPP. The laboratory will adhere to both the UWS and their lab SOPs.

Participating Monitoring Groups will be responsible for conducting field work and analyses following the requirements presented in the UWS SOPs. Monitoring Group Leads or designated appointees will complete all required training. Monitoring Group members will complete all

required data sheets and chain of custody forms. Any problems or deviance from this QAPP or SOPs will immediately be reported to the Monitoring Program Field Coordinator who will confer with the Monitoring Program Quality Assurance Officer on corrective course of action.

How the proposed sampling plan supports the Monitoring Program objectives

Data collected under this QAPP will be collected in a manner to allow the data to be used as part of the UWS. The UWS is a coordinated effort among groups monitoring Long Island Sound embayments with the goal of comparing water quality and macrophyte abundance within and among embayments.

Overview of data handling processes

Sampling event and field data will be collected on standardized field and instrument calibration sheets. These standardized datasheets are in Appendix B of this document.

If a field team is delivering samples to a centralized location for laboratory analysis by a member of the Monitoring Group, the field data sheet is sufficient as a chain of custody record. In this scenario a chain of custody form will not be required as sufficient information is contained on the sample event datasheet.

If a field team is delivering a sample for analysis by a lab external to the monitoring group, the UWS Chlorophyll a Chain of Custody Form or UWS Nutrient Chain of Custody Form is required. These forms are in Appendix B of this document.

The type of sample information that can be collected under this QAPP includes:

- GPS location to identify and track station locations
- Total water depth of the sample station; and depth of sample location
- Temperature
- Conductivity (Salinity)
- Dissolved oxygen concentration and percent saturation
- Chlorophyll a concentrations (filtered water sample)
- Chlorophyll a concentrations (*in situ* fluorescence)
- Turbidity
- Light
- Qualitative assessment of macrophytes
- Quantitative assessments of macrophytes
- Nitrogen forms to measure nutrient levels
- Phosphorous forms to measure nutrient levels

A.5.b. Maps of Study Area

Figure 1a-am: All UWS study sites. Reporting regions if present are clearly delineated. Red circles are water quality station locations. The maps are overlain by a hexagonal grid. The grid was used to select stations to represent the water quality of the entire embayment using a probability-based sampling design[2], as in the EPA National Coastal Assessment[3]. In some cases, hexagons have been joined to represent a local area considered similar or if a hexagon included large sections of land.

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[2] Paul, J.F., J.L. Copeland, M. Charpentier, P.V. August, and J.W. Hollister. 2003, Overview of GIS applications in estuarine monitoring and assessment research. Marine Geodesy Journal 26: 63-72.

[3] EPA, U.S. 2001. National Coastal Assessment: Field Operations Manual. U. S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Gulf Ecology Division, Gulf Breeze, FL. EPA 620/R-01/003. 72 p.

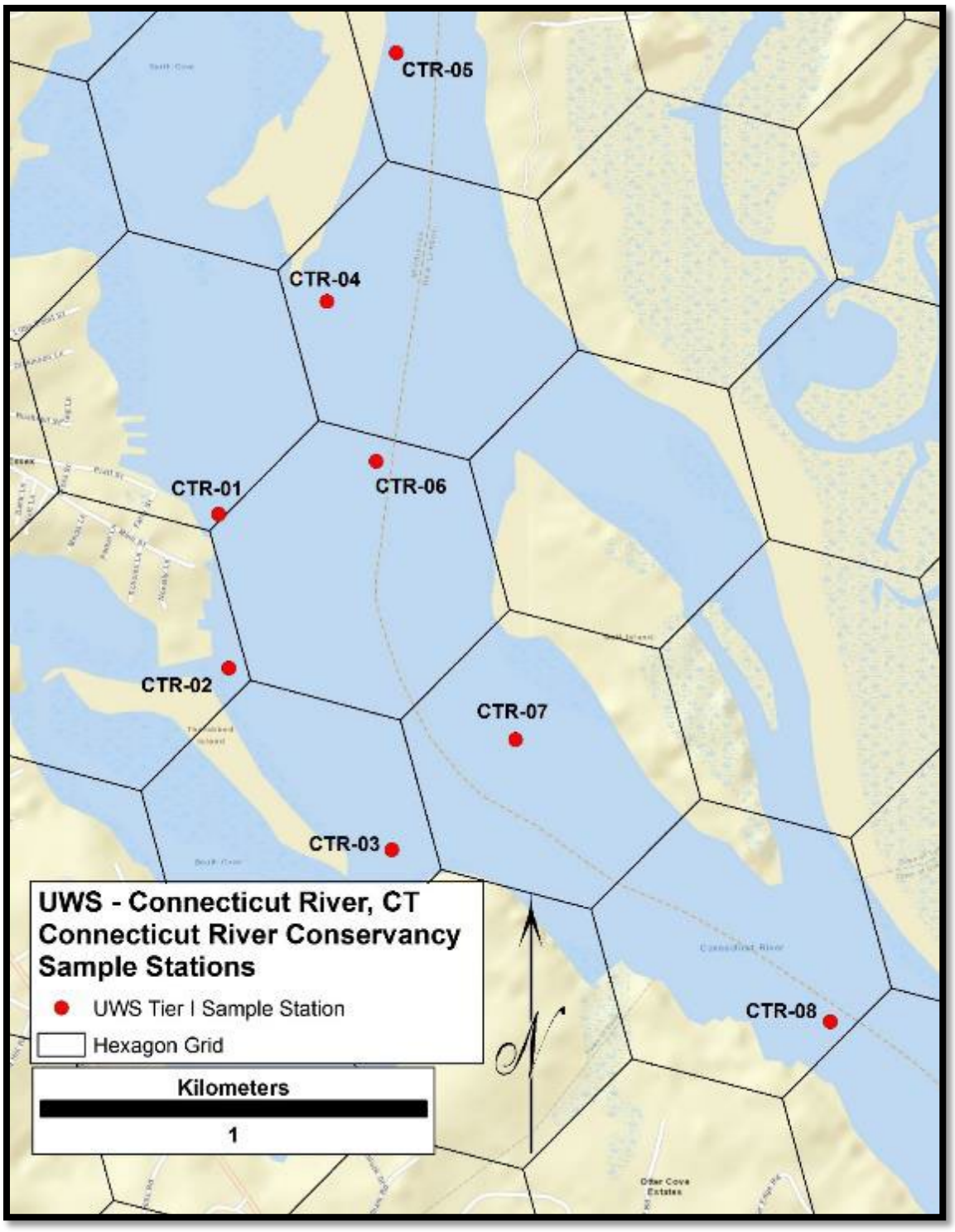

Figure 1a Connecticut River, CT

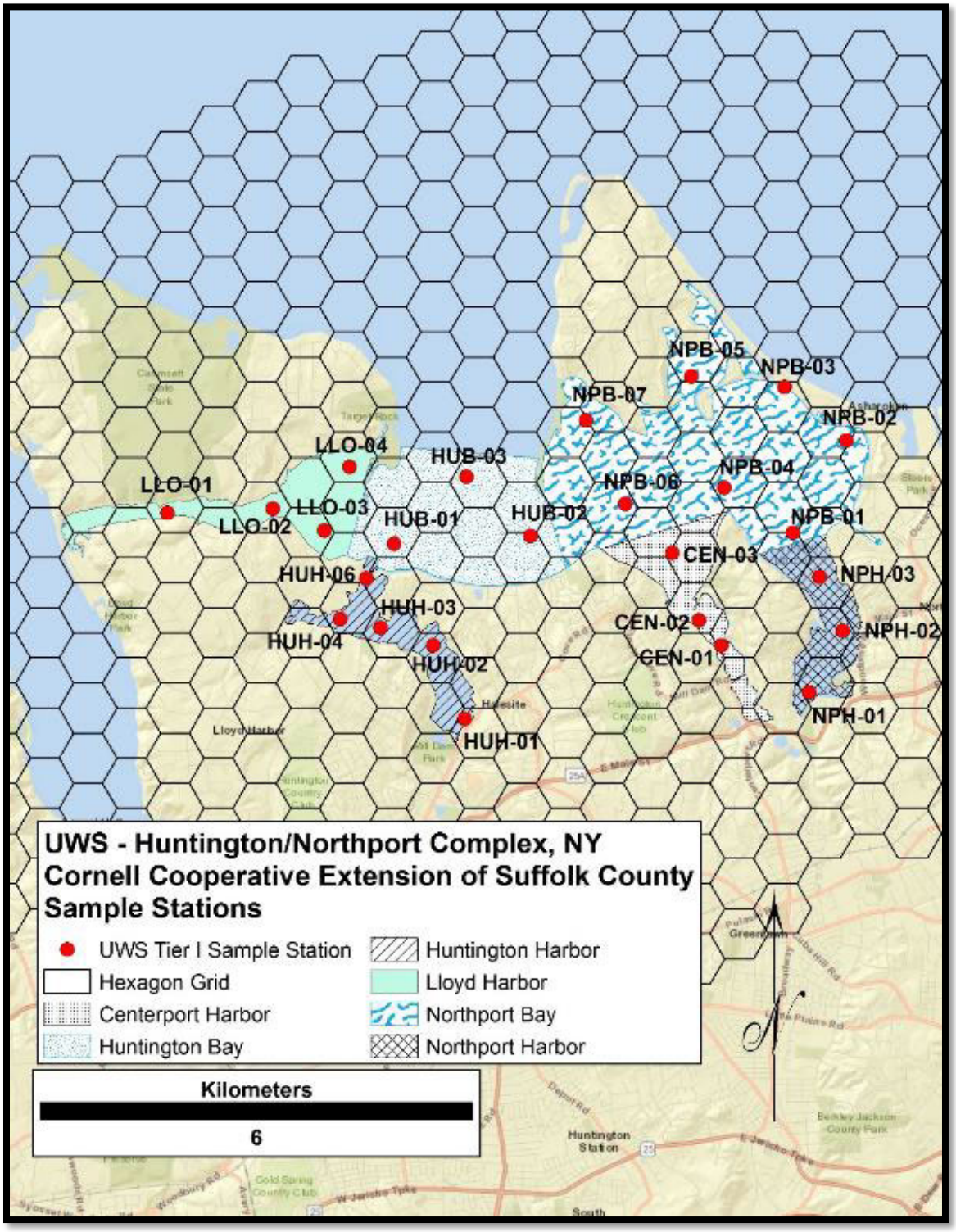

Figure 1b Huntington/Northport Complex, NY

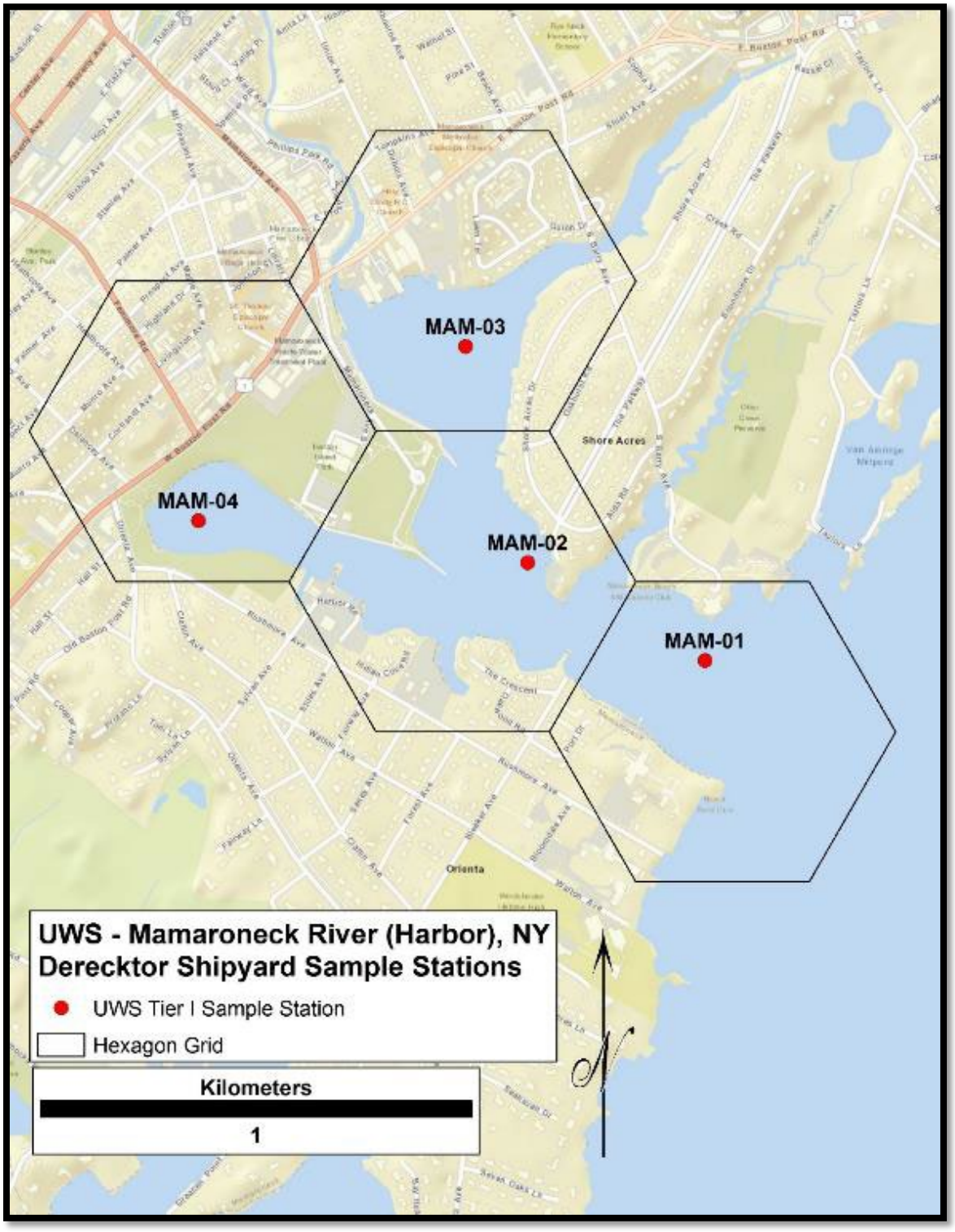

Figure 1c Mamaroneck River (Harbor), NY

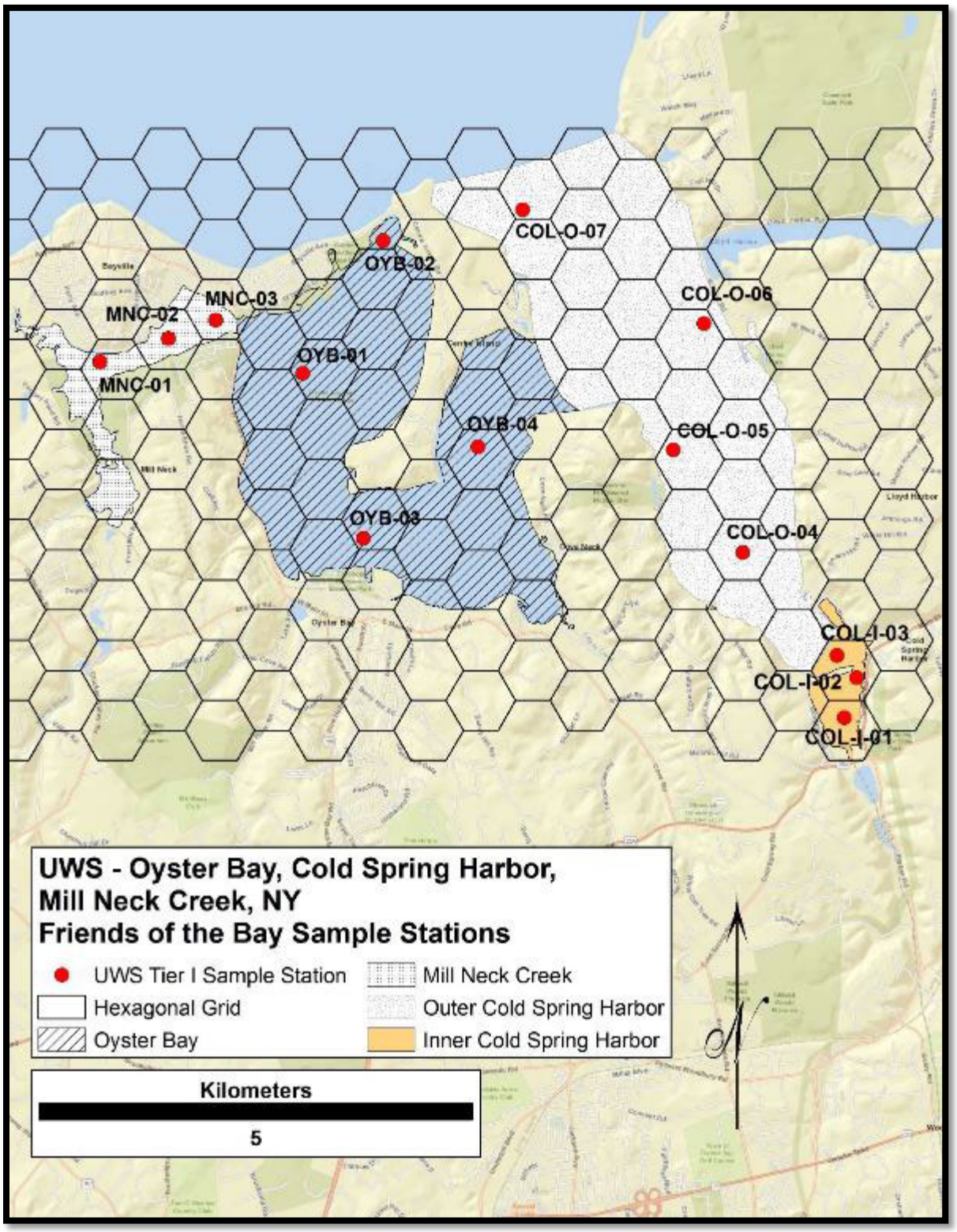

Figure 1d Oyster Bay, Cold Spring Harbor, Mill Neck Creek, NY

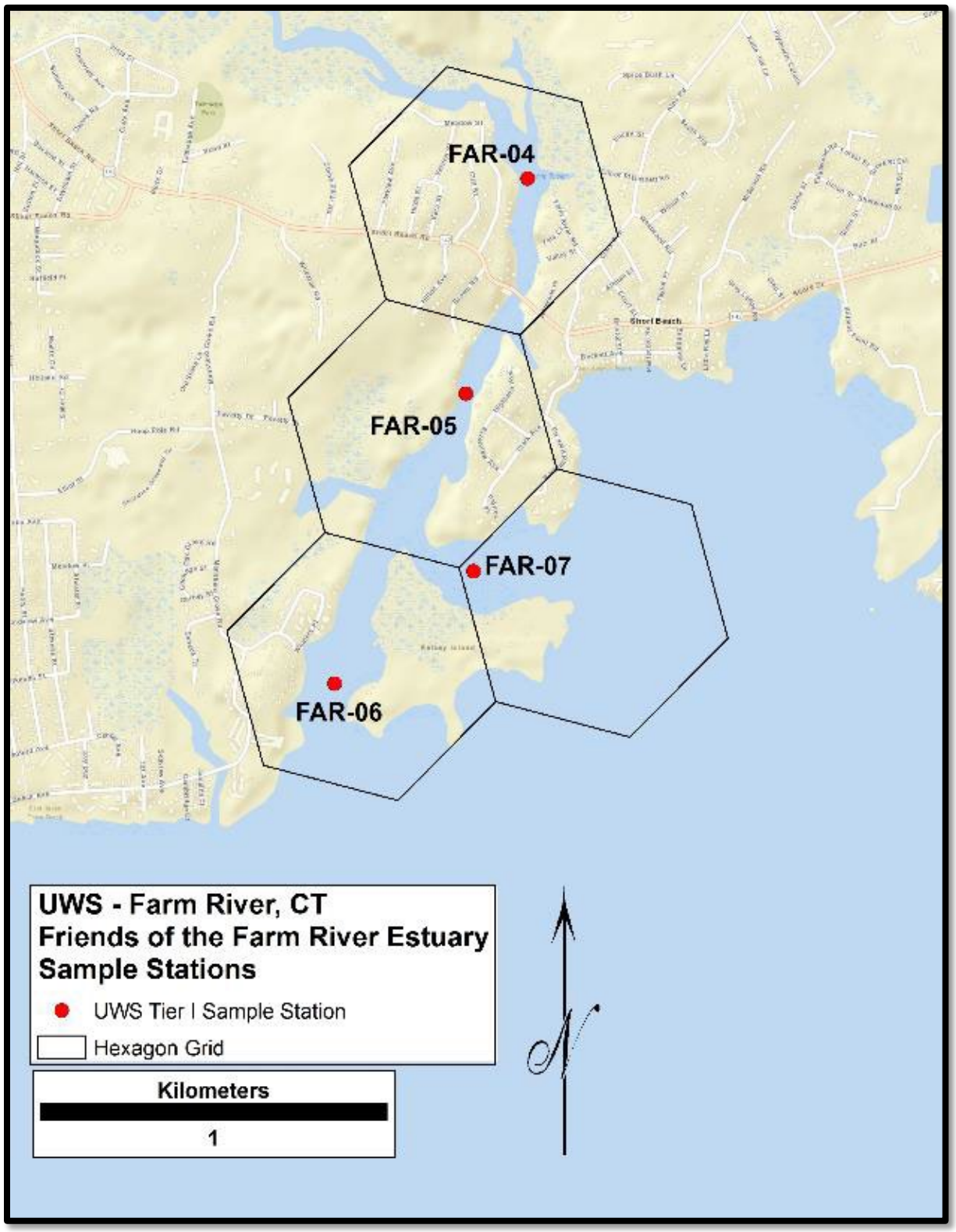

Figure 1e Farm River, CT

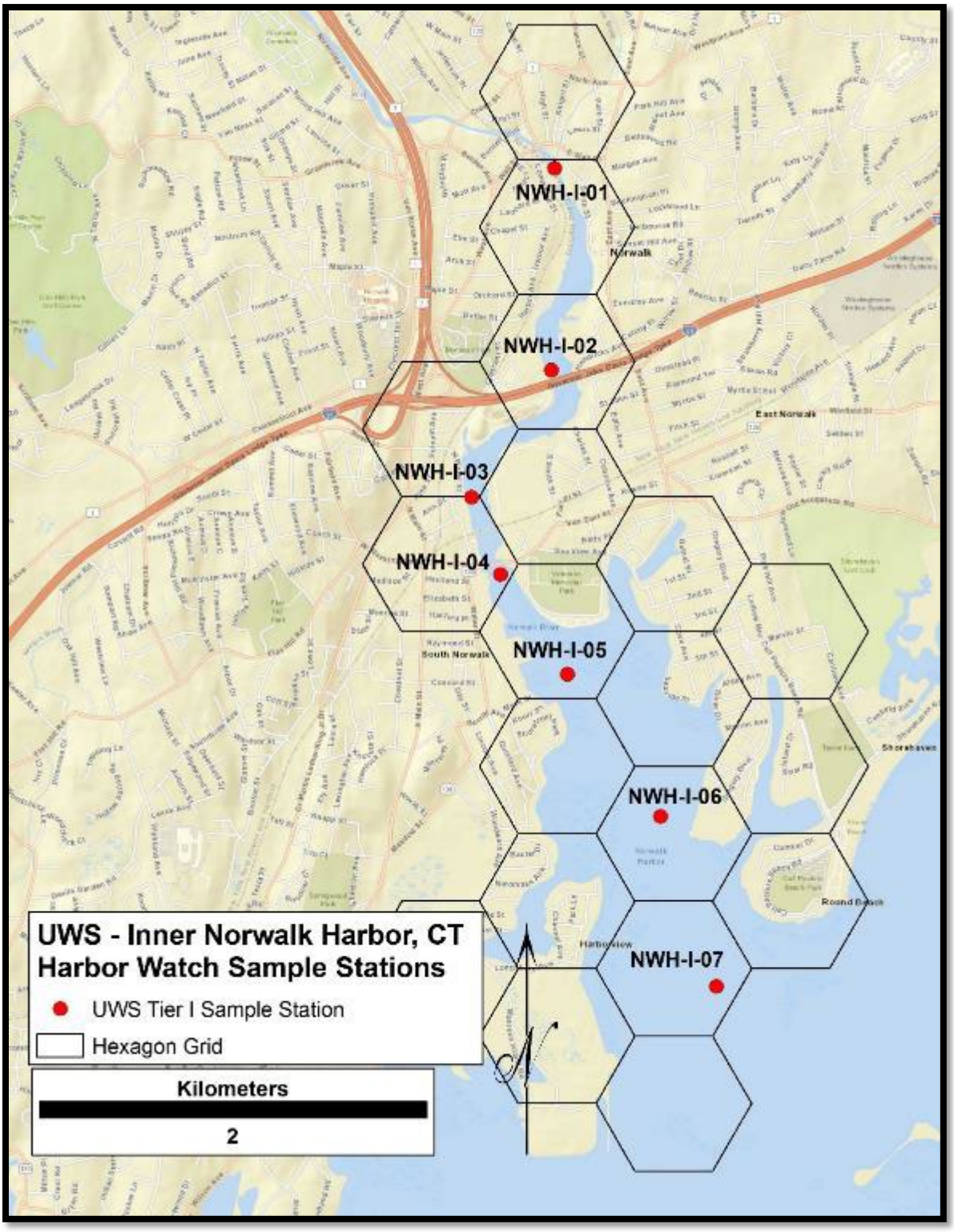

Figure 1f Inner Norwalk Harbor, CT

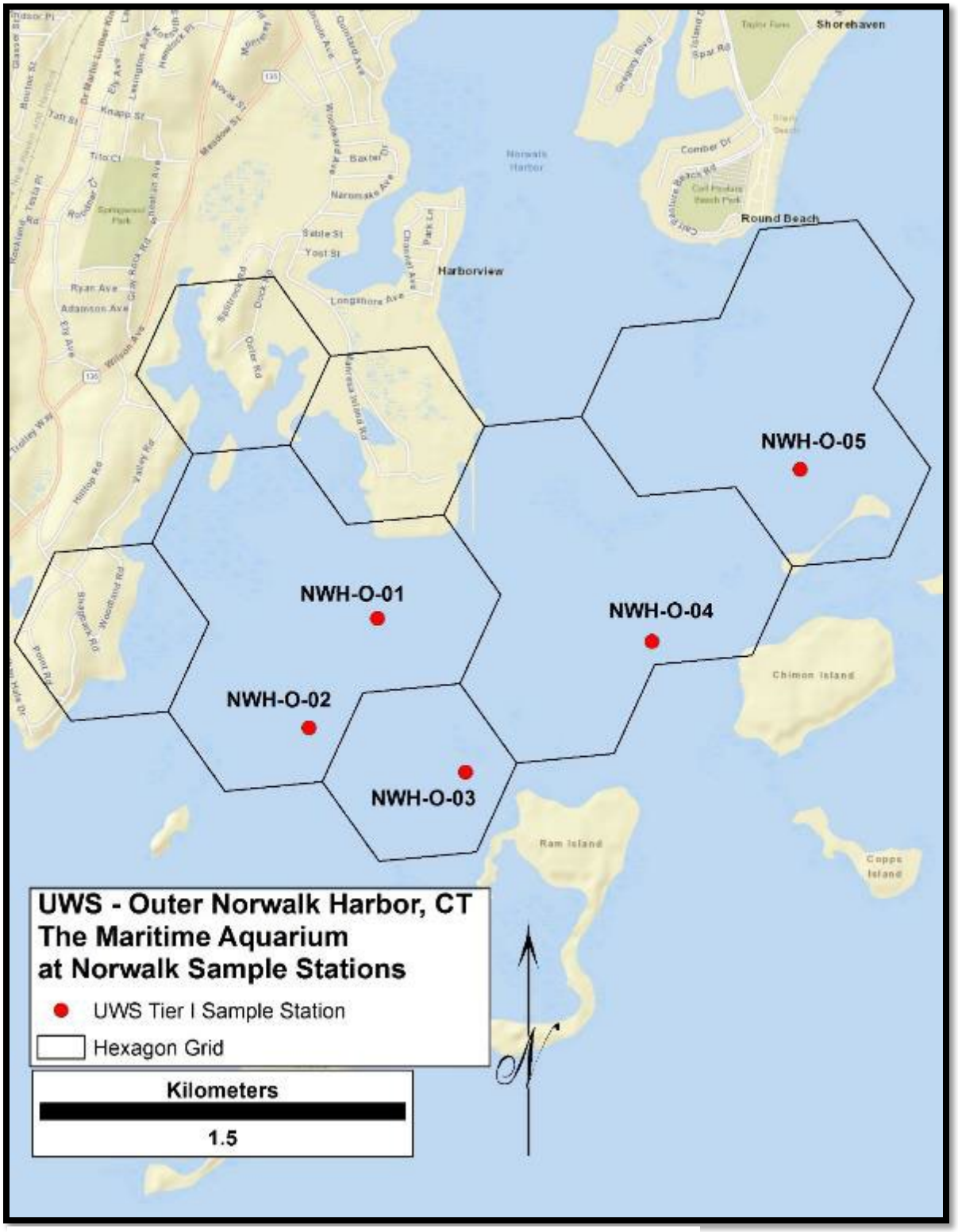

Figure 1g Outer Norwalk Harbor, CT

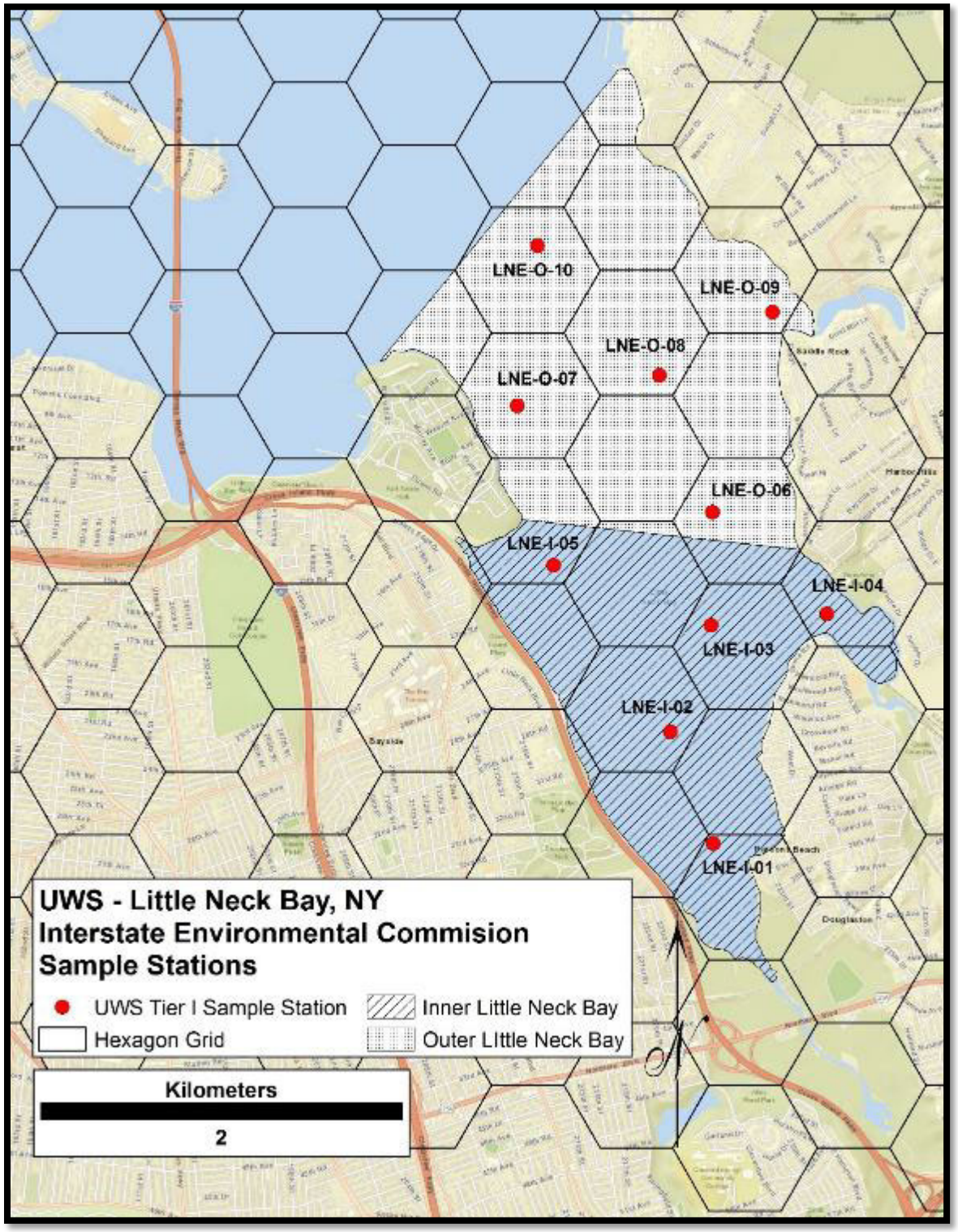

Figure 1h Little Neck Bay, NY

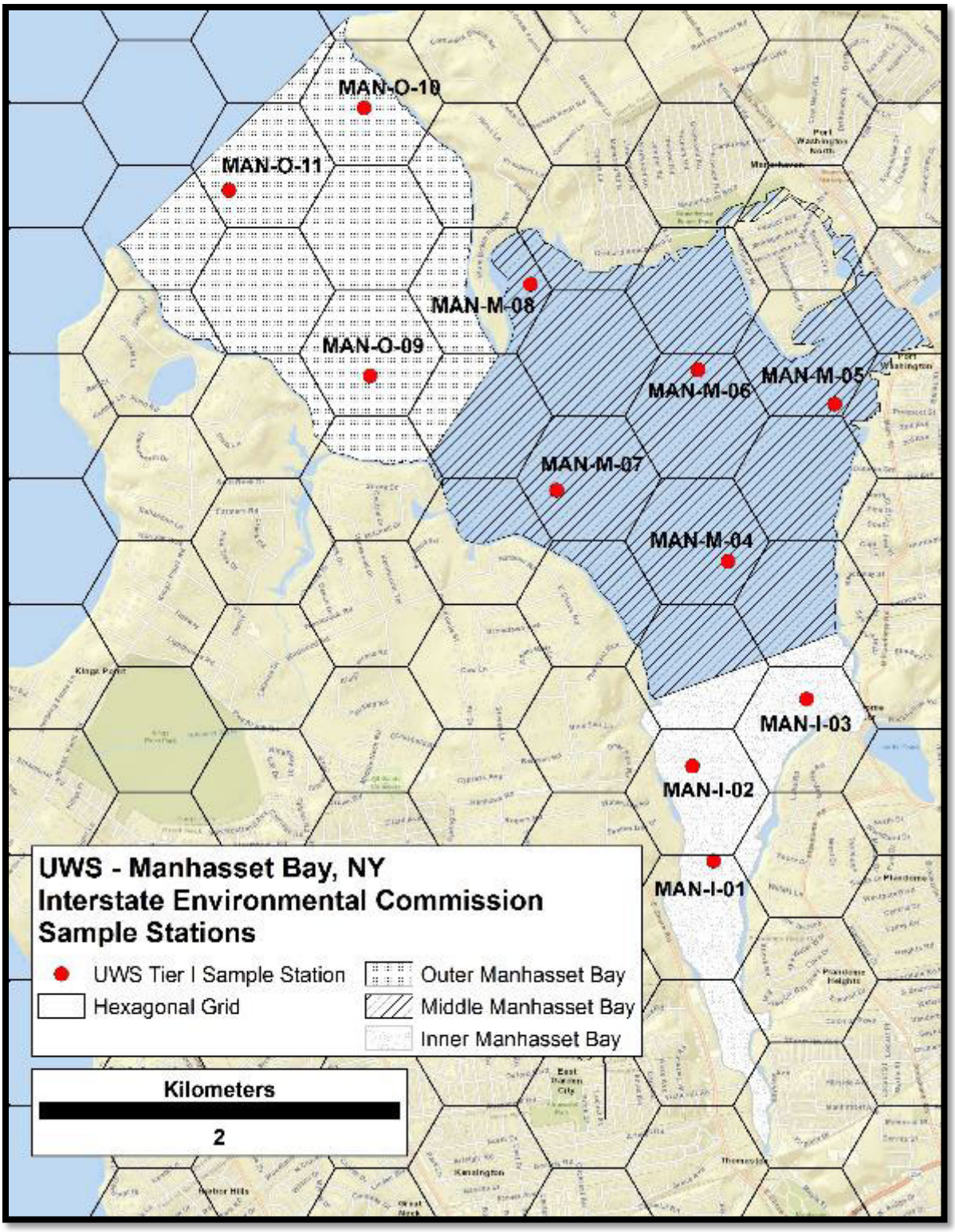

Figure 1i Manhasset Bay, NY

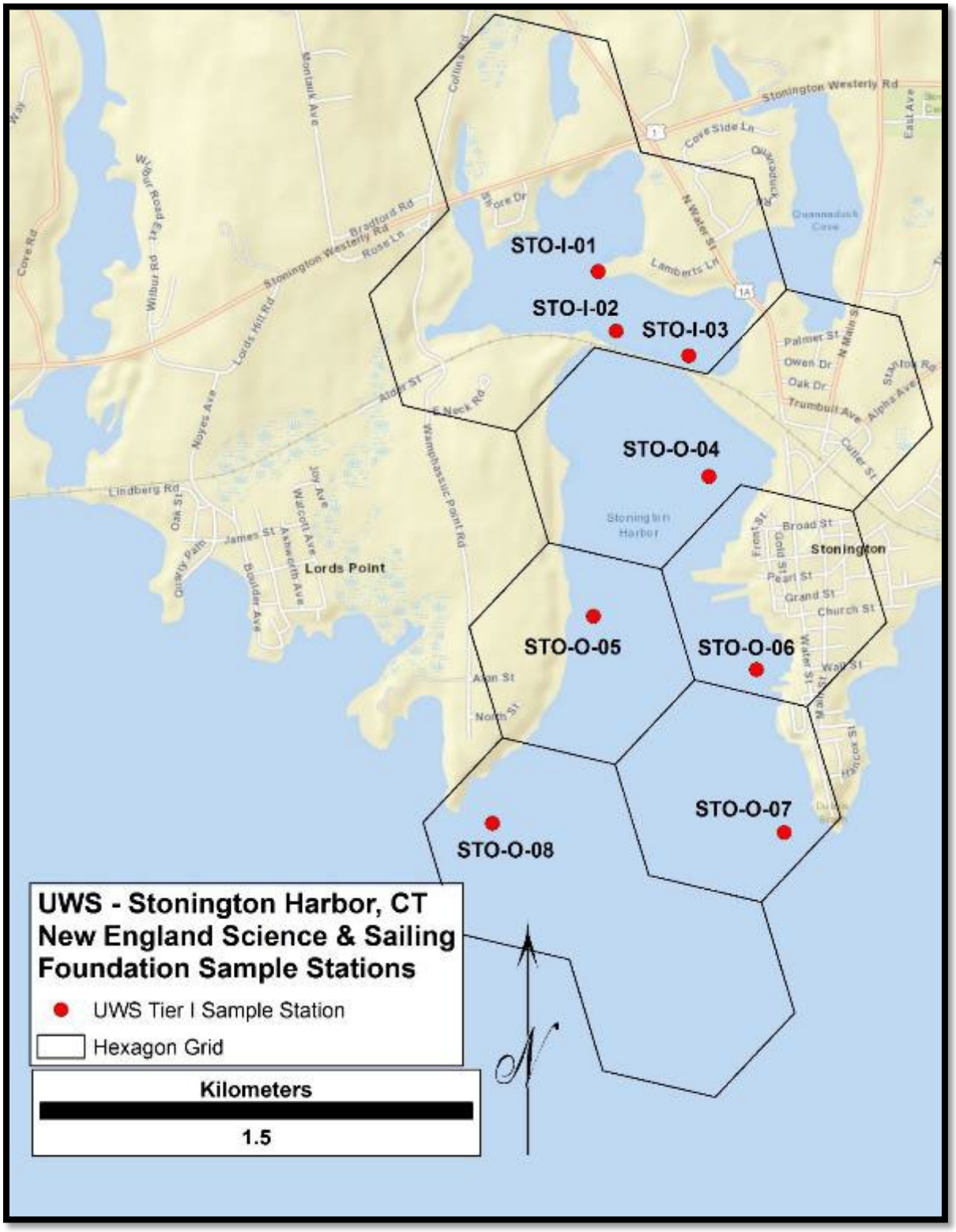

Figure 1j Stonington Harbor, CT

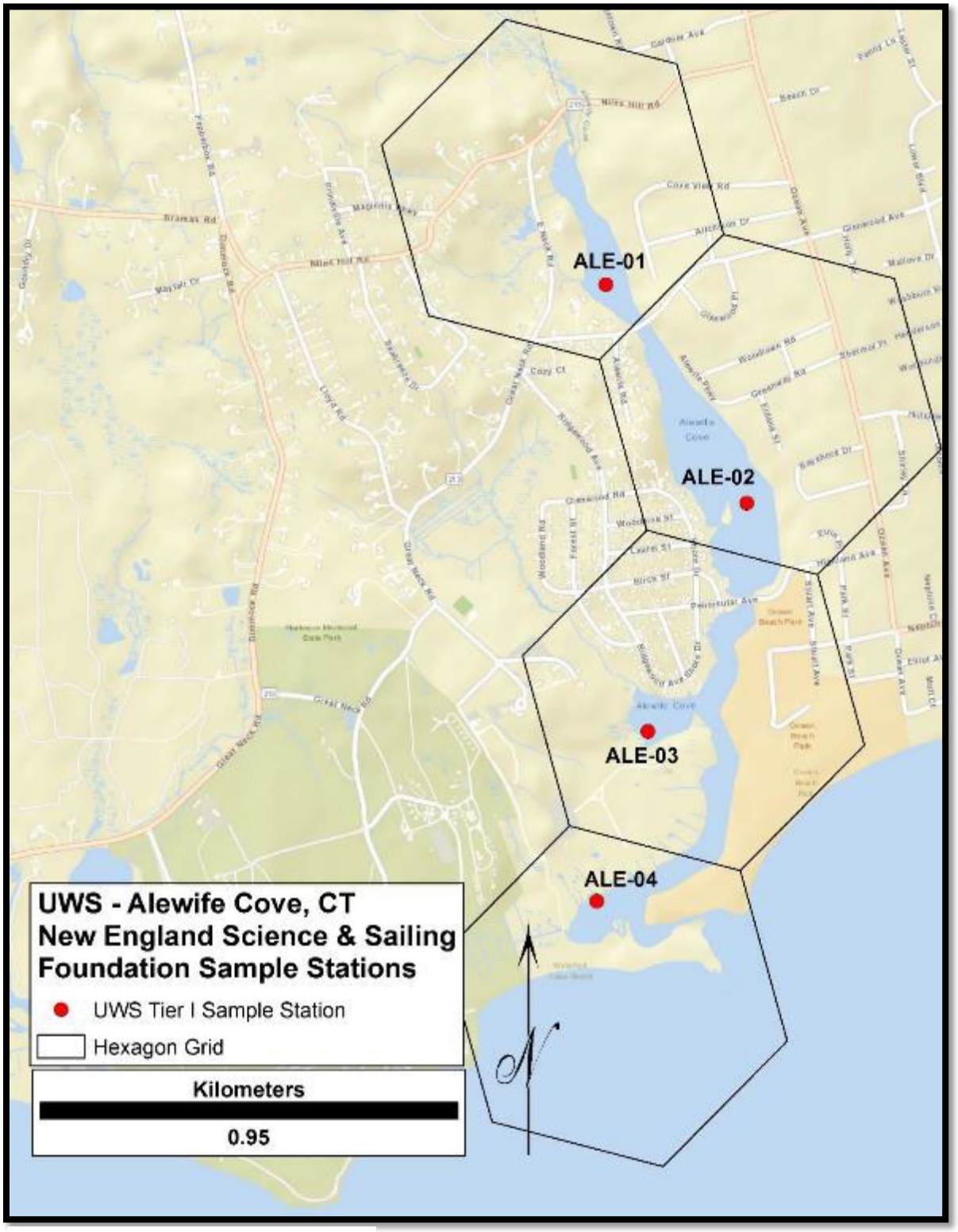

Figure 1k Alewife Cove, CT

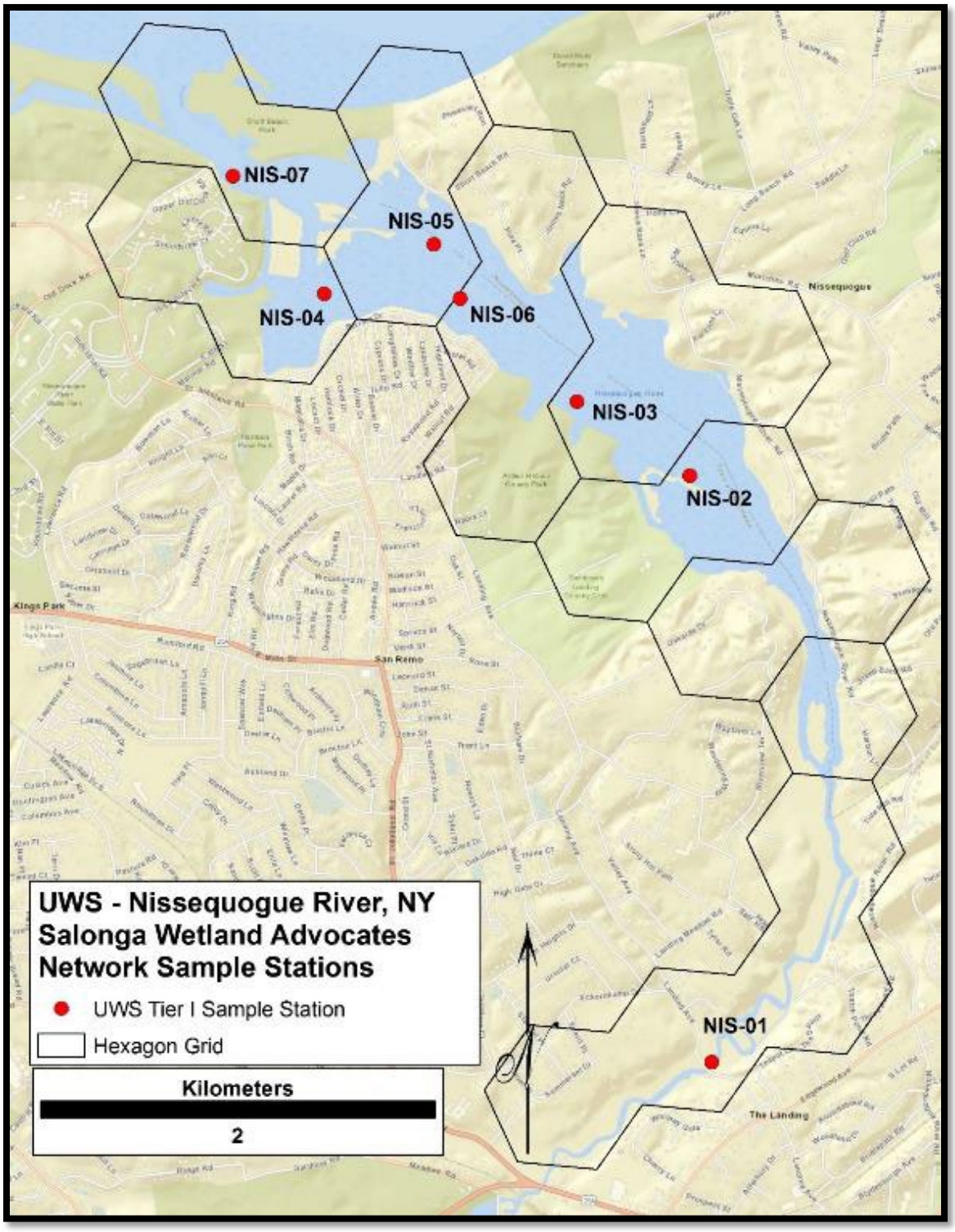

Figure 1l Nissequogue River, NY

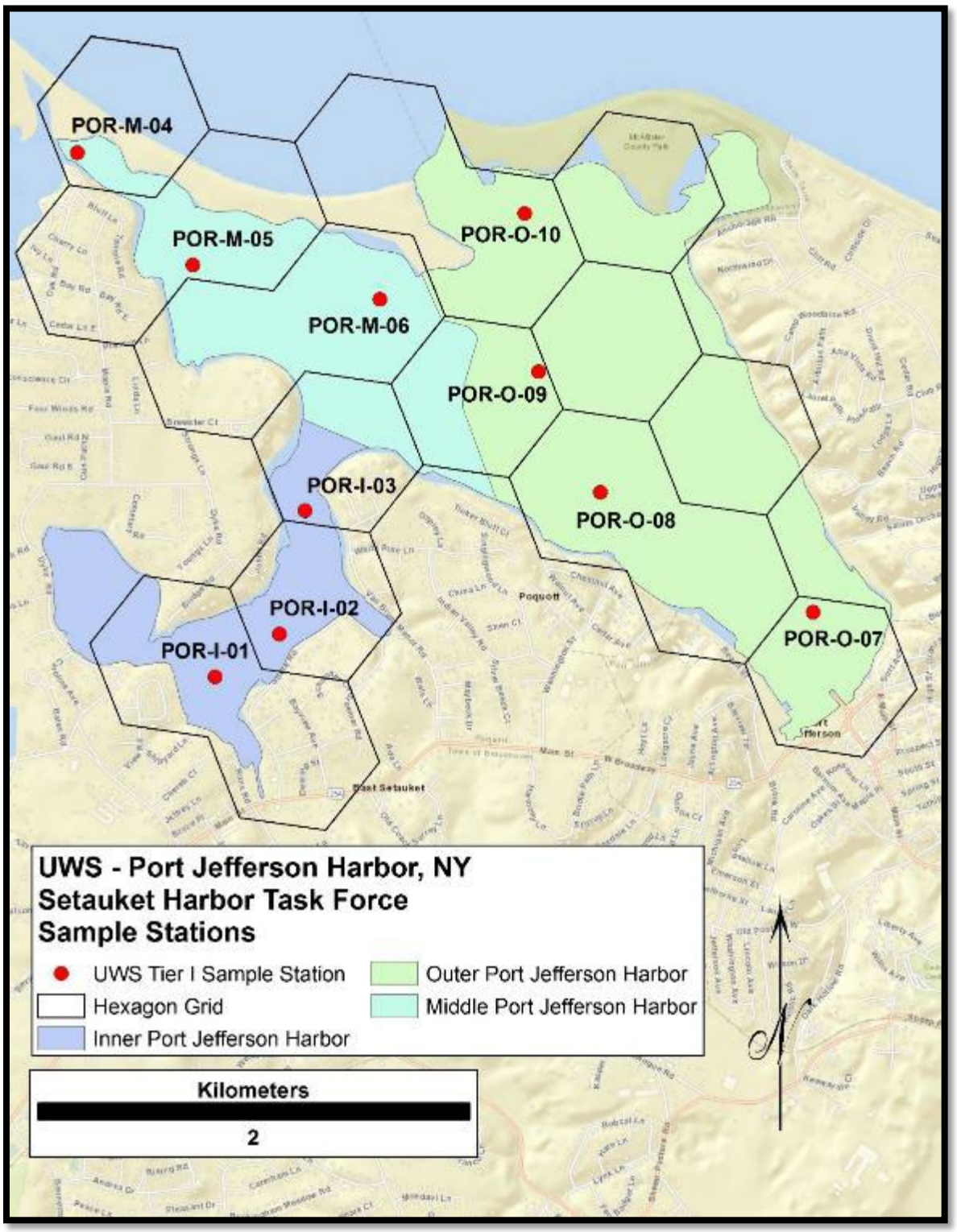

Figure 1m Port Jefferson Harbor, NY

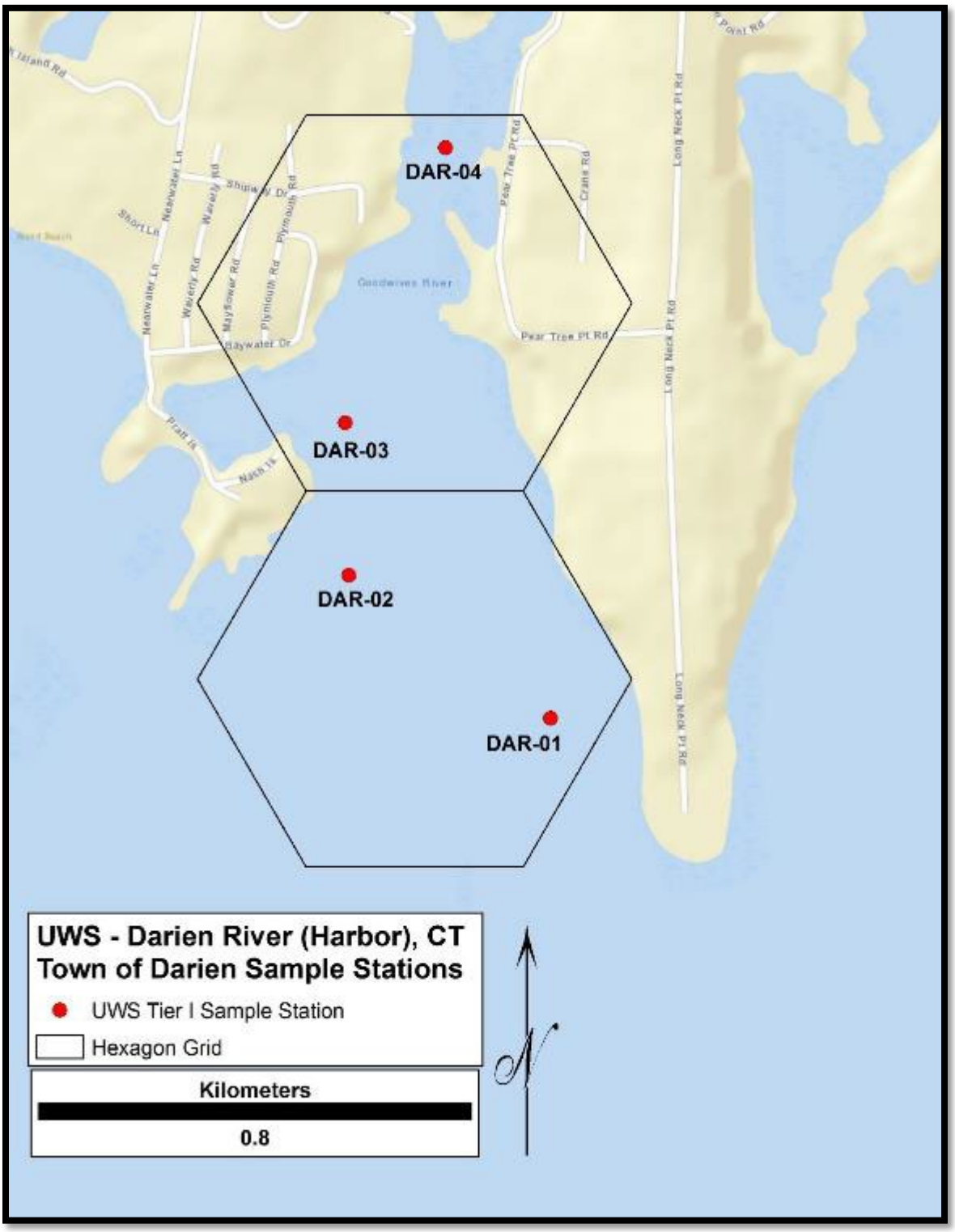

Figure 1n Darien River (Harbor), CT

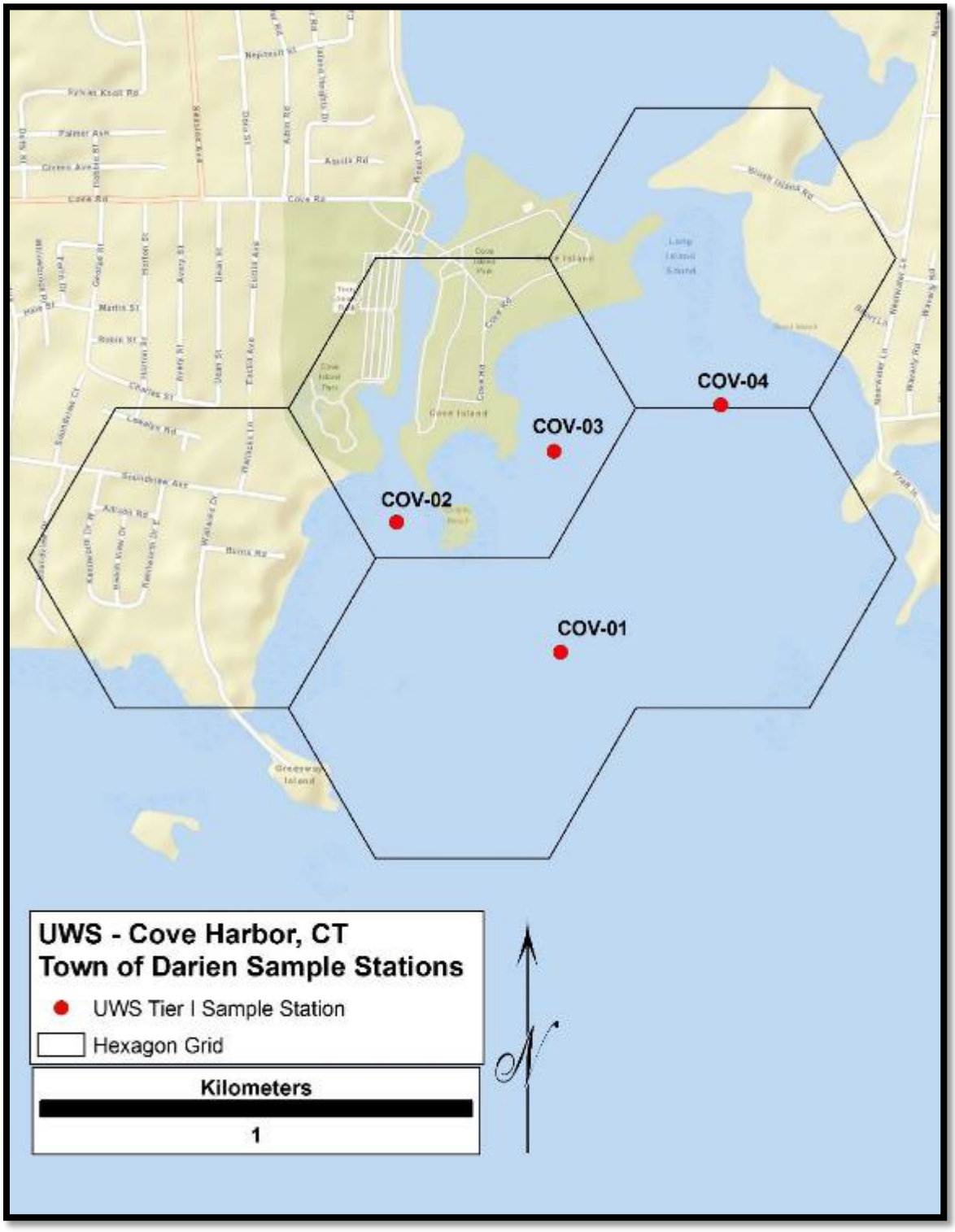

Figure 1o Cove Harbor, CT

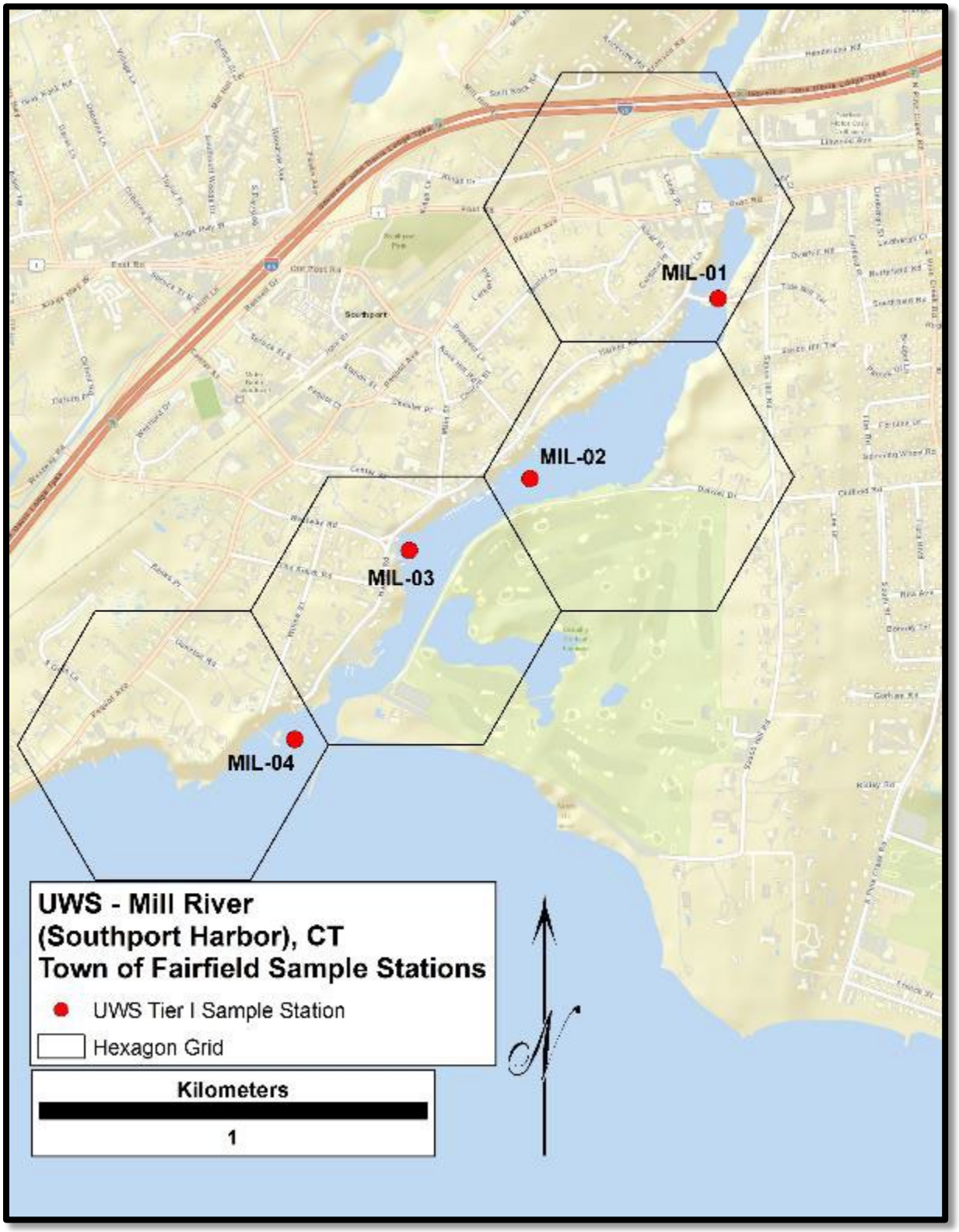

Figure 1p Mill River (Southport Harbor), CT

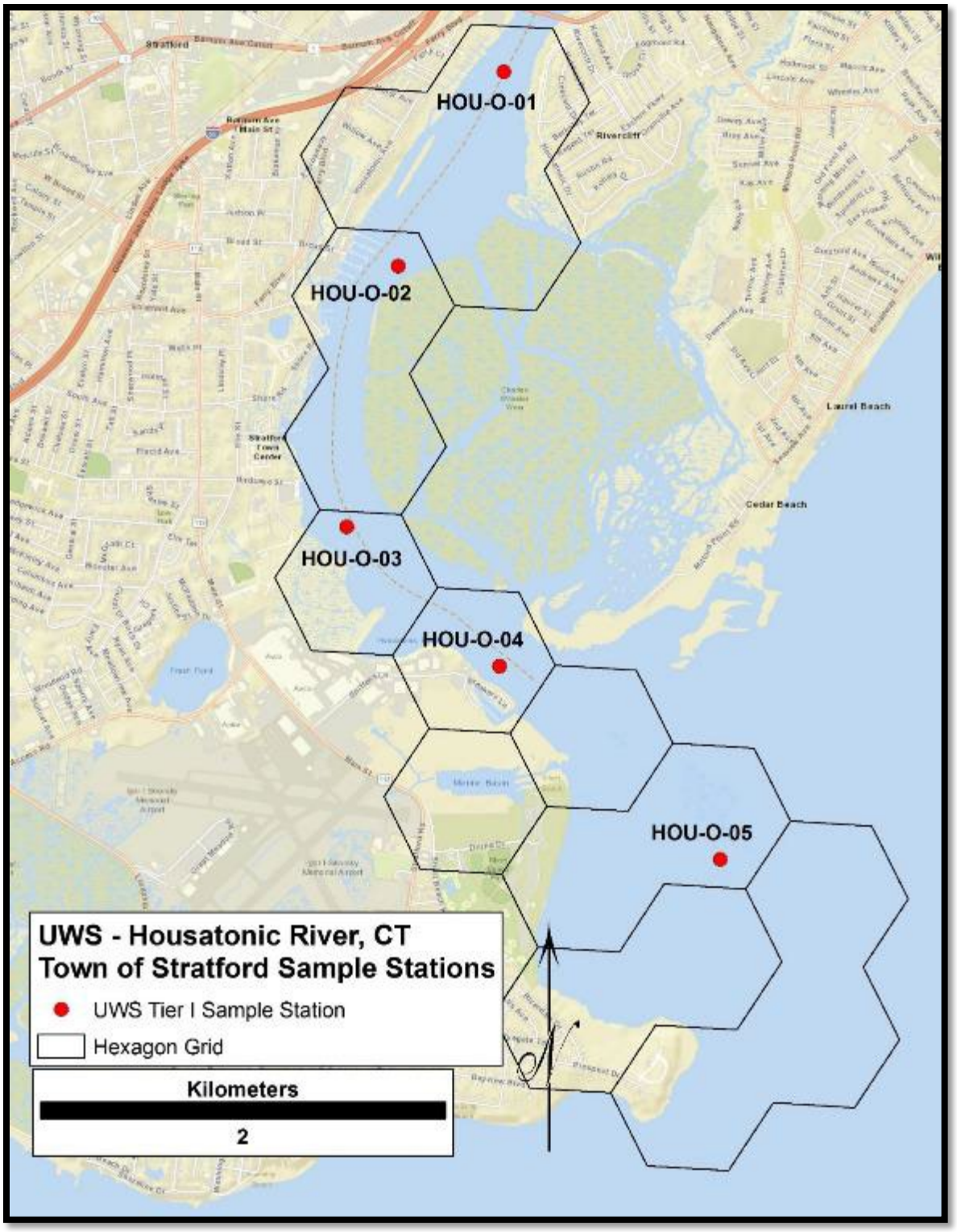

Figure 1q Housatonic River, CT

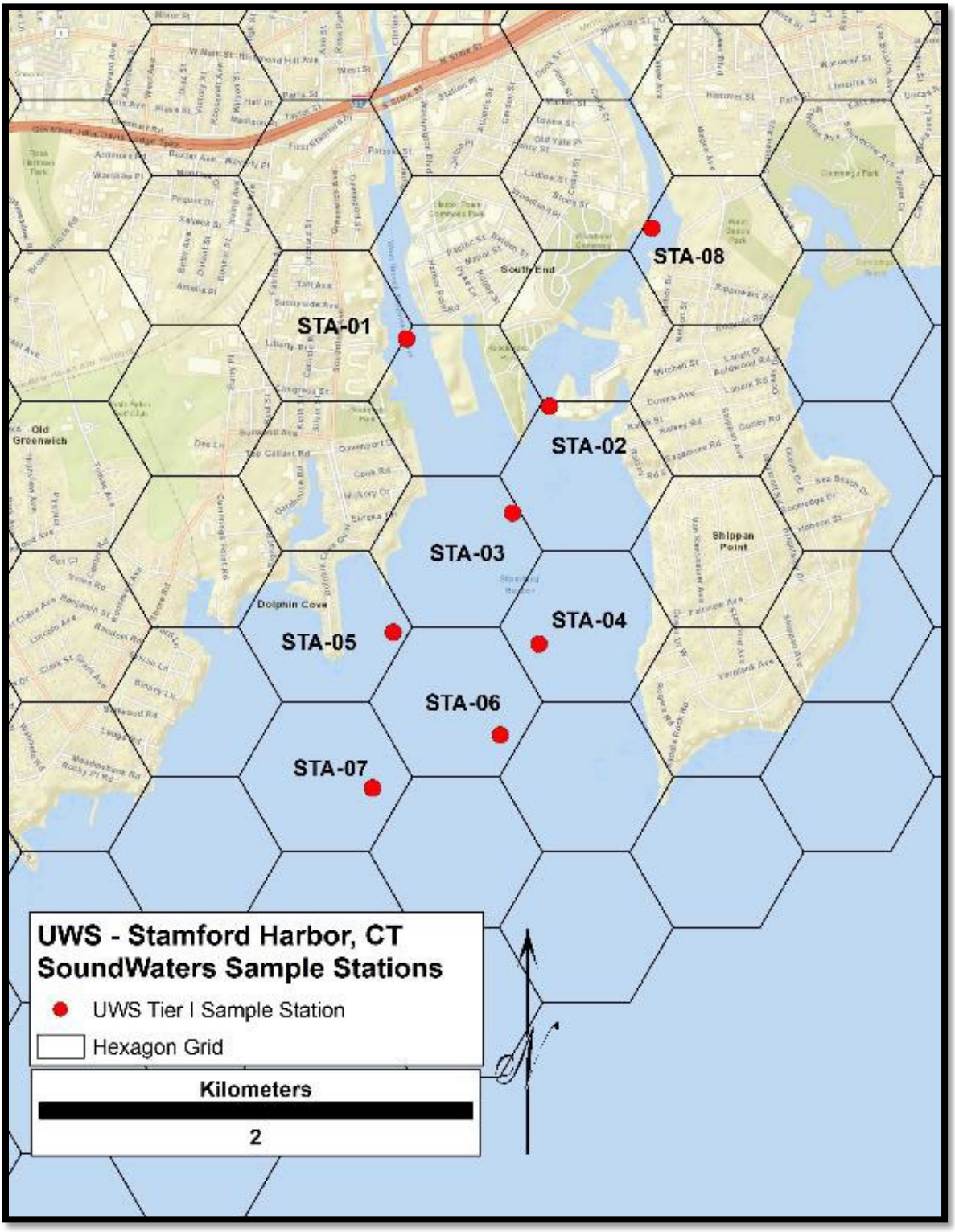

Figure 1r Stamford Harbor, CT

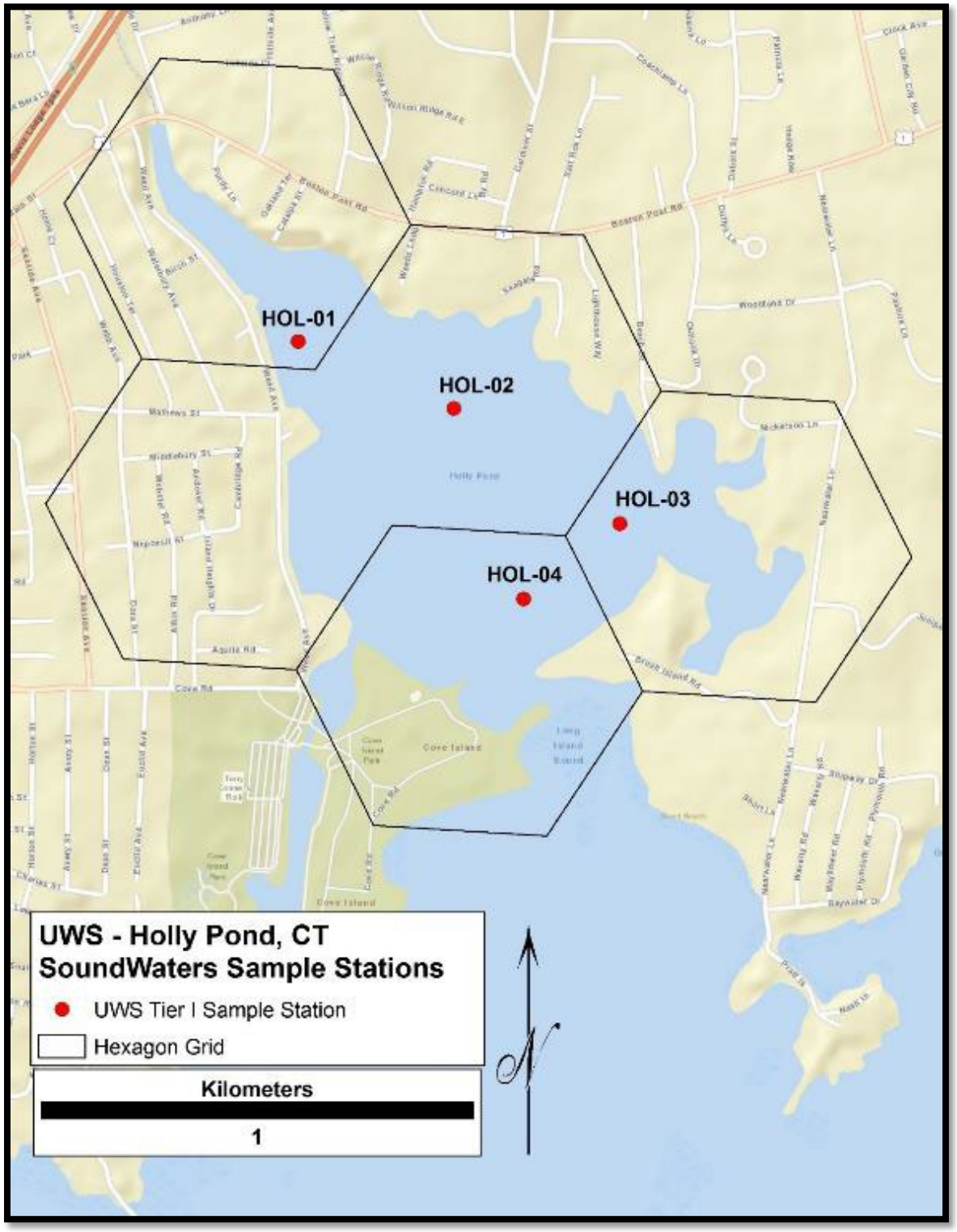

Figure 1s Holly Pond, CT

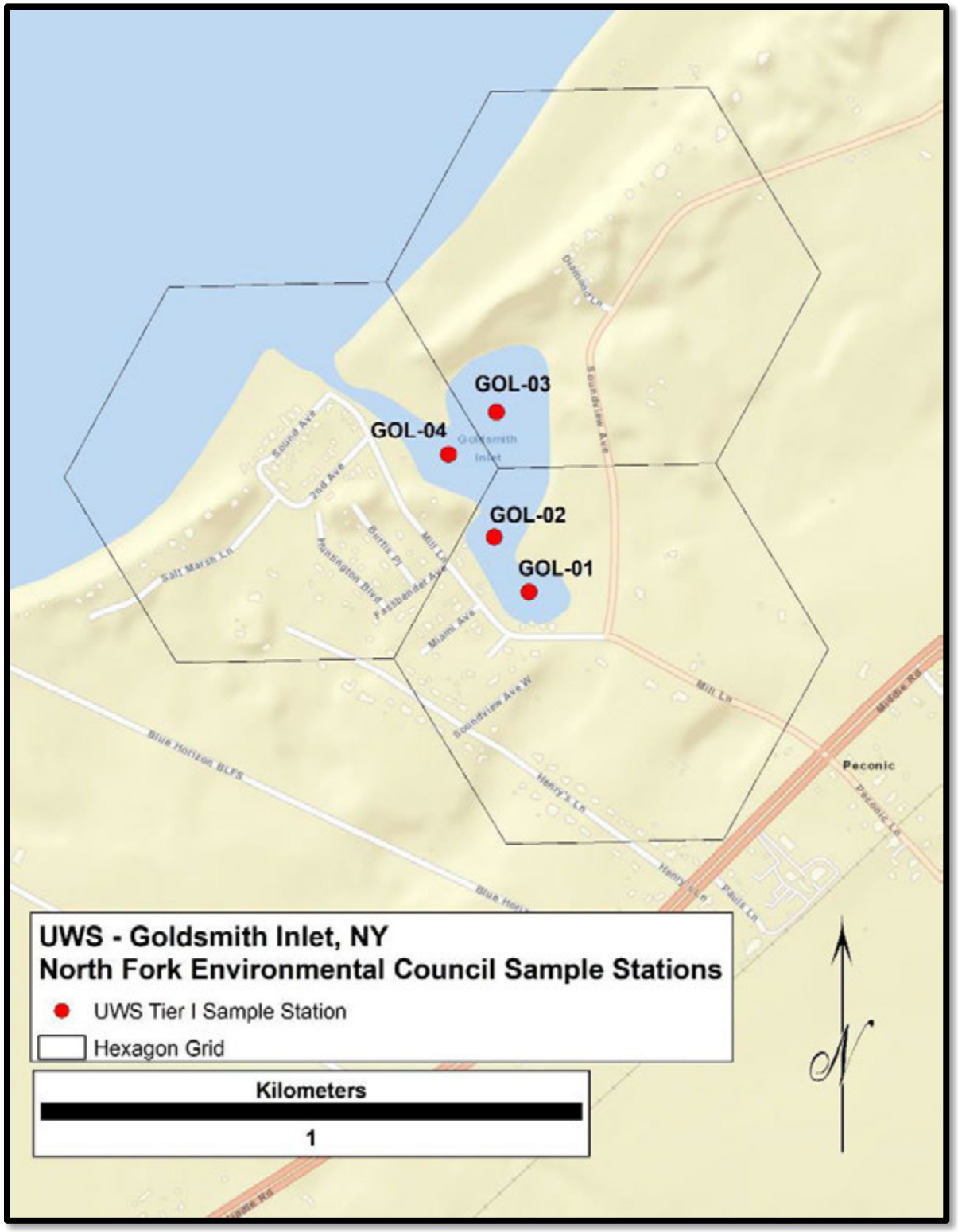

Figure 1t Goldsmith Inlet, NY

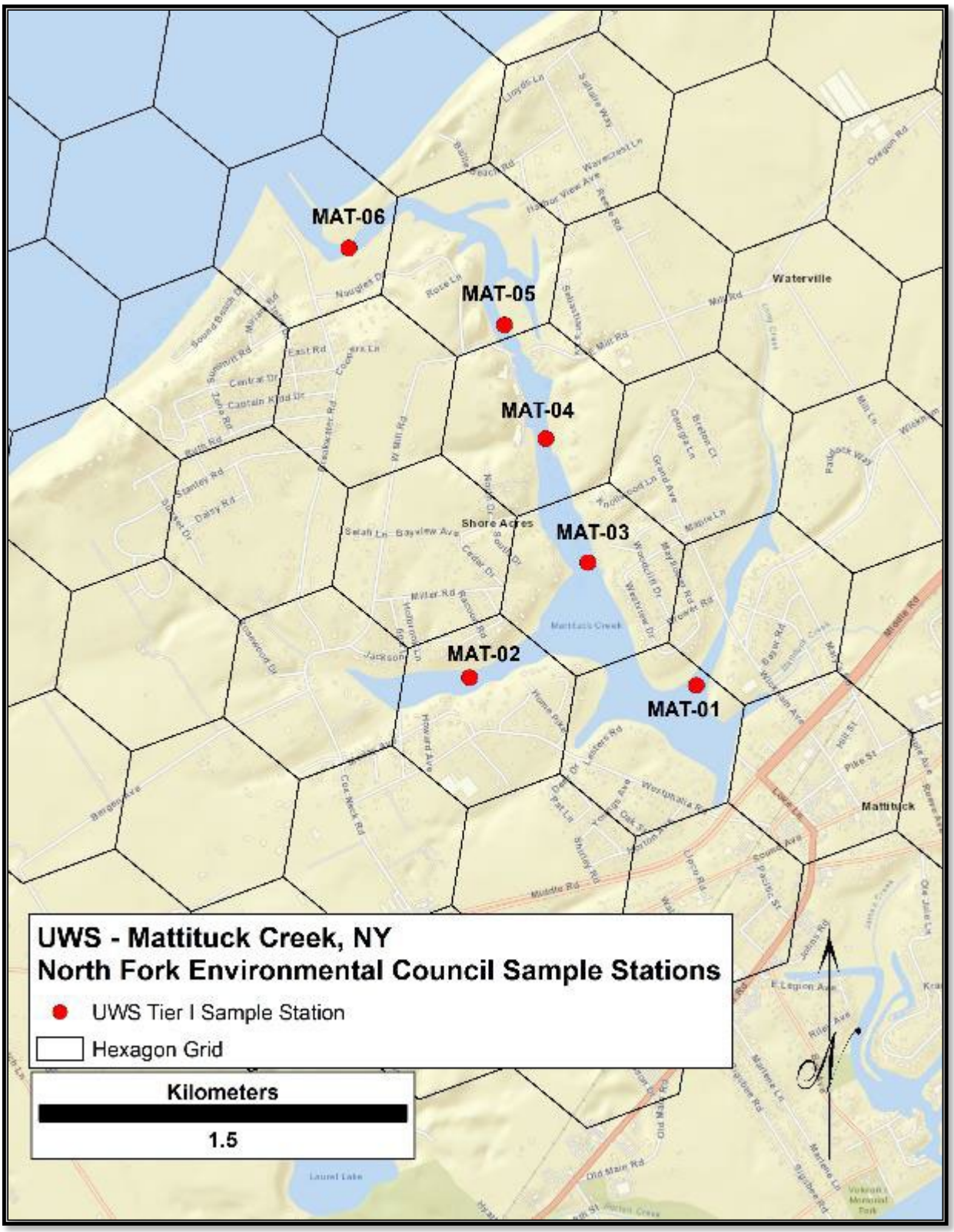

Figure 1u Mattituck Creek, NY

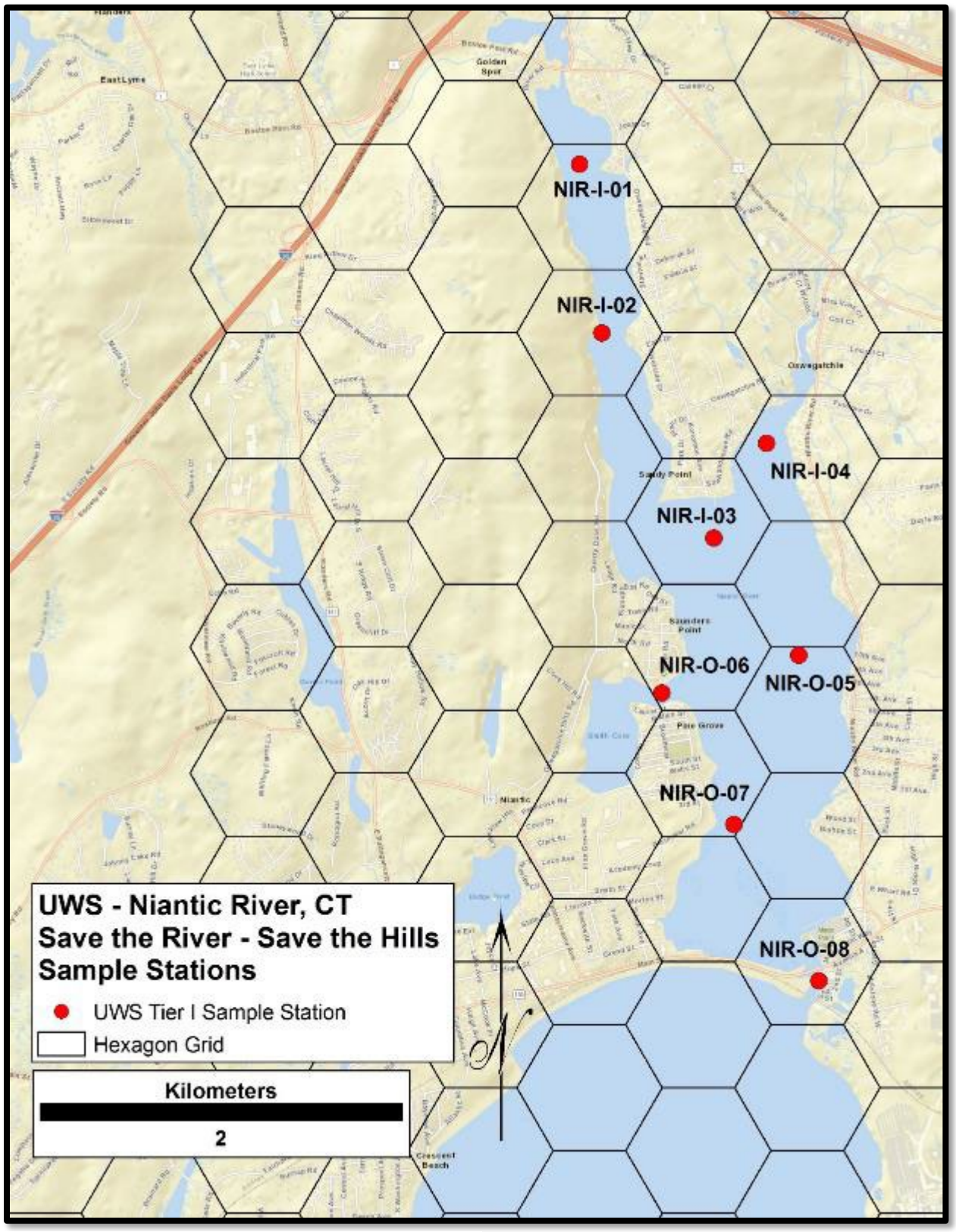

Figure 1v Niantic River, CT

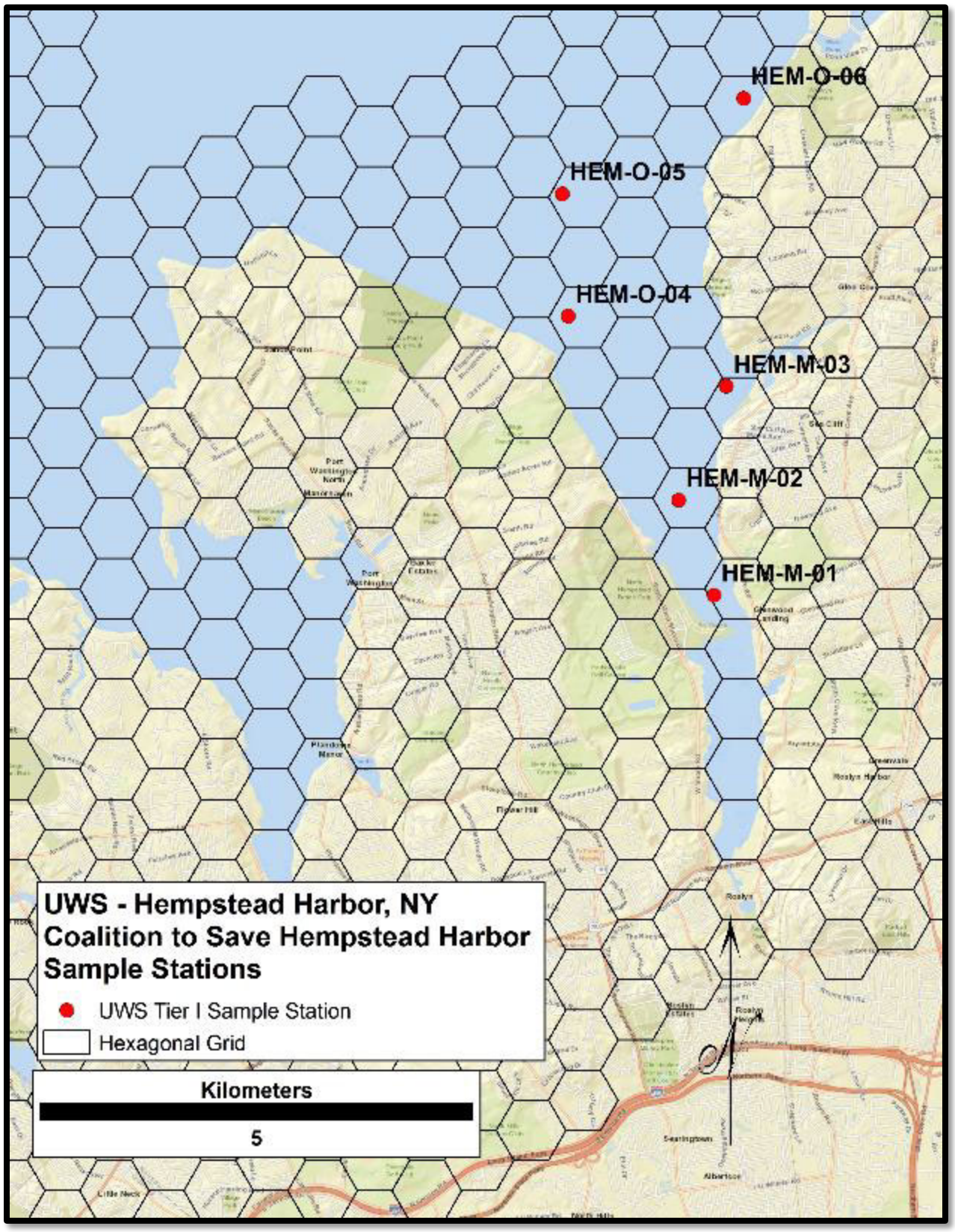

Figure 1w Hempstead Harbor, NY

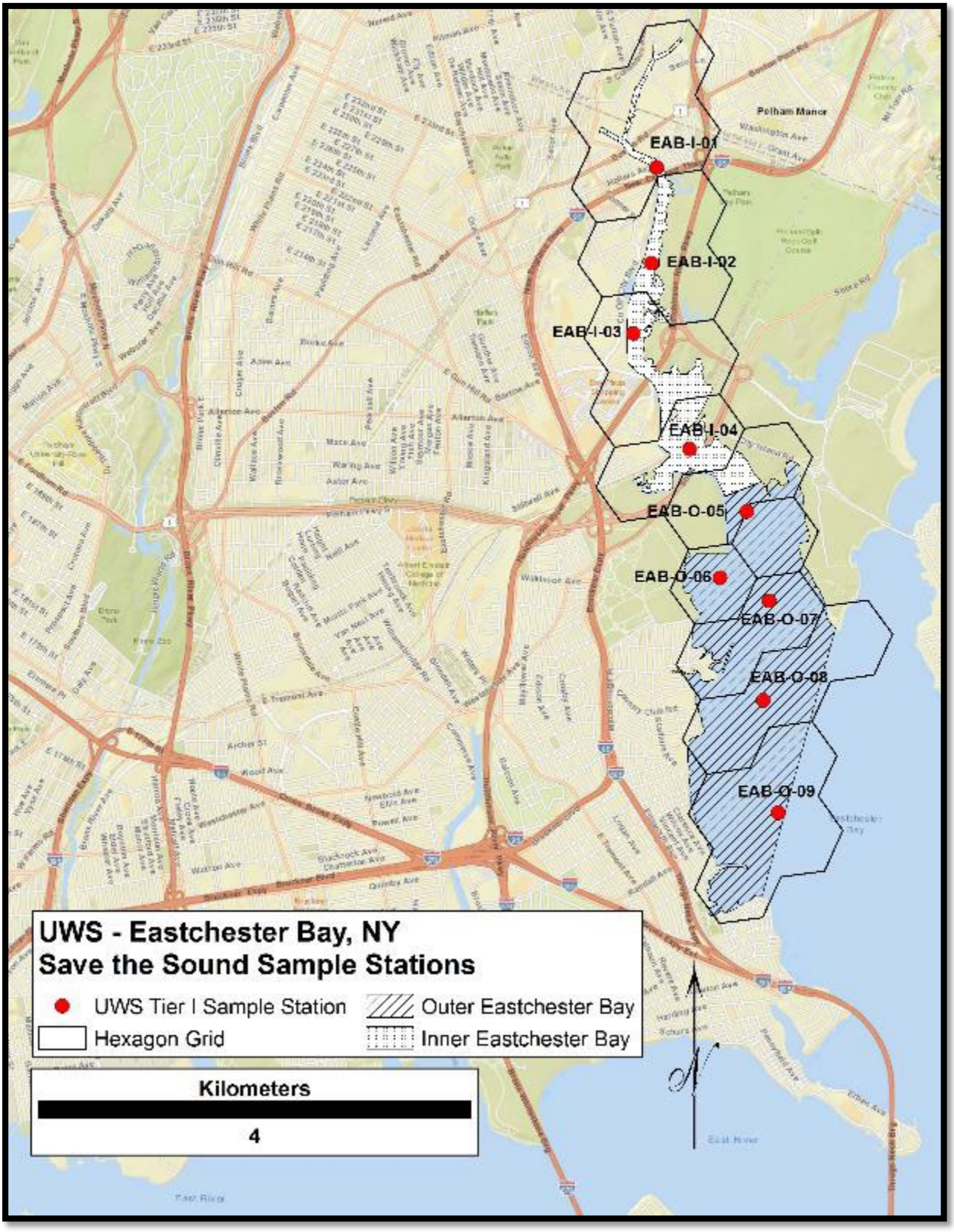

Figure 1x Eastchester Bay, NY

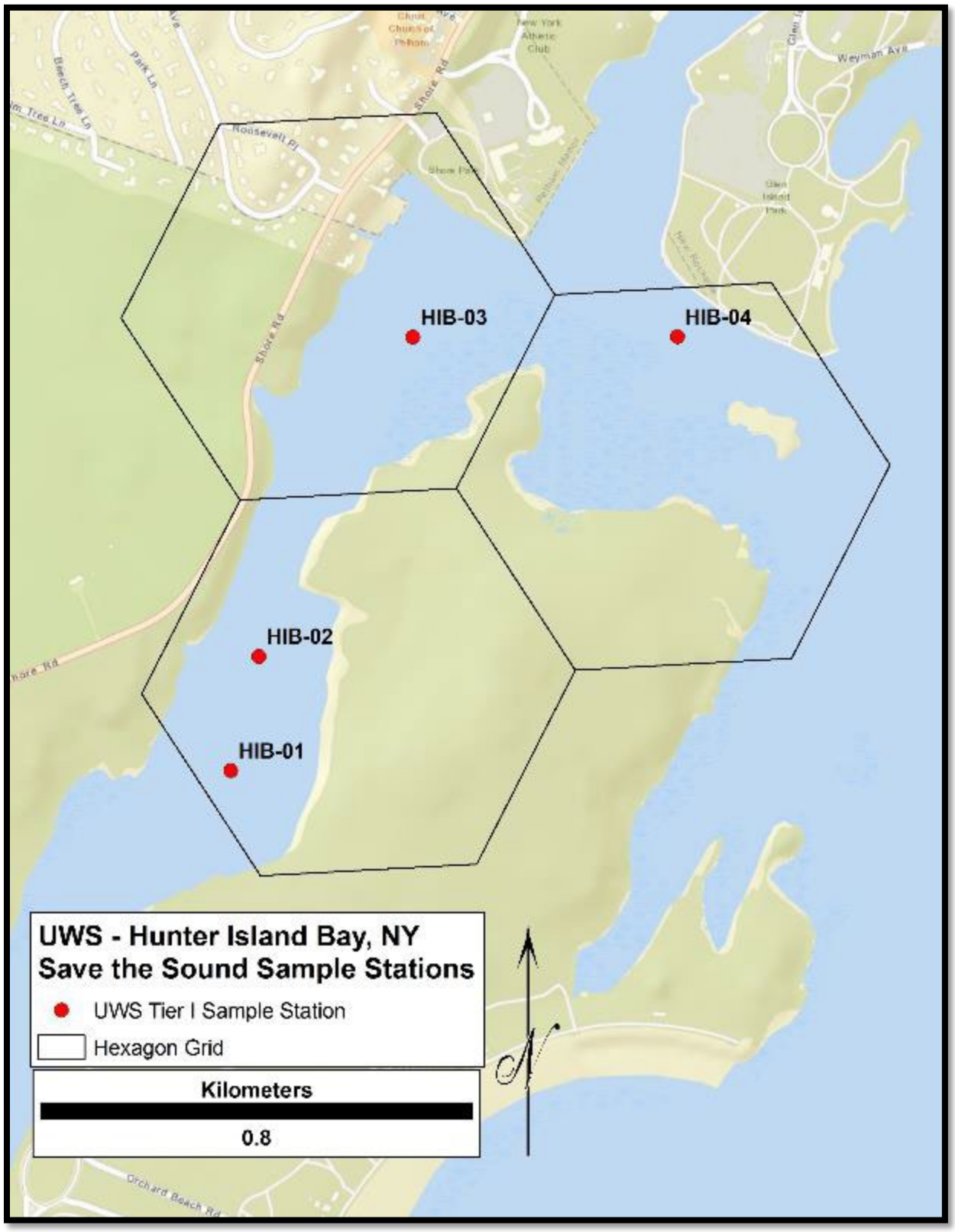

Figure 1y Hunter Island Bay, NY

Figure 1z New Rochelle Harbor, NY

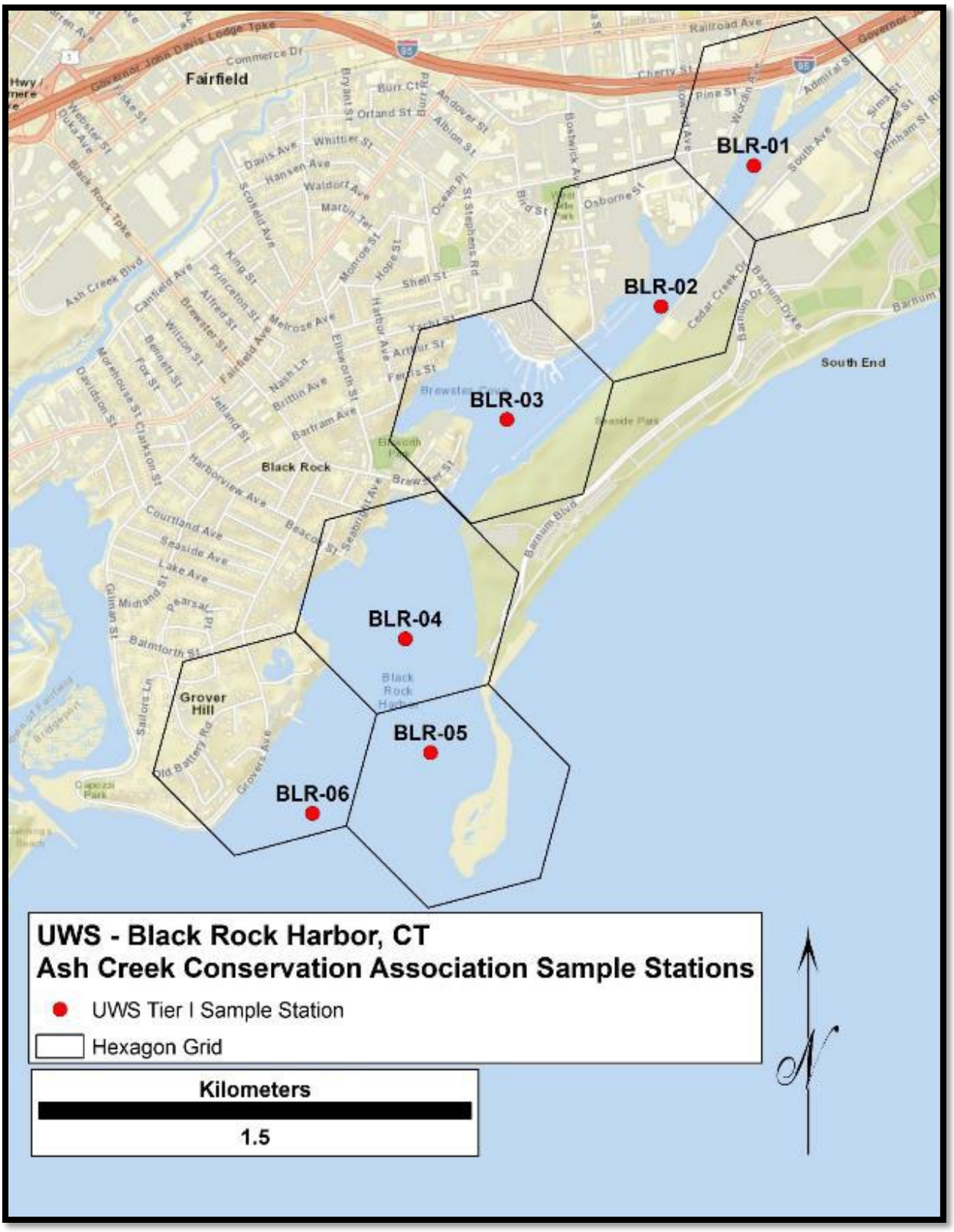

Figure 1aa Black Rock Harbor, CT

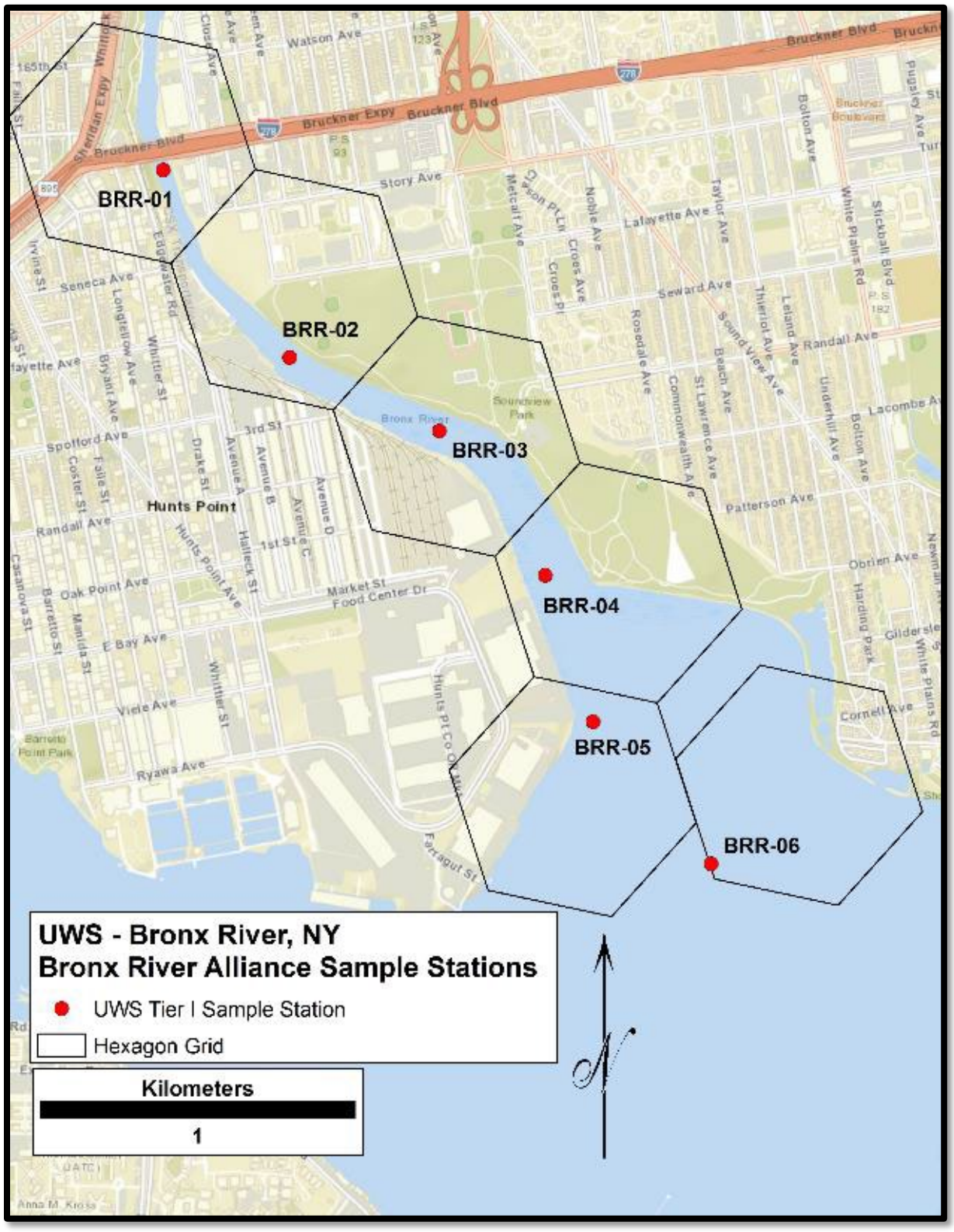

Figure 1ab Bronx River, NY

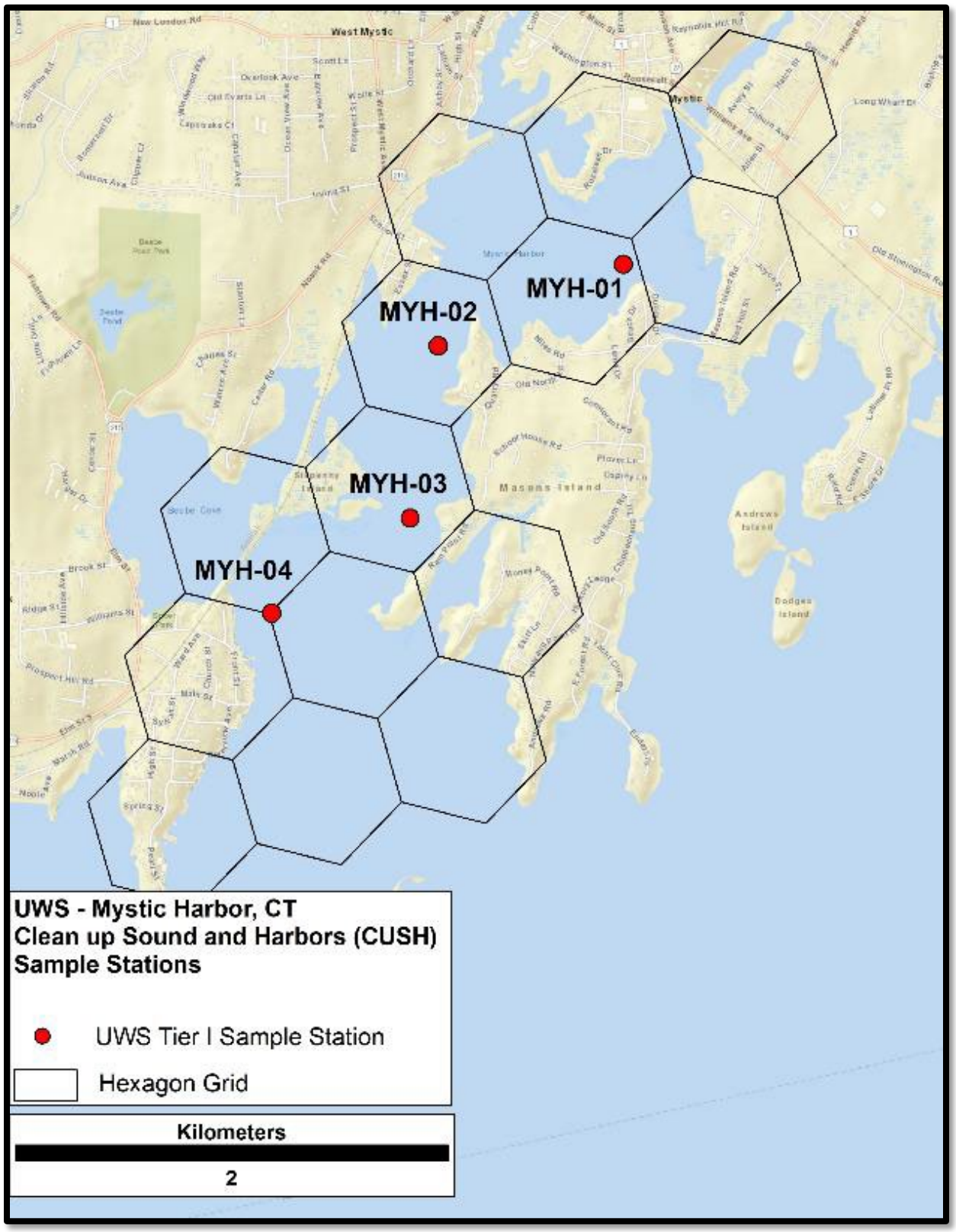

Figure 1ac Mystic Harbor, CT

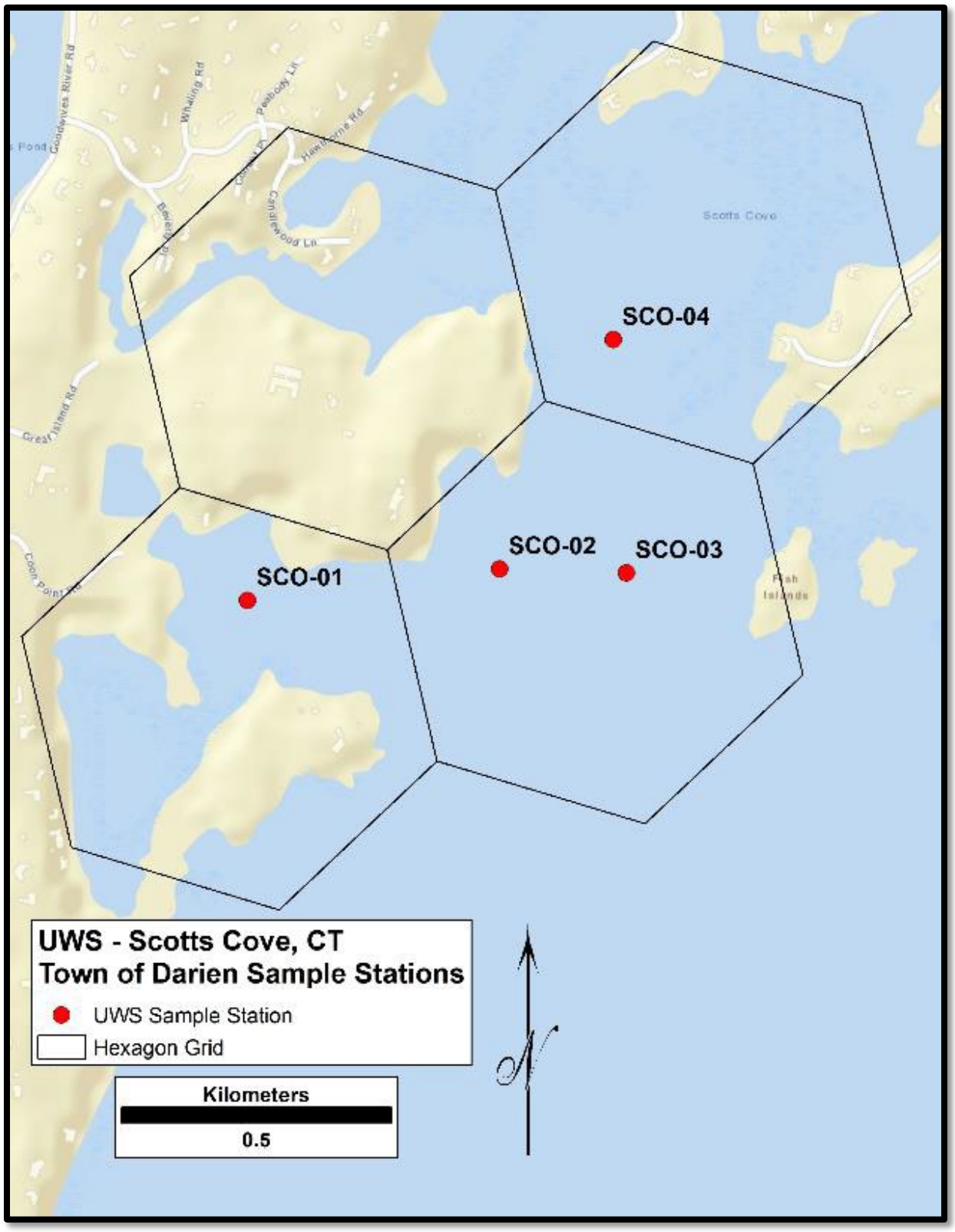

Figure 1ad Scotts Cove, CT

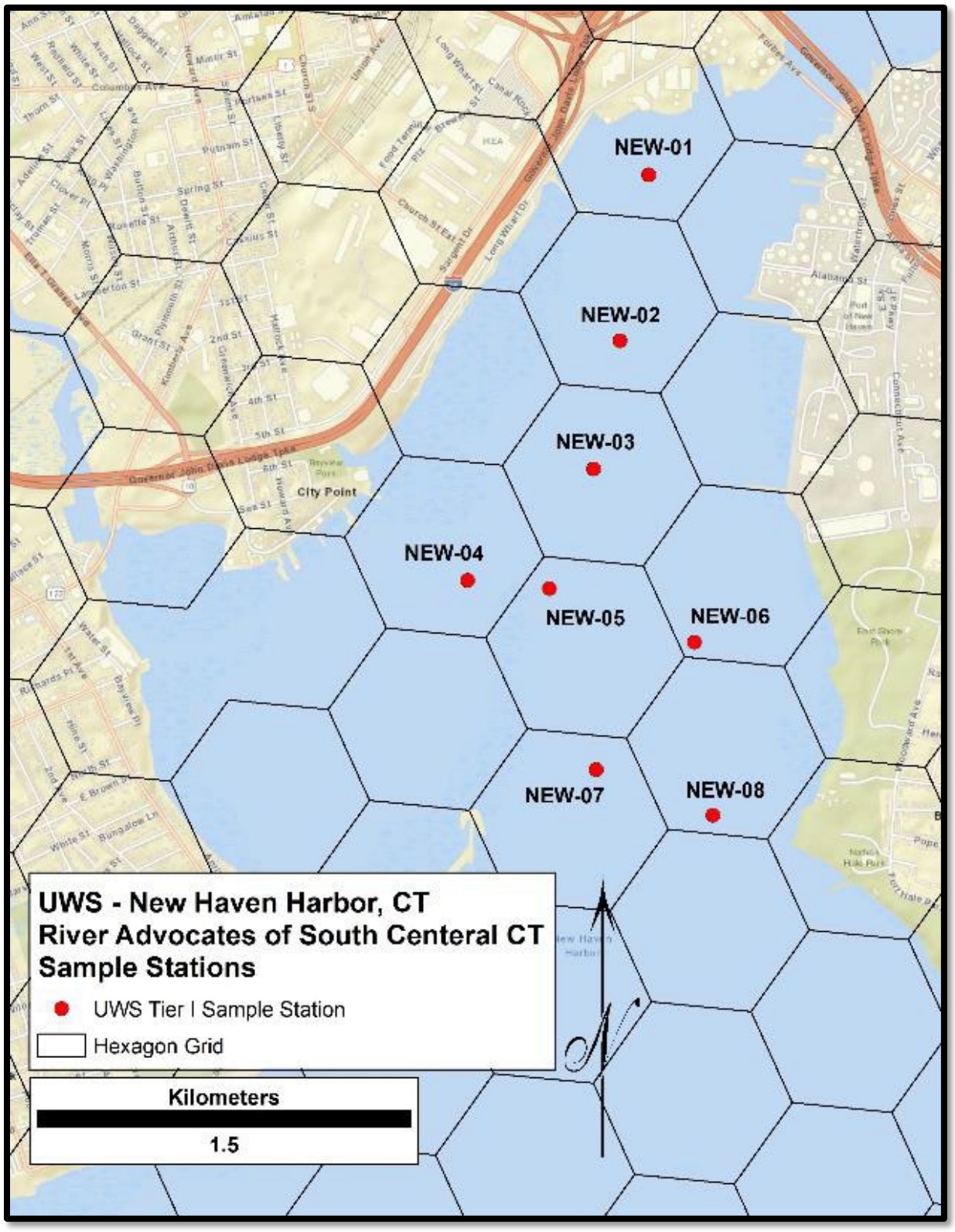

Figure 1ae New Haven Harbor, CT

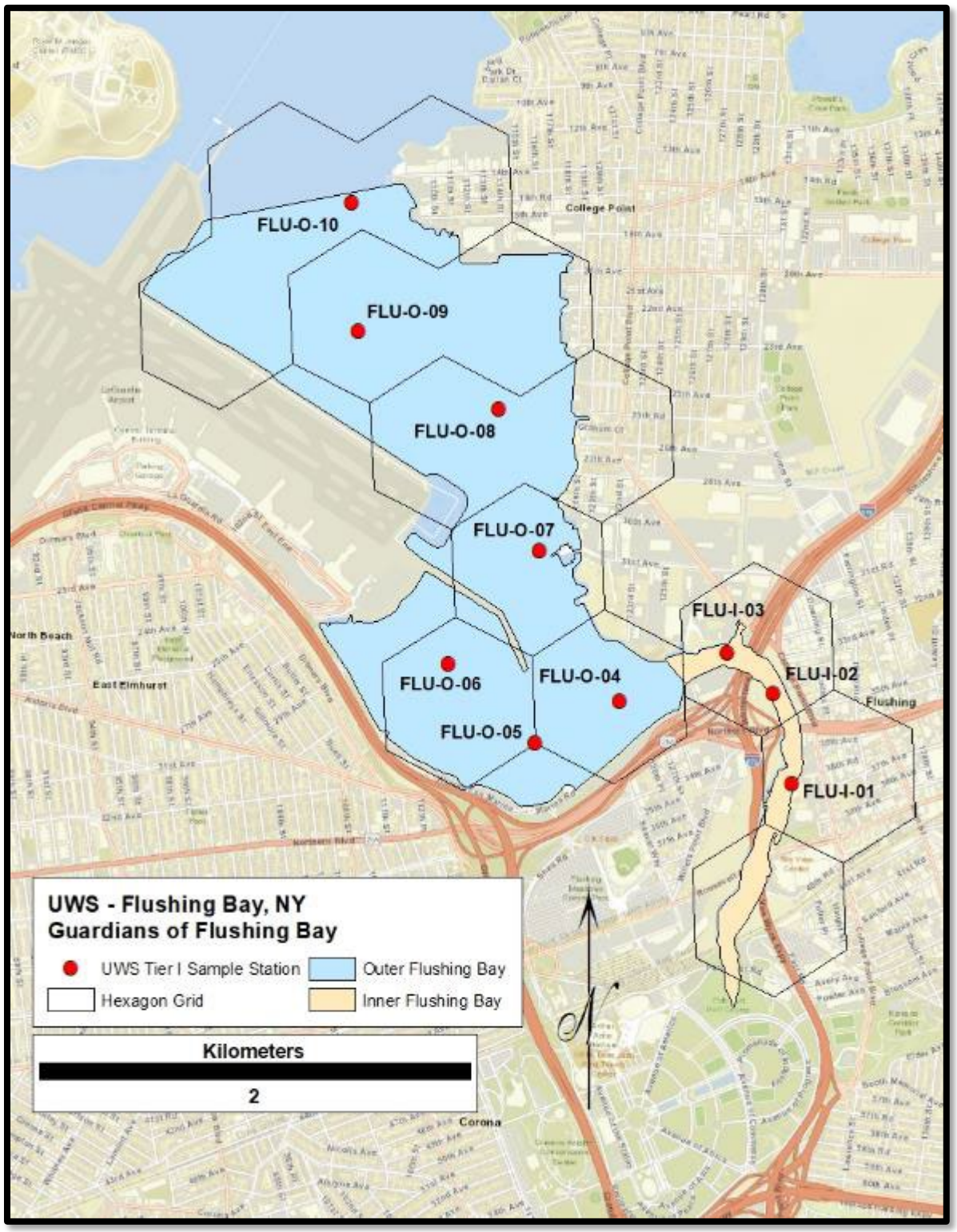

Figure 1af Flushing Bay, NY

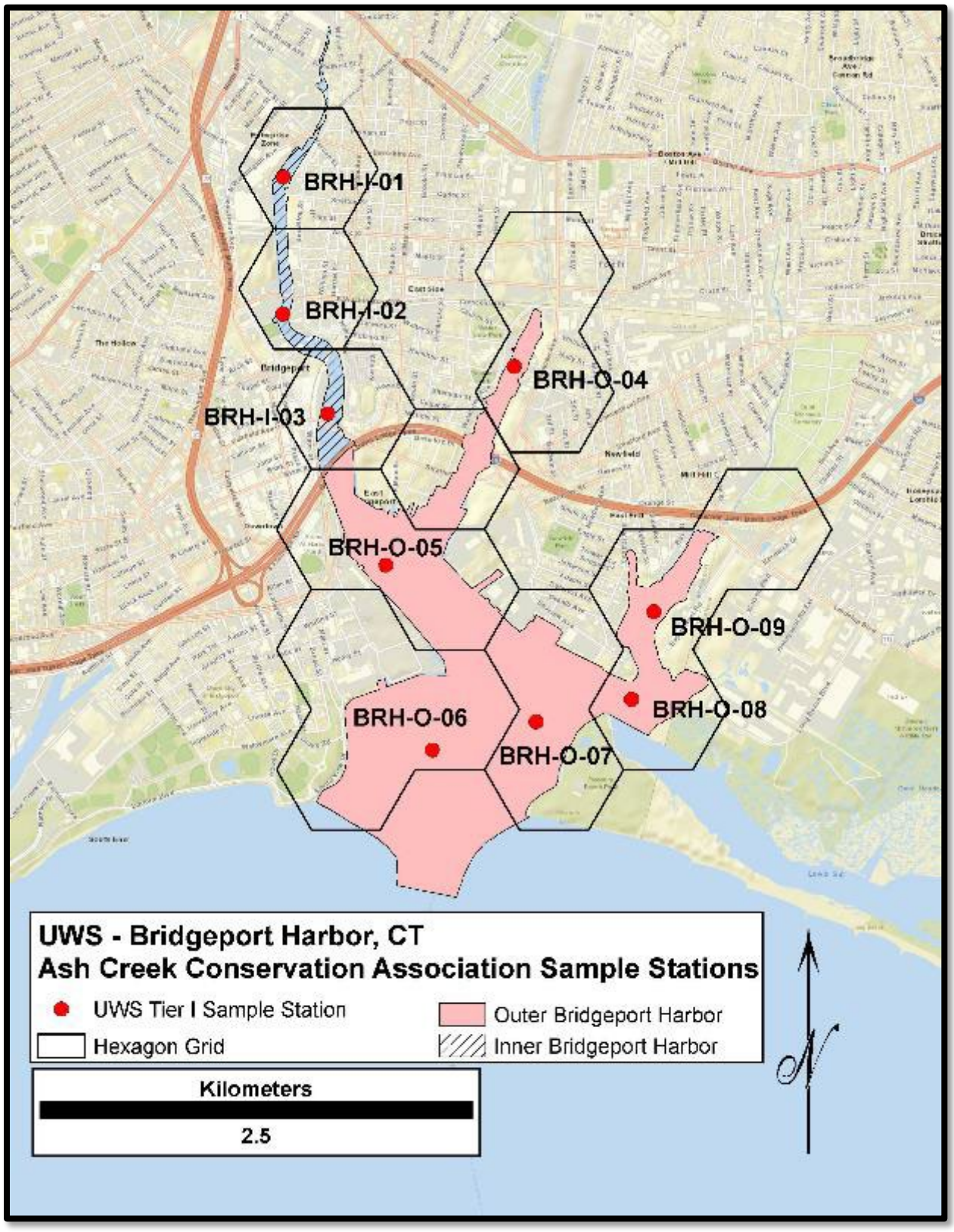

Figure 1ag Bridgeport Harbor, CT

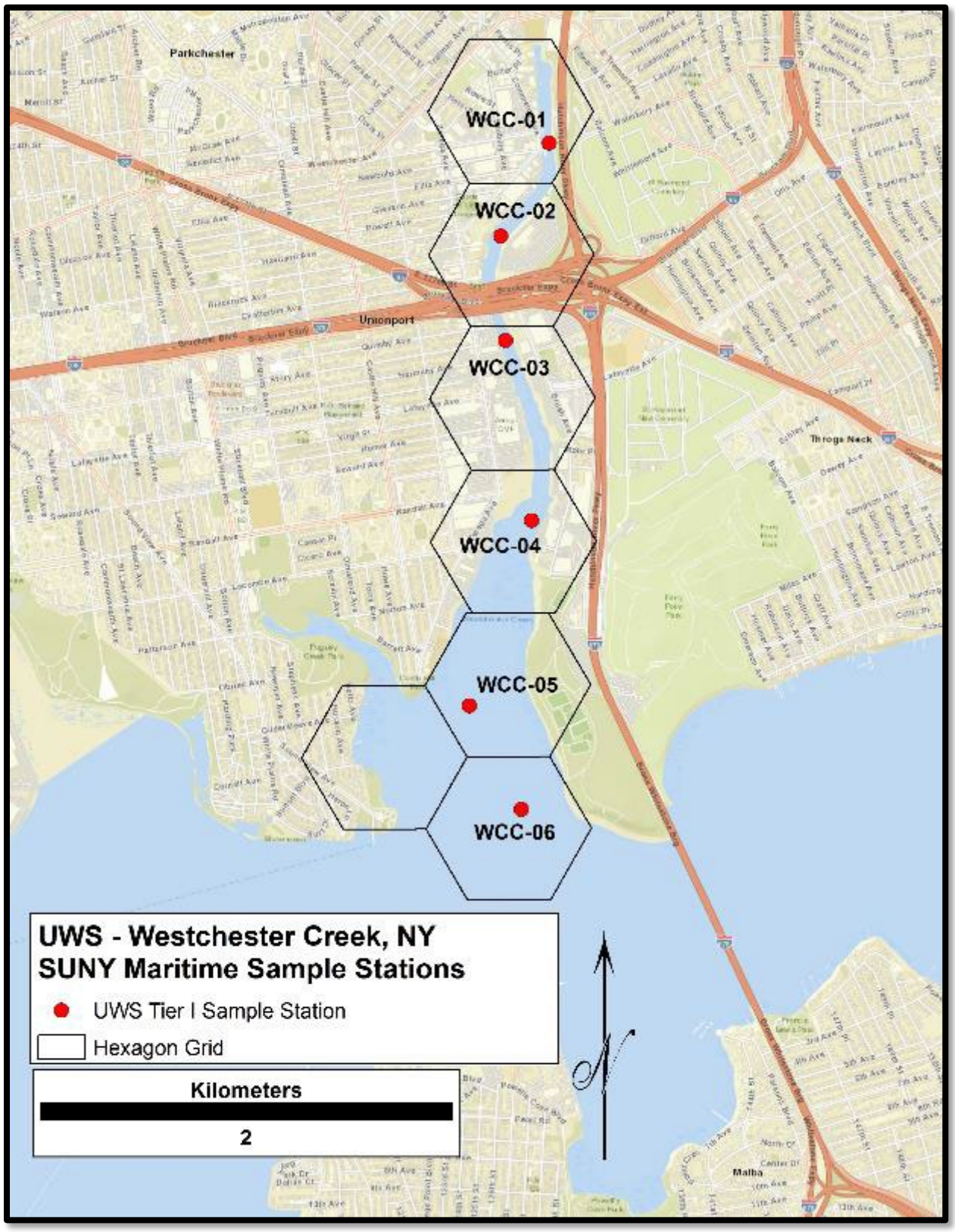

Figure 1ah Westchester Creek, NY

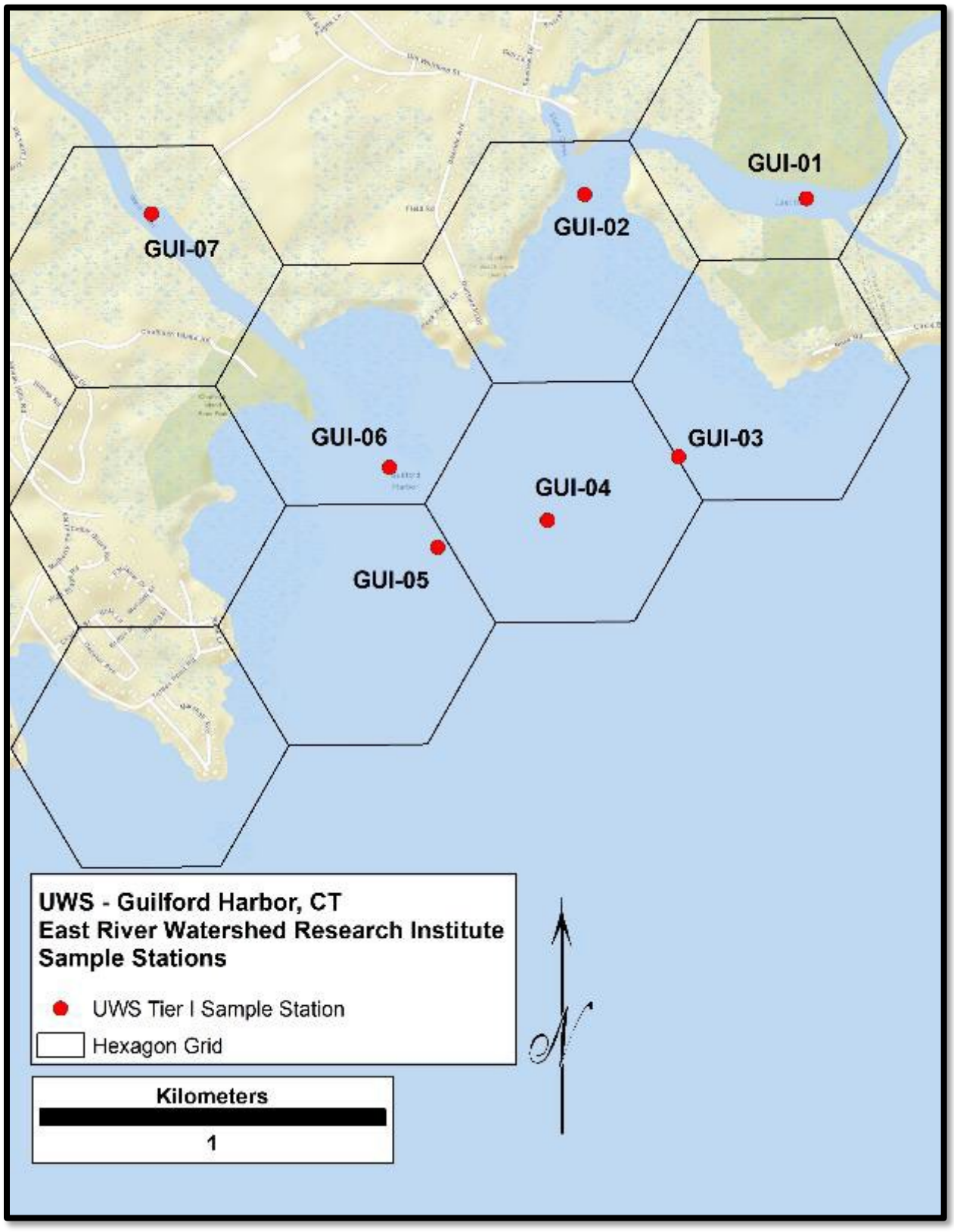

Figure 1ai Guildford Harbor, CT

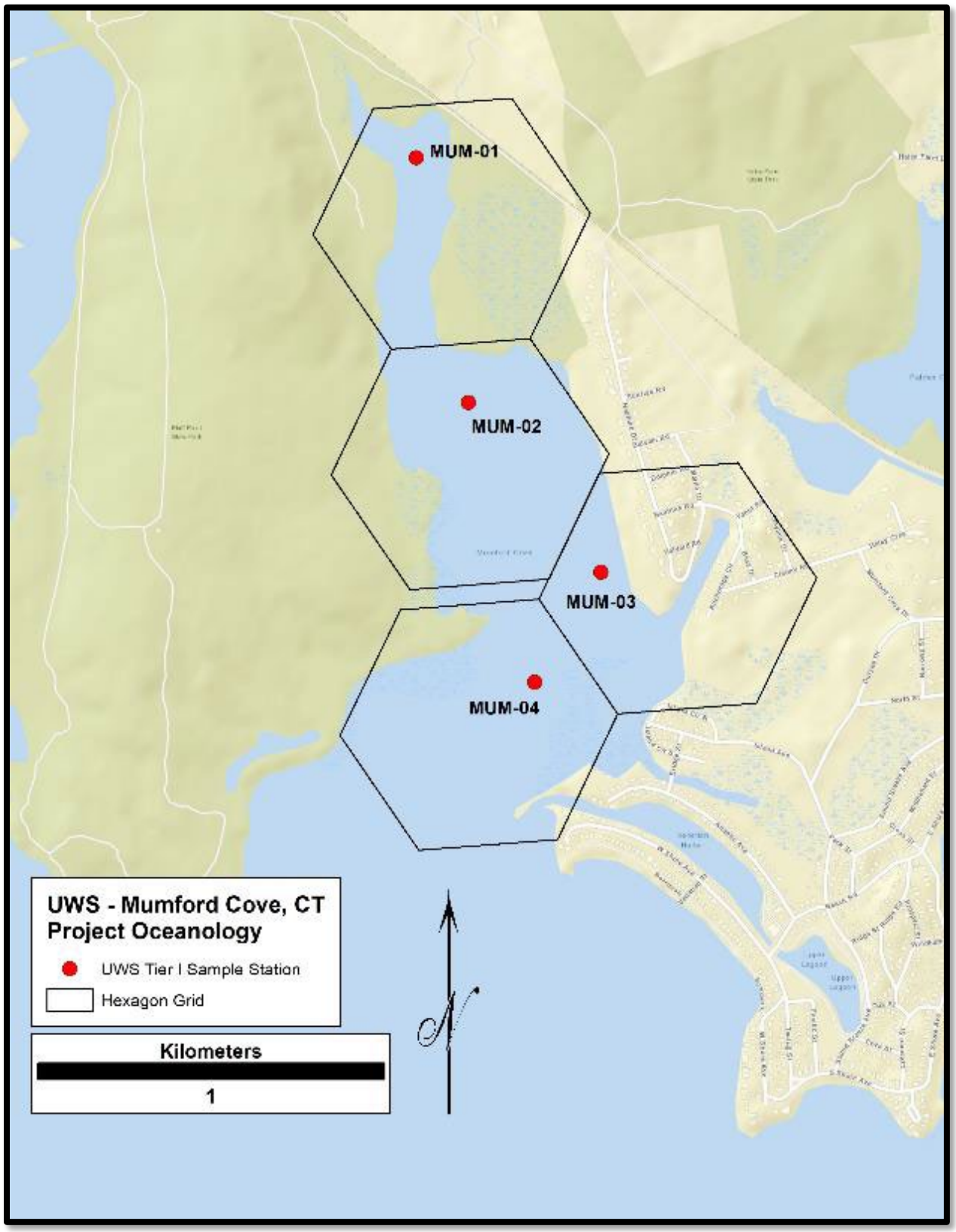

Figure 1aj Mumford Cove, CT

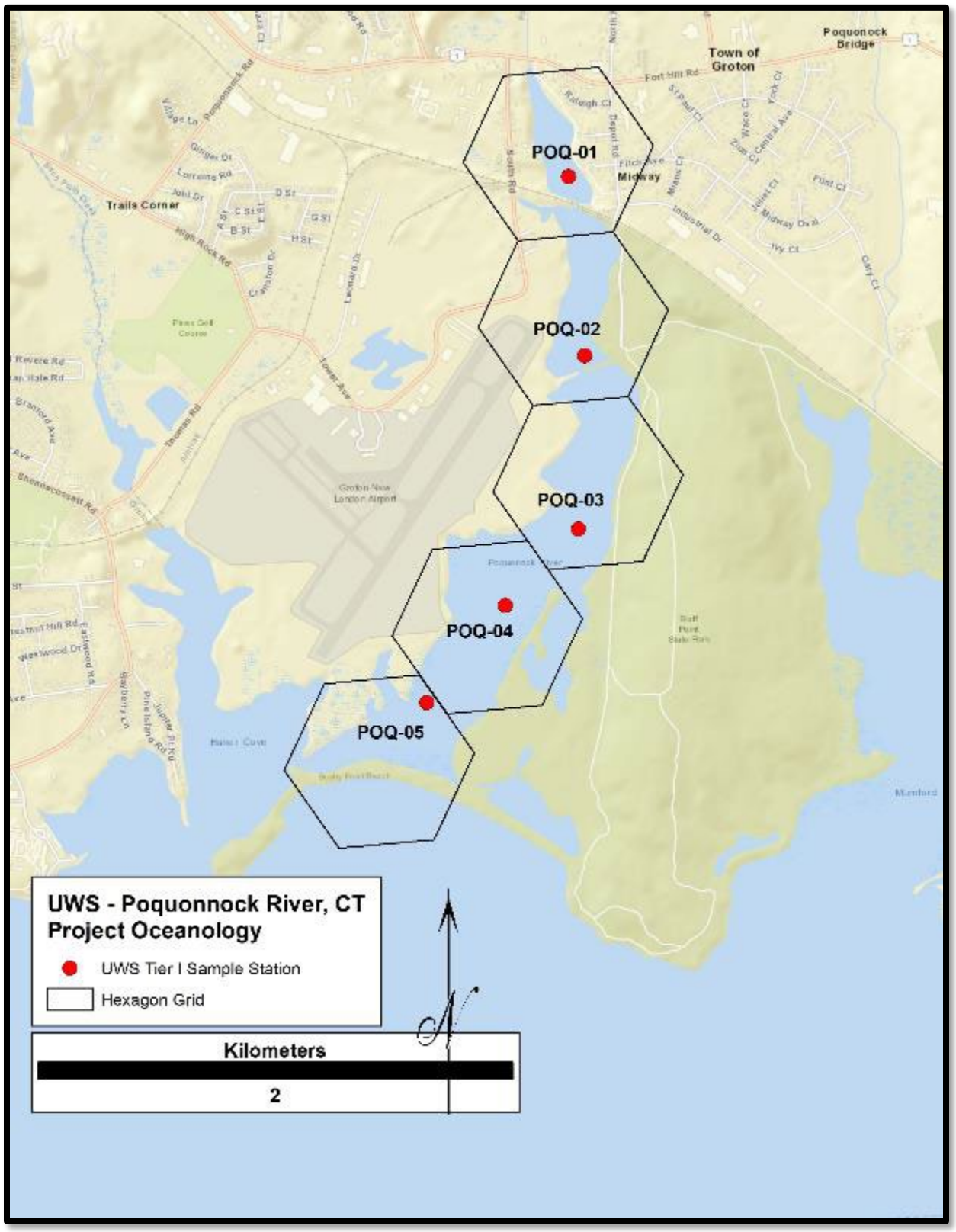

Figure 1ak Poquonnock River, CT

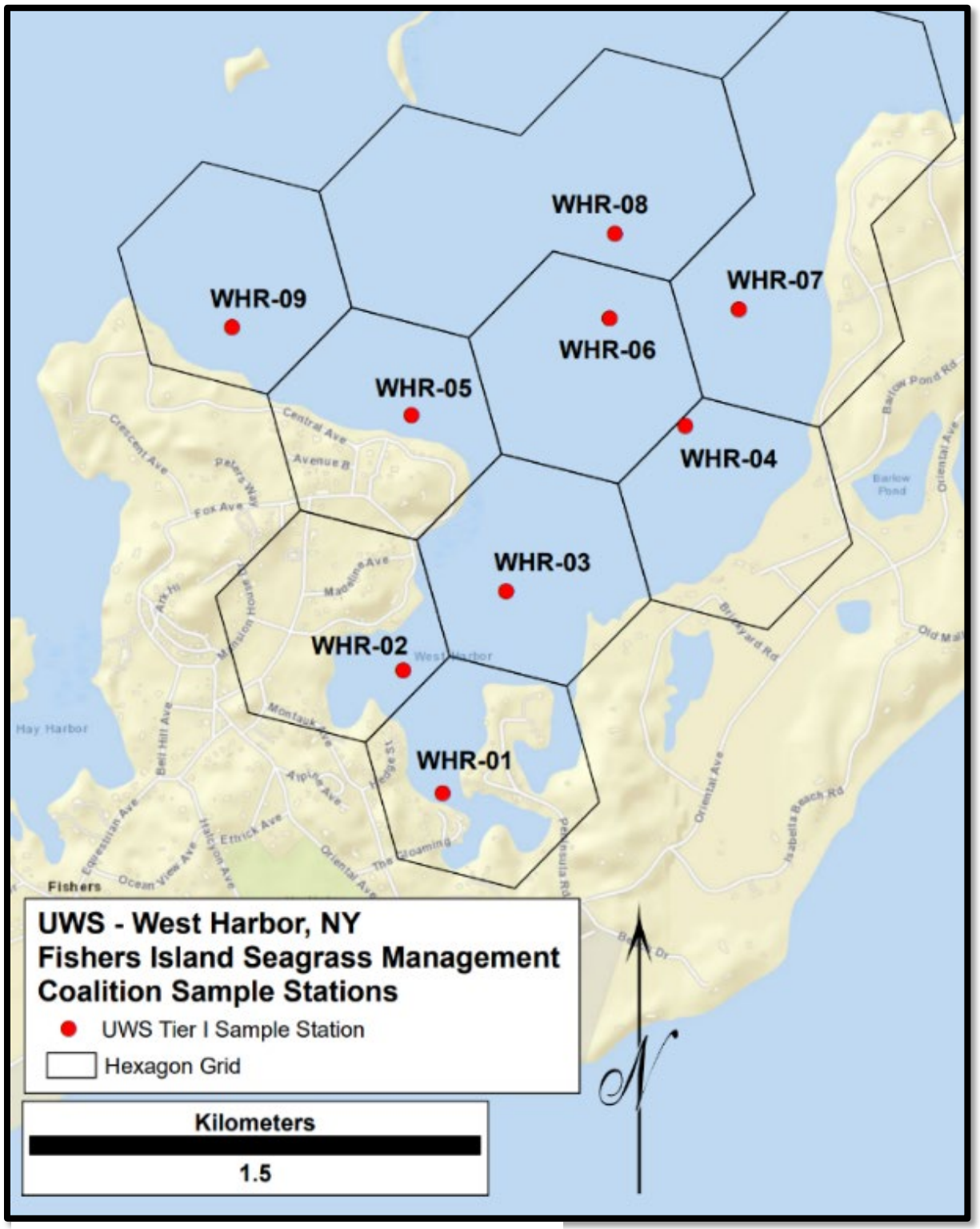

Figure 1al West Harbor, NY

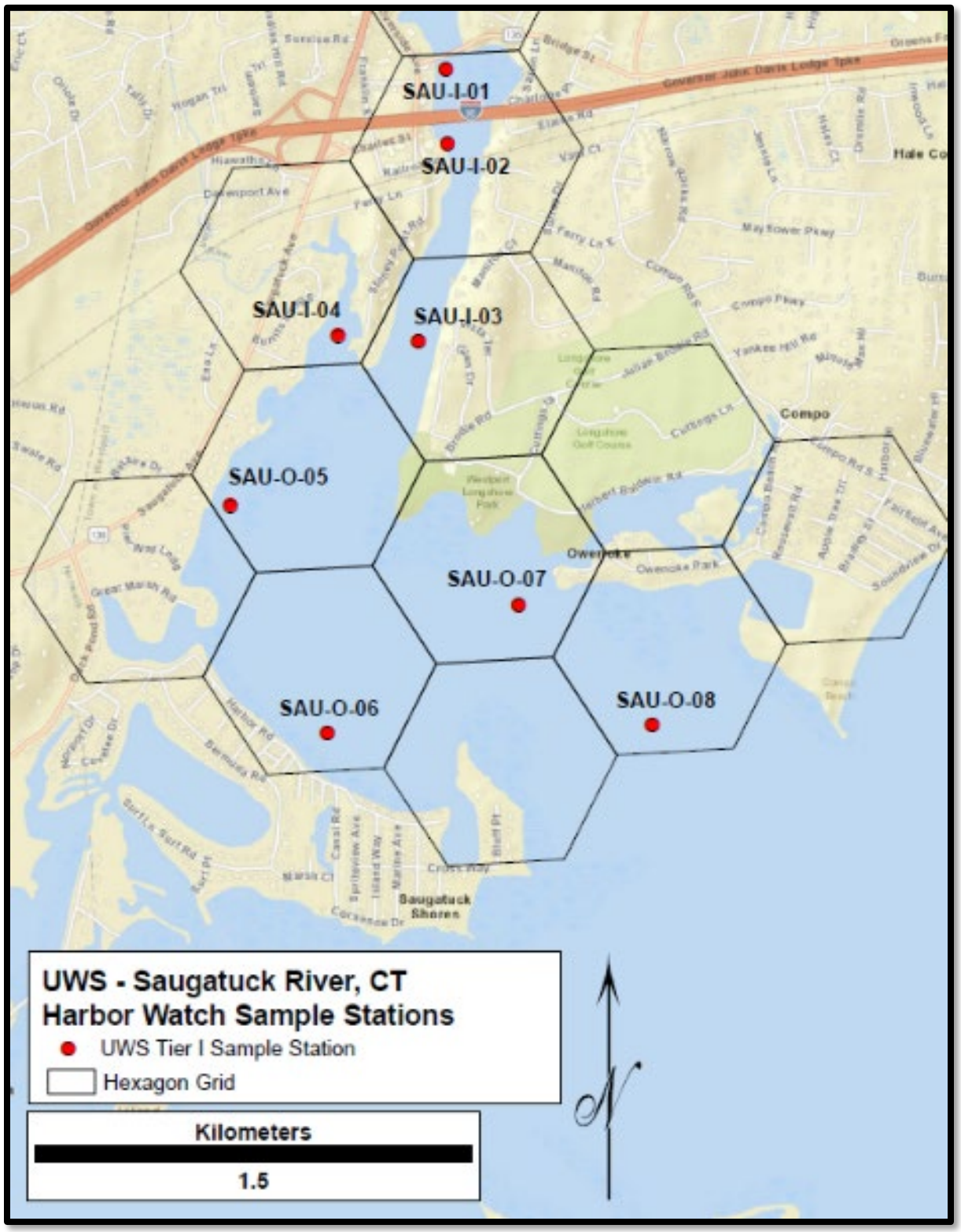

Figure 2am Saugatuck River, CT

Table 1: Station Coordinates in NAD_83 for Tier I Water Quality and Tier II Nutrients Stations* in the UWS

Station ID	Embayment	Longitude	Latitude
ALE-01	Alewife Cove, CT	-72.10449	41.31814
ALE-02	Alewife Cove, CT	-72.10069	41.31364
ALE-03	Alewife Cove, CT	-72.10343	41.30898
ALE-04	Alewife Cove, CT	-72.10485	41.3055
BLR-01*	Black Rock Harbor, CT	-73.20513	41.16387
BLR-02	Black Rock Harbor, CT	-73.20895	41.15945
BLR-03*	Black Rock Harbor, CT	-73.21531	41.15589
BLR-04	Black Rock Harbor, CT	-73.21946	41.14901
BLR-05	Black Rock Harbor, CT	-73.21839	41.14545
BLR-06*	Black Rock Harbor, CT	-73.22326	41.14353
BRR-01	Bronx River, NY	-73.88403	40.82226
BRR-02	Bronx River, NY	-73.87916	40.81694
BRR-03	Bronx River, NY	-73.87346	40.81489
BRR-04	Bronx River, NY	-73.86939	40.81079
BRR-05	Bronx River, NY	-73.86751	40.80661
BRR-06	Bronx River, NY	-73.86299	40.80257
CEN-01*	Centerport Harbor, NY	-73.37583	40.89694
CEN-02	Centerport Harbor, NY	-73.37952	40.90007
CEN-03*	Centerport Harbor, NY	-73.38401	40.90849
COL-I-01*	Cold Spring Harbor, NY	-73.46501	40.8625
COL-I-02	Cold Spring Harbor, NY	-73.46333	40.86667
COL-I-03*	Cold Spring Harbor, NY	-73.46605	40.86898
COL-O-04*	Cold Spring Harbor, NY	-73.47908	40.8796
COL-O-05	Cold Spring Harbor, NY	-73.48873	40.89025
COL-O-06	Cold Spring Harbor, NY	-73.48468	40.90344
COL-O-07*	Cold Spring Harbor, NY	-73.50969	40.91512
CTR-01	Connecticut River, CT	-73.3842	41.352

CTR-02	Connecticut River, CT	-72.3839	41.34842
CTR-04	Connecticut River, CT	-72.38082	41.35696
CTR-05	Connecticut River, CT	-72.37864	41.36275
CTR-06	Connecticut River, CT	-72.37932	41.35323
CTR-07	Connecticut River, CT	-72.37504	41.34672
CTR-08	Connecticut River, CT	-72.36533	41.34011
COV-01	Cove Harbor, CT	-73.49904	41.03958
COV-02	Cove Harbor, CT	-73.5036	41.04227
COV-03	Cove Harbor, CT	-73.49928	41.04377
COV-04	Cove Harbor, CT	-73.49468	41.04477
DAR-01	Darien River, CT	-73.4814	41.03846
DAR-02	Darien River, CT	-73.48587	41.04082
DAR-03	Darien River, CT	-73.48598	41.04336
DAR-04	Darien River, CT	-73.48382	41.04796
EAB-I-01*	Eastchester Bay, NY	-73.8207	40.88621
EAB-I-02	Eastchester Bay, NY	-73.82118	40.87824
EAB-I-03	Eastchester Bay, NY	-73.82306	40.8724
EAB-I-04*	Eastchester Bay, NY	-73.81672	40.8628
EAB-O-05*	Eastchester Bay, NY	-73.81038	40.85766
EAB-O-06	Eastchester Bay, NY	-73.81319	40.85211
EAB-O-07	Eastchester Bay, NY	-73.80781	40.85024
EAB-O-08	Eastchester Bay, NY	-73.80829	40.84192
EAB-O-09*	Eastchester Bay, NY	-73.80649	40.83259
FAR-04	Farm River, CT	-72.85192	41.26209
FAR-05	Farm River, CT	-72.85405	41.25649
FAR-06	Farm River, CT	-72.85857	41.24893
FAR-07	Farm River, CT	-72.85378	41.25186
GOL-0	Goldsmith Inlet, NY	-72.46946	41.05073
GOL-02	Goldsmith Inlet, NY	-72.47022	41.05165
GOL-03	Goldsmith Inlet, NY	-72.47017	41.05373

GOL-04	Goldsmith Inlet, NY	-72.47123	41.05303
HEM-M-01	Hempstead Harbor, NY	-73.65353	40.83189
HEM-M-02	Hempstead Harbor, NY	-73.65854	40.84172
HEM-M-03	Hempstead Harbor, NY	-73.65216	40.85365
HEM-O-04	Hempstead Harbor, NY	-73.67396	40.86077
HEM-O-05	Hempstead Harbor, NY	-73.67493	40.87349
HEM-O-06	Hempstead Harbor, NY	-73.65016	40.88365
HOL-01	Holly Pond, CT	-73.50337	41.05624
HOL-02	Holly Pond, CT	-73.49906	41.05487
HOL-03	Holly Pond, CT	-73.49446	41.0525
HOL-04	Holly Pond, CT	-73.4971	41.05092
HOU-O-01	Housatonic River, CT	-73.11245	41.1976
HOU-O-02	Housatonic River, CT	-73.11861	41.18895
HOU-O-03	Housatonic River, CT	-73.12158	41.17737
HOU-O-04	Housatonic River, CT	-73.11256	41.17121
HOU-O-05	Housatonic River, CT	-73.09952	41.16267
HIB-01	Hunter Island Bay, NY	-73.79606	40.87446
HIB-02	Hunter Island Bay, NY	-73.79547	40.87637
HIB-03	Hunter Island Bay, NY	-73.79217	40.88172
HIB-04	Hunter Island Bay, NY	-73.78636	40.88178
HUB-01*	Huntington Bay, NY	-73.42993	40.90936
HUB-02*	Huntington Bay, NY	-73.40746	40.91044
HUB-03	Huntington Bay, NY	-73.41805	40.91777
HUH-01*	Huntington Harbor, NY	-73.41805	40.88749
HUH-02	Huntington Harbor, NY	-73.42333	40.89666
HUH-03	Huntington Harbor, NY	-73.43205	40.89881
HUH-04	Huntington Harbor, NY	-73.43865	40.89988
HUH-06*	Huntington Harbor, NY	-73.43445	40.90499
LNE-I-01	Little Neck Bay, NY	-73.75791	40.77224
LNE-I-02	Little Neck Bay, NY	-73.7608	40.7778

LNE-I-03	Little Neck Bay, NY	-73.75823	40.78314
LNE-I-04	Little Neck Bay, NY	-73.75061	40.78377
LNE-I-05	Little Neck Bay, NY	-73.76862	40.78606
LNE-O-06	Little Neck Bay, NY	-73.7582	40.7888
LNE-O-07	Little Neck Bay, NY	-73.77112	40.794
LNE-O-08	Little Neck Bay, NY	-73.76179	40.79561
LNE-O-09	Little Neck Bay, NY	-73.75442	40.79884
LNE-O-10	Little Neck Bay, NY	-73.76992	40.80202
LLO-01*	Lloyd Harbor, NY	-73.46734	40.91296
LLO-02	Lloyd Harbor, NY	-73.45	40.91361
LLO-03	Lloyd Harbor, NY	-73.44147	40.91093
LLO-04*	Lloyd Harbor, NY	-73.43738	40.91889
MAM-01*	Mamaroneck River, NY	-73.72225	40.94088
MAM-02	Mamaroneck River, NY	-73.72717	40.94288
MAM-03*	Mamaroneck River, NY	-73.72894	40.94737
MAM-04*	Mamaroneck River, NY	-73.73625	40.94367
MAN-I-01	Manhasset Bay, NY	-73.71316	40.80772
MAN-I-02	Manhasset Bay, NY	-73.71461	40.81244
MAN-I-03	Manhasset Bay, NY	-73.70714	40.81586
MAN-M-04	Manhasset Bay, NY	-73.71242	40.82271
MAN-M-05	Manhasset Bay, NY	-73.70551	40.83064
MAN-M-06	Manhasset Bay, NY	-73.71454	40.83228
MAN-M-07	Manhasset Bay, NY	-73.72375	40.82616
MAN-M-08	Manhasset Bay, NY	-73.72564	40.83644
MAN-O-09	Manhasset Bay, NY	-73.73613	40.83179
MAN-O-10	Manhasset Bay, NY	-73.73672	40.84517
MAN-O-11	Manhasset Bay, NY	-73.74556	40.84097
MAT-01	Mattituck Creek, NY	-72.53983	40.99671
MAT-02	Mattituck Creek, NY	-72.55082	40.99702
MAT-03	Mattituck Creek, NY	-72.54506	41.00124

MAT-04	Mattituck Creek, NY	-72.5471	41.0058
MAT-05	Mattituck Creek, NY	-72.5491	41.00997
MAT-06	Mattituck Creek, NY	-72.55664	41.01282
MNC-01*	Mill Neck Creek, NY	-73.5675	40.89888
MNC-02	Mill Neck Creek, NY	-73.55809	40.90138
MNC-03*	Mill Neck Creek, NY	-73.55167	40.90333
MIL-01	Mill River, CT	-73.27468	41.13761
MIL-02	Mill River, CT	-73.28045	41.13339
MIL-03	Mill River, CT	-73.28416	41.1317
MIL-04	Mill River, CT	-73.28766	41.12727
MYH-01	Mystic Harbor, CT	-71.96392	41.34344
MYH-02	Mystic Harbor, CT	-71.97418	41.34013
MYH-03	Mystic Harbor, CT	-71.97581	41.33295
MYH-04	Mystic Harbor, CT	-71.98351	41.32905
NRH-01	New Rochelle Harbor, NY	-73.77759	40.89548
NRH-02	New Rochelle Harbor, NY	-73.78096	40.89031
NRH-03	New Rochelle Harbor, NY	-73.78444	40.88806
NRH-04	New Rochelle Harbor, NY	-73.7881	40.88382
NIR-I-01	Niantic River, CT	-72.19166	41.36423
NIR-I-02	Niantic River, CT	-72.19027	41.35582
NIR-I-03	Niantic River, CT	-72.18295	41.34556
NIR-I-04	Niantic River, CT	-72.17941	41.35027
NIR-O-05	Niantic River, CT	-72.17737	41.3397
NIR-O-06	Niantic River, CT	-72.18646	41.33786
NIR-O-07	Niantic River, CT	-72.18174	41.33128
NIR-O-08	Niantic River, CT	-72.1762	41.32346
NIS-01	Nissequogue River, NY	-73.20069	40.86397
NIS-02	Nissequogue River, NY	-73.20219	40.89071
NIS-03	Nissequogue River, NY	-73.20899	40.89408
NIS-04	Nissequogue River, NY	-73.22424	40.89892

NIS-05	Nissequogue River, NY	-73.21767	40.90121
NIS-06	Nissequogue River, NY	-73.21607	40.89874
NIS-07	Nissequogue River, NY	-73.22976	40.90427
NPB-01	Northport Bay, NY	-73.36417	40.91111
NPB-02*	Northport Bay, NY	-73.35544	40.92265
NPB-03	Northport Bay, NY	-73.36616	40.92906
NPB-04	Northport Bay, NY	-73.37555	40.91666
NPB-05*	Northport Bay, NY	-73.38112	40.93054
NPB-06*	Northport Bay, NY	-73.39183	40.91458
NPB-07	Northport Bay, NY	-73.39841	40.92496
NPH-01*	Northport Harbor, NY	-73.36131	40.89117
NPH-02	Northport Harbor, NY	-73.35583	40.89888
NPH-03*	Northport Harbor, NY	-73.35972	40.90561
NWH-I-01	Norwalk Harbor, CT	-73.41105	41.11738
NWH-I-02*	Norwalk Harbor, CT	-73.41117	41.10799
NWH-I-03*	Norwalk Harbor, CT	-73.416	41.10205
NWH-I-04	Norwalk Harbor, CT	-73.41419	41.09846
NWH-I-05*	Norwalk Harbor, CT	-73.41003	41.09385
NWH-I-06*	Norwalk Harbor, CT	-73.40425	41.08727
NWH-I-07	Norwalk Harbor, CT	-73.40073	41.07939
NWH-O-01	Norwalk Harbor, CT	-73.41195	41.06843
NWH-O-02*	Norwalk Harbor, CT	-73.41526	41.06435
NWH-O-03	Norwalk Harbor, CT	-73.40758	41.06275
NWH-O-04	Norwalk Harbor, CT	-73.39851	41.06764
NWH-O-05*	Norwalk Harbor, CT	-73.39131	41.07406
OYB-01*	Oyster Bay, NY	-73.53963	40.89789
OYB-02*	Oyster Bay, NY	-73.52878	40.91181
OYB-03	Oyster Bay, NY	-73.53113	40.88073
OYB-04*	Oyster Bay, NY	-73.51553	40.89036
POR-I-01	Port Jefferson Harbor, NY	-73.10422	40.94861

POR-I-02	Port Jefferson Harbor, NY	-73.10069	40.9504
POR-I-03	Port Jefferson Harbor, NY	-73.09931	40.95557
POR-M-04	Port Jefferson Harbor, NY	-73.11192	40.97045
POR-M-05	Port Jefferson Harbor, NY	-73.10555	40.96579
POR-M-06	Port Jefferson Harbor, NY	-73.09524	40.9644
POR-O-07	Port Jefferson Harbor, NY	-73.07133	40.95141
POR-O-08	Port Jefferson Harbor, NY	-73.08307	40.95637
POR-O-09	Port Jefferson Harbor, NY	-73.08649	40.96139
POR-O-10	Port Jefferson Harbor, NY	-73.08729	40.968
STA-01	Stamford Harbor, CT	-73.54388	41.0363
STA-02	Stamford Harbor, CT	-73.53599	41.03353
STA-03	Stamford Harbor, CT	-73.53796	41.02906
STA-04	Stamford Harbor, CT	-73.53645	41.02362
STA-05	Stamford Harbor, CT	-73.54446	41.02405
STA-06	Stamford Harbor, CT	-73.53853	41.01981
STA-07	Stamford Harbor, CT	-73.54553	41.01754
STA-08	Stamford Harbor, CT	-73.53044	41.041
STO-I-01	Stonington Harbor, CT	-71.91511	41.34485
STO-I-02	Stonington Harbor, CT	-71.9144	41.34298
STO-I-03	Stonington Harbor, CT	-71.91138	41.3422
STO-O-04	Stonington Harbor, CT	-71.9106	41.33843
STO-O-05	Stonington Harbor, CT	-71.91545	41.33408
STO-O-06	Stonington Harbor, CT	-71.90871	41.33237
STO-O-07	Stonington Harbor, CT	-71.90762	41.32727
STO-O-08	Stonington Harbor, CT	-71.91973	41.32764
SCO-01	Scotts Cove, CT	-73.47318	41.04985
SCO-02	Scotts Cove, CT	-73.46762	41.05041
SCO-03	Scotts Cove, CT	-73.46483	41.05037
SCO-04	Scotts Cove, CT	-73.46516	41.05425
NEW-01	New Haven Harbor, CT	-72.91249	41.29462

NEW-02	New Haven Harbor, CT	-72.91387	41.28861
NEW-03	New Haven Harbor, CT	-72.91511	41.28396
NEW-04	New Haven Harbor, CT	-72.92178	41.28159
NEW-05	New Haven Harbor, CT	-72.91722	41.27964
NEW-06	New Haven Harbor, CT	-72.91025	41.27771
NEW-07	New Haven Harbor, CT	-72.91496	41.27309
NEW-08	New Haven Harbor, CT	-72.90936	41.27144
FLU-I-01	Flushing Bay, NY	-73.83682	40.76045
FLU-I-02	Flushing Bay, NY	-73.83789	40.76416
FLU-I-03	Flushing Bay, NY	-73.84044	40.76584
FLU-O-04	Flushing Bay, NY	-73.8463	40.76379
FLU-O-05	Flushing Bay, NY	-73.85089	40.76199
FLU-O-06	Flushing Bay, NY	-73.85573	40.76525
FLU-O-07	Flushing Bay, NY	-73.85081	40.76998
FLU-O-08	Flushing Bay, NY	-73.85314	40.77587
FLU-O-09	Flushing Bay, NY	-73.8609	40.77904
FLU-O-10	Flushing Bay, NY	-73.86131	40.78441
BRH-I-01	Bridgeport Harbor, CT	-73.18912	41.19232
BRH-I-02	Bridgeport Harbor, CT	-73.18911	41.18517
BRH-I-03	Bridgeport Harbor, CT	-73.18597	41.17997
BRH-O-04	Bridgeport Harbor, CT	-73.17312	41.1825
BRH-O-05	Bridgeport Harbor, CT	-73.1819	41.1721
BRH-O-06	Bridgeport Harbor, CT	-73.17863	41.16247
BRH-O-07	Bridgeport Harbor, CT	-73.17147	41.16398
BRH-O-08	Bridgeport Harbor, CT	-73.16489	41.16516
BRH-O-09	Bridgeport Harbor, CT	-73.16339	41.16975
WCC-01	Westchester Creek, NY	-73.83933	40.83521
WCC-02	Westchester Creek, NY	-73.84203	40.8311
WCC-03	Westchester Creek, NY	-73.84169	40.82654
WCC-04	Westchester Creek, NY	-73.84005	40.81868

WCC-05	Westchester Creek, NY	-73.8435	40.81054
WCC-06	Westchester Creek, NY	-73.84045	40.80605
GUI-01	Guilford Harbor, CT	-72.6573	41.27003
GUI-02	Guilford Harbor, CT	-72.66496	41.27013
GUI-03	Guilford Harbor, CT	-72.66174	41.26328
GUI-04	Guilford Harbor, CT	-72.66627	41.26163
GUI-05	Guilford Harbor, CT	-72.67005	41.26093
GUI-06	Guilford Harbor, CT	-72.67172	41.26301
GUI-07	Guilford Harbor, CT	-72.67993	41.26964
MUM-01	Mumford Cove, CT	-72.02225	41.33216
MUM-02	Mumford Cove, CT	-72.02052	41.32578
MUM-03	Mumford Cove, CT	-72.016	41.32134
MUM-04	Mumford Cove, CT	-72.01832	41.3185
POQ-01	Poquonnock River, CT	-72.03608	41.34227
POQ-02	Poquonnock River, CT	-72.03534	41.33548
POQ-03	Poquonnock River, CT	-72.03574	41.32892
POQ-04	Poquonnock River, CT	-72.03945	41.32604
POQ-05	Poquonnock River, CT	-72.04345	41.32239
WHR-01	West Harbor, NY	-72.00847	41.26103
WHR-02	West Harbor, NY	-72.01001	41.26472
WHR-03	West Harbor, NY	-72.0059	41.26708
WHR-04	West Harbor, NY	-71.99871	41.27199
WHR-05	West Harbor, NY	-72.00959	41.27238
WHR-06	West Harbor, NY	-72.00167	41.27524
WHR-07	West Harbor, NY	-71.99653	41.27546
WHR-08	West Harbor, NY	-72.00144	41.27777
WHR-09	West Harbor, NY	-72.01669	41.27506
SAU-I-01	Saugatuck River, CT	-73.36917	41.12226
SAU-I-02	Saugatuck River, CT	-73.36907	41.11998
SAU-I-03	Saugatuck River, CT	-73.37022	41.11384

SAU-I-04	Saugatuck River, CT	-73.37351	41.11402
SAU-O-05	Saugatuck River, CT	-73.37788	41.10873
SAU-O-06	Saugatuck River, CT	-73.37383	41.10173
SAU-O-07	Saugatuck River, CT	-73.36604	41.10570
SAU-O-08	Saugatuck River, CT	-73.36053	41.10204

*These stations will be sampled for Tier II nutrients.

A.5.c. Annual Task Calendar

The annual task calendar describes when certain activities will occur.

Table 2: Annual Task Calendar
These tasks are repeated annually.

Activity	J	F	M	A	M	J	J	A	S	O	N	D
Kickoff meeting with UWS project team	x	x										
Develop draft QAPP and submit to UWS & EPA	x	x	x									
Finalize QAPP and annual review of QAPP, responding to comments from EPA			x	x	x							
Application process and group admittance to UWS; includes station selection and funding	x	x	x	x			x					
Equipment inventory, purchase, inspection, and testing	x	x	x	x							x	X
Field training and database-related training session(s)			x	x								
Contact with analytical laboratory (for chlorophyll a and nutrient sampling samples)		x	x	x								
Field audits & midseason check in with Monitoring Group Leads or designated appointees					x	x		x				
Monthly check ins with Monitoring Groups					x	x	x	x	x	x	x	x
Technical support to Monitoring Groups	x			x	x	x	x	x	x	x	x	x
Sampling events					x	x	x	x	x	x		
Data entry					x	x	x	x	x	x	x	x
Data review and validation of data entry	o	o	o	o	o	x	x	x	x	x	x	x
Data uploads to STS-UWS website and WQX (must follow data review)						o						
Draft report								o				
Final annual report									o			
o indicates the year following sampling events												

A.6. INFORMATION/DATA QUALITY OBJECTIVES, AND PERFORMANCE/ACCEPTANCE CRITERIA

Taken together, precision, accuracy and bias, representativeness, comparability, completeness, and sensitivity comprise the major data quality indicators used to assess the quality of the program's data. A summary of criteria are provided in Table 3.

Definitions of these data quality indicator terms:

- **Precision** is the degree of agreement among repeated field measurements of the same indicator and gives information about the consistency of methods. It is typically defined as relative percent difference, or RPD.

- **Accuracy** is a measure of confidence that describes how close a measurement is to its "true" or expected value; it includes a combination of random error (precision) and systematic error (bias) components of both sampling and analytical operations.

- **Bias** is the systematic or persistent distortion of a measurement process that causes errors in one direction.

- **Representativeness** is the extent to which measurements actually represent the true environmental condition. Parameters, station selection (including location of sampling point within the water column), time, and frequency of sample collection can all play a role in determining how representative a sample is.

- **Comparability** is the extent to which data can be compared between sample locations or periods of time within a project, or between different sites.

- **Completeness** is the comparison between the amount of valid or usable data the program originally intended to collect versus how much was actually collected.

- **Sensitivity** is the capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest.

Table 3: Measurement Performance Criteria

Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Criteria
Precision – overall	RPD ≤ value indicated in Table 4	field duplicates
Precision – analytical	RPD ≤ value indicated in Table 4	analytical duplicates
Accuracy / Bias	85% ≤ recovery ≤ 115%	certified reference material
Comparability	standard procedures followed	NA
Completeness	data from surface, mid (if applicable) and bottom at each station meet data quality objectives	data completeness check
Sensitivity	value ≥ MDL*	sample value check

* MDL = method detection limit. This is a reporting limit based on the lowest standard accurately analyzed in the analysis.

Precision - Precision objectives are listed in Table 4. Precision is evaluated in the field by participants taking replicate measurements for at least 5% of samples, where applicable.

For UWS Tier I water quality sample events, a replicate profile at one station per field day.

For water samples filtered and analyzed for extracted chlorophyll-*a*, two field replicates will be collected per sample day.

For estuary and tributary stations sampled for nutrients, a field replicate will be collected at each station.

For qualitative macrophyte stations, multiple pictures will be taken for rake toss sampling and beach sampling.

For quantitative macrophyte sampling, multiple analyses of the stills to determine percent coverage will be undertaken.

When a multiparameter sonde is used, standards will be read before and following a trip, within one day of the field day. Calibration of sondes will happen within one day of the sampling event. Multiparameter sondes can hold their calibrations for weeks. The pre and post sampling event readings can identify any potential drift outside of manufacturer recommendations for calibration. These values will be kept with all other data for review at the end of the project interval.

The Onset HOBO loggers (dissolved oxygen) and Star-Oddi loggers (temperature, conductivity, depth) will be deployed in a common water bath before deployment and following deployment. Conductivity, temperature and oxygen will be varied in the bath, allowing for

multiple values for intercomparison. The temperature, conductivity, and oxygen of the bath will be determined with the instruments being used for conducting Tier I water quality profiles. These pre- and post-baths will serve to cross-calibrate all instruments and to determine if the deployed loggers exhibited any drift over the course of the deployment. The deployed loggers will be intercalibrated by applying a multiplicative correction if initial values differ by more than 10% from the reference value (as determined from the YSI EXO1 or YSI ProDSS sondes).

The frequency of field replicate measurements for each parameter are described in Table 7.

Relative percent difference (RPD) of replicate samples is used as one index of precision; see Table 4. This is defined as the absolute difference between the replicates divided by the average of the replicates. The allowable RPDs for each parameter are provided in Table 4. A difference greater than the designated RPD requires further investigation of the sample run. If the difference is large enough, it indicates failure (unless the average of the two samples is less than 10 times the method detection limit), and results in potential disqualification or flagging of data from that station depth, unless there is a reasonable and supported explanation for the inconsistency. Replicate precision will be analyzed by calculating the RPD using the equation:

$$RPD\ (\%) = |x1 - x2| \ / \ ((x1 + x2)/2) * 100$$

where x1 is the original sample concentration and x2 is the replicate sample concentration.

The Microsoft Excel formula for calculating the RPD is:

$$= ABS(X1-X2) \ / \ ((X1+X2) \ / \ 2) * 100$$

where X1 is the original sample concentration and X2 is the replicate sample concentration. The RPD is automatically calculated in the UWS data entry template for replicate profiles and field samples.

Accuracy and Bias - Accuracy objectives are listed in Table 4. Procedures used to test or ensure accuracy are described in Table 12. While training and audits help to ensure measurement accuracy and precision, quantitative measures of accuracy for water quality monitoring are estimated using laboratory QC data (blank results, fortified matrix results, known QC samples, etc.). When a multiparameter sonde is used, standards will be read before and following a trip, within one day of the field day. Extracted chlorophyll a analysis will include a field replicate, laboratory blank and reference standards. Nutrient analysis will include a laboratory blank, field blank, and reference standards. Data loggers will be calibrated prior to and after deployment. Biweekly comparative readings between loggers and sonde will be recorded to keep a log of any drift occurring with loggers. These data will be evaluated with the log data in the final report and during the season.

Representativeness – Tier I water quality sample stations and quantitative Tier II macrophyte stations are selected to represent the entire embayment using a probability-based sampling design[4], as in the EPA National Coastal Assessment[5]. In this approach, a 0.42 km^2 hexagonal grid is overlain on the site map. Three random stations are generated in ArcGIS in each section of the embayment within a hexagon. Large embayments will have hexagons for random station generation selected with the UWS Science Advisors. A minimum of four stations will be sampled in each embayment, with larger sites having up to twelve stations. The location of the station in each hexagon will be randomly generated, with at least two alternate locations also randomly generated, in case the original location is deemed unusable (e.g. too shallow or in the middle of a navigation channel). If none of the three random stations are accessible, a station will be determined as close as possible to a randomly generated station unless bias circumstances are identified. The Monitoring Program Coordinator will oversee station selection, providing GIS-based maps and station coordinates to groups participating in the Unified Water Study. At least one Scientific Advisor affiliated with the UWS will also advise on the choice of station locations. Stations used previously by a group are evaluated for bias before inclusion in the UWS.

Tier II nutrient stations are a subset of the Tier I water quality stations selected in consultation with the UWS Science Advisors. A pilot test of nutrient sampling was conducted in Mamaroneck River, NY and Little Neck Bay, NY in 2017. In this pilot test, all Tier I water quality stations were sampled for nutrients. The approach to selecting a subset of stations (2-3) for Tier II nutrient analysis to yield a regional average was compared to the regional average using all stations in a region (3-5). The approach described below yields the most accurate regional average when sampling a subset of Tier I water quality stations for nutrients.

At a minimum, there will be two stations per embayment. In embayments with multiple regions, there will be a minimum of two stations per region. These stations are located at the boundaries of region delineations or the entire embayment, when regions are not identified.

Embayment size, salinity, and best judgment of the UWS Science Advisors determine if more stations may be needed in a region. Additional stations are required when the geometry of the embayment is not linear. For example, the Y shape of Mamaroneck River, NY requires three stations as seen in this QAPP. Salinity within a region that has a range greater than 2 ppt

[4] Paul, J.F., J.L. Copeland, M. Charpentier, P.V. August, and J.W. Hollister. 2003, Overview of GIS applications in estuarine monitoring and assessment research. Marine Geodesy Journal 26: 63-72.

[5] EPA, U.S. 2001. National Coastal Assessment: Field Operations Manual. U. S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Gulf Ecology Division, Gulf Breeze, FL. EPA 620/R-01/003. 72 p.

triggers a closer inspection of available salinity data by the UWS Science Advisors, to insure selected stations are sufficient to characterize the region.

Stations that have salinity data of less than 5 ppt are not acceptable as representative embayment stations. In embayments with the minimum Tier I water quality stations (4 stations), a station where salinity is episodically below 5 ppt may be deemed acceptable if the UWS Science Advisors deem inclusion of the station as important to estimating the regional average. The next station downstream is evaluated for inclusion in cases where a station is rejected.

Tier II nutrients stations (tributary and Long Island Sound reference) are chosen based on access, location, and salinity values under 1 PPT.

Data logging stations are selected with at least one station per reporting region. Access to station is a strong consideration in the selection process. The final station locations will be conferred with UWS Science Advisors before deployment.

Qualitative macrophyte surveys are targeted qualitative assessments of areas in the embayment known to harbor macrophytes thus the random station generation does not apply to selecting these locations. Sample collection timing and frequency for water quality stations are selected to capture data that are representative of embayment conditions. While tidal stage will vary among sampling dates, the timing relative to dawn was considered of greatest importance when sampling Tier I water quality stations to evaluate hypoxia in embayments. These very shallow systems are typically dominated by benthic primary producers (macroalgae, benthic microalgae, and seagrass) versus pelagic primary producers (pelagic microalgae / phytoplankton). When the sun rises, these primary producers quickly replenish the dissolved oxygen in the water column. One of the goals of this study is to evaluate the incidence of hypoxia in embayments, thus sampling close to dawn is more important than sampling at a specific tidal stage. Time of high and low tide and precipitation volumes are recorded and will be considered in the analysis of results. Any abnormal or episodic conditions that may affect the representativeness of sample data are noted and maintained as metadata.

Comparability - The comparability of the data collected can be assured by using known protocols and documenting methods, analysis, sampling sites and stations, times and dates, sample storage and transfer, as well as laboratories and identification specialists; so that future surveys can produce comparable data by following similar procedures. Examples of project procedures are available in the collection of Standard Operating Procedures (SOPs) provided in Appendix A of this document.

Completeness –Minimum sample events for inclusion for Tier I and Tier II monitoring are included in section A.5.a of this document.

Sensitivity – Sensitivity objectives are listed in Table 4. Sensitivity is the lowest detection limit of the method or instrument for each of the measurement parameters of interest. For analytical methods, these are the method detection limits (MDLs).

Table 4: Data Quality Objectives

Parameter	Units	Accuracy	Precision (allowable RPD)	Approx. Expected Range	Sensitivity (Resolution or MDL)
Depth (calibrated line)	meters (m)	± 0.1 m	20%	0 - 50 m	0.1 m
Barometric Pressure (ONSET HOBO U20L-01)	Kilopascal (kPa)	0.62 kPa maximum error	10%	3.7 - 4.1 kPa	< 0.02 kPa
Depth (YSI EXO 1)	meters (m)	0 to 10 m ± 0.04% FS or ± 0.004 m 0 to 100 m ± 0.04% FS or ± 0.04 m 0 to 250 m ± 0.04% FS or ± 0.10 m	20%	0 - 50 m	0.001 m
Depth (YSI ProDSS)	meters (m)	±0.004 m for 1, 4 and 10-m cables ±0.04 m for cables 20-m and longer	20%	0 - 50 m	0.001 m
GPS coordinates	decimal degrees (dec. deg.)	± 7.8 m http://www.gps.gov/systems/gps/performance/accuracy/	for reference point on land, within 10 m (=0.0001 dec. deg.)	NA	1.02 m
Temperature (YSI EXO 1)	degrees Celsius (°C)	-5 to 35 °C ±0.01°C 35 to 50 °C ± 0.05 °C	10%	4 - 26 °C	0.001 °C
Temperature (YSI ProDSS)	degrees Celsius (°C)	±0.2°C	10%	4 - 26 °C	0.1°C
Conductivity (YSI EXO 1)	millisiemens (mS/cm)	0 to 100 mS/cm ± 5% of reading or 0.0001 mS/cm; whichever is greater 100 to 200 mS/cm ± 1% of reading	10%	0 - 50 mS/cm	0.0001 to 0.01 mS/cm, range-dependent

Parameter	Units	Accuracy	Precision (allowable RPD)	Approx. Expected Range	Sensitivity (Resolution or MDL)
Conductivity (YSI ProDSS)	millisiemens (mS/cm)	0 to 100 mS/cm ± 5% of reading or 0.0001 mS/cm; whichever is greater 100 to 200 mS/cm ± 1% of reading	10%	0 - 50 mS/cm	0.0001 to 0.01 mS/cm, range-dependent
Conductivity (Star-Oddi DST CT)	millisiemens (mS/cm)	13-50 mS/cm ± 1.5 mS/cm	10%	13 - 50 mS/cm	0.01 mS/cm within range
Dissolved oxygen (YSI EXO 1)	milligrams per liter (mg/L) = parts per million (ppm); percent saturation (% sat.)	0 to 20 mg/L: ±0.1 mg/L or 1% of reading or whichever is greater 20 to 50 mg/l: ± 5% of reading 0 to 200%: ± 1% reading or 1% saturation, whichever is greater 200 to 500%: ± 5% reading	20%	0 - 14 mg/L 0 - 120 %	0.01 mg/L 0.1 % sat.
Dissolved oxygen (YSI ProDSS)	milligrams per liter (mg/L) = parts per million (ppm); percent saturation (% sat.)	0 to 20 mg/L: ±0.1 mg/L or 1% of reading or whichever is greater 20 to 50 mg/l: ± 8% of reading 0 to 200%: ± 1% reading or 1% saturation, whichever is greater 200 to 500%: ± 8% reading	20%	0 - 14 mg/L 0 - 120 %	0.01 mg/L 0.1 % sat.

Parameter	Units	Accuracy	Precision (allowable RPD)	Approx. Expected Range	Sensitivity (Resolution or MDL)
Dissolved oxygen (ONSET HOBO U26)	milligrams per liter (mg/L) = parts per million (ppm)	0 to 8 mg/l ± 0.2 mg/l 8 to 20 mg/l ± 0.5 mg/l	20%	0 - 14 mg/L	0.02 mg/l
Chlorophyll a (as measured in lab)	microgram per liter (µg/L)	75 - 125 % recovery of a lab QC sample with known µg/L	15%	0 - 30 µg/L; though higher concentrations may occur	0.7 µg/L
Chlorophyll a (YSI EXO 1)	Relative Fluorescence Units (RFU), microgram per liter (µg/L)	Chl: R^2 > 0.999 for serial dilution of Rhodamine WT Solution from 0 to 400 µg/L Chl *a* equivalent	20%	0 - 30 µg/L; though higher concentrations may occur	0.01 RFU 0.01 µg/L
Chlorophyll a (YSI ProDSS)	Relative Fluorescence Units (RFU), microgram per liter (µg/L)	$R^2 \geq 0.999$ for Rhodamine WT across full range	20%	0 - 30 µg/L; though higher concentrations may occur	0.01 RFU 0.01 µg/L
Turbidity (YSI EXO 1)	FNU*	0 to 999 FNU: ± 2% of reading or 0.3 FNU, whichever is greater 1000 to 4000 FNU: ±5% of reading	20%	0 - 30 FNU	0 – 999 FNU: 0.01 FNU 1000 – 9999 FNU: 0.1 FNU
Turbidity (YSI ProDSS)	FNU*	0 to 999: 0.3 or ±2% of reading, whichever is greater 1000 to 4000: ±5% of reading	20%	0 - 30 NTU	0.1 FNU
Light (ONSET UA-002-08)	Lux (lx)	In water: 5 minutes to 90% accuracy	20%	0 - 108,000 lx	1 lx
Dissolved ammonia - NH3 (as measured in lab)	mg/L NH_3 (= ppm = g/m3)	85% - 115% recovery of lab fortified matrix (LFM)	Field Replicate 30% Analytical Replicate 15%	0 - 1 mg/l	0.020 mg/l
Dissolved nitrate[ǂ] - NO_{3-} (NO_x- NO_{2-})	mg/l NO_3 (= ppm = g/m3)	Value calculated from multiple N analyses	NA	0 - 2 mg/l	NA

Parameter	Units	Accuracy	Precision (allowable RPD)	Approx. Expected Range	Sensitivity (Resolution or MDL)
Dissolved nitrite - NO2- (as measured in lab)	mg/L NO2 (= ppm = g/m3)	85% - 115% recovery of lab fortified matrix (LFM)	Field Replicate 30% Analytical Replicate 15%	0 - 0.7 mg/l	0.004 mg/l
Nitrate-nitrite – NO_X or NO_{3^-} + NO_{2^-} (as measured in lab)	mg/L NOx (= ppm = g/m3)	85% - 115% recovery of lab fortified matrix (LFM)	Field Replicate 30% Analytical Replicate 15%	0 - 2.5 mg/l	0.004 mg/l
Dissolved inorganic nitrogen‡ – DIN ($NH3+NO_x$)	mg/L DIN (= ppm = g/m3)	Value calculated from multiple N analyses	NA	0 - 4 mg/l	NA
Total dissolved nitrogen – TDN (as measured in lab)	Mg/l TDN (= ppm = g/m3)	85% - 115% recovery of lab fortified matrix (LFM)	Field Replicate 30% Analytical Replicate 15%	0 - 5 mg/l	0.05 mg/l
Total Nitrogen (as measured in lab)	mg/l TDN (= ppm = g/m3)	85% - 115% recovery of lab fortified matrix (LFM)	Field Replicate 30% Analytical Replicate 15%	0 - 8 mg/l	0.05 mg/l
Total inorganic nitrogen‡ – TIN ($NH3+NO_x$)	mg/L TIN (= ppm = g/m3)	value calculated from multiple N analyses	NA	0 - 4 mg/l	NA
Total organic nitrogen‡ – TON (TN - TIN)	mg/L TON (= ppm = g/m3)	value calculated from multiple N analyses	NA	0 - 5 mg/l	NA
Dissolved organic nitrogen‡ - DON (TDN - DIN)	mg/L DON (= ppm = g/m3)	value calculated from multiple N analyses	NA	0 - 4.5 mg/l	NA
Particulate nitrogen‡ – PN (TN-TDN)	mg/L PN (= ppm = g/m3)	value calculated from multiple N analyses	NA	0 - 0.5 mg/l	NA
Total phosphorus – TP (as measured in lab)	mg/L TP (= ppm = g/m3)	85% - 115% recovery of lab fortified matrix (LFM)	Field Replicate 30% Analytical Replicate 15%	0 - 0.5 mg/l	0.01 mg/l
Dissolved organic nitrogen‡ - DON (TDN - DIN)	mg/L DON (= ppm = g/m3)	value calculated from multiple N analyses	NA	0 - 4.5 mg/l	NA

Parameter	Units	Accuracy	Precision (allowable RPD)	Approx. Expected Range	Sensitivity (Resolution or MDL)
Dissolved orthophosphate – PO_4^{3-} or DIP (as measured in lab)	mg/L PO_4^{3-} mg/L DIP (= ppm = g/m3)	85% - 115% recovery of lab fortified matrix (LFM)	Field Replicate 30% Analytical Replicate 15%	0 - 0.3 mg/l	0.001 mg/l
Quantitative macrophyte amount	% coverage bare, macrophytes, and animals of bottom	Estimates from three analyses are compared. If the relative percent difference among the three estimates is greater than 5%, the Monitoring Group Lead examines the image and the three estimates, choosing the appropriate value. The three estimates will not be changed, values are retained to show the inconsistency. The Monitoring Group Lead decides on the final value for the estimate.			
Qualitative macrophyte amount	choice of: none, some, lots	This is a qualitative assessment, not quantitative. Photos are reviewed by a UWS Science Advisor or trained designee to confirm choice of amount.			

*: FNU and NTU are interchangeable in the UWS. All data reported as NTU.

ǂ: This parameter is calculated rather than measured analytically, so MDL is not computed. RPD is also not relevant for this parameter.

A.7. DISTRIBUTION LIST

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A.8. PROJECT ORGANIZATION

Table 5: Project Organization
Key project personnel and their corresponding responsibilities.

Name(s)	***Project Title*** - Responsibility
Peter Linderoth	***Monitoring Program Project Manager*** – Oversees all aspects of project that incorporate the monitoring program including: fiscal management, project objectives, data uses, program changes, etc.
Peter Linderoth	***Monitoring Program Coordinator*** – Monitoring Group recruitment and training. Develops the QAPP. Produces monitoring report. Produces or oversees outreach efforts, in coordination with project manager.
Ameera Khan	***Monitoring Program Field Coordinator*** – Responsible for assistance in training and quality assurance of monitoring groups for field work. Ensures field datasheets are properly filled out, samples and forms are transported to laboratories as needed, Standard Operations Procedures (SOPs) are being followed in entirety; and performs QA checks, including field audits, to make sure procedures are followed or corrected as needed (in collaboration QA officer and UWS Science Advisors).
Elena Colón	***Monitoring Program Lab Coordinator*** – Makes arrangements with any lab(s) used to perform analyses according to QAPP. Ensures correct procedures are used, holding times are met, and adequate documentation is provided.
Elena Colón	***Monitoring Program Data Management Coordinator*** – Maintains the data systems for the program. Performs/oversees data entry and checks entries for accuracy against field and lab forms. Responsible for data entry into EPA Water Quality Exchange (WQX) (epa.gov/waterdata/water-quality-data)
Peter Linderoth	***Monitoring Program Quality Assurance Officer*** – Runs Quality Assurance (QA) program.
Jamie Vaudrey and Jason Krumholz	**UWS Science Advisors –** Science consultants offering guidance and participating in trainings and station selection among other aspects of the project including quality assurance.
See Distribution List	**UWS Monitoring Group Leads** – Undertake UWS in their respective embayment(s) following all aspects of this QAPP.
Changes by year. Individual names are not listed.	***Monitoring Program Field Staff*** – Sample, perform field analyses, and assist in laboratory analyses and/or data entry.
Elizabeth Tanzi	***USEPA Project Officer*** – Oversees US EPA Cooperative Agreement compliance including processing recipient/subrecipient requests for QA/QC within EPA Regions
Erwin Smieszek	***USEPA Quality Assurance Officer*** – Reviews, comments and approves QAPP.

A.9. Project Quality Assurance Manager Independence

The Monitoring Program Quality Assurance Officer is also serving as the Project Manager and Monitoring Program Coordinator for this project. The tasks associated with the Project Manager and the Monitoring Program Coordinator do not involve direct collection of environmental information in the field and thus do not directly conflict with Project Quality Assurance Officer responsibilities.

Save the Sound is a respectively smaller organization and there may be times where the staff member holding the joint responsibilities of the Monitoring Program Quality Assurance Officer, Project Manager, and Monitoring Program Coordinator needs to cover tasks of other responsibilities (e.g. such as operating the sampling vessel if the Monitoring Field Coordinator is unable to report to work on a sampling event). These instances are rare but are allowable if required to maintain work towards project completion and QAPP compliance.

A.10. Project Organizational Chart and Communications

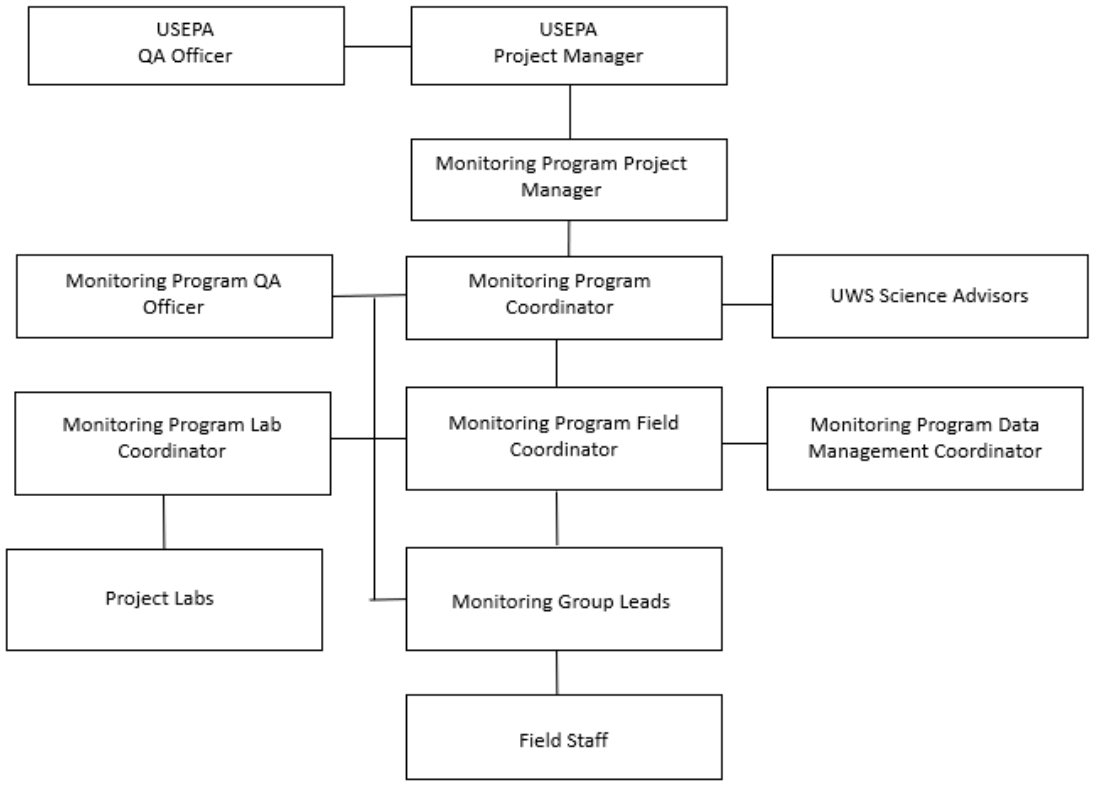

Figure 2: Organizational Chart
Lines between boxes indicate direct communication.

Communications between project personnel will primarily be conducted via email with secondary communications allowable using the personnel listed in Table 5 and the distribution list contained in section A.7. of this QAPP. The USEPA Project Manager is the primary contact at EPA Region 2 for the Monitoring Program Project Manager to discuss any topics. Figure 2 in this QAPP and Table 5 detail the lines of communication and the roles of project personnel.

The Monitoring Group Leads will communicate any concerns they may have with QAPP compliance to the personnel listed in Table 5 of this QAPP. Contacts for different issues are presented in the annual training. For example, complications with sonde calibration will be directed to the Monitoring Program Lab Coordinator but issues with sampling schedule will be directed to the Monitoring Program Field Coordinator. Microsoft Teams is used so that all Save the Sound project personnel have access and can track any given issue, and the communications surrounding it, that arises. All participating groups have access to the main Unified Water Study Microsoft Teams Channel created for this project for general communications. Group-specific channels for items that directly relate to their respective efforts are also created for all participating groups.

The Monitoring Program Quality Assurance Officer will detail any issued with QAPP compliance in the final report and will take actions as described in Section C. of this QAPP.

A.11. Special Training / Certification

UWS trainings are hands on full day events*. They are designed for a wide range of experience in water quality monitoring; ranging from groups with an extensive existing water quality monitoring programs to groups with little to no water quality monitoring experience. The trainings help to ensure all groups are on the same understanding of project QAPP and SOPs. All Monitoring Groups are provided the SOPs and QAPP. They are required to read these documents. Monitoring Groups take notes on the project SOPs during training events to clarify any points that require extra attention. The objective of trainings is to have all Monitoring Groups, regardless of previous experience, following the project requirements in a unified manner.

The Monitoring Program Coordinator shall ensure that all UWS Monitoring Groups receive appropriate training by organizing and conducting training events. The trainings are mandatory for new and veteran groups and have hands on elements for sonde calibration and usage, filling in datasheets, macrophyte assessments, logger calibration and usage, nutrient sample collection, and filtering chlorophyll a. All topics are covered in guided step by step approach. Training will be assessed as described by checks in Section C.1 Assessment and Response Actions.

The Monitoring Program Coordinator enters training into the project database and records the following information: subject matter (i.e. what type of monitoring and procedures are

covered), training course title, date and agenda, name and qualification of trainers, and names of participants trained with associated monitoring group name. The trainings and technical support offered through the Monitoring Program Coordinator, Monitoring Program Field Coordinator, and Science Advisors is in place for the duration of the project. This will ensure new and veteran groups have a reliable source for prompt answers to their inquiries. Groups are prompted to email or call the Monitoring Program Coordinator or Monitoring Program Field Coordinator with their questions. If needed, the Science Advisors will be consulted. This support is mentioned throughout the project duration and emphasized at the trainings. Trainers remind trainees to call at any hint of a question or issue so it can be resolved.

The Monitoring Program Coordinator worked closely with the Science Advisor signatories on this QAPP to confirm procedures are appropriate. He was part of the three-person team leading UWS Tier I trainings around Long Island Sound in 2017. The Coordinator oversees Save the Sound's Water Quality Program which samples water for pathogen-indicator bacteria and participates in the UWS Tier I & II monitoring.

*: UWS trainings for the 2020 season were held remotely due to concerns and timing in regard to spread of the Coronavirus (Covid-19).

The Coordinator holds a Bachelor of Science Degree in Environmental Studies from University California Santa Barbara and a Master's of Science Degree in Environmental Science and Management from Sacred Heart University. it

Project training shall take place as specified in Table 6.

Table 6: Project-Specific Training

Training: Type & Description	Trainer(s)	Training Date(s)	Trainees	Location of Training Records
UWS Standard Operating Procedures and Methods, QAPP, and Data Entry Training - General water quality parameter information - Sonde calibration and field training - Chlorophyll a field collection, filtering, preservation, & transport - Nutrient sampling collection, filtering, preservation, & transport - Qualitative macrophyte assessment procedure - Quantitative macrophyte assessment procedure - Data logger calibration and field training - QAPP review and data entry	UWS Monitoring Program Coordinator, UWS Field Coordinator, UWS Science Advisor(s), and other personnel under the supervision of the listed trainer(s)	Annual; Spring before sampling season commences	All participating UWS groups will send 1-3 representatives	Office of the UWS Monitoring Program Coordinator; digital record of attendees and agenda stored on computer and backed up on Save the Sound S-Drive

A.12. DOCUMENTS AND RECORDS

Calibration Datasheet, Sample Event Datasheet and Field Datasheet will be completed by Monitoring Groups before, during, and after Tier I water quality station sampling event.

Qualitative Macrophyte Field Datasheet will be completed upon every qualitative macrophyte survey. Photographs must accompany and be identified in this datasheet.

UWS Nutrient Sample Event Datasheet, Calibration Datasheet, Field Datasheet will be completed upon every Tier II nutrients sampling event. The calibration datasheet will only contain the parameters being recorded in the field: conductivity (salinity).

UWS Quantitative Macrophyte Field Datasheet will be completed upon every quantitative macrophyte survey.

UWS Logger Retrieval Sample Event Datasheet, Field Datasheet, and Calibration Datasheet will be completed upon every data retrieval of data loggers in the field. The calibration datasheet will only contain the parameters being recorded in the field: dissolved oxygen and conductivity.

Sample Labels will be put on all sample containers. Labels will include the station name, organization name, date, time, sample id, and type of sample. Samples needing containers with labels are filters for extracted chlorophyll a and nutrients. Detailed instructions for chlorophyll a filters and nutrient samples are provided in the UWS SOP Chlorophyll, UWS SOP Filtered Nutrients, and UWS SOP Total Nitrogen and Total Phosphorous SOP in Appendix A.

Chain of Custody (COC) forms will accompany samples from collection sites to laboratories. COC forms will be signed by collectors and all individuals who gain custody of the samples until they arrive at a lab. Information will agree with the label information on the sample containers and field datasheet. UWS Chain of Custody forms are in Appendix B.

Training records and field audit information will be kept by the Monitoring Program Coordinator.

The electronic project database shall be organized and protected from loss and damage through proper back-up of digital data on Save the Sound's S-Drive.

No scientific collecting permits or certificates of permission are required.

The specific forms to be used for this project are provided in Appendix B.

B. Implementing Environmental Information Operations

B.1. Identification of Project Environmental Information Operations

Tier I water quality sample stations, Tier II nutrients stations (estuary), and quantitative Tier II macrophyte stations were selected to represent the water quality of the entire embayment using a probability-based sampling design[6], as in the EPA National Coastal Assessment[7]. Monitoring Program Coordinator and a UWS Science Advisor advised on the choice of station locations. The UWS assigned unique ID codes for the embayments, reporting regions of the embayment, and stations. Water quality stations can be viewed in section A.5.b of this document.

Qualitative macrophyte stations are selected based on local knowledge and observation of the embayment during the course of the May and June sampling events. They are targeted to areas of macrophyte abundance. Monitoring Program Coordinator and a UWS Science Advisor advised on the choice of station locations. UWS SOP Qualitative Macrophytes describes the process for sampling locations for macrophytes. These stations are selected using an adaptive process that requires observations during May and June sampling events. These observations identify the best locations for high macrophyte abundance. The qualitative macrophyte sampling can be classified as judgmental design resulting in directed sampling information to complement the water quality station data. Macrophyte stations may change from year to year but records of locations are maintained by the UWS Monitoring Program Coordinator.

Data logging stations were selected with at least one station per reporting region. Access to station is a strong consideration in the selection process. The final station locations will be conferred with Monitoring Program Coordinator and the UWS Science Advisors before deployment.

Tier II nutrients stations (tributary) were selected based on access and salinity <1 ppt. Parameters, number and location of sampling sites, sampling time of day, frequency, and season are selected to meet the monitoring objectives referred to in Section A.5.a.

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[6] Paul, J.F., J.L. Copeland, M. Charpentier, P.V. August, and J.W. Hollister. 2003, Overview of GIS applications in estuarine monitoring and assessment research. Marine Geodesy Journal 26: 63-72.

[7] EPA, U.S. 2001. National Coastal Assessment: Field Operations Manual. U. S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Gulf Ecology Division, Gulf Breeze, FL. EPA 620/R-01/003. 72 p.

Sampling design components are described below:

Sampling Safety. Personal safety shall be a primary consideration in all activities, including selection of sampling stations, dates, and training programs. No sampling shall occur when personal safety is thought to be compromised. The Monitoring Group Lead of each participating group on this QAPP shall confer with their respective field teams before each sampling event to decide whether adverse weather or other conditions pose a threat to safety and will cancel/postpone sampling when necessary. Sampling shall take place in teams of two or more. Samplers shall wear life vests when required, in adverse conditions in boats, or wading in waters under difficult conditions. Samplers shall wear proper clothing to protect against the elements.

Design Considerations. A summary of design considerations incorporated into this project are included in Table 7. Specifics on the design approaches to the number of stations, depth of sampling, and frequency of sampling and time of day of sampling are included in the SOPs in Appendix A. A summary of general design approaches to the number of stations, depth of sampling, frequency of sampling, and time of day are included here:

There are 254 Tier I water quality stations and approximately 127 qualitative macrophyte station monitored across all the study sites. 16 data logging stations will be monitored. 75 quantitative macrophyte stations will be monitored. 49 Tier II nutrient stations will be monitored. The qualitative macrophyte stations are confirmed by the beginning of the macrophyte monitoring window described in UWS SOP Macrophytes. Sonde profiles for water quality parameters at water quality stations will be sampled 0.5 m below the surface, 0.5 m above bottom, mid-depth if total depth >10 m; if total depth is less than 1.5 m, only a mid-depth reading will be collected. Extracted chlorophyll a samples will be taken from a bucket. Two filters and a corresponding chlorophyll a sonde reading will be taken per sampling event. Land-based qualitative macrophyte stations will be photographed from land. Rake toss qualitative macrophyte stations will be photographed from land or boat. Quantitative macrophyte stations are recorded from a boat. These are the same locations as the Tier I water quality stations in the respective embayments. Tier II nutrients stations are collected 0.5 below the surface. New Tier II nutrients tributary stations are confirmed by field work prior to collecting the first batch of nutrient samples for the season. Data logging stations are 0.5 m off the bottom and record data every 15 minutes. These stations are selected and confirmed with the Monitoring Program Coordinator and a UWS Science Advisor prior to commencement of the season.

Table 7: Sampling Approaches
Assessment Type: Tier I water quality Stations.

Indicators	Number of sample locations	Frequency, duration, special conditions	Field survey QC
GPS: latitude & longitude in decimal degrees; NAD83 coordinate system or record system used	every station	Twice a month from May - October, within 3 hours of sunrise,	repeat readings every time a station is sampled. coordinates indicating a 100 m or greater discrepancy will be assessed and documented in final report. reference land site, once per sampling event once per field day, take readings twice at the last station sampled
station depth			
sample depth	every station: if station depth < 1.5 m, mid-depth; if station depth > 1.5 m & < 10 m, 0.5 m below surface and 0.5 m above bottom; if station depth > 10 m, 0.5 m below surface, 0.5 m above bottom, and mid-depth		once per field day, take readings twice for replicate at the last station sampled calibration per SOPs
temperature			
salinity			
dissolved oxygen			
turbidity	every station , 0.5 m below surface once per sampling event from bucket at reference station		
chlorophyll a			take readings twice for replicate at the last station sampled calibration per SOPs collect filter and sonde readings at reference station

Stations are representative, defined clearly in respective SOPs

Assessment Type: Qualitative Macrophyte Surveys.

Indicators	Number of sample locations	Frequency, duration, special conditions	Field survey QC
GPS: latitude & longitude in decimal degrees; NAD83 coordinate system or record system used	Every station	Sample 3 days during the 3-week period starting July 15 and ending August 7. Try to sample once per week. If this is not possible, sample such that you maximize the days between sampling. All three days cannot be sampled in the same 7-day window. 2 sampling events or an event outside this time criteria may be accepted in unforeseeable circumstances. Consultation with Monitoring Program Coordinator and UWS Science Advisor is necessary for this decision. See UWS SOP Macrophytes for additional details.	repeat readings every time a station is sampled. coordinates indicating a 100 m or greater discrepancy will be assessed and documented in final report reference land site, once per sampling event
Macrophyte Abundance			Photos and assessment (none, some, lots) of each sample are reviewed by the Monitoring Program Coordinator and UWS Science Advisor

Stations are targeted, defined clearly in SOP

Assessment Type: Tier II nutrients Stations.

Indicators	Number of sample locations	Frequency, duration, special conditions	Field survey QC
GPS: latitude & longitude in decimal degrees; NAD83 coordinate system or record system used	Every station	Each visit to sample station; at least monthly (May – October), with 14 days separation	Repeat readings every time the station is sampled to verify coordinates. Coordinates indicating a 100 m or greater discrepancy from documented coordinates will be assessed and documented in data notes.
Salinity	Every station	Each visit to sample station; at least monthly (May – October), with 14 days separation	Probe calibration prior to survey; post sampling event readings in standard
Nutrients	Every station	Each visit to sample station; at least monthly (May – October), with 14 days separation	At minimum one field replicate per sampling event

Stations are representative.

Assessment Type: Data logging stations.

Indicators	Number of sample locations	Frequency, duration, special conditions	Field survey QC
GPS: latitude & longitude in decimal degrees; NAD83 coordinate system or record system used	Every station	Each visit to sample station	Repeat readings every time the station is sampled to verify coordinates . Coordinates indicating a 100 m or greater discrepancy from documented coordinates will be assessed and documented in data notes.
Conductivity	Every station	Each visit to sample station	Probe calibration prior to survey; post sampling event readings in standard
Dissolved oxygen	Every station	Each visit to sample station	Probe calibration prior to survey; post sampling event readings in standard
Barometric pressure	Every station	Each visit to sample station	Not applicable
Light	Every station	Each visit to sample station	Not applicable

Stations are selected for access and other considerations addressed in this QAPP and UWS Data Logging SOP.
Assessment Type: Quantitative Macrophyte Surveys.

Indicators	Number of sample locations	Frequency, duration, special conditions	Field survey QC
GPS: latitude & longitude in decimal degrees; NAD83 coordinate system or record system used	Every station	Each visit to sample station while conducting all camera descents to bottom. Obtained from GPS track	Not applicable
Bottom coverage (% macroalgae, % bare, % eelgrass)	Every station	Each visit to sample station with specifications in SOP on image count and analysis	Not applicable

Stations are representative.

B.2 METHODS FOR ENVIRONMENTAL INFORMATION ACQUISITION

Pre-coordination shall occur with the external lab to ensure that sample collection procedures meet lab needs. The project labs for this study are below:

Chlorophyll a

Save the Sound, John and Daria Barry Foundation Water Quality Laboratory (Environmental Laboratory Approval Program Identification Number NY12180), contact: Peter Linderoth & Elena Colón, plinderoth@savethesound.org; ecolon@savethesound.org, 914-381-3140, 1385 Boston Post Rd, 2nd Fl, Larchmont, NY 10538

Tier II Nutrients

Center of Environmental Sciences and Engineering (EPA Laboratory Identification Number CT01022 & Environmental Laboratory Certification Program CT Registration Number PH-0778), contact: Chris Perkins, christopher.perkins@uconn.edu, 860-486-2668, Box U-4210, University of Connecticut, 3107 Horsebarn Hill Rd, Building #4 Annex, Storrs, CT 06269

A laboratory of equal or higher certification than Save the Sound or Center of Environmental Sciences and Engineering can be considered if Save the Sound or Center of Environmental Services and Engineering are unable to complete project analyses. This surrogate laboratory must adhere to analytical methods in Table 10.

To comply with UWS program guidelines, all sample collections for this project shall follow detailed methods on how samples will be collected and preserved as stated in the standard operating procedures (SOPs) contained in Appendix A of this document. The lab has reviewed the UWS SOPs and confirms they are appropriate for the select analyses.

B.2.a. Sample Collection Methods

A summary overview of sample collection methods is provided in Table 8. A summary of field sampling considerations is provided in Table 9.

Any filters or nutrient sample bottles collected for analysis will be stored in a cooler, on ice during the sampling trip. The cooler designated for these samples will not be used for the storage of macrophytes.

All deviations from the Standard Operating Procedures of this QAPP will be documented and subsequently reviewed by the Monitoring Program Coordinator and the project UWS Science Advisors. This information will be available to all signatories at the completion of this project at which time acceptability of data will be determined.

Table 8: Overview of Sample Collection Methods
Assessment Type: Tier I water quality Parameters **(NA = not applicable)**

Parameter(s)	Container Type(s) and Preparation	Minimum Sample Quantity per Sample Depth (unless otherwise noted)	Sample Preservation	Maximum Holding Time
GPS: latitude & longitude in decimal degrees; NAD83 coordinate system or record system used	*in situ*	1 / station	transfer to digital format, maintain back-up copies of digital data	NA
Station depth	*in situ*	1 / station	transfer to digital format, maintain back-up copies of digital data	NA
Sample depth (metered line)	*in situ*	1, and for remainder of the sampling event if the intercomparison with project sonde and line is > 0.3 m	transfer to digital format, maintain back-up copies of digital data	NA
Multiparameter sonde: • depth • temperature • salinity • dissolved oxygen • turbidity • chlorophyll a	*in situ*	1 / sample depth and a second reading for each depth at the last station of the day	transfer to digital format, maintain back-up copies of digital data	NA

Parameter(s)	Container Type(s) and Preparation	Minimum Sample Quantity per Sample Depth (unless otherwise noted)	Sample Preservation	Maximum Holding Time
chlorophyll a (extracted, fluorometric analysis)	*Large bucket rinsed three times with surface water. Bucket volume must accommodate sonde for reading in situ*	Filtered sample volume must be sufficient to provide "color" on the filter pad; 10 mL to 180 mL. 2 filters collected and one sonde reading from bucket per sampling event	GF/F filter is blown dry with a 60mL syringe and stored in the dark (foil wrapped), on ice; transferred to -20°C freezer within 12 hours	28 days

Assessment Type: Qualitative Macrophyte Abundance **(NA = not applicable)**

Parameter(s)	Container Type(s) and Preparation	Minimum Sample Quantity	Sample Preservation	Maximum Holding Time
GPS: latitude & longitude in decimal degrees; NAD83 coordinate system or record system used	*in situ*	1 / station	transfer to digital format, maintain back-up copies of digital data	NA
Macrophyte abundance	digital photos	1 / sample (a sample is a single rake toss or required distance for soft shoreline photo)	transfer to a computer, upload to online datasheet	NA

Assessment Type: Tier II Nutrients Parameters **(NA = not applicable)**

Parameter(s)	Container Type(s) and Preparation	Minimum Sample Quantity	Sample Preservation	Maximum Holding Time
GPS: latitude & longitude in decimal degrees; NAD83 coordinate system or record system used	*in situ*	NA	transfer to digital format; maintain back-up copies of digital data	NA
Multiparameter sonde: • Salinity	*in situ*	NA	transfer to digital format; maintain back-up copies of digital data	NA

Parameter(s)	Container Type(s) and Preparation	Minimum Sample Quantity	Sample Preservation	Maximum Holding Time
Inorganic nutrients	high density polyethylene (HDPE) polypropylene (new containers washed with ASTM Type 1 Ultrapure Water, used containers pre-acid-washed with 10% hydrochloric acid)	120 mL per station	ice or refrigerate filtered water samples at a temperature of <4 C while in the field, store at <-20 C	holding time of ~1 year once frozen
Total nutrients	high density polyethylene (HDPE) polypropylene (new containers washed with ASTM Type 1 Ultrapure Water, used containers pre-acid-washed with 10% hydrochloric acid)	120 mL per station	ice or refrigerate water samples at a temperature of <4 C while in the field, freeze at <-20 C	holding time of ~1 year once frozen

Assessment Type: Quantitative Macrophyte Abundance

Parameter(s)	Container Type(s) and Preparation	Minimum Sample Quantity	Sample Preservation	Maximum Holding Time
Macrophyte abundance (% bare, % macroalgae, % eelgrass)	Field data sheets and computer storage	20 still images per station; more if heterogeneity is observed. Detailed procedure in SOP	maintain back-up copies of digital data	NA

Table 9: Overview of Field Sampling Considerations

Sample Type	Parameter(s)	Sampling Considerations
In-situ sampling	Station depth	Note the tidal stage and time of day. Depth varies greatly over the tidal cycle.
In-situ sampling, GPS	GPS: latitude & longitude in decimal degrees; NAD83 or WGS84 coordinate system, record system used	NAD83 or WGS84 coordinate system, record system used; check GPS accuracy relative to a known, fixed location
in-situ Tier I water quality sampling, multiparameter sonde	Depth Temperature Salinity Dissolved oxygen Turbidity Chlorophyll a fluorescence	Sample within 3 hours of sunrise. Inspection, maintenance, pre-calibration and post-checking of probes and instruments are critical to achieving accurate and precise measurements.

Sample Type	Parameter(s)	Sampling Considerations
Data logging stations	Dissolved Oxygen, Conductivity (Salinity), Barometric Pressure, Light	Inspection, maintenance as specified by manufacturer, and calibration of instruments are critical to achieving accurate and precise measurements, especially for DO. Loggers are rinsed and cleaned with freshwater after each retrieval and use.
Grab samples - i.e. collection of a water sample	Chlorophyll a	Keep careful and accurate track of volume of water passed through each filter pad, quantitation is impossible without this value.
Qualitative macrophyte abundance	Macrophyte abundance	Be sure to photograph all sites and samples. Record identifier for each photo on the datasheet.
Quantitative macrophyte abundance	Macrophyte abundance	Maintain low speed to minimize potential damage to camera. Monitoring Group Lead and two additional members of the sampling team, under Monitoring Group Lead supervision, will analyze the macrophyte videos as described in SOP
Grab samples - i.e. collection of a water sample in bottle	Inorganic and total nutrients	Triple-rinse sample container in ambient water immediately prior to sample collection. Care must be taken to avoid contact between fingers and inside surfaces of containers, including bottle caps. New, pre-washed bottles preferred; if not, containers for nutrient samples should be acid-washed and rinsed with deionized water. This process is overseen by the Monitoring Coordinator. These bottles will be obtained by appropriate suppliers such as Fischer Scientific. Field filtration preferred for dissolved fractions. If filtering water, triple-rinse container with *filtered* water immediately prior to sample collection, not ambient water.

B.2.b. Analyses Methods

To comply with the requirements of the UWS Program, all analytical methods used in the Monitoring Program, including methods used by laboratories performing analyses for the project, shall be based on standardized laboratory methods.

All analytical methods used for this project are provided in Appendix C.

Table 10 provides an overview of the analytical methods utilized in this Monitoring Program. The SOPs associated with these methods are included in Appendix C.

Table 10: Overview of Analytical Methods

Parameter	Method #	Source of Method	MDL	Alternative Applications Special Provisions/Certifications
Chlorophyll a	EPA 445.0	EPA	0.7 µg/l	John and Daria Barry Foundation Water Quality Laboratory (Environmental Laboratory Approval Program Identification NY12180). This is not a certified parameter.
Nitrite	EPA 353.2	EPA	0.004 mg/l	Center of Environmental Sciences and Engineering (EPA Laboratory Identification Number CT01022 & Environmental Laboratory Certification Program CT Registration Number PH-0778). This is a certified parameter.
Nitrate+Nitrite	EPA 353.2	EPA	0.004 mg/l	Center of Environmental Sciences and Engineering (EPA Laboratory Identification Number CT01022 & Environmental Laboratory Certification Program CT Registration Number PH-0778). This is a certified parameter.
Ammonia	EPA 350.1	EPA	0.020 mg/l	Center of Environmental Sciences and Engineering (EPA Laboratory Identification Number CT01022 & Environmental Laboratory Certification Program CT Registration Number PH-0778). This is a certified parameter.
Total Dissolved Nitrogen	EPA 353.2	EPA	0.05 mg/l	Center of Environmental Sciences and Engineering (EPA Laboratory Identification Number CT01022 & Environmental Laboratory Certification Program CT Registration Number PH-0778). This is not a certified parameter.
Orthophosphate (DIP)	EPA 365.1	EPA	0.001 mg/l	Center of Environmental Sciences and Engineering (EPA Laboratory Identification Number CT01022 & Environmental Laboratory Certification Program CT Registration Number PH-0778). This is a certified parameter.
Total Nitrogen	EPA 353.2	EPA	0.05 mg/l	Center of Environmental Sciences and Engineering (EPA Laboratory Identification Number CT01022 & Environmental Laboratory Certification Program CT Registration Number PH-0778). This is not a certified parameter.
Total Phosphorous	EPA 365.1	EPA	0.01 mg/L	Center of Environmental Sciences and Engineering (EPA Laboratory Identification Number CT01022 & Environmental Laboratory Certification Program CT Registration Number PH-0778). This is a certified parameter.

B.2.c. Existing Information

To provide high-quality data to enhance the interpretation of data collected as part of this Monitoring Program, data may be acquired from qualified sources approved by Monitoring Program Coordinator. NOAA tide gauges will be used for tide information. Precipitation will be

acquired from local weather stations that log reasonable (in respect to northeastern USA conditions) volumes. Precipitation data out of the expected annual volumes and the observed conditions will be flagged and discussed with Monitoring Program Coordinator and shared with quality assurance personnel for review and potential disqualification. External data sources are described in Table 11.

Table 11: Non-Project Data Validity
The following data will be used as part of the Monitoring Program. This is a 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 in use of the data due to questions about data quality.
Time of low and high tide	NOAA tide gauges recorded on field data sheet	N	NOAA has internal requirements for data suitability. High and low tide data are not generally available at the embayment. Data from NOAA tide gauges are acceptable; data are used in broad scale, to determine the potential impact of stage in tidal cycle on the day of sampling.	Data quality is acceptable. However, local tidal stage will differ from the nearest NOAA gauge even when corrected for difference in location. These data are rough predictors only.
High and low temperature and precipitation within the 24 hours prior to the field trip	Local weather station recorded on field data sheet	N	Air temperature within the last 24 hours are not generally available at the embayment. Data from nearby weather stations are acceptable; data are used in broad scale, to determine the potential impact of weather on the day of sampling.	Data will be used in comparing among embayments or among dates, as a general indication of weather during the day prior to sampling.

B.3. INTEGRITY OF ENVIRONMENTAL INFORMATION

Sample handling and labeling procedures shall comply with project Standard Operating Procedures (SOPs). Chlorophyll a filters and nutrient samples will be transported on ice in a cooler to the freezer on the same day as sampling occurs. Filters and nutrient samples will always be transported on ice with no more than 24 hours out of freezer to avoid thawing.

Sample labels will be associated with: station name, date, time, volume filtered, sample id, type of sample, and organization name. These details may be written on the label. Information will also be filled in the field data sheet.

Chain of Custody shall be tracked as detailed in the SOPs. The project Chain of Custody forms are provided in in Appendix B.

The following steps shall be taken to avoid sample mislabeling:

Labels will be prepared in advance and cross checked with the field datasheet before sampling event. Field team will check data sheet versus sample filter labels before storing in the cooler for transport to a freezer. A white board with name of the embayment, site and station id, and date will be filmed prior to recording every station in the macrophyte video surveys.

B.4. QUALITY CONTROL

Lab Quality Control (QC) protocols shall be discussed with the external lab facility or contractor analyzing chlorophyll a and nutrient samples prior to sampling to ensure acceptability.

Quality control shall be discussed and defined prior to sampling (e.g., during training).

Details on quality control procedures are provided in Table 12.

Table 12: Quality Control Measures
Note that 5% of field samples equates to one station per field day sampled as replicate.

Sample Type	Instrument/ Parameter	Accuracy Checks	Precision Checks	% Field QC Samples (blanks and field duplicates)
GPS coordinates	GPS or Smart Phone app / GPS coordinates	Compare location of reference site to Google Earth coordinates	Readings at a land-based reference point and duplicate readings at one station	1 / field day
Station depth	metered line / depth	re-measure line	replicate readings at one station	5%
Multiparameter sonde and data loggers	Depth, temperature, conductivity, dissolved oxygen, turbidity, chlorophyll a, light	Pre-survey calibration and post-survey checks, including "zero" DO standard check	field duplicates or 3-5 minutes stable readings recorded	5% or verify repeatability in the field
Water samples - grab	Fluorometric determination of extracted chlorophyll a	Acetone blank, standard	QC check for multiparameter sonde	100%
Qualitative Macrophyte abundance	Observation / macrophyte abundance	Photos of all assessments	Photos of all assessments	100% photos are required for inclusion of the data in the UWS

Sample Type	Instrument/ Parameter	Accuracy Checks	Precision Checks	% Field QC Samples (blanks and field duplicates)
Water samples – grab	TP, P fractions TN, N fractions	Field: blanks Lab: analysis of lab-fortified matrix (spiked samples) and/or lab QC standard	Field duplicates Lab duplicates	Minimum 5%
Quantitative Macrophyte abundance	% coverage bare, macrophytes, and animals of bottom	Still images of all assessments	Still images of all assessments	100% still images are required for inclusion of the data in the UWS

B.5. INSTRUMENT/EQUIPMENT CALIBRATION, TESTING, INSPECTION, AND MAINTENANCE

B.5.a Instrument/Equipment Testing, Inspection, and Maintenance

Maintenance of instruments and equipment shall occur as needed during the field season. Annual maintenance and intercalibration assurance will be conducted by Save the Sound.

Records of equipment inspection, maintenance, repair and replacement shall be kept in a logbook. A backup of the logbook will be kept in a separate location. If the logbook is digital, appropriate backups of the computer files will be maintained by Monitoring Program Coordinator.

Table 13: Instrument / Equipment Inspection and Testing Procedures

Equipment Type	Inspection Frequency	Type Inspection	Maintenance, Corrective Action
GPS unit	before each sampling date	battery life	charge batteries
Depth line	Annually, or when a potential problem is noted	Check the calibrated line against a meter tape	Wipe tape after each use, if line has stretched or is damaged, replace immediately and note recent data as questionable
Multiparameter sonde	Before each sampling date	Battery life, electrical connections, sensor condition	Charge batteries, spare sensors as appropriate, batteries
Filtering apparatus (chlorophyll a)	Before each use	Proper functioning, clean storage	Spare filters and syringe
Collection rake, rope	Before each collection	Visually for integrity	Repair, replace keep spares on hand

Equipment Type	Inspection Frequency	Type Inspection	Maintenance, Corrective Action
Filtering apparatus (nutrients)	Before each use	Proper functioning, clean storage	Spare syringe, spare filters, spare pump tubing
Logging sensors	Every 7-10 days or as needed	Biofouling and battery check	Clean off fouling organisms, check battery life from data log
Underwater camera and equipment	Before each use	Battery life, test video	Recharge/replace batteries and clean lens if required

B.5.b. 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 back-ups). Calibration records shall be maintained for a minimum of four years, ideally longer. Monitoring Groups will deliver calibration records to the Monitoring Program Coordinator. These records and digital backups will be saved on Save the Sound's S-Drive for duration of the project.

A summary of calibration procedures for instruments and equipment is provided in Table 14.

Detailed calibration procedures are described in SOPs contained in Appendices A.

Table 14: Instrument / Equipment Calibration Procedures

Instrument	Inspection and Calibration Frequency	Standard of Calibration Instrument Used	Calibration Acceptance Criteria	Corrective Action
Calibrated lines (for depth)	Annually	Tape measure	Within 0.1 m of tape measure	Recalibrate or replace with calibrated line
Multiparameter sonde	Before each sampling run	Standard solutions	According to manufacturer's instruction or when not provided a maximum difference of %10 of the calibration standard value	According to UWS and manufacturer's instruction
Logging sensors	Before and after deployment	Standard solutions, according to manufacturer's recommendations	According to manufacturer's instruction or when not provided a maximum difference of %10 of the calibration standard value	According to UWS and manufacturer's instruction

B.6. Inspection / Acceptance of Supplies and Consumables

The procedures for inspection and acceptance of supplies and consumables listed in Table 15 shall be followed by the Monitoring Groups.

Table 15: 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, filters	Before each sampling date	Visual inspection of quantity, integrity	Spares	Storage according to manufacturer's recommendations
Field and lab sample sheets	Before each sampling date	Visual	Additional copies	
Cooler	Before each sampling date	Cleanness, ice packs		Annually or as needed
Sample bottles	Before each sampling date	Integrity, cleanness and seal for nutrient bottles, verified sterility of bacterial sample bottles	One set of spare bottles	Clean after use (note that nutrient bottles require acid washing before reuse)

B.7. Environmental Information Management

Field teams shall record data on field sheets, review them, and turn over to respective Monitoring Group Lead or designated appointee.

Monitoring Group Leads or designated appointees shall review sheets and confer with field teams on any needed corrective action.

The designated person shall fill out the chain-of-custody form for forwarding samples to the external laboratory. Each person who handles or transports samples shall also sign the custody form upon receipt of the samples. Chain of custody forms will follow samples to the lab and back to Monitoring Program Lab Coordinator by mail or pickup after each analysis run is completed. Alternatively, scanned copies may be emailed or faxed. These copies will be sent to Monitoring Group Leads or designated appointees.

Once laboratory analyses are complete, the laboratory personnel shall deliver (digital or hard copy) lab results to the Monitoring Program Lab Coordinator or arrange for pickup. These results will be sent to all Monitoring Group Leads or designated appointees.

The Monitoring Group Lead or other trained designee will enter raw field and lab data into the project computer system.

Computer-entered data shall be compared with field sheets for accuracy.

Original data sheets will be stored by the Monitoring Group Leads or designated appointees, following data entry into the UWS data entry template.

Digital back-ups and copies of the non-digitized data will be made and stored in a separate location designated by the Monitoring Group Lead or designated appointees and delivered to the Monitoring Program Coordinator.

Documentation of data recording and handling, including all problems and corrective actions, shall be included in all preliminary and final reports.

Table 16 in this document accurately represents the procedures utilized by the UWS for data management, review, validation, and verification.

Table 16: 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 of Monitoring Groups performing calibrations and demonstrating field procedures.	Monitoring Program Field Coordinator or appointed designee	Correct any discrepancies with this QAPP or SOPs
Check labels just prior to sampling, to ensure correct labeling of container.	Field sampler	Correct label
At time of sampling, record data, sign field sheets.	Field sampler	Remind samplers of proper procedures; retrain if needed.
Fill out, sign chain of custody (COC) forms for any samples going to lab.	Field sampler or designated person	Remind person of proper procedures; retrain if needed.
Before turning field sheets over to Monitoring Group Lead or designated appointee, check for reasonableness to expected range, completeness.	Field sampler	Resample if feasible; otherwise, flag suspect data.
Upon receipt of field sheets, recheck for reasonableness to expected range, completeness, accuracy, and legibility.	Monitoring Group Lead or designated appointee	Confer with field sampler(s) immediately or within 24 hours. Resample if feasible; otherwise, flag suspect data.
Upon receipt of samples, field sheets and COC forms, check to see that sheets and forms correspond to number of samples, condition of samples as stated on COC forms. Sign COC forms. Copies of field sheets and COC forms are made, given to Monitoring Program Coordinator.	Monitoring Group Lead or designated appointee	Contact field samplers as needed to locate missing samples, data records. In case of missing/spoiled samples or data records, authorize resampling as needed and feasible. If resampling is not feasible, flag all suspect data.
Upon completion of laboratory analyses, fill out lab sheets, including data on QC tests.	External Lab	Re-analyze if possible. If not, confer with Monitoring Program Laboratory Coordinator. Flag all suspect data.
Upon receipt of lab data, review for completeness and legibility.	Monitoring Group Lead or designated appointee	Confer with Monitoring Program Laboratory Coordinator.

Activity	By whom	Corrective action, if needed
Upon completion of data entry, compare with field/lab sheets for accuracy.	Monitoring Group Lead or other volunteer. Data entry personnel may review their own work, but it cannot be on the same day as data entry.	Re-enter or correct data.
Translate data into preliminary data reports: run statistical analyses and/or prepare graphical summaries of data. Check for agreement with QC objectives for completeness.	Monitoring Program Coordinator	Confer with QA Officers and UWS Science Advisor(s). Flag or discard suspect data.
In-season (at least once) and end of season review of collected data sets (individual sample runs and season-total compilations); review for completeness and agreement with QC objectives and DQOs.	Monitoring Group Lead or designated appointee	Flag suspect data. Confer with Monitoring Program Quality Assurance Officer.

Data Management Systems – spreadsheets, databases, statistical or graphical software packages, location of data records (paper and electronic), are described here:

All data will be entered from field data sheets to an Excel spreadsheet for storage and retrieval by Monitoring Group Leads and appointed individuals. Digital copies of all datasheets will be kept on file on the S-Drive server in Save the Sound office for at least 4 years with a plan to keep records for duration of the project and beyond. The S-Drive is backed up weekly.

C. Assessment, Response Actions, and Oversight

C.1. Assessment and Response Actions

The Monitoring Program Coordinator and UWS Science Advisors 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 Program Coordinator or appointed designees will check at the end of every month from May - October 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. Retraining or other corrective action is implemented at the first hint of non-compliance with the QAPP or SOPs.
g. 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.
h. Data management is being handled properly, i.e. data are entered on a timely basis, is properly backed up, is easily accessed, and raw data are properly stored in a safe place.
i. Procedure for developing and reporting the results exists.

Monitoring Groups will be assessed on their ability to follow UWS procedures during field audits overseen by the Monitoring Program Quality Assurance Officer and Field Coordinator. The Monitoring Program Field Coordinator or designee will observe each monitoring group undertaking calibrations and field procedures once in May-June and follow up calls with Monitoring Groups will be scheduled after initial field audits. Field procedures will be reviewed from a set location on the water that does not need to be a UWS monitoring station. A dock or boat in a slip will be appropriate for these field audits. The CTDEEP and NYSDEC representative on this QAPP distribution list will be provided dates for field audits being held in embayments within their respective management areas. CTDEEP and NYSDEC staff have the option to attend the field audits as observers. The Monitoring Program Quality Assurance Officer or designee will conduct a midseason check in call in August to all Monitoring Groups.

The Monitoring Program Coordinator shall confer with the UWS Science Advisors as necessary to discuss any problems that occur and what corrective actions are needed to maintain program integrity. In addition, the Monitoring Program Coordinator and UWS Science Advisors 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.6. of this document the Monitoring Program Coordinator shall review the program and correct problems as needed. Corrections may include retraining groups; rewriting sampling instructions; replacement of staff/Monitoring Group(s); alteration of sampling schedules, sites, stations or methods; or other actions deemed necessary. This information will be logged and maintained by the Monitoring Program Quality Assurance Officer. It will also be included in the QAPP Final Report.

C.2. Oversight and Reports to Management

Data that have passed the project quality assurance may be posted on the organization's web site, shared with the local media or at other venues (e.g. kiosks at recreation access sites), and

submitted to the Long Island Sound Study, New England Interstate Water Pollution Control Commission, Interstate Environmental Commission, New York State Department of Environmental Conservation, New York City Department of Environmental Protection and/or Connecticut Department of Energy and Environmental Protection. 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 sampling season.

The Monitoring Program Coordinator will write a final report. This will be sent to the distribution list on this QAPP. A final workbook of data from all embayments will accompany the report. The final report will also include (updated as necessary) any tables and graphs that were developed for initial data distribution efforts (i.e. the web site and media), and it will describe the program's goals, methods, quality control results, 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 17: Report Mechanisms, Responsibilities, and Distribution

Reporting Mechanism	Person Responsible for writing report	Distribution list
Monitoring Group Master Data Entry Template	Monitoring Group Lead or designated appointee	Monitoring Program Coordinator
Final Monitoring Report	Monitoring Program Coordinator	All signatories of this QAPP
Final Monitoring Data	Monitoring Program Coordinator	Signatories on this QAPP, EPA, NYS DEC, CTDEEP, NYCDEP, and other management groups

D. Environmental Information Review and Usability Determination

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.

Data collected before the 2018 season will be flagged as not being conducted under this QAPP when distributed. Save the Sound will be tasked with maintaining this QAPP in all aspects for the duration of the Unified Water Study.

The Monitoring Group Lead or designated appointee will review field data after each sampling run and take corrective actions as described in Table 16 of this document. At least once during the season, at the end of the season and if questions arise, the Monitoring Group Lead or designated appointee will share the data with the UWS 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.

All project data and metadata are reviewed and approved as usable data, or as un-usable data.

Data verification and validation will occur as described in Table 16, and will include checks on:

- Completion of all fields on data sheets; missing data sheets
- Completeness of sampling runs (e.g. number of stations visited / samples taken vs. number proposed, were all parameters sampled / analyzed)

- Completeness of QC checks (e.g. number and type 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.2. USEABILITY DETERMINATION

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.6. 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, monitoring groups, etc. produced poor results), the Monitoring Program Coordinator, Quality Assurance Officer, and respective Monitor Group Lead 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.

E. Appendices

Appendix A. Standard Operation Procedures

Appendix B. Data Forms, Checklists, and Chain of Custody Forms

Appendix C. Project Laboratories - Analytical Method

Appendix A-1

UWS Standard Operating Procedure – Station Selection

Table of Contents

1 POINT OF CONTACT

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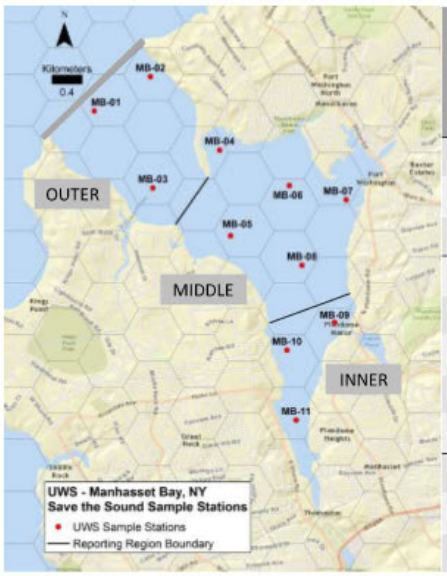
2 OBJECTIVE

Select sample locations to represent the entire embayment in a statistically sound manner. The Unified Water Study (UWS) will assign unique ID codes for the embayment, reporting sections of the embayment, and stations.



Local Naming Convention	Unique Site ID (assigned by UWS)	Unique Region ID (assigned by UWS)	Unique Station ID (assigned by UWS)
MB-01	MAN	outer	MAN-O-11
MB-02	MAN	outer	MAN-O-10
MB-03	MAN	outer	MAN-O-09
MB-04	MAN	middle	MAN-M-08
MB-05	MAN	middle	MAN-M-07
MB-06	MAN	middle	MAN-M-06
MB-07	MAN	middle	MAN-M-05
MB-08	MAN	middle	MAN-M-04
MB-09	MAN	inner	MAN-I-03
MB-10	MAN	inner	MAN-I-02
MB-11	MAN	inner	MAN-I-01

Figure 1: Visual representation of terminology. The grey line at the mouth of Manhasset Bay, NY represents the boundary of the embayment; this whole area is termed the SITE. Manhasset Bay includes three reporting regions, termed the Regions; the black lines show the divisions between the inner, middle, and outer regions. Each region includes a minimum of three STATIONS, represented by the red dots. Monitoring groups may use their existing station IDs. When entering data into the UWS template and submitting data, the assigned UWS station ID must also be included.

3 OVERVIEW

Sample stations are selected to represent the water quality of the entire embayment using a probability-based sampling design (Paul et al., 2003), as in the EPA National Coastal Assessment (EPA, 2001). A UWS Scientific Advisor and UWS Monitoring Program Coordinator advise on the choice of station locations. Historic sites are evaluated for bias and inclusion in the UWS.

Station selection occurs only once, at the time of an embayment joining the UWS. Once stations are determined, these should be consistent in future years. Re-evaluation of stations in future years should be conducted under advisement with the UWS Monitoring Program Coordinator and the UWS Science Advisors

Details on sampling frequency and timing during a day are covered in the UWS SOP Sampling Plan. The information below provides a general overview of the timing of sampling at the different stations.

4 SOURCES

This station selection design is based on methods used in the EPA National Coastal Assessment (EPA, 2001).

5 MATERIALS AND EQUIPMENT

- nautical charts of embayment or local knowledge of typical depth contours
- ArcGIS, access through the UWS Monitoring Program
- UWS subwatershed and embayment delineations for general reference
- hexagonal tessellation grid for use in ArcGIS

6 METHODS

6.1 Water Quality Station Selection

The location of stations will be determined or verified using a probability-based sampling design (Paul et al., 2003), as in the EPA National Coastal Assessment (EPA, 2001). This approach allows for the use of probability-based statistics in data analysis, without bias introduced by non-random station choice.

In this approach, a 0.42 km^2 hexagonal grid is overlain on the site map (Figure 2).

A minimum of four stations will be sampled in each embayment. If an embayment is divided into reporting regions, a minimum of three sites will be selected within each reporting region.

In cases where many hexagons are located in the embayment, sampling of some hexagons may be eliminated, if they are likely to be similar to neighboring stations. Exclusion of hexagons from the sampling plan should only be undertaken under advisement with the UWS Monitoring Program Coordinator and UWS Scientific Advisors. Nine stations per embayment are considered reasonable. Twelve stations and above are likely candidates for eliminating hexagons from the sampling plan. An example of eliminated hexagons is provided for Little Neck Bay, NY (Figure 2).

When a monitoring group has existing stations, those stations may be evaluated by the UWS Monitoring Program Coordinator and UWS Scientific Advisors for inclusion in the study.

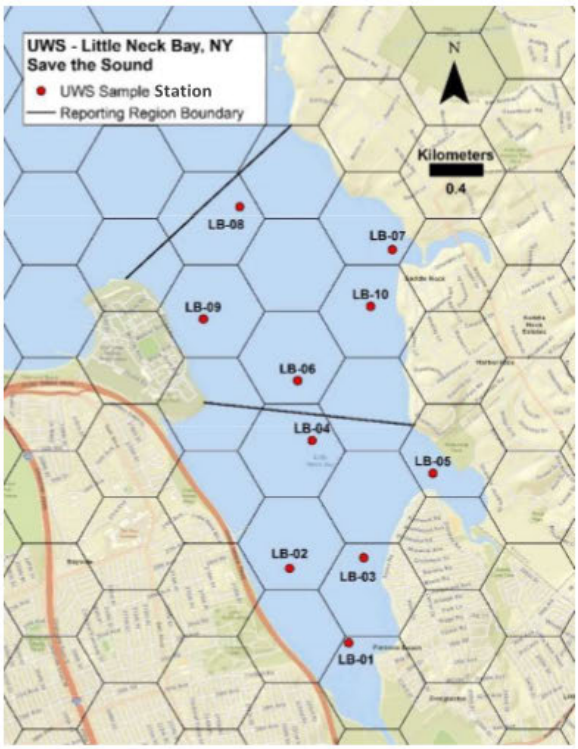


Figure 2: Hexagons overlaying Little Neck Bay, NY. Numbers indicate station locations. Eight of the hexagons overlaying embayment water do not contain stations. This is an example of how some hexagons may be eliminated from sampling for larger embayments. Criteria for eliminating hexagons include an assessment of representability of neighboring stations, hexagons which include a large proportion of land, and stations closer to Long Island Sound likely to be well-mixed and similar to neighboring stations.

6.1.1 Assigning New Stations

Three stations are randomly generated for each hexagon targeted for sampling, identified in order of preference from low value to high. Stations will not be allowed in the center of navigational channels or in unnavigable waters. Stations will not be situated close to point sources of nutrients; this will be determined by consulting maps, local knowledge, and an on-site assessment on the first field day. The random generation of stations is conducted by the UWS Monitoring Program Coordinator in ArcGIS.

The final location of the station in each hexagon will be determined in the field. A trial sampling run is recommended to verify the stations chosen are accessible and can be sampled in the required time frame (for timeframe, see UWS SOP Sampling Plan). From the three random stations, a Monitoring Group may determine a station is unsuitable based on navigation considerations (too shallow, too much current to anchor, too rocky, etc.). If the first station is considered unsuitable, the field leader, UWS Monitoring Program Coordinator, and UWS Scientific Advisor, will evaluate the second, then third station. If all are deemed unacceptable, the collective group may choose a station within the hexagon that is close to the first random station with above considerations reviewed.

Once chosen, the station location is considered the permanent location and will not change on future sampling dates. Because the station will be permanent, the field leader should pay particular attention to the station depth in relation to the stage of the tide; the goal should be to have enough water at low tide to be able to sample the location.

6.1.2 Evaluating Existing Stations

Existing stations in each hexagon will be evaluated for any potential biases that are present. These can include proximity to nutrient sources, disproportional sampling of beach sites, or other targeted sampling locations. Stations that are unbiased in a hexagon will be the first options for inclusion in the study. Stations deemed biased will not be included in the UWS. Monitoring

6.2 Macrophyte Station Selection

The number of stations sampled per embayment depends upon the size of the embayment, expected variability in macroalgae coverage, and access to sampling sites. An initial site visit of many locations can aid with determining the viability of sampling stations. A minimum of 3 sample stations is recommended for all embayments. More may be needed for larger embayments. The UWS Monitoring Program Coordinator, UWS Scientific Advisor, and Monitoring Group will consult to select these stations.

Station selection for macrophytes is complex. Refer to the UWS SOP Qualitative Macrophyte for this process. Macrophyte sampling occurs at different time scales and different stations than water quality parameters.

6.3 GPS Coordinate Reference Station

Select one land-based station to assess the precision of your GPS device. This station does not need to be located near the embayment being sampled. This is a land-based station that is easily accessible to the person with the GPS device.

The GPS coordinates at this station are read within 1 days of a field sampling day.

Each GPS unit or smart phone used for GPS must collect GPS coordinates form a land reference station.

7 TROUBLESHOOTING / HINTS

Station selection should be conducted in coordination with the UWS Monitoring Program Coordinator and UWS Scientific Advisors. A monitoring group is not expected to select stations without assistance.

8 DATA PROCESSING AND STORAGE

The UWS Monitoring Program Coordinator will be the custodian of the initial station selection maps and final maps determined after the first complete field day. The UWS Monitoring Program Coordinator will maintain a database which includes the unique site codes, section codes, and station codes for the embayment. Each unique station code will be affiliated with the corresponding GPS for the station.

The monitoring group is responsible for obtaining the GPS coordinates for each station during sample events.

The monitoring group is responsible for assuring that the correct unique station ID assigned by the UWS is properly matched with the local organizations station ID codes. Both codes (monitoring group's

station code and UWS unique station ID) will be entered into the data template, along with the GPS coordinates.

9 REFERENCES

EPA, U.S. 2001. National Coastal Assessment: Field Operations Manual. U. S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Gulf Ecology Division, Gulf Breeze, FL. EPA 620/R-01/003. 72 p.

Paul, J.F., J.L. Copeland, M. Charpentier, P.V. August, and J.W. Hollister. 2003, Overview of GIS applications in estuarine monitoring and assessment research. Marine Geodesy Journal 26: 63-72.

10 APPENDIX - LIST OF EMBAYMENT CODES

For record keeping purposes, each embayment is assigned a unique three letter code for the UWS. Contact the UWS Monitoring Program Coordinator to verify the names of specific waterbodies. Site names in this list may differ from the local names used for a site.

sorted by RI to NY order			*sorted by embayment name*		
Site Name	RI - NY order	UWS Site ID	Site **Name**	RI - NY order	UWS Site ID
Pawcatuck River, RI	1	PAW	Alewife Cove, CT	18	ALE
Little Narragansett Bay, CT	2	LNA	Ash Creek, CT	57	ASH
Wequetequock Cove, CT	3	WEQ	Baker Cove, CT	16	BAK
Quanaduck Cove, CT	4	QUA	Bebee Cove, CT	10	BEB
Stonington Harbor, CT	5	STO	Black Hall River, CT	28	BLH
Quiambog Cove, CT	6	QUI	Black Rock Harbor, CT	56	BLR
Wilcox Cove, CT	7	WXC	Branford Harbor, CT	45	BRA
Williams Cove, CT	8	WIL	Bride Brook, CT	25	BRB
Mystic River, CT	9	MYS	Bridgeport Harbor, CT	54	BRH
Bebee Cove, CT	10	BEB	Byram River, CT	82	BYR
West Cove, CT	11	WST	Calf Pen Meadow Creek, CT	50	CAL
Palmer Cove, CT	12	PAL	Captain Harbor, CT	81	CAP
Venetian Harbor, CT	13	VEN	Centerport Harbor, NY	106	CEN
Mumford Cove, CT	14	MUM	Clinton Harbor, CT	36	CLI
Poquonock River, CT	15	POQ	Cockenoe Harbor, CT	65	COC
Baker Cove, CT	16	BAK	Cold Spring Harbor, NY	103	COL
Thames River, CT	17	THA	Compo Cove, CT	62	COM
Alewife Cove, CT	18	ALE	Connecticut River, CT	29	CTR
Goshen Cove, CT	19	GOS	Conscience Bay, NY	112	CON
Jordan Cove, CT	20	JOR	Cove Harbor, CT	73	COV
Gardners Pond, CT	21	GAR	Darien River, CT	71	DAR
Niantic River, CT	22	NIR	Dosoris Pond, NY	99	DOS

sorted by RI to NY order			*sorted by embayment name*		
Site Name	RI - NY order	UWS Site ID	Site Name	RI - NY order	UWS Site ID
Niantic Bay, CT	23	NIB	East River, NY	95	EAR
Pattagansett River, CT	24	PAT	Eastchester Bay, NY	92	EAB
Bride Brook, CT	25	BRB	Echo Bay, NY	90	ECH
Four Mile River, CT	26	FOU	Farm River, CT	47	FAR
Threemile River, CT	27	THR	Fence Creek, CT	38	FEN
Black Hall River, CT	28	BLH	Five Mile River, CT	68	FIV
Connecticut River, CT	29	CTR	Four Mile River, CT	26	FOU
South Cove, CT	30	SOU	Frost Creek, NY	100	FRO
Indiantown Harbor, CT	31	ITH	Gardners Pond, CT	21	GAR
Oyster River, Old Saybrook, CT	32	ORO	Goldsmith's Inlet, NY	116	GOL
Hagar Creek, CT	33	HAG	Gorham Pond, CT	70	GOR
Patchogue River, CT	34	PAC	Goshen Cove, CT	19	GOS
Menunkesucket River, CT	35	MEN	Greenwich Cove, CT	76	GRC
Clinton Harbor, CT	36	CLI	Greenwich Harbor, CT	80	GRH
Toms Creek, CT	37	TOM	Guilford Harbor, CT	39	GUI
Fence Creek, CT	38	FEN	Hagar Creek, CT	33	HAG
Guilford Harbor, CT	39	GUI	Hempstead Harbor, NY	98	HEM
Indian Cove, CT	40	INC	Holly Pond, CT	72	HOL
Sachem Head Harbor, CT	41	SAC	Housatonic River, CT	52	HOU
Joshua Cove, CT	42	JOS	Hunter Island Bay, NY	91	HIB
Island Bay, CT	43	ISL	Huntington Bay, NY	109	HUB
Little Harbor, CT	44	LIH	Huntington Harbor, NY	105	HUH
Branford Harbor, CT	45	BRA	Indian Cove, CT	40	INC
Pages Cove, CT	46	PAG	Indian Harbor, CT	78	INH
Farm River, CT	47	FAR	Indiantown Harbor, CT	31	ITH
New Haven Harbor, CT	48	NEW	Island Bay, CT	43	ISL
Oyster River, Milford, CT	49	ORM	Jordan Cove, CT	20	JOR
Calf Pen Meadow Creek, CT	50	CAL	Joshua Cove, CT	42	JOS
Milford Harbor, CT	51	MIF	Kirby Pond, NY	83	KIR
Housatonic River, CT	52	HOU	Larchmont Harbor, NY	88	LAR
Lewis Gut, CT	53	LEW	Lewis Gut, CT	53	LEW
Bridgeport Harbor, CT	54	BRH	Little Harbor, CT	44	LIH
Pequonnock River, CT	55	PEQ	Little Narragansett Bay, CT	2	LNA
Black Rock Harbor, CT	56	BLR	Little Neck Bay, NY	96	LNE
Ash Creek, CT	57	ASH	Lloyd Harbor, NY	104	LLO
Pine Creek, CT	58	PIN	Mamaroneck River, NY	87	MAM
Mill River, CT	59	MIL	Manhasset Bay, NY	97	MAN
Sasco Brook, CT	60	SAS	Mattituck Creek, NY	115	MAT
Sherwood Millpond, CT	61	SHE	Menunkesucket River, CT	35	MEN

sorted by RI to NY order			*sorted by embayment name*		
Site Name	RI - NY order	UWS Site ID	Site Name	RI - NY order	UWS Site ID
Compo Cove, CT	62	COM	Mianus River, CT	77	MIA
Saugatuck River, CT	64	SAU	Milford Harbor, CT	51	MIF
Cockenoe Harbor, CT	65	COC	Mill Neck Creek, NY	101	MNC
Norwalk Harbor, CT	66	NWH	Mill River, CT	59	MIL
Sheffield Island Harbor, CT	67	SIH	Milton Harbor, NY	85	MIT
Five Mile River, CT	68	FIV	Mount Sinai Harbor, NY	114	MOU
Scotts Cove, CT	69	SCO	Mumford Cove, CT	14	MUM
Gorham Pond, CT	70	GOR	Mystic River, CT	9	MYS
Darien River, CT	71	DAR	New Haven Harbor, CT	48	NEW
Holly Pond, CT	72	HOL	Niantic Bay, CT	23	NIB
Cove Harbor, CT	73	COV	Niantic River, CT	22	NIR
Wescott Cove, CT	74	WES	Nissequogue River, NY	110	NIS
Stamford Harbor, CT	75	STA	Northport Bay, NY	108	NPB
Greenwich Cove, CT	76	GRC	Northport Harbor, NY	107	NPH
Mianus River, CT	77	MIA	Norwalk Harbor, CT	66	NWH
Indian Harbor, CT	78	INH	Oyster Bay, NY	102	OYB
Smith Cove, CT	79	SMI	Oyster River, Milford, CT	49	ORM
Greenwich Harbor, CT	80	GRH	Oyster River, Old Saybrook, CT	32	ORO
Captain Harbor, CT	81	CAP	Pages Cove, CT	46	PAG
Byram River, CT	82	BYR	Palmer Cove, CT	12	PAL
Kirby Pond, NY	83	KIR	Patchogue River, CT	34	PAC
Playland Lake, NY	84	PLA	Pattagansett River, CT	24	PAT
Milton Harbor, NY	85	MIT	Pawcatuck River, RI	1	PAW
Van Amringe Millpond, NY	86	VAN	Pequonnock River, CT	55	PEQ
Mamaroneck River, NY	87	MAM	Pine Creek, CT	58	PIN
Larchmont Harbor, NY	88	LAR	Playland Lake, NY	84	PLA
Premium Millpond, NY	89	PRE	Poquonock River, CT	15	POQ
Echo Bay, NY	90	ECH	Port Jefferson Harbor, NY	113	POR
Hunter Island Bay, NY	91	HIB	Premium Millpond, NY	89	PRE
Eastchester Bay, NY	92	EAB	Pugsley Creek, NY	94	PUG
Westchester Creek, NY	93	WCC	Quanaduck Cove, CT	4	QUA
Pugsley Creek, NY	94	PUG	Quiambog Cove, CT	6	QUI
East River, NY	95	EAR	Sachem Head Harbor, CT	41	SAC
Little Neck Bay, NY	96	LNE	Sasco Brook, CT	60	SAS
Manhasset Bay, NY	97	MAN	Saugatuck River, CT	64	SAU
Hempstead Harbor, NY	98	HEM	Scotts Cove, CT	69	SCO
Dosoris Pond, NY	99	DOS	Sheffield Island Harbor, CT	67	SIH
Frost Creek, NY	100	FRO	Sherwood Millpond, CT	61	SHE
Mill Neck Creek, NY	101	MNC	Smith Cove, CT	79	SMI

sorted by RI to NY order			*sorted by embayment name*		
Site Name	RI - NY order	UWS Site ID	Site **Name**	RI - NY order	UWS Site ID
Oyster Bay, NY	102	OYB	South Cove, CT	30	SOU
Cold Spring Harbor, NY	103	COL	Stamford Harbor, CT	75	STA
Lloyd Harbor, NY	104	LLO	Stonington Harbor, CT	5	STO
Huntington Harbor, NY	105	HUH	Stony Brook Creek, NY	111	SBC
Centerport Harbor, NY	106	CEN	Thames River, CT	17	THA
Northport Harbor, NY	107	NPH	Threemile River, CT	27	THR
Northport Bay, NY	108	NPB	Toms Creek, CT	37	TOM
Huntington Bay, NY	109	HUB	Van Amringe Millpond, NY	86	VAN
Nissequogue River, NY	110	NIS	Venetian Harbor, CT	13	VEN
Stony Brook Creek, NY	111	SBC	Wequetequock Cove, CT	3	WEQ
Conscience Bay, NY	112	CON	Wescott Cove, CT	74	WES
Port Jefferson Harbor, NY	113	POR	West Cove, CT	11	WST
Mount Sinai Harbor, NY	114	MOU	Westchester Creek, NY	93	WCC
Mattituck Creek, NY	115	MAT	Wilcox Cove, CT	7	WXC
Goldsmith's Inlet, NY	116	GOL	Williams Cove, CT	8	WIL

UWS Standard Operating Procedure – Tier I Sampling Plan

Table of Contents

1 POINT OF CONTACT

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2 OBJECTIVE

Sample water quality and macrophytes within an embayment following guidelines of the Unified Water Study (UWS). Frequency of sampling and daily order of events are specified.

3 DEFINITIONS AND ABBREVIATIONS

Embayment: A recess in a coastline or an indentation off a shoreline which forms a bay. In Long Island Sound, the names of embayments often include the words Harbor, River, Cove, Bay, Creek; with a few including the names Brook, Gut, Inlet, or Lake.

Field Team: Person or group of people working together to sample a station.

Macroalgae (macroalga, singular.): Commonly referred to as seaweed. This is a group of plant-like organisms. They do not have the vascular system and roots of a true plant. The "macro" prefix indicates these organisms are visible with the naked eye, no magnification is required to view the whole organism; although, magnification with a hand lens or loupe may be necessary to view the structure of the organism. In comparison, microalgae are the phytoplankton in the water which are too small to see with the naked eye.

Macrophyte: Plants and macroalgae that are viewable with the naked eye. This term includes macroalgae, seagrass (eelgrass, *Zostera marina*; widgeon grass, *Ruppia maritima*), and marsh grass.

Monitoring Group: The group conducting the field work.

Seagrass: A true plant, not an alga; they have the vascular system and roots of a land plant. These plants are fully submerged at all times (though there are a few species not found in Long Island Sound which are intertidal). Long Island Sound has two species of seagrass: *Zostera marina* (eelgrass), which is the most commonly seen seagrass in our area; and *Ruppia maritima* (widgeon grass).

Region: The reporting regions for the UWS. Each section must include a minimum of three stations. Sections will be assigned a unique name by the UWS; examples are included below.

Number of Sections	1	2		3		
Name of Sections	whole	inner	outer	inner	middle	outer
Abbreviations for Sections	W	I	O	I	M	O

Site: The whole embayment, as defined by the UWS list. Each site has a unique three letter code assigned by the UWS; for example, Little Neck Bay, NY is "LNE". Each site will have a minimum of four water quality stations.

Sonde: An instrument probe that automatically transmits information about its surroundings underground, under water, in the atmosphere, etc.

SOP: Standard operating procedure; this document is a SOP.

Station: The location where samples are collected, identified by a GPS location.

UWS: Unified Water Study

UWS Monitoring Program Coordinator: The person designated as the point of contact for the UWS.

UWS Scientific Advisor: Estuarine or water quality scientists designated as advisors to the UWS.

4 OVERVIEW

Sampling occurs in the months of May through October, though a shorter season is acceptable for inclusion in the UWS.

Two types of stations are included:

1) *Water quality stations* are sampled within three hours of sunrise between the months of May through October. A minimum of four stations per embayment are required. If multiple regions of the embayment are delineated, a minimum of three stations are required per region. Monitoring groups will plan to sample water quality stations at a minimum every two weeks. However, if unforeseeable circumstances make this plan not possible, a minimum of six sample events between May and October are required for inclusion in the UWS; including at least one sample event in each of the months of June, July, August, and September.

2) *Macrophyte stations* are land-based or boat-based. They are sampled only mid-summer and may be sampled on different days from the water quality stations. Sampling occurs on three separate days between July 15 and August 7. Two sample days or a date slightly outside of the date criteria may be sufficient in the event of unforeseen complications. This decision will be made by the Monitoring Program Quality Assurance Officer and UWS Science Advisor(s).

5 SOURCES

These procedures are based on the EPA Volunteer Estuary Monitoring Manual (EPA, 2007) and follows methods used in the EPA National Coastal Assessment (EPA, 2001). The EPA Volunteer Estuary Monitoring Manual (EPA, 2007) provides a wealth of specific data for monitoring groups. All groups should refer to the EPA manual for specific guidance. This SOP provides specific monitoring details relevant to the UWS.

6 MATERIALS AND EQUIPMENT

6.1 Safety

- safety plan – every volunteer should have a copy
    - Find out the location and telephone number of the nearest telephone and write it down, or have a cellular phone available.
    - Locate the nearest medical center and write down directions for guiding emergency

personnel to your stations.
    - Have each member of the sampling team complete a medical form that includes emergency contacts, and relevant health information such as allergies, diabetes, epilepsy, etc. ***Please note*** – this form should be kept confidential. Whoever coordinates the Monitoring Group efforts should have a copy and should review the form. A second copy should be kept with the field team in the event of an emergency; the form for each team member should be sealed in an envelope with their name.
    - Each team member should have contact information for all field team members. This list could be kept in your field box or use packing tape to affix it to the back of a clipboard or some other item you always have in the field.
        - full name
        - cell phone
        - home phone
        - email address
        - car color, make, model, and license plate
        - emergency contact information
- Every monitoring team should have a shore-based check-in for each sampling day. This is a person who knows who is on the team, where they will be, and the time they are expected back. If the field team does not check in, the shore person should know the procedures to follow to report the team missing. The following is an example:
    - Call the cell phones and home phones of all team members.
    - Check the site for parked vehicles – if the vehicle is present, start a search.
    - If the team is considered missing at sea, contact the Coast Guard; if the team is missing on land, contact the police.
- first aid kit – suggested items
    - telephone numbers of emergency personnel (e.g., police, ambulance service)
    - first aid manual which outlines diagnosis and treatment procedures
    - antibacterial or alcohol wipes
    - first aid cream or ointment
    - acetaminophen and ibuprofen for relieving pain and reducing fever
    - several band-aids
    - several gauze pads, 3 or 4 inches square
    - 2-inch roll of gauze bandage
    - triangular bandage
    - large compress bandage
    - 3-inch wide elastic bandage
    - needle for removing splinters
    - tick spoon for removing ticks
    - doctor-prescribed antihistamine for any participant who is allergic to bee stings
- cell phone
- water
- appropriate shoes and clothes (and extras); protection from the sun
- other items to consider:
    - flash light
    - back pack for sampling equipment, so hands are free

6.2 Sampling Gear – All Stations

REQUIRED (PUT IN A SMALL TOOL BOX)

- site maps with stations on map
- list of UWS unique station IDs with GPS coordinates for the site
- clip boards
- pencils
- pencil sharpener
- permanent marker
- field data sheets
- Chlorophyll a labels

OPTIONAL, BUT VERY USEFUL (PUT IN A SMALL TOOL BOX)

- clear packing tape (can be used to cover writing on bottles or affix a label that is not sticking)
- extra batteries for any electrical sampling gear
- tailor's tape measure (seamstress measuring tape), with metric scale – comes in handy when you need to re-mark a line
- basic tools (pliers, wrench, screw drivers, etc.)
- plastic baggies
- scissors, pocket knife, nail clippers
- cable ties
- electrical tape (this tape works well underwater; comes in many colors)
- duct tape (very useful in many situations)

7 METHODS

7.1 Parameters to Sample

Monitoring groups must collect the following data to be included in the UWS:

- for each water quality station
    - GPS coordinates of stations, recorded each sample date
    - date and time
    - total water depth
  - 0.5 m below the surface, 0.5 m above bottom, mid-depth if total depth >10 m; if total depth is less than 1.5 m, only a mid-depth reading will be collected
    - temperature
    - conductivity (salinity)
    - dissolved oxygen
    - chlorophyll a
    - turbidity
  - at the last station per field day undertake a replicate profile including all parameters
- obtain from an online NOAA tide table and noted weather station:
  - time of high and low tide nearest time of sampling
  - high and low air temperature for 24 hours preceding field sampling
  - precipitation out a week preceding sampling event
- within 1 day of the field sampling day, read the GPS of a land-based reference station

- for each macrophyte station
    - GPS coordinates of stations
    - date and time
    - photos of macrophytes
- within 1 days of the field sampling day, read the GPS of a land-based reference station

7.2 Timing of Sampling

7.2.1 Timing During the Year

WATER QUALITY STATIONS

The target sampling frequency is two sampling events per month, May through October. Sampling dates should be 10 to 18 days apart.

All water quality parameters should be sampled during a sampling event. At one station per field day, conduct a replicate profile.

In the occurrence of equipment failure or other unforeseen difficulty, a minimum of six sample events between May and October are required for inclusion in the UWS; including at least one sample event in each of the months of June, July, August, and September.

Macrophyte Survey Sampling Frequency

Macrophyte surveys will occur between July 15 and August 7 of every sampling season, with 3 survey events total. One survey per week is best. If this is not possible, maximize the days between sampling. All three days cannot be sampled in the same 7-day window. 2 sampling events or one outside of the interval may be considered for inclusion in the UWS. This decision will be made by the Monitoring Program Quality Assurance Officer and UWS Science Advisor(s).

Overview of Sampling Frequency

The calendar below provides an example of sampling frequency throughout the season. Dates highlighted in orange are water quality sampling dates (e.g. May 11). The green text (July 15 – August 7) are potential dates for macrophyte sampling. The dates highlighted in green are the 3 planned macrophyte sampling dates (e.g. July 21).

MAY

S	M	T	W	T	F	S
1	2	3	4	5	6	7
8	9	10	11	12	13	14
15	16	17	18	19	20	21
22	23	24	25	26	27	28
29	30	31	1	2	3	4
5	6	7	8	9	10	11

JUNE

S	M	T	W	T	F	S
29	30	31	1	2	3	4
5	6	7	8	9	10	11
12	13	14	15	16	17	18
19	20	21	22	23	24	25
26	27	28	29	30	1	2
3	4	5	6	7	8	9

JULY

S	M	T	W	T	F	S
26	27	28	29	30	1	2
3	4	5	6	7	8	9
10	11	12	13	14	15	16
17	18	19	20	21	22	23
24	25	26	27	28	29	30
31	1	2	3	4	5	6

AUGUST

S	M	T	W	T	F	S
31	1	2	3	4	5	6
7	8	9	10	11	12	13
14	15	16	17	18	19	20
21	22	23	24	25	26	27
28	29	30	31	1	2	3
4	5	6	7	8	9	10

SEPTEMBER

S	M	T	W	T	F	S
28	29	30	31	1	2	3
4	5	6	7	8	9	10
11	12	13	14	15	16	17
18	19	20	21	22	23	24
25	26	27	28	29	30	1
2	3	4	5	6	7	8

OCTOBER

S	M	T	W	T	F	S
25	26	27	28	29	30	1
2	3	4	5	6	7	8
9	10	11	12	13	14	15
16	17	18	19	20	21	22
23	24	25	26	27	28	29
30	31	1	2	3	4	5

7.2.2 Timing During a Sample Day

Sampling of dissolved oxygen occurs in the morning (within 3 hours of sunrise), to capture the lowest

dissolved oxygen values in the system.

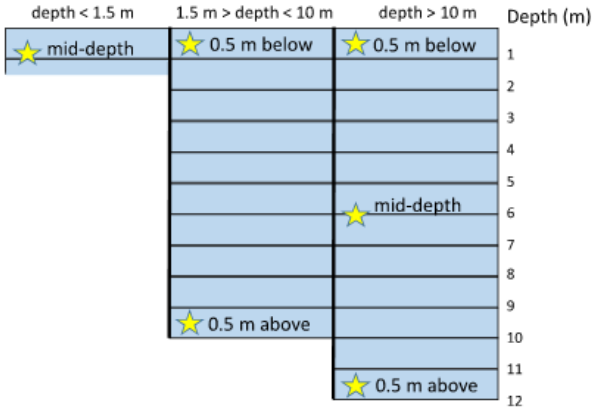
Chlorophyll a and turbidity should be sampled at the same time as dissolved oxygen, to allow for linking of these parameters to their corresponding temperature, salinity, and dissolved oxygen (Tables 1).

Table 1: Text summary of required sampling times within a sample day

Parameter/Survey	Required time interval
Dissolved Oxygen (mg/l, % sat.)	Collected within 3 hours of sunrise
Temperature	Collected within 3 hours of sunrise (with dissolved oxygen)
Salinity	Collected within 3 hours of sunrise (with dissolved oxygen)
Chlorophyll a	Collected within 3 hours of sunrise (with dissolved oxygen)
Turbidity (NTU)	Collected within 3 hours of sunrise (with dissolved oxygen)
Total and Sample Station Depth	At time of sampling
Macrophyte Survey	close to low tide for wrackline survey, close to high tide for hardened shorelines, boat surveys any time of day

7.3 Sampling Depths

7.3.1 Temperature, Salinity, Dissolved Oxygen, Chlorophyll a, Turbidity



If total depth at the station is greater than 10 m, take three samples: one at 0.5 m below the surface, one at mid depth, and another at 0.5 m above the bottom.

If total depth at the station is less than 10 m, take two samples: one at 0.5 m below the surface and the other at 0.5 m above the bottom.

If total depth at the station is less than 1.5 m, take one sample halfway to the bottom and record as mid depth.

Always record the depth of the sample.

7.4 Required Replicates and Verification

During a field day, use the field data sheet as a reminder for the number of replicates required for each parameter.

Table 2: Required replicates, blanks, and verification readings.

parameter & technique	replicates required	verification and/or blank
GPS coordinates	1 reading per station at 1 station per day, take a second reading before leaving the station	read a land-based reference station within 2 days of the field sampling day
sampling with multiparameter sonde	1 reading at each depth, wait for reading to stabilize before recording at 1 station per day (typically the last station), do two replicate profiles – do one complete profile, then do a second	verify depth by lowering sonde to known depth verify Chlorophyll a by reading water in a bucket and filtering 2 samples from the bucket read standards before and after a sample day (salinity, oxygen in 100% water saturated air, turbidity, chl-a); day before and after sample day is acceptable
filtered Chlorophyll a	2 filtered samples of a single water sample collected from 0.5 m below the surface at all stations	duplicate from same bucket used as a second calibration point for Chlorophyll a for a sampling event
macrophytes	3-6 stations per embayment	photos of each rake toss or the beach being sampled, reviewed by UWS Monitoring Program Coordinator and Science Advisors

7.5 Order of Events When Sampling a Water Quality Station

7.5.1 Prepare for Sampling Trip

A. Calibrate all instruments.

B. Gather all field supplies.

C. Complete the pre-sampling event portions of the UWS datasheet.

D. Arrange for a shore person. This is someone to check on you if you don't come back at the designated time.

7.5.2 Water Quality Station Sampling – within 3 hours of sunrise

A. Record station information on the data sheet. *Be sure to complete all sections of the data sheet completely, for every data entry.*

B. Obtain total depth of the station, determine sampling depths for water quality parameters

C. Collect profile data using the multiparameter sonde.

   a. Sample the surface, then mid-depth, then bottom with Sonde; or depths necessary according to total depth and respective sample depth criteria, sampling from top to bottom.

D. At one station per day repeat measurements where only one profile is typically collected. The last station of the day is the ideal choice in terms of time management.

   a. Repeat the sonde profile. Complete the first profile, sampling at each depth. Complete a second profile.

   b. Record the depth and GPS coordinates a second time, just before leaving the station.

E. Read a calibration standard just following calibration and following the field trip to verify readings, for all parameters where this applies.

7.5.3 End of Field Day

A. If using a multiparameter sonde to sample Chlorophyll a, place the sonde in a bucket of estuarine water, read the sonde, and filter samples for Chlorophyll a analysis for verification of the sonde readings.

B. Verify all sections of the data sheet have been completed.

C. Store Chlorophyll a samples according to the UWS SOP Filtered Chlorophyll.

D. Within 1 days of sampling, record the GPS of a reference station on land to verify the accuracy and precision of the GPS coordinates.

8 TROUBLESHOOTING / HINTS

- Gather field equipment the day prior to sampling. Check the field equipment in the morning, before

you head out into the field. Creating a checklist is very helpful in prepping for your field day. Include personal items (sunscreen, bug spray, etc.) and safety equipment on the checklist.

- Always carry a copy of this SOP and the relevant parameter-specific SOPs.
- Print out the "quick sheets" for relevant SOPs to use as a reminder in the field. Do not laminate these as you will want to add notes. A plastic page-protector taped close can be used to keep these sheets dry.

9 DATA PROCESSING AND STORAGE

The UWS Monitoring Program Coordinator will be the custodian of the finalized data files.

The monitoring group is responsible for obtaining data, entering data into the UWS data template, and delivering the data to the UWS Monitoring Program Coordinator.

The monitoring group is responsible for assuring that the correct unique station ID assigned by the UWS is properly matched with the local organizations station ID codes. Both codes (monitoring group's station code and UWS unique station ID) will be entered into the data template, along with the GPS coordinates.

10 REFERENCES

EPA, 2007, Volunteer Estuary Monitoring, A Methods Manual, Second Edition. Orhrel Jr., R.L., Register, K.M. (Eds.). The Ocean Conservancy & EPA. 396 p. https://www.epa.gov/sites/production/files/2015-09/documents/2007_04_09_estuaries_monitoruments_manual.pdf

EPA, U.S. 2001. National Coastal Assessment: Field Operations Manual. U. S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Gulf Ecology Division, Gulf Breeze, FL. EPA 620/R-01/003. 72 p.

11 Quick Sheet – Tier I Sampling Plan

Check your equipment list the day before a field day and again on the morning of a field day.

Calibrate instruments the day before sampling.

Read a calibration standard just following calibration and following the sampling event to verify readings, for all parameters where this applies.

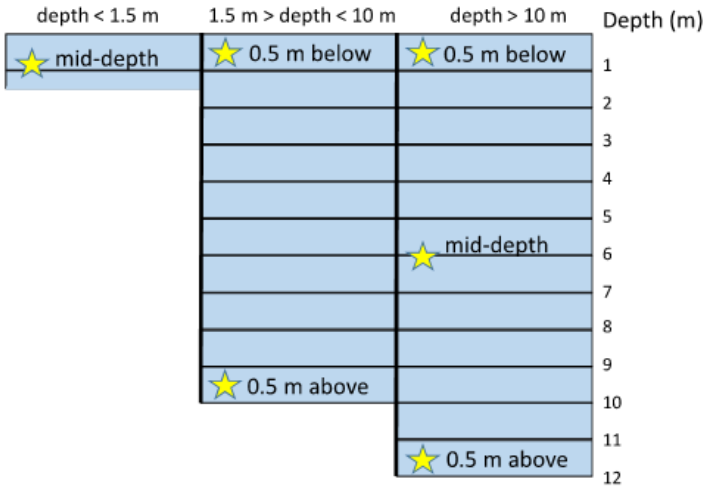
Bring the relevant SOPs and quick sheets with you into the field.

Remember – rinse equipment in sample water before collecting a sample.

Water quality stations - Sample depths are shown in chart to the right.

Use the field data sheet as a reminder for the number of replicates required for each parameter. Sample 1 station / day as a replicate for sonde profiles, GPS, and depth.

For filtered Chlorophyll a, filter four samples per day with corresponding sonde reading.



MACROPHYTE STATIONS – use quick sheet from Macrophyte SOP

GPS REFERENCE CHECK

- Within 1 days of sampling, record the GPS of a reference station on land to verify the accuracy and precision of the GPS coordinates.

WATER QUALITY STATIONS (sample within 3 hours of sunrise)

- At one station per day repeat measurements where only one profile is typically collected. The last station of the day is a good choice in terms of time management. (sonde, GPS and depth)

Appendix A-3

UWS Standard Operating Procedure – Depth and GPS Coordinates

Table of Contents

1 POINT OF CONTACT

NAME: Peter Linderoth, Save the Sound, Director of Water Quality
ADDRESS: 1385 Boston Post Rd, 2nd Floor, Larchmont, NY 10538
EMAIL: plinderoth@savethesound.org
PHONE: 914-381-3140 ext.200

2 OBJECTIVE

Determine the total depth and sample depth at station. Determine the GPS coordinates of the station.

3 OVERVIEW

A graduated line is weighted and used for recording total depth (m) and sample depth (m) at a station. Acceptable alternatives include multiparameter sonde depth reading.

A GPS unit is used to obtain GPS coordinates for the station on each field day. A Smart Phone app is an acceptable alternative as backup. GPS position of your actual location at each station for each sample date is required. A second reading is taken at one station per embayment per sample day to assess precision. If unforeseen circumstances make recording GPS points impossible and dead reckoning is used, your data may still be used as part of the UWS but will be flagged and reviewed in the quality assurance process.

4 SOURCES

These procedures are based on the EPA Volunteer Estuary Monitoring Manual (EPA, 2007). The EPA Volunteer Estuary Monitoring Manual (EPA, 2007) provides a wealth of specific data for monitoring groups.

5 MATERIALS AND EQUIPMENT

- Depth sampling device. Options include:
  - weighted, graduated line, with divisions every 0.1 m
    - This can be the cable attached to a multiparameter sonde
  - multiparameter sonde with depth sensor
- GPS coordinate sampling device. Options include:
  - Handheld GPS unit
  - Apps are available for your smart phone that allow you to easily log and return to GPS coordinates. The accuracy of the GPS on your phone is dependent on Wi-Fi signals and cellular signals.
  - Dead reckoning to get yourself on station should only be used if your GPS options have failed. This will need to be included in field notes for the sampling event. Data will be reviewed in the quality assurance process.

6 METHODS

6.1 Preparation

- Weighted line:
  - Examine the line for wear or damage.
  - Measure the increments to ensure line has not stretched or shrank.
- If using a multiparameter sonde:
  - Calibrate the depth sensor prior to the sampling event and the morning of on the sampling vessel according to the manufacturer's instructions.

- GPS device
  - Check batteries
  - Within 1 day of the sampling trip, read the GPS coordinates of a reference station on land (refer to "UWS Station Selection SOP" for more details on this reference station). These readings will be used to assess the precision of your GPS method.

6.2 Field Collection and Processing

Metered Line

1. Attach weight to line.
   a. A weighted sonde attached to a cable with 0.1 m increments is considered a weighted line.
2. Slowly lower line until the weight reaches the bottom.
3. Mark the line at the surface of the water (pinch with finger).
4. Determine the depth of the station.
5. Record max depth to the nearest 0.1 m on field data sheet.
6. Following UWS SOP Sampling Plan for number of samples and locations in the water column associated with total depth, sample all target depths using steps 2-5 replacing "weight reaches the bottom" to deliver sonde to target depth using increments on cable.
7. At least once per day per embayment (usually the last station of the day), take the reading again.

Multiparameter Sonde

1. Slowly lower until the weighted sonde reaches the bottom.
2. Determine the depth of the station by reading the display.
   a. Add the length from the depth sensor to the weight for total depth.
3. Record max depth to the nearest 0.1 m on field data sheet.
4. Following UWS SOP Sampling Plan for number of samples and location in the water column associated with total depth, sample all target depths using steps 1-3 replacing "weight reaches the bottom" to deliver sonde to target depth using handheld display. If depth sensor is not located with sonde attachments, compensate by lowering the sonde to the depth reading required. For example, if the sonde attachments are .25 m below the depth sensor and the target sample depth is 5 m the sampler should lower sonde to a depth reading 4.75 m on the display.
5. At least once per sampling day (prior to first station), lower the sonde to a known depth and verify the reading. If the depth reading from sonde does not agree within 0.3 m, use the metered line procedures.
6. At least once per sampling day per embayment (usually the last station of the day), take the reading again.

GPS DEVICE

1. Determine the GPS coordinates of the station by reading the display.
2. At least once per sampling day per embayment (usually the last station of the day), take the reading again.
3. Within 1 day of the sampling trip, read the GPS coordinates of a reference station on land.

6.3 Sample Storage

Not applicable.

6.4 Laboratory Analysis

Not applicable.

7 TROUBLESHOOTING / HINTS

- Always carry a copy of this SOP and the relevant parameter-specific SOPs.
- Print out the "quick sheets" for relevant SOPs to use as a reminder in the field. Do not laminate these as you will want to add notes. A plastic page-protector taped close can be used to keep these sheets dry.

8 DATA PROCESSING AND STORAGE

The monitoring group is responsible for obtaining data, entering data into the UWS data template, and delivering the data to the UWS Monitoring Program Coordinator.

The monitoring group is responsible for assuring that the correct unique station ID assigned by the UWS is properly matched with the local organizations station ID codes. Both codes (monitoring group's station code and UWS unique station ID) will be entered into the data template, along with the GPS coordinates.

9 REFERENCES

EPA, 2007, Volunteer Estuary Monitoring, A Methods Manual, Second Edition. Orhrel Jr., R.L., Register, K.M. (Eds.). The Ocean Conservancy & EPA. 396 p. https://www.epa.gov/sites/production/files/2015-09/documents/2007_04_09_estuaries_monitoruments_manual.pdf

10 Quick Sheet – Depth & GPS Coordinates

For depth and GPS - At least once per sampling day per embayment (usually the last station of the day), take the reading again.

Preparation

- If using a weighted line:
  - Examine the line for wear or damage.
  - Measure the increments to ensure line has not stretched or shrank.
- If using a multiparameter sonde:
  - Calibrate the depth sensor according to the manufacturer's instructions. This may be done in the field.
  - Bring a weighted line (can be sonde cable) for verification of readings (prior to sampling first station) and in case sonde depth is inaccurate.
- GPS device
  - Check batteries
  - Within 1 days of the sampling trip, read the GPS coordinates of a reference station on land. This will be used to assess the precision of your GPS method.

Field Collection and Processing

METERED LINE

1. Attach weight to line.
   a. A weighted sonde attached to a cable with 0.1 m increments is a weighted line.
2. Slowly lower line until the weight reaches the bottom.
3. Mark the line at the surface of the water (pinch with finger).
4. Determine the depth of the station.
5. Record max depth and sample depth(s) to the nearest 0.1 m on field data sheet.

MULTIPARAMETER SONDE

1. Determine the depth of the station by reading the display.
2. Record max depth and sample depth(s) to the nearest 0.1 m on field data sheet.
3. At least once per sampling day (prior to first station), use a metered line to confirm the accuracy of the depth reading. If the depth reading from sonde does not agree within 0.3 m, use the metered line.

GPS DEVICE

1. Determine the GPS coordinates of the station by reading the display.
2. Within 1 days of the sampling trip, read the GPS coordinates of a reference station on land.

Appendix A-4

UWS Standard Operating Procedure – Sonde Profile

Table of Contents

1 POINT OF CONTACT

NAME: Peter Linderoth, Save the Sound, Director of Water Quality
ADDRESS: 1385 Boston Post Rd, 2nd Floor, Larchmont, NY 10538
EMAIL: plinderoth@savethesound.org
PHONE: 914-381-3140 ext.200

2 OBJECTIVE

Determine the sample depth (m), temperature (°C), salinity (ppt), dissolved oxygen concentration (mg/L = ppm), and dissolved oxygen percent (% sat.) in the surface (0.5 m below surface) and bottom water (0.5 m above bottom) at the station using a multiparameter sonde. When total water depth is greater than 10 m, parameters at mid-depth will also be determined.

UWS Standard Operating Procedure – Sonde Profile

Table of Contents

1 POINT OF CONTACT

NAME: Peter Linderoth, Save the Sound, Director of Water Quality
ADDRESS: 1385 Boston Post Rd, 2nd Floor, Larchmont, NY 10538
EMAIL: plinderoth@savethesound.org
PHONE: 914-381-3140 ext.200

2 OBJECTIVE

Determine the sample depth (m), temperature (°C), salinity (ppt), dissolved oxygen concentration (mg/L = ppm), and dissolved oxygen percent (% sat.) in the surface (0.5 m below surface) and bottom water (0.5 m above bottom) at the station using a multiparameter sonde. When total water depth is greater than 10 m, parameters at mid-depth will also be determined.

3 OVERVIEW

A multiparameter sonde is used to determine the sample depth (m), temperature (°C), salinity (ppt), dissolved oxygen concentration (mg/L = ppm), and dissolved oxygen percent (% sat.) in the surface (0.5 m below surface) and bottom water (0.5 m above bottom) at the station. When total water depth is greater than 10 m, parameters at mid-depth will also be determined. Multiparameter sondes may also include probes for turbidity (NTU) and chlorophyll a (RFU, µg/L). Frequency of sampling and daily order of events are specified in the "UWS Sampling Plan SOP."

At one station per day (typically the last station), do two replicate profiles – do one complete profile, then do a second. This allows for the precision of the sonde to be assessed.

4 SOURCES

These procedures are based on the EPA Volunteer Estuary Monitoring Manual (EPA, 2007) and follows methods used in the EPA National Coastal Assessment (EPA, 2001). The EPA Volunteer Estuary Monitoring Manual (EPA, 2007) provides a wealth of specific data for monitoring groups. All groups should refer to the EPA manual for specific guidance.

5 MATERIALS AND EQUIPMENT

- YSI EXO1 or YSI ProDSS Multiparameter Sonde, setup to record:
  - depth
  - temperature
  - conductivity (salinity)
  - dissolved oxygen
  - chlorophyll a
  - turbidity
- 5 gallon bucket
- See UWS SOP Filtered Chlorophyll. The field team will need all equipment and material listed for collecting chlorophyll a samples. Filter two samples per field day for verification of sonde readings.
- ASTM Type I reagent grade water or equivalent for 0 NTU turbidity standard solution and 0 µg/L (and 0 RFU) for chlorophyll a calibration
- YSI Turbidity Standard, 124 FNU (or NTU), SKU: 607300
- YSI Conductivity Calibrator Solution, 3169: 50,000 µS/cm, SKU: 060660

6 METHODS

6.1 Preparation

- Check the battery power. Pack extra batteries in the field tool kit.
- Calibrate the sonde the day before or morning of each field day. Follow the manufacturer's instructions for calibration steps.

- Conductivity – Conduct calibration using the 50,000 µS/cm conductivity standard.
- Dissolved Oxygen – Conduct an air calibration, using water saturated air for calibrating 100% saturation.
- Chlorophyll a - Conduct a one-point calibration using the 0 µg/L (ASTM Type I reagent grade water)
- Turbidity - Conduct a two-point calibration using the 0 NTU (ASTM Type I reagent grade water) and 124 NTU standard solutions.
- Depth – Calibrate the depth following manufacturer's guidelines.
- The instrument will be factory calibrated and serviced at the manufacturer's recommended interval.

- After each calibration, take a verification reading in each of the standard solutions. This can be done directly after the calibration with solution still in the calibration cup.
- Record calibration information in the calibration section of the UWS datasheet. The following information will be entered into the UWS data entry template:
  - dissolved oxygen - post calibration reading in 100% saturated air
  - conductivity standard for sonde - manufacturer and value (µS/cm)
  - conductivity standard for sonde - lot number
  - conductivity standard for sonde - expiration date
  - conductivity on sonde - post calibration reading in standard (µS/cm)
  - chlorophyll a fluorescence on sonde - post calibration reading (µg/L and RFU)
  - turbidity standard - manufacturer and value (FNU/NTU)
  - turbidity standard - lot number
  - turbidity standard - expiration date
  - turbidity - post calibration reading in standard (FNU/NTU)

6.2 Field Collection and Processing

6.2.1 Sampling at a Station

- Turn on the sonde.
- If sampling from a boat, anchor the boat or stay on station with short engine adjustments.
- Determine sampling depths as described in the UWS SOP Sampling Plan.
- If wading in to sample, take extra precaution to not stir up sediment. Samples should be taken from an area that is not disturbed from the sampler's approach.
- Lower sonde to sample depth. Be sure that the probe ends are at the desired depth, versus other sections of the sonde. Be careful not to let the probe contact the sediments as this could foul the probes and give inaccurate readings.

- Allow the sonde to equilibrate for at least 90 seconds. Watch the salinity first. Once salinity is steady, watch the dissolved oxygen. The value may fluctuate in response to real variability in the water column. You are waiting for the readings to hover around a value, versus consistently rising or falling. Do not wait for turbidity or chlorophyll a to stabilize, these probes respond quickly to real variability in the water column. These values should be listed as the middle point between the high and low displayed back and forth on the screen.
- Record readings on the field data sheet.
- At one station per day (typically the last station), do a replicate profile – do one complete profile, then do a second. This allows for the precision of the sonde to be assessed.

6.2.2 Verification of Water Quality Parameters and Sonde Depth

- Take and record sonde values in standards up to a day before and after a sampling day (conductivity, dissolved oxygen in 100% air-saturated water, 0 µg/L chl-*a*, 0 NTU turbidity and 124 NTU turbidity).
- Verify sonde depth by lowering sonde to a known depth following the procedures listed in UWS SOP Depth SOP.

6.2.3 Verification of Chlorophyll a – Bucket Sample

If a chlorophyll a probe is on the sonde, verify the chlorophyll a readings from the sonde once per day and send to an analytical lab for analysis. This may be conducted at a dock; it does not need to occur at a water quality station.

- Rinse the bucket three times with surface water.
- Fill the bucket with surface water.
- Place the sonde in the bucket and stir for 10 seconds, allow to equilibrate, record chlorophyll a reading.
- Filter four samples from the bucket following the procedures in the UWS SOP Filtered Chlorophyll. Prior to withdrawing a sample from the bucket, be sure to stir the water in the bucket, using the sonde.

6.3 Sample Storage

Not applicable for the sonde. Follow instructions in the UWS SOP Filtered Chlorophyll SOP for filtered chlorophyll a samples.

6.4 Laboratory Analysis

Not applicable for the sonde. Follow instructions in the UWS SOP Filtered Chlorophyll SOP for filtered chlorophyll a samples.

7 TROUBLESHOOTING / HINTS

- Always make sure to wait until readings have stabilized before calibrating or logging a reading.

- If the probe does not appear to be operating or calibrating properly, contact the Monitoring Group Lead to make a decision on proceeding with the sampling event. Immediately notify the UWS Monitoring Program Coordinator if a sonde continues to not operate properly.

8 DATA PROCESSING AND STORAGE

The UWS Monitoring Program Coordinator will be the custodian of the finalized data files.

The monitoring group is responsible for obtaining data, entering data into the UWS data template, and delivering the data to the UWS Monitoring Program Coordinator.

The monitoring group is responsible for assuring that the correct unique station ID assigned by the UWS is properly matched with the local organizations station ID codes. Both codes (monitoring group's station code and UWS unique station ID) will be entered into the data template, along with the GPS coordinates.

9 REFERENCES

EPA, 2007, Volunteer Estuary Monitoring, A Methods Manual, Second Edition. Orhrel Jr., R.L., Register, K.M. (Eds.). The Ocean Conservancy & EPA. 396 p. https://www.epa.gov/sites/production/files/2015-09/documents/2007_04_09_estuaries_monitoruments_manual.pdf

EPA, U.S. 2001. National Coastal Assessment: Field Operations Manual. U. S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Gulf Ecology Division, Gulf Breeze, FL. EPA 620/R-01/003. 72 p.

10 Quick Sheet – Sonde Water Quality Profile

Preparation

- Check the battery power. Pack extra batteries in the field tool kit.
- Calibrate the sonde the day before each field day. Follow the manufacturer's instructions for calibration.
- After calibrating, use the sonde to take a verification reading in each of the standard solutions.
- Record calibration information in the calibration section of the UWS datasheet.

Field Collection and Processing

- If sampling from a boat, anchor the boat or stay on station with short engine adjustments.
- Determine sampling depths as described in the UWS SOP Sampling Plan.
- If wading in to sample, take extra precaution to not stir up sediment.
- Lower sonde to sample depth. Be sure that the probe ends are at the desired depth, versus other sections of the sonde. Be careful not to let the probe contact the sediments as this could foul the probes and give inaccurate readings.
- Allow the sonde to equilibrate for at least 90 seconds.
  - Watch the salinity first.
  - Once salinity is steady, watch the dissolved oxygen.
  - The value may fluctuate in response to real variability in the water column. You are waiting for the readings to hover around a value, versus consistently rising or falling. This will typically take about one minute, but may take longer. Do not wait for turbidity or chlorophyll a to stabilize, these probes respond quickly to real variability in the water column.
- Record readings on the field data sheet.
- At one station per day (typically the last station), do a replicate profile – do one complete profile, then do a second. This allows for the precision of the sonde to be assessed.

Verification of Water Quality Parameters and Sonde Depth

- Take and record sonde values in standards up to a day before and after a sampling day (conductivity, dissolved oxygen in 100% air-saturated water, 0 µg/L chl-*a*, 0 NTU turbidity and 124 NTU turbidity).
- Verify sonde depth by lowering sonde to a known depth following the procedures listed in UWS SOP Depth GPS.

Verify chlorophyll a by sampling in a bucket.

Verify the chlorophyll a readings from the sonde once per day and send to an analytical lab for analysis. This may be conducted at a dock; it does not need to happen at a station.

- Rinse the bucket three times with surface water, fill the bucket with surface water.
- Place the sonde in the bucket, stir for 10 seconds, and then allow to equilibrate, record chlorophyll a reading.
- Filter two samples from the bucket following the procedures indicated in the UWS SOP Filtered Chlorophyll. Prior to withdrawing a sample from the bucket, be sure to stir the water in the bucket with sonde.

Appendix A-5

UWS Standard Operating Procedure – Filtered Chlorophyll a

Table of Contents

1 POINT OF CONTACT

NAME: Peter Linderoth, Save the Sound, Director of Water Quality
ADDRESS: 1385 Boston Post Rd, 2nd Floor, Larchmont, NY 10538
EMAIL: plinderoth@savethesound.org
PHONE: 914-381-3140 ext. 200

2 OBJECTIVE

Determine the concentration of chlorophyll a in the surface water, 0.5 m below the surface, following guidelines of the Unified Water Study (UWS). Frequency of sampling and daily order of events are specified in the UWS SOP Sampling Plan.

3 OVERVIEW

A water sample is collected, filtered, and analyzed at an analytical lab to determine the chlorophyll a

concentration using the fluorometric technique (90% acetone extraction). Phytoplankton, the microscopic plant-like organisms living in the water, contain chlorophyll a. Thus, chlorophyll a concentration provides a rough approximation of the amount of phytoplankton in the water column. This is considered a rough approximation because individual phytoplankton contain varying amounts of chlorophyll a based on species, size, and environmental factors.

At each station, a chlorophyll a sonde reading is collected from 0.5 m below the surface according to the UWS SOP Sonde Profile. Once per sampling event a bucket of surface water is collected. A sonde reading for chlorophyll a and four water samples from the bucket are filtered through a glass fiber filter with pore size of 0.7 µm. The filters are dried by passing air through the filter. The filters are stored in the dark on ice until it can be transferred to a freezer (within 12 hours of the initial sample collection).

4 SOURCES

These procedures are based on the EPA Volunteer Estuary Monitoring Manual (EPA, 2007) and follows methods used in the EPA National Coastal Assessment (EPA, 2001). The EPA Volunteer Estuary Monitoring Manual (EPA, 2007) provides a wealth of specific data for monitoring groups.

Analytical methods follow EPA method #445.0, "*In Vitro* Determination of Chlorophyll a and Pheophytin *a* in Marine and Freshwater Algae by Fluorescence" (Arar and Collins, 1997) or Standard Methods 10200 H3, "Fluorometric Determination of Chlorophyll a" (Eaton et al., 2005).

5 MATERIALS AND EQUIPMENT

- 5 gallon bucket or larger
- Glass fiber filters (Whatman GF/F with nominal pore size of 0.7 µm), 2.5 cm diameter
- Filter holders, 2.5 cm: Pall brand, 25 mm Easy Pressure Syringe Filter Holder, Delrin Plastic
- 60 mL syringe
- Forceps for handling filters
- Unused and unbleached coffee filter cut into strips
- Aluminum foil
- Airtight container
- Cooler

6 METHODS

6.1 Preparation

- Check that field equipment is prepped and operational.

- Prepare labels for filters. The pre-labeled information should include the monitoring group, UWS unique station ID, date, sample type, sample volume, and replicate ID ("a" or "b"). For example:
    - "Save the Sound LNE-I-01a 6/8/17 Vol. 60 mL" & " Save the Sound LNE-I-01b 6/8/17 Vol. 60 mL"
- Prep aluminum foil squares for projected number of samples (4 per reference station) plus extras.
- Load all available filter holders with filters. Have at least 4 ready for use.

6.2 Field Collection and Processing

1. Collect water in 5 gallon bucket.
    - Rinse the bucket three times with sample water from the surface. Fill bucket with sample water.
2. If not prepped, load filters into the filter holder.
    - Preloading all filter holders with filters before the sampling event begins is strongly advised.
3. Rinse the 60 mL syringe with ~5 mL of sample water. Repeat for a total of three rinses.
4. Mix the sample well by stirring for 10 seconds with sonde.
5. Record chlorophyll a (µg/L and RFU) data from sonde.
6. Fill the 60 mL syringe with sample water taken close to where sonde reading was recorded. Note the volume of water in the syringe – knowing the exact volume filtered is critical to analyzing the chlorophyll a concentration.
7. Connect the filter holder to the syringe.
8. Gently expel water through the filter. The pressure applied to the plunger of the syringe should be slow and steady. If you encounter more than mild resistance, the filter may be clogged (e.g. jellyfish, algae) or you may have filtered sufficient sample.
9. After filtering 60 mL, inspect the filter for color. If a visible light green or light brown color is present, there is sufficient material on the filter for analysis, skip to step 10.
    - If no color is visible, filter another 60 mL and re-inspect.
    - On some occasions, if chlorophyll a levels are very high, filtering may become difficult after as little as 30 mL. If this occurs, and the filter is colored, stop filtering and proceed to step 10.
10. Record volume recorded on field data sheet and sample label when possible. Recording the exact volume filtered is critical to analyzing the chlorophyll a concentration. If you are uncertain of the volume filtered, discard the sample and start over.
11. Use the 60 mL syringe to dry the filter by expelling air through the filter.
    - With the syringe NOT attached to the filter holder, draw air into the syringe.

- Attach syringe to holder and expel air forcefully through the filter. Do this until no "mist" is aspirated from the filter holder, a minimum of 3 times.
- DO NOT draw air backwards through the filter. Syringe should be taken off holder each time plunger is drawn up.

12. Remove filter with forceps.
    - If forceps are dirty, wipe with a Kimwipe or rinse with distilled water.
    - Only touch the filter on the edges. You may use clean fingers to steady the filter by touching the edge (do not touch the green or brown part).
    - Fold filter in half with forceps and place it in an absorbent pad (unbleached coffee filter). Wrap in aluminum foil by folding the foil around the filter.
13. Filters should be placed in an airtight container and stored in a cooler on ice. Ice should surround the airtight container.

6.3 Sample Storage

14. Store samples in the freezer (-20°C). Frozen samples must be analyzed within 28 days.

6.4 Laboratory Analysis

15. Bring filters to partner lab for analysis or transport group; using UWS Chain of Custody. Frozen samples must be analyzed within 28 days.

7 TROUBLESHOOTING / HINTS

- Make sure filters are dry before storing.
- Gather field equipment the day prior to sampling. Check the field equipment in the morning, before you head out into the field.
- Always carry a copy of this SOP and the relevant parameter-specific SOPs.
- Print out the "quick sheets" for relevant SOPs to use as a reminder in the field. Do not laminate these as you will want to add notes. A plastic page-protector taped close can be used to keep these sheets dry.

8 DATA PROCESSING AND STORAGE

The monitoring group is responsible for obtaining data, entering data into the UWS data template, and delivering the data to the UWS Monitoring Program Coordinator.

The monitoring group is responsible for assuring that the correct unique station ID assigned by the UWS is properly matched with the local organizations station ID codes. Both codes (monitoring group's station code and UWS unique station ID) will be entered into the data template, along with the GPS coordinates.

9 REFERENCES

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10 Quick Sheet – Filtered Chlorophyll a

SAMPLE from 5 gallon Bucket

Recording the exact volume filtered is critical to analyzing the chlorophyll a concentration. If you are uncertain of the volume filtered, discard the sample and start over.

The labels should include the UWS unique station ID, monitoring group, replicate ID ("a" or "b"), sample volume, and date. For example:

- station 1: Save the Sound LNE-I-01a 6/8/17 Vol. 60 mL &
  Save the Sound LNE-I-01b 6/8/17 Vol. 60 mL

1. Collect surface water in a 5 gallon bucket. Rinse bucket three times with sample water prior to filling.
2. Mix the sample well by stirring for 10 seconds with sonde. Record data from sonde
3. Rinse the 60 mL syringe with ~5 mL of sample water. Repeat for a total of three rinses.
4. ***Note the volume of water in the syringe – knowing the exact volume filtered is critical to analyzing the chlorophyll a concentration.***
5. Gently expel sample water through the filter. The pressure applied to the plunger of the syringe should be slow and steady. If you encounter more than mild resistance, the filter may be clogged (e.g. jellyfish, algae) or you may have filtered sufficient sample.
   - After filtering 60 mL, inspect the filter for color. If a visible light green or light brown color is present, there is sufficient material on the filter for analysis. If no color is visible, filter another 60 mL and re-inspect. On some occasions, if chlorophyll a levels are very high, filtering may become difficult after as little as 30 mL.

6. ***Recording the exact volume filtered is critical to analyzing the chlorophyll a concentration. If you are uncertain of the volume filtered, discard the sample and start over.***
7. Use the 60 mL syringe to dry the filter by expelling air through the filter.
   - Attach syringe to holder and expel air forcefully through the filter. Do this until no "mist" is aspirated from the filter holder, a minimum of 3 times. DO NOT draw air backwards through the filter. Syringe should be taken off holder each time plunger is drawn up.
8. Remove filter with forceps.
   - Only touch the filter on the edges. You may use clean fingers to steady the filter by touching the edge (do not touch the green part).
   - Fold filter in half with forceps, place in an absorbent pad (unbleached coffee filter), wrap in aluminum foil and apply the label.
9. Labeled, foil wrapped filters should be placed in an airtight container and stored in a cooler on ice. Ice should surround the airtight container.
10. Store samples in the freezer (-20°C). Bring filters to partner lab for analysis. Frozen samples must be analyzed within 28 days.

Appendix A-6

UWS Standard Operating Procedure – Qualitative Macrophytes

Table of Contents

1 POINT OF CONTACT

NAME: Peter Linderoth, Save the Sound, Director of Water Quality
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EMAIL: plinderoth@savethesound.org
PHONE: 914-381-3140 ext.200

2 OBJECTIVE

Identify problematic macroalgae blooms and the presence of eelgrass in neighboring waters by examining the wrack line on a beach or sampling submerged areas with a rake.

3 OVERVIEW

The goal is to identify areas with problematic amounts of macroalgae and areas with eelgrass (a beneficial condition). This is not intended to be a quantitative assessment. Macrophyte surveys will complement chlorophyll *a* concentrations to better understand the dominant primary producer in the system. Methods for conducting an assessment vary by the location to be assessed. If a soft shoreline is available, photos of the beach area are used to characterize the amount of macroalgae in the neighboring water. Alternatively, a rake is used to assess what is on the bottom when submerged areas are sampled.

METHOD OVERVIEW (please see text below for a full explanation)

- Sample 3 days during the 3-week period starting July 15 and ending August 7. Try to sample once per week. If this is not possible, please sample such that you maximize the days between sampling. All three days cannot be sampled in the same 7-day window. Two sample days or a date slightly outside of the date criteria may be sufficient in the event of unforeseen complications. This decision will be made by the Monitoring Program Quality Assurance Officer and UWS Science Advisor(s).
- For soft shorelines, take an overview photo of the area, focused on the beach (not the water). Take a close-up photo of each of the dominant macroalgae types on the beach. Complete the datasheet.
- For sampling submerged areas, toss the rake 6 times, 2 tosses in each of 3 directions. Photograph each rake, even empty rakes. Complete the datasheet.
- Enter the data into data entry excel template and upload photos onto SharePoint platform.

BACKGROUND

Later on, in this SOP, you will see that you are characterizing macroalgae by morphology (hair-like, twig/leaf-like, sheets) and color (green, other). Macroalgae can be hard to identify, thus we are not attempting to identify the genus or species of algae present. The morphology will allow us to identify algae that are nutrient-loving, and thus may represent a water quality problem. Hair-like algae of all colors tend to be nutrient-lovers. Some branching algae in the twig/leaf-like category are also nutrient-lovers, especially if they fall into the red algae category. Sheets of green or red are problematic, while sheets of brown (e.g. kelp) can be indicative of good water quality. Based on these assessments, you may notice that color of the algae is important. Macroalgae fall into three taxonomic divisions denoted by the color of the algae: red (*Rhodophyta*), green (*Chlorophyta*), and brown (*Phaeophyta*). These colors refer to the types of photosynthetic pigments present in the organisms of each division. While a *Rhodophyta* often looks reddish, it can appear gold, green, brown, or black. The same is true of the other divisions. Green macroalgae typically appear green. Almost all green algae found in Long Island Sound is indicative of high nutrient availability. Thus, we ask that you distinguish between green algae and those of other colors. Good photos of the algae you are seeing will aid in follow-up analysis of these data.

MATERIALS AND EQUIPMENT

- GPS unit
  - GPS unit or GPS app for a smart phone
- Digital camera with resolution >5 megapixels (most smartphone cameras meet this criteria)
- Bucket or plastic bin, for putting macroalgae in if it is very muddy or falling off rake
- Bow rake with ~7 m (~20 feet) of rope attached to the tine-end of the rake and attached to the handle (cable tie, duct tape, etc.).
  - The rake should be a heavy duty bow rake with forged steel rake head, 16 inches wide, with 15 or 16 tines. The total length (handle to tines) should be around 60 inches. A rake with an ash wood handle is appropriate; however, fiberglass or another handle material is also acceptable.
- Weight that can be attached to the rake, to help it sink to the bottom. For example, a dive weight or large fishing weights.
- Local tidal information for survey site (for soft shoreline surveys).

4 METHODS

4.1 Station Selection

The number of stations sampled per embayment depends upon the size of the embayment, expected variability in macroalgae coverage, and access to sampling areas. An initial site visit of many locations can aid with determining the viability of sampling stations. A minimum of 3 sample stations is recommended for all embayments. More may be needed for larger embayments. Consultation with the Monitoring Program Coordinator and UWS Science Advisors will aid with the determination of how many to include. ***We cannot assess how much macroalgae is in an embayment using this method.*** Instead, the goal is to identify embayments which have widespread macroalgae problems and those which have problem areas for macroalgae but not throughout the whole system. Additionally, eelgrass will be noted when present in the survey.

4.1.1 Considerations for Choosing a Station

Must be legally accessible. This includes areas with public access and private areas where permission has been granted by the owner or manager of the area. Roadways closed to pedestrian traffic and all train tracks ARE NOT considered areas with public access, prior permission and official escort are typically required for these areas.

Must be safe to access. The station should not endanger personnel. For example, areas to avoid include: steep inclines, roadways with insufficient buffers from passing cars, areas overrun with poison ivy, areas with excessive debris, etc.

Look for areas where macroalgae is likely to collect. The goal is to assess what is out in the system. If you

choose an area that is too deep or where the current is sweeping away all of the macroalgae, you may miss an issue that is occurring in shallower, calmer waters. However, if the overall system is deep and scoured by the current or wind driven waves, then sample these areas, as they do indeed represent the system. To assess how representative an area is, try sampling in a few spots in a general area of the embayment. If macroalgae is widespread, make a note of this. If the macroalgae you are sampling is at a spot where macroalgae tends to collect, also make a note of this.

4.1.2 Station Selection Guidance for Soft Shoreline (Beaches)

For soft shoreline assessments, the method calls for taking a photo of the beach and close-ups of the dominant macroalgae types. This is the quicker assessment when compared to a rake survey. You are looking for an area with the following characteristics:

- A beach composed of sand or gravel.
- Avoid marshes (though you may use a rake from a marsh).
- Avoid rocky intertidal zones.
- Areas with attached brown macroalgae (rockweed, knotted wrack) are fine if the area also collects free-floating macroalgae.
- An area you know is **not raked** or otherwise maintained by municipalities or local residents.

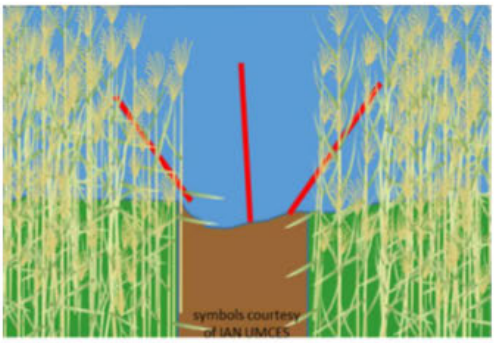
4.1.3 Guidance for Submerged Areas (Sampling from Boats, Docks, Jetties, etc.)

For sampling submerged areas, the method calls for tossing in a garden rake attached to a rope and slowly and steadily pulling in the rake. Two tosses are conducted in three directions, for a total of six tosses. A photo is taken of each rake, including when only mud is collected. Potential areas include:

- Marinas, docks, or jetties can be suitable locations, if their depth is representative of the overall area. Even deep boat slips can be acceptable as macroalgae tends to collect in the deeper locations. Avoid areas where prop scour is likely to push macroalgae away. If your rake toss looks similar to what you see in shallower areas, the areas should be suitable. *Note – when sampling from a dock, be considerate of private property: avoid areas where your actions may be misconstrued as potentially damaging to boats. In other words, choose an area of the dock where you have some room to move, not an area with little space between boats. Always check in with the office or property owner before sampling, to let them know you have permission to sample and so they know who you are and what you are doing.*
- Causeways, seawalls, and shorelines without a beach deemed safe to access are suitable sampling locations. Avoid areas scoured clean by the water flow (i.e., the mouth of a culvert). Be sure to choose areas where you will not catch brown macroalgae attached to rocks at the shoreline (rockweed, knotted wrack). We are interested in the beneficial shoreline macroalgae.
- Boat sampling is acceptable if the depth of the area is representative of the embayment. In other words, you should not sample in the deepest or the shallowest locations.

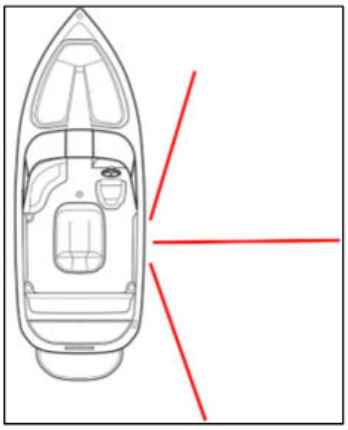
4.1.4 Examples of Sample Locations

When sampling from a dock, jetty, causeway, or other hardened shoreline, choose three locations and do two rake tosses from each location (red lines indicate direction and length of rake toss). Note that sampling is not done from the finger docks in the image below; these docks can be too skinny to safely accommodate two people and allow for proper framing of the photograph.



If you are in a location which inhibits moving around, do two rake tosses in each of three directions. For example, a kayak launch amidst a dense stand of *Phragmites* can provide limited access to the shoreline. In this case, two rakes tosses are directed straight out into the water, two upstream, and two downstream.

When sampling from a boat at anchor, we assume the boat is shifting slightly with the wind and current. You may do all six tosses from the same location in the boat, tossing the rake in different directions. However, if you feel that you are sampling the same location six times, you will need to shift to a new location on the boat between tosses. If your boat is drifting, you may toss in the same direction each time, as you will be floating over new substrate.



4.2 Preparation

- Ensure battery power and available storage is sufficient on camera or smartphone.
- Ensure battery power is sufficient on GPS unit or smartphone.
- Collect equipment and ensure all is in working order.
- Always carry a copy of this SOP and the relevant parameter-specific SOPs.
- Print out the "quick sheets" for relevant SOPs to use as a reminder in the field. Do not laminate these as you will want to add notes. A plastic page-protector taped close can be used to keep these sheets dry.

4.3 Field Collection and Processing

Sampling at each station should be quick. In field trials, the UWS Science Advisors completed sampling at a station in 10 to 15 minutes, though getting a rake hung up on a rock can increase the time needed. Soft shoreline (beach) areas can go even quicker. Please keep in mind this is a qualitative survey, so

spending additional time to quantify the macroalgae is not necessary. You are making a call of "not much here", "wow, that's a lot of macroalgae", or "this could be a problem, but I'm not sure." The first station may take a bit longer, as you get acquainted with the datasheet.

4.3.1 Option 1: Soft Shoreline Station (Beaches)

- Conduct the assessment within 3 hours of low tide (this gives you a 6-hour window).
- Complete the station information on the datasheet.
  - IMPORTANT: Record GPS points as decimal degrees (e.g. 41.56437 N, -71.87634 W). Please do not report GPS in hours and minutes. For example, a location with decimal degrees of 41.56437 N, -71.87634 W can also be reported in hours and minutes as 41° 33' 51.7314", -71° 52' 34.8234". Note that the numbers are different, decimal degrees are not just leaving out the symbols for hours (') and minutes ("). We ask for decimal degrees because hours and minutes do not translate well in a spreadsheet. If you do not understand this distinction, please ask an advisor to explain.
- Record the amount of macroalgae on the beach as "none", "some", or "lots".
  - None – essentially nothing on the beach, only attached macroalgae is present.
  - Some – ranges from a small bit of macroalgae on the beach to large wrack lines of macroalgae present on the beach. This is qualitative, the Monitoring Program Coordinator and UWS Science Advisors will review when comparing stations, so do not worry too much about what truly constitutes some versus lots.
  - Lots – covers > 50% of the beach. May be a thin covering, in thick wrack lines, or a thick layer covering the whole beach.
- Examine the macroalgae and use the guide to identify macroalgae morphology (hair-like, twig/leaf like, sheets) and color (green, other). You only need to record macroalgae that constitutes more than 10% of the macroalgae present on the beach.
- Take two overview photos, showing the overall appearance of the shoreline. One should include upland areas for context, the next should be slightly closer, showing macroalgae (or lack of macroalgae) on the beach (examples below).
  - Zoom in on the overview photo and confirm the beach is in focus (versus something in the background or foreground).
  - Do not submit any overview photos deemed unacceptable.
  - The two overview photos should be sufficient. However, if lighting or size of the station requires, you may take multiple photos.
  - Record an identifier for the photo on the datasheet. For a camera, this may be the filename. For a smartphone, record the time associated with the photo; this can be located by viewing the photo, the time the photo was taken should be on the screen.

Example overview photos:

Wide scale overview shot of station X.

Closer overview shot of station X.

Wide scale overview shot of station Y.

Closer overview shot of station Y.

- For the dominant macroalgae types, take a close-up photo of each macroalgae.
  - This is a rough assessment of the dominant macroalgae types; you DO NOT need to photograph each type of macroalgae present on the beach.
  - Add something to the photo to provide a size reference. This could be a ruler, your foot, a brick, your keys, etc. It needs to be something with a known size (not a stick you pick up, which can be any size).
  - Zoom in on the macroalgae photo and confirm the macroalgae is in focus (versus something in the background or foreground).
  - Be sure that the lighting allows for realistic colors in the photo.
  - The photo should not include the shadow of the photographer.
  - Record an identifier for the photo on the datasheet. For a camera, this may be the filename. For a smartphone, record the time associated with the photo; this can be located by viewing the photo, the time the photo was taken should be on the screen.

Example close-up photo of macroalgae:

Close-up of macroalgae at station X.

Close-up of macroalgae at station Y.

4.3.2 Option 2: Submerged Station

- *Note* – a YouTube video demonstrating how to properly toss a rake is available at: https://www.youtube.com/watch?v=yMqpSaA6ZWY or find the video by searching for "macroalgae rake toss."
- The timing of sampling is not critical. The only criterion is that low tide has not exposed the sediment at the sampling station
- Complete the station information on the datasheet. An example of a completed datasheet is included on page 14 of this SOP.
    - IMPORTANT: Record GPS points as decimal degrees (e.g. 41.56437 N, -71.87634 W). Please do not report GPS in hours and minutes. For example, a location with decimal degrees of 41.56437 N, -71.87634 W can also be reported in hours and minutes as 41° 33' 51.7314", -71° 52' 34.8234". Note that the numbers are different, decimal degrees are not just leaving out the symbols for hours (') and minutes ("). We ask for decimal degrees because hours and minutes do not translate well in a spreadsheet. *If you do not understand this distinction, please ask the UWS Monitoring Program Coordinator to explain.*
- Select a sampling station at your location.
    - If the station allows, conduct 2 rake tosses at each of 3 different spots. An example would be moving to three different areas on a dock. See Section 4.1.4 (page 5) for diagrams of where to sample.
    - If the station does not allow you to move around, conduct 2 tosses in each of 3 different directions. An example would be an opening in a marsh that allows access to the embayment. The rake is tossed upstream, downstream, and straight out into the water. See Section 4.1.4 for diagrams of where to sample.

- Confirm that the line is securely attached to the rake. Place your foot on the end of the rope, to keep it from going into the water.
- Face the embayment and hold the rake such that your dominant hand is at the end of the rake (ready to push the rake).
- Push the rake out into the water a distance of ~2 rake lengths. The motion is similar to an underhand slow pitch, rather than a javelin throw.
- If the toss is too short or too long, bring back and try again.
- The tines of the rake should be downward. If the rake lands with tines up, bring back and try again.
- After a successful toss, allow rake to settle on the floor then ***slowly and steadily*** pull the line so the teeth of the rake drag on the embayment bottom.
    - If the rake gets hooked on a rock or other object, try taking up the slack in the rope and pulling up on the rake, or moving to the left and to the right. If you feel that macroalgae was likely dislodged, try tossing again. For some rocks, freeing the rake is easy enough that macroalgae is mostly intact on the rake. For these cases, you do not need to toss again.
    - When removing the rake from the water, do so such that macroalgae does not fall off of the rake.
    - Make certain that you DO NOT pick up macroalgae removed from the rake on a previous toss. Be aware of where you discard macroalgae from the rake so that you are not capturing the same macroalgae with each toss.
- Record the amount of macroalgae on the rake as “none”, “some”, or “lots” (using sample photos shown below to assist).
    - None – no macroalgae on the rake.
    - Some – some tines are still bare.
    - Lots – all tines hold macroalgae. This includes anything from a thin coat of a slimy macroalgae to thick clumps of a wiry or leafy macroalgae.
    - If you get a lot of mud, put into a bucket or bin and rinse; mud that clumps on the rake is often being held together by fine macroalgae
- Take a photo of the rake (and macroalgae) after each toss.
    - Include all of the rake tines and macroalgae in the photo. If a portion of the rake tines is not included, take another photograph. You will want to be about 4 feet from the rake. *Do not get too close* – some cameras do not focus at shorter distances. With the resolution required, zooming in to look at macroalgae can be done on the computer. You do not need to get super close to get a good shot of the macroalgae, further back is better.
    - Frame the shot such that the light is behind the photographer (or at a slight angle), so that the light is good and the photographer’s shadow is not cast on the macroalgae.
    - Be aware of the background and change your location for the photo as needed. Light colors in the background make the macroalgae look darker; avoid light backgrounds (e.g. a white boat).
    - Zoom in on the photo and confirm the macroalgae is in focus (versus something in the background or foreground).

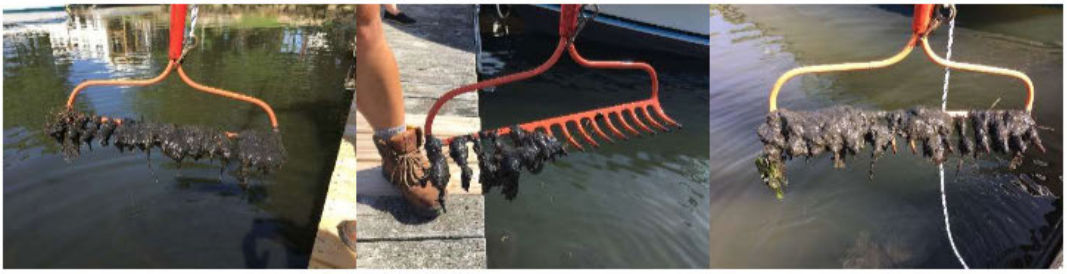
- Be sure that the lighting allows for realistic colors in the photo.
- Record an identifier for the photo on the datasheet. For a camera, this may be the filename. For a smartphone, record the time associated with the photo; this can be located by viewing the photo, the time the photo was taken should be on the screen.

➢ Sort through the macroalgae and use the guide to identify macroalgae morphology (hair-like, twig/leaf like, sheets) and color (green, other). You only need to record macroalgae that constitutes more than 10% of the macroalgae present on the rake.

Example photos of rakes:

Station 1: Wequetequock Cove, Stonington Marina, 7/13/2016

Lots Some Lots



Some Some Some

Station 2: Wequetequock Cove, kayak launch near Saltwater Farm Vineyard, 7/13/2016

Some Some Some

Some Some Lots

Station 3: Wequetequock Cove, Elihu Island causeway, 7/13/2016

Overview – Lots Lots

Close-up of dominant macroalgae (all beach looked like this photo, only 1 photo necessary).

The macroalgae collected on the soft shoreline at Elihu Island causeway is characterized as "lots." To verify that it represents the area, we also tossed a rake off the causeway, about midway between the mainland and the island. Each toss had "lots," confirming the beach survey was indeed representative. Eelgrass is visible on these rakes and was visible on the beach. The red branching macroalgae on the rakes was not a large component of what was on the beach. It is fine if the macroalgae composition varies, we are most interested in the amount of macroalgae.

Wequetequock Cove, Elihu Island causeway, mid-embayment, 7/13/2016

4.4 Sample Storage

Not applicable.

4.5 Laboratory Analysis

Not applicable.

5 TROUBLESHOOTING / HINTS

- Organize all volunteers well before sampling events.
- Check tide information before initiating the surveys.
- Bring backup rake and line, if possible.
- Always carry a copy of this SOP and the relevant parameter-specific SOPs.
- Print out the "quick sheets" for relevant SOPs to use as a reminder in the field. Do not laminate these as you will want to add notes. A plastic page-protector taped close can be used to keep these sheets dry.

6 DATA PROCESSING AND STORAGE

The monitoring group is responsible for obtaining data, entering data into the UWS data template, and delivering the data to the UWS Monitoring Program Coordinator.

The monitoring group is responsible for assuring that the correct unique station ID assigned by the UWS is properly matched with the local organizations station ID codes. Both codes (monitoring group's station code and UWS unique station ID) will be entered into the data template, along with the GPS coordinates.

Macroalgae assessment data and photos will be submitted onto a SharePoint platform. This will allow for consistent formatting in the data, easy transference and a storage system for the photos, and immediate access to the photos for the Monitoring Program Coordinator and UWS Scientific Advisors. Once uploaded by UWS participants, the data will be downloaded and stored by Save the Sound.

7 REFERENCES

None

8 Quick Sheet – Qualitative Macrophytes

Method Overview

- Sample 3 days during the 3-week period starting July 15 and ending August 7. Try to sample once per week. If this is not possible, please sample such that you maximize the days between sampling. All three days cannot be sampled in the same 7-day window. Two sample days or a date slightly outside of the date criteria may be sufficient in the event of unforeseen complications. This decision will be made by the Monitoring Program Quality Assurance Officer and UWS Science Advisor(s).
- For soft shorelines, take an overview photo of the area, focused on the beach (not the water). Take a close-up photo of each of the dominant macroalgae types on the beach. Complete the datasheet.
- For sampling submerged areas, toss the rake 6 times, 2 tosses in each of 3 directions (if limited by access to a single point) or 3 areas (if you have room to move to another location at the station). Photograph each rake, even empty rakes. Complete the datasheet.
- Enter the data into the data entry excel template and upload your photos to the SharePoint platform.

Preparation

- Gather field equipment.
- Ensure battery power and available storage is sufficient on camera or smartphone.
- Ensure battery power is sufficient on GPS unit or smartphone.
- Always carry a copy of this SOP and the relevant parameter-specific SOPs.
- Print out the "quick sheets" for relevant SOPs to use as a reminder in the field. Do not laminate these as you will want to add notes. A plastic page-protector taped close can be used to keep these sheets dry.

Field Collection and Processing

Option 1: Soft Shoreline Station (Beaches)

- Conduct the assessment within 3 hours of low tide (this gives you a 6-hour window).
- Complete the station information on the datasheet. IMPORTANT: Record GPS points as decimal degrees (e.g. 41.56437 N, -71.87634 W).
- Take two overview photos, showing the overall appearance of the shoreline. One should include upland areas for context, the next should be slightly closer, showing macroalgae (or lack of macroalgae) on the beach (examples below).
- For the dominant macroalgae types, take a close-up photo of each macroalgae.
- Record the amount of macroalgae on the beach as "none", "some", or "lots".
  - None – essentially nothing on the beach, only attached macroalgae is present.
  - Some – ranges from a small bit of macroalgae on the beach to large wrack lines of macroalgae present on the beach. This is qualitative, the science advisors will review when comparing stations, so do not worry too much about what truly constitutes some versus lots.
  - Lots – covers > 50% of the beach. May be a thin covering, in thick wrack lines, or a thick layer covering the whole beach.
- Examine the macroalgae and use the guide to identify macroalgae morphology (hair-like, twig/leaf like, sheets) and color (green, other). You only need to record macroalgae that constitutes more than 10% of the macroalgae present on the beach.
- Remember – we are ***looking for*** large amounts of seaweed. If there is nothing on the beach, but you see lots of seaweed (that are not the beneficial brown seaweed) in the water, then try a rake toss in

the water.

Option 2: Submerged Station

- The timing of sampling is not critical. The only criterion is that low tide has not exposed the sediment at the sampling station.
- *Note* – a YouTube video demonstrating how to properly toss a rake is available at: https://www.youtube.com/watch?v=yMqpSaA6ZWY.
- Complete the station information on the datasheet. IMPORTANT: Record GPS points as decimal degrees (e.g. 41.56437 N, -71.87634 W).
- Confirm that the line is securely attached to the rake. Place your foot on the end of the rope, to keep it from going into the water. Face the embayment and hold the rake such that your dominant hand is at the end of the rake (ready to push the rake). Push the rake out into the water a distance of ~2 rake lengths. The motion is similar to an underhand slow pitch, rather than a javelin throw.
  - If the toss is too short or too long, bring back and try again.
  - The tines of the rake should be downward. If the rake lands with tines up, try again.
- After a successful toss, allow rake to settle on the floor then ***slowly and steadily*** pull the line so the teeth of the rake drag on the embayment bottom.
  - If the rake gets hooked on a rock or other object, try taking up the slack in the rope and pulling up on the rake, or moving to the left and to the right. If you feel that macroalgae was likely dislodged, try tossing again.
  - When removing the rake from the water, do not let macroalgae fall off of the rake.
  - Make certain that you DO NOT pick up macroalgae removed from the rake on a previous toss.
  - If you get a lot of mud, put into a bucket or bin and rinse; mud that clumps on the rake is often being held together by fine macroalgae.
- Take a photo of the rake (and macroalgae) after each toss.
  - Include all of the rake tines and macroalgae in the photo. If a portion of the rake tines is not included, take another photograph. You will want to be about 4 feet from the rake. *Do not get too close* – some cameras do not focus at shorter distances. With the resolution required, zooming in to look at macroalgae can be done on the computer. You do not need to get super close to get a good shot of the macroalgae, further back is better.
  - Frame the shot such that the light is behind the photographer.
  - Be aware of the background and change your location for the photo as needed. Light colors in the background make the macroalgae look darker; avoid light backgrounds (e.g. a white boat).
  - Zoom in on the photo and confirm the macroalgae is in focus (versus something in the background or foreground).
  - Be sure that the lighting allows for realistic colors in the photo.
  - Record an identifier for the photo on the datasheet. For a camera, this may be the filename. For a smartphone, record the time associated with the photo; this can be located by viewing the photo, the time the photo was taken should be on the screen.
- Record the amount of macroalgae on the rake as “none”, “some”, or “lots”.
  - None – no macroalgae on the rake.
  - Some – some tines are still bare.
  - Lots – all tines hold macroalgae. This includes anything from a thin coat of a slimy macroalgae to thick clumps of a wiry or leafy macroalgae.
  - If you get a lot of mud, put into a bucket or bin and rinse; mud that clumps on the rake is often being held together by fine macroalgae
- Examine the macroalgae and use the guide to identify macroalgae morphology (hair-like, twig/leaf like, sheets) and color (green, other). You only need to record macroalgae that constitutes more

than 10% of the macroalgae present on the rake.

Appendix A-7

POINT OF CONTACT

NAME: Peter Linderoth, Save the Sound, Director of Water Quality
ADDRESS: 1385 Boston Post Rd, 2nd Floor, Larchmont, NY 10538
EMAIL: plinderoth@savethesound.org
PHONE: 914-381-3140 ext.200

I. OBJECTIVE:

Determine the ammonia, nitrite, nitrate, total dissolved nitrogen, and orthophosphate concentrations in the water column.

II. OVERVIEW:

Water samples are collected from the surface of the water column. This water is filtered through GF/F filters and delivered into clean HDPE bottles. The samples are analyzed on a Lachat 8500 QuikChem®Autoanalyzer (manifold reaction unit, colorimetric detector, Omnion software data system) or SEAL Analytical AQ400 Discrete Analyzer (colorimetric method, AQ software system with QCProTM Data Quality Assurance System).

IV. MATERIALS AND EQUIPMENT:

A. FIELD COLLECTION AND STORAGE OF SAMPLES

- Plastic bottles, 60 mL, HDPE, (Fisher Scientific Catalog Number: 03-313-11B)
- Plastic bottles, 1 L, HDPE, (Fischer Scientific Catalog Number: 02-925-3E)
- Glass Fiber Filters (GF/F), 2.5 cm diameter, retains particles down to 0.7 µm, (Fisher Scientific Catalog Number: 09-874-64; Whatman Number:1825-025)
- Filter holders, 2.5 cm (*preferred*: Pall brand, 25 mm Easy Pressure Syringe Filter Holder, Delrin Plastic; *second choice*: Millipore Swinnex Filter Holder, 25 mm polypropylene with silicon gasket, Fisher Scientific Catalog Number: SX00 025 00; Millipore Number:SX0002500)
- Forceps for handling filters
- Acid Bath: 1 N (Certified) hydrochloric acid (Fisher Scientific Catalog Number: SA48-4)
- 2 L of ASTM type I (ultrapure) for field blank

Equipment for getting water samples:

- option 1 – Master flex pump with silicone tubing sufficient for sample depth
- option 2 – Homemade sampling poles with 1 L Bottle

Equipment for delivering sample through filter to 60 mL bottles:

- option 1 – Masterflex pump with silicone tubing
- option 2 – 60 mL syringe

V. METHODS

A. PREPARATION

- Check that the pump or other sampling equipment are operational
  Prepare the sample bottles:
  - Wear powder-free nitrile gloves
  - Rinse 1 L bottles with ultrapure, ASTM type 1 (ultrapure) water. Allow to dry and store with caps on
  - If 60 mL HDPE bottles are new and un-used, rinse the vials three times with ultrapure, ASTM type I (ultrapure) water. Allow to dry and store with caps on
  - If 60 mL HDPE bottles have been used, acid wash the bottles. Acid washing entails soaking the bottles in a 1 N hydrochloric acid bath for 60 minutes followed by rinsing three times with ultrapure, ASTM type I (ultrapure) water. Allow to dry and store full of ultrapure, ASTM type 1 (ultra-pure) water with caps on

B. FIELD COLLECTION AND STORAGE OF SAMPLES

A slightly different procedure is used based on the sampling method. Choose the protocols for your sampling method

Masterflex Pump

1. Rinse the sampling equipment with sample water. This involves rinsing with three times the volume of the sampling device. Place the intake 0.5 m below the surface, allow the pump to run long enough to pass a minimum of three times the volume of the tubing through the system. Discharge this water over the boat, do not collect.

2. Assemble the filtering mechanism. Connect the filter holder (with filter loaded into the holder) to the pump. Change filter if needed during collection.
3. Rinse the sample bottles with water from target sampling depth. Cap the bottle and shake to rinse. Discard the sample used as a rinse. Repeat three times for each bottle.
4. Fill sample bottle with water from target sampling depth.
5. Sample bottle is immediately stored in cooler full of ice for transport to lab.

Note: Sample(s) can be collected in either the 1 L bottle or three 60 mL HDPE bottles. If only filling the 1 L bottle, filtering can occur when 60 mL bottles are filled as seen lower in this SOP under sample preparation. If filling 60 mL bottles in the field, only collect up to 50 mL in the bottle.

Note: About mid-way through the sampling day, perform a field blank. Follow the procedures for sampling above, but use ASTM Type I (ultrapure) water brought out on the boat in place of the field water.

Homemade Sampling Poles with 1 L Bottle

A sampling pole can be fabricated by a member of your organization. The key criteria for acceptability is the ability to sample from a specific depth without contaminating the sample. The method involves reaching into the water with the sample bottle inverted and full of air, then righting the bottle and allowing it to fill at the appropriate depth.

Homemade poles will typically work only for 0.5 m below the surface; deeper depths require alternate methods of sampling.

- Remove the cap from the bottle.
- Rinse the bottle three times with surface water. Fill bottle, cap bottle, invert, then discard rinse.
- Holding the bottle with the mouth down, lower it to 0.5 m below the surface.
- Invert the bottle so that air empties out of the bottle and the bottle fills with water.
- Bring to the surface and cap.
- Sample bottle is immediately stored in cooler full of ice until being filtered.

Note – About mid-way through the sampling day, perform a field blank. Follow the procedures for sampling above, but use ASTM Type I (ultrapure) Water brought out on the boat in place of the field water.

The following steps apply to when using a Masterflex for sample preparation:

Masterflex Pump – after collecting sample in 1 L bottle and storing on ice

1. Rinse the sampling equipment with sample water. This involves rinsing with three times the volume of the sampling device. Place the intake into the sample bottle, allow the pump to run long enough to pass a minimum of three times the volume of the tubing through the system. Discharge this water, do not collect.
2. Assemble the filtering mechanism. Connect the filter holder (with filter loaded into the holder) to the pump. Run approximately 15 mL through the filter before next step.
3. Rinse the sample bottles. Deliver a small volume of the filtered sample into the sample bottles. Cap the vials and shake to rinse. Discard the sample used as a rinse. Repeat for a total of three small volume rinses per bottle.
4. Deliver between 45 mL and 50 mL of sample (through the filter) to the bottles. Be sure to keep the volume in the bottle under 50 mL, this head space will allow for expansion during freezing. Change the filter if needed.
5. Store the bottles *upright* in the freezer (- 20° C).

A sample, replicate, and sample in reserve are collected from each station.

The following steps apply when using a syringe for sample preparation:

1. Rinse the sampling equipment with sample water. This involves rinsing with three times the volume of the sampling device.
2. Assemble the filtering mechanism. Connect the filter holder (with filter loaded into the holder). Rinse the 60 mL syringe with 5 mL of sample water. Repeat for a total of three rinses. Fill the 60 mL syringe with sample water.

3. Rinse the HDPE bottles. Deliver a small volume of the filtered sample into the HDPE bottles. Cap the bottles and shake to rinse. Discard the sample used as a rinse. Repeat for a total of three small volume rinses per bottle.
4. Deliver between 45 mL and 50 mL of sample (through the filter) to the bottles. Be sure to keep the volume below 50 mL, this head space will allow for expansion during freezing. Change the filter as needed.
5. Upon return to the lab, store the bottles in the freezer (- 20° C).

A sample, replicate, and sample in reserve are collected at each station.

C. LABORATORY ANALYSIS

- The nutrients are analyzed on a Lachat 8500 QuikChem®Autoanalyzer or SEAL Analytical AQ400 Discrete Analyzer or similar instrument, at the Interstate Environmental Commission (IEC). Instrument operations are detailed in the IEC Laboratory SOP which is contained in the UWS QAPP.

VI. TROUBLE SHOOTING / HINTS

- Avoid contaminating the samples – do not touch: the insides of the bottle caps, the mouth of the bottles, the insides of the graduated cylinders, the filter pads
- Two people working in tandem will speed the process. One person focuses on filtering while the other handles the sample bottles and filters. The person filtering the sample can lend a hand when s/he gets ahead of the sample handler.

VII. DATA PROCESSING AND STORAGE

- Enter the data on the field sheet. Be sure to fill out the data sheet completely.
- Enter data when returned from the lab into the Excel template.

VIII. QUICK SHEET

Refer to the SOP for details, this list is only a reminder!!

FIELD

Rinse everything three times before collecting sample

Store in cooler on ice while in the field

STORAGE

1 L sample bottle remains on ice immediately after collection. Filtering must commence the same day of sampling.

Store samples *upright* in the freezer

Separate replicates a and b (samples to be analyzed) from c (sample held in reserve)

ANALYSIS

Follow any potential guidelines established for analytical lab

Appendix A-8

Standard Operating Procedure
Total Nitrogen and Total Phosphorous
Sample Collection

revised March 2023
Page 1 of 6

POINT OF CONTACT

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I. OBJECTIVE:

Determine the dissolved total nitrogen and total phosphorous concentrations in the water column.

II. OVERVIEW:

Water samples are collected from the surface in the water column. The samples are analyzed on a Lachat 8500 QuikChem®Autoanalyzer (manifold reaction unit, colorimetric detector, Omnion software data system) or SEAL Analytical AQ400 Discrete Analyzer (colorimetric method, AQ software system with QCProTM Data Quality Assurance System).

III. SOURCE:

IV. MATERIALS AND EQUIPMENT:

A. FIELD COLLECTION AND STORAGE OF SAMPLES

- Plastic bottles, 60 mL, HDPE, (Fisher Scientific Catalog Number: 03-313-11B)
- Plastic bottles, 1 L, HDPE, (Fischer Scientific Catalog Number: 02-925-3E)
- Acid Bath: 1 N (Certified) hydrochloric acid (Fisher Scientific Catalog Number: SA48-4)
- 2 L of ASTM type I (ultrapure) for field blank

Equipment for getting water samples:

- option 1 – MasterFlex pump with silicone tubing sufficient for sample depth
- option 2 – Homemade sampling poles with 1 L Bottle

Equipment for delivering sample to 60 mL bottles:

- option 1 – MasterFlex pump with silicone tubing
- option 2 – 60 mL syringe

B. LABORATORY ANALYSIS

Included in IEC Lab SOPs in QAPP.

V. METHODS

A. PREPARATION

- Check that the pump or other sampling equipment are operational
- Prepare the sample bottles:
  - Wear powder-free nitrile gloves
  - Rinse 1 L bottles with ASTM type I (ultrapure) Allow to dry and store with caps on.
  - If 60 mL HDPE bottles are new and un-used, rinse the vials three times with ultrapure, ASTM type I water. Allow to dry and store with caps on.
  - If 60 mL HDPE bottles have been used, acid wash the bottles. Acid washing entails soaking the bottles in a 1 N hydrochloric acid bath for 60 minutes followed by rinsing three times with ultrapure, ASTM type I water. Allow to dry and store full of ASTM type 1, ultrapure, water with caps on.

B. FIELD COLLECTION AND STORAGE OF SAMPLES

A slightly different procedure is used based on the sampling method. Choose the protocols for your sampling method.

Masterflex Pump

1. Rinse the sampling equipment with sample water. This involves rinsing with three times the volume of the sampling device and bottle. Place the intake into the target sampling depth, allow the pump to run long enough to pass a minimum of three times the volume of the tubing through the system. Discharge this water over the boat, do not collect.
2. Rinse the sample bottle with water from target sampling depth. Cap the bottle and shake to rinse. Discard the sample used as a rinse. Repeat three times.
3. Fill sample bottle with water from target sampling depth.
4. Sample bottle is immediately stored in cooler full of ice for transport to lab.

Note: Sample(s) can be collected in either the 1 L bottle or three 60 mL HDPE bottles. If filling 60 mL bottles in the field, only collect up to 50 mL in the bottle.

Note: About mid-way through the sampling day, perform a field blank. Follow the procedures for sampling above, but use ASTM type I (ultrapure) out on the boat in place of the field water.

Homemade Sampling Poles with 1 L Bottle

A sampling pole can be fabricated by a member of your organization. The key criteria for acceptability is the ability to sample from a specific depth without contaminating the sample. The method often involves reaching into the water with the sample bottle inverted and full of air, then righting the bottle and allowing it to fill at the appropriate depth.

Homemade poles will typically work only for 0.5 m below the surface; deeper depths require alternate methods of sampling.

- Remove cap from bottle.
- Rinse the bottle three times with surface water. Fill bottle, cap bottle, invert, then discard rinse.
- Holding the bottle with the mouth down, lower it to 0.5 m below the surface.
- Invert the bottle so that air empties out of the bottle and the bottle fills with water.
- Bring to the surface and cap.
- Sample bottle is immediately stored in cooler full of ice until being filtered.

Note – About mid-way through the sampling day, perform a field blank. Follow the procedures for sampling above, but use ASTM type I (ultrapure) brought out on the boat in place of the field water.

The following steps apply when using a Masterflex for sample preparation:

Masterflex Pump – after collecting sample in 1 L bottle and storing on ice

1. Rinse the sampling equipment with sample water. This involves rinsing with three times the volume of the sampling device. Place the intake into the sample bottle, allow the pump to run long enough to pass a minimum of three times the volume of the tubing through the system. Discharge this water, do not collect.

2. Rinse the sample bottles. Deliver a small volume of the sample into the sample bottles. Cap the vials and shake to rinse. Discard the sample used as a rinse. Repeat for a total of three small volume rinses per bottle.
3. Deliver between 45 mL and 50 mL of sample to the bottles. Be sure to keep the volume in the bottle under 50 mL, this head space will allow for expansion during freezing. Change the filter if needed.
4. Store the bottles *upright* in the freezer (- 20° C).

A sample, replicate, and sample in reserve are collected from for station.

The following steps apply when using a syringe for sample preparation:

1. Rinse the sampling equipment with sample water. This involves rinsing with three times the volume of the sampling device.
2. Rinse the 60 mL syringe with 5 mL of sample water. Repeat for three rinses. Fill the 60 mL syringe with sample water.
3. Rinse the HDPE bottles. Deliver a small volume of the sample into the HDPE bottles. Cap the bottles and shake to rinse. Discard the sample used as a rinse. Repeat for a total of three small volume rinses per bottle.
4. Deliver between 45 mL and 50 mL of sample to the bottles. Be sure to keep the volume below 50 mL, this head space will allow for expansion during freezing.
5. Upon return to the lab, store the bottles in the freezer (- 20° C).

A sample, replicate, and sample in reserve are collected at each station.

C. LABORATORY ANALYSIS

The nutrients are analyzed on a Lachat 8500 QuikChem®Autoanalyzer or SEAL Analytical AQ400 Discrete Analyzer or similar instrument, at the Interstate Environmental Commission (IEC). Instrument operations are detailed in the IEC Laboratory SOP which is contained in the UWS QAPP.

VI. TROUBLE SHOOTING / HINTS

- Avoid contaminating the samples – do not touch: the insides of the vial caps, the mouth of the vials, the insides of the graduated cylinders.
- Two people working in tandem will speed the process.

VII. DATA PROCESSING AND STORAGE

- Enter the data on the field sheet. Be sure to fill out the data sheet completely.
- Enter data when returned from lab into the Excel template.

VIII. QUICK SHEET

Refer to the SOP for details, this list is only a reminder!!

FIELD

Rinse everything three times before collecting sample (pump / sample collection vessel; vials)

store in cooler on ice while in the field

STORAGE

Store samples *upright* in the freezer

Separate replicates a and b (samples to be analyzed) from c (sample held in reserve)

ANALYSIS

Follow any potential guidelines established for analytical lab

Appendix A-9

POINT OF CONTACT

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PHONE: 914-381-3140

I. OBJECTIVE:

Determine the dissolved oxygen (DO) concentration and saturation in addition to light over a period of time at select intervals.

II. OVERVIEW:

Continuous dissolved oxygen sampling instruments – dissolved oxygen, conductivity, light, and barometric pressure loggers – are deployed in the field to log light, dissolved oxygen and saturation. Light, Dissolved oxygen and conductivity are logged at approximately 0.5 meters off the bottom and barometric pressure is logged in a secure location near the other loggers.

III. SOURCE:

IV. MATERIALS AND EQUIPMENT:

A. CONTINUOUS LOGGING STATIONS

- Dissolved oxygen logger (Onset HOBO U26)
- Barometric pressure logger (Onset HOBO U20L-01)
- Conductivity Logger (Star-Oddi DST-CT, 13-50 mS/cm range)
- Light logger (ONSET UA-002-08)
- Aquarium water pump for inter-comparison of loggers and sonde
    - Aquarium air stone for inter-comparison of loggers and sonde
- Sodium sulfite DO calibration solution (Onset HOBO U26-CAL-SOL)
- Ice/tap water for adjusting conductivity in water bath
- Multiparameter sonde (YSI EXO1 or YSI ProDSS) with DO and conductivity sensors
- Conductivity Standard (YSI: 50,000 µS/cm) for calibrating sonde
- Q-tips for cleaning inside of anti-fouling guard of DO loggers

B. LABORATORY ANALYSIS

No laboratory analysis.

V. METHODS

A. Logger Inter-comparison (Prior to Field Deployment)

- Check that all sampling equipment are operational and ready for deployment.
- Calibrate conductivity and DO on multiparameter sonde to manufacturer recommendations the day before or morning of this logger comparison.
- Calibrate all loggers according to manufacturer recommendations the day before or morning of this logger comparison.
- Synchronize loggers and multiparameter sonde to same time. Set loggers to 15-minute interval readings (:00, :15, :30, :45).
- Prepare a water bath with water similar to deployment stations; enough volume to fit all loggers for comparison and sonde.
- Place DO and conductivity loggers ready for deployment in the water bath and note the time the loggers will be taking readings.
- Run the aquarium pump to keep water flowing in water bath. Do not allow bubbles to come into direct contact with sensors end of the loggers or sonde.
- Record DO and conductivity readings with the multiparameter sonde at the same time the loggers record data.
- Add ice or tap water to adjust the salinity concentration in the water bath. Ensure that the salinity (conductivity) in the water bath does not go out of the logger's conductivity range.
- Record DO and conductivity readings with the multiparameter sonde at the same time the loggers record data.
- Add sodium sulfite solution to lower the DO level in the water bath. This should be done slowly
    - NOTE: Do not leave equipment in this low-oxygen solution for too long. Two readings will suffice
- Record DO and conductivity readings with the multiparameter sonde at the same time the loggers record data
- Logger data is retrieved from loggers and stored with multiparameter sonde readings. The salinity correction will need to be applied through the HOBOware software for correct DO concentration

B. Logger Inter Comparison (After Field Deployment)

- Bring all loggers back to office or lab.
- Prepare a water bath with water similar to deployment stations; enough volume to fit all loggers for comparison and sonde.
- Place DO and conductivity loggers from the field in the water bath without cleaning any fouling and note the time the loggers will be taking readings.
- Run the aquarium pump to keep water flowing in water bath. Do not allow bubbles to come into direct contact with sensors end of the loggers or sonde.
- Record DO and conductivity readings with the multiparameter sonde at the same time the loggers record data.
- Clean all sensors before proceeding to the next steps.
- Place DO and conductivity loggers ready for deployment in the water bath and note the time the loggers will be taking readings.
- Run the aquarium pump to keep water flowing in water bath. Do not allow bubbles to come into direct contact with sensors end of the loggers or sonde.
- Record DO and conductivity readings with the multiparameter sonde at the same time the loggers record data.
- Add ice or tap water to adjust the salinity concentration in the water bath. Ensure that the salinity (conductivity) in the water bath does not go out of logger's conductivity range.
- Record DO and conductivity readings with the multiparameter sonde at the same time the loggers record data.
- Add sodium sulfite solution to lower the DO level in the water bath. This should be done slowly
    - NOTE: Do not leave equipment in this low-oxygen solution for too long. Two readings will suffice.
- Record DO and conductivity readings with the multiparameter sonde at the same time the loggers record data.
- Logger data is retrieved from loggers and stored with multiparameter sonde readings. The salinity correction will need to be applied through the HOBOware software for correct DO concentration.

C. FIELD DATA COLLECTION

1. Logger Deployment and Data Collection

- Dissolved oxygen, light, and conductivity loggers are deployed at approximately 0.5 m off bottom. Loggers need to be actively logging when deployed to obtain initial sonde/logger comparison in field. The bottom light logger is attached above the dissolved oxygen and conductivity loggers. A second light logger is attached above the bottom light logger for

reference readings. The distance between the two is recorded and dependent on expected conditions over the deployment.

- Barometric pressure logger is deployed above water at a secure and close location.
    - Logger needs to be actively logging prior to deployment
- All loggers are set to record at 15-minute intervals (:00, :15, :30, :45).
- Station visits are required every 7-10 days for cleaning and comparison with multiparameter sonde.
    - Conductivity, dissolved oxygen, and barometric pressure are all recorded at the station at 0.5 m off bottom using sonde and handheld
    - Readings must coincide with a known time the loggers are recording data
    - Record readings on field data sheet
- Retrieve submerged loggers and clean all fouling organisms.
- Couple loggers with data retrieval method of choice and collect data for storage.
- Repeat the comparison sampling procedure after the loggers are cleaned and redeployed.
- Bring data retrieval instrument to the laboratory/office and upload data to analysis software provided by manufacturer.

IX. QUICK SHEET

Refer to the SOP for details, this list is only a reminder!!

INTER COMPARISON

Zero DO solution needs to be added very slowly to avoid adding too much. Obtain a full reserve of water for use in the event the DO plummets quickly and below the preferred accuracy range of the instruments.

FIELD

Secure all loggers with backup ropes and security measures. All loggers need to be set to 15-minute intervals. Inter comparison readings are taken before and after cleaning loggers of fouling organisms. The bottom light logger is deployed above the setup to avoid shadowing by deployment materials. The distance between the light loggers must be recorded and maintained during deployment.

STORAGE

Data sheets are filed and digital logs of data are stored on local computer/server prior to being sent to Save the Sound.

ANALYSIS

Upload data from field onto manufacturer software for analysis.

Appendix A-10

POINT OF CONTACT

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I. OBJECTIVE:

To quantify the percent coverage of macrophytes and determine bottom type at select locations.

II. OVERVIEW:

An underwater camera (video or still) is used to capture images of the bottom in the area of a water quality station. Bottom type is identified and the percent cover of macrophytes is calculated.

III. SOURCE:

IV. MATERIALS AND EQUIPMENT:

A. FIELD COLLECTION AND STORAGE OF SAMPLES

- camera (e.g. SeaViewer video system, still camera)
- method for keeping camera a set distance from the bottom (to maintain consistent areal size in the field of vision)
- GPS unit

B. LABORATORY ANALYSIS

not applicable

V. METHODS

A. PREPARATION

- check the charge on the GPS battery (SeaViewers has built-in GPS)
- check the charge on the camera battery
- check the camera system for proper functioning

- check the deployment rig for the camera system (must have a size reference in the field of vision)

B. FIELD COLLECTION AND STORAGE OF SAMPLES

- samples stored on the SD card of the camera
- collect between 20 and 40 bottom images – in areas with greater heterogeneity, collect more samples (~40), if an area is fairly homogenous (e.g. sand, oyster, cobble) you may collect fewer (~20)

C. LABORATORY ANALYSIS

not applicable

VI. TROUBLE SHOOTING / HINTS

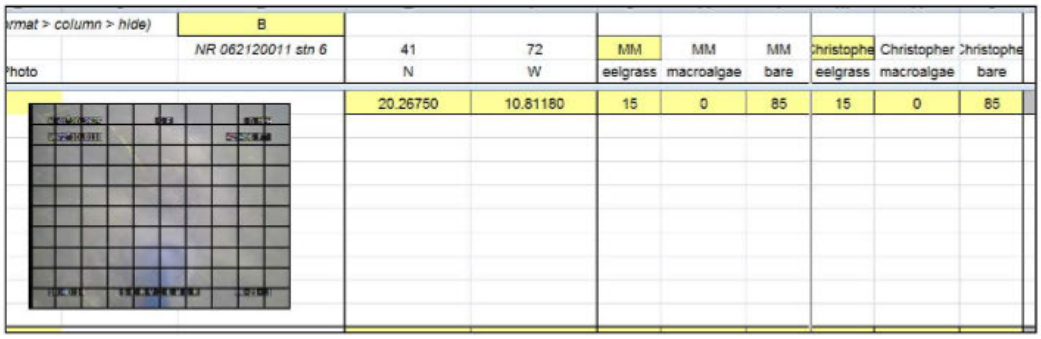
- for the video system – keep the speed of the boat low, so as not to put too much tension on the pole (the pole will snap at high speeds)

VII. DATA PROCESSING AND STORAGE

- Video (or still photos) will be downloaded the following day and stored in a cloud-service platform (providing back-up on multiple computers and the remote server).
- For video - A trained analyst will watch the video and do a screen-capture for all instances where the base of the pole is resting on the bottom (Figure 1).
- The bottom images will be pasted into the Excel camera work template (Figure 2).
- A 100-cell grid is overlaid on the image in cases where the coverage is not 0 % or 100%. The first analyst reviews the image and enters the % cover in three categories: eelgrass, macroalgae, bare sediment. The first analyst also enters the GPS coordinates, when available. The first analyst hides their columns of data, so that other analysts cannot see the first set of estimates.
- A second analyst reviews the images and makes an independent assessment of percent cover. The second analyst also checks the GPS coordinate data entry. The second analyst hides their columns of data, so that the other analysts cannot see their estimates.
- A third analyst performs the same tasks as the second analyst.

- The lab manager reviews a minimum of 10% of the images for accuracy of percent coverage estimates.
- INSERT ANY QUESTIONS INTO THE "COMMENTS" COLUMN
- In the Excel template, data are condensed into a table. Estimates from the three analysts are compared. If the relative percent difference among the three estimates is greater than 5%, the lab manager examines the image and the three estimates, choosing the appropriate value. The three estimates will not be changed, values are retained to show the inconsistency. The lab manager decides on the final value for the estimate. If a specific analyst's estimate consistently differs, the analyst will receive further training or may be removed from conducting future estimates.
- See Figure 3 for examples of coverage estimates and how to handle sparse coverage.

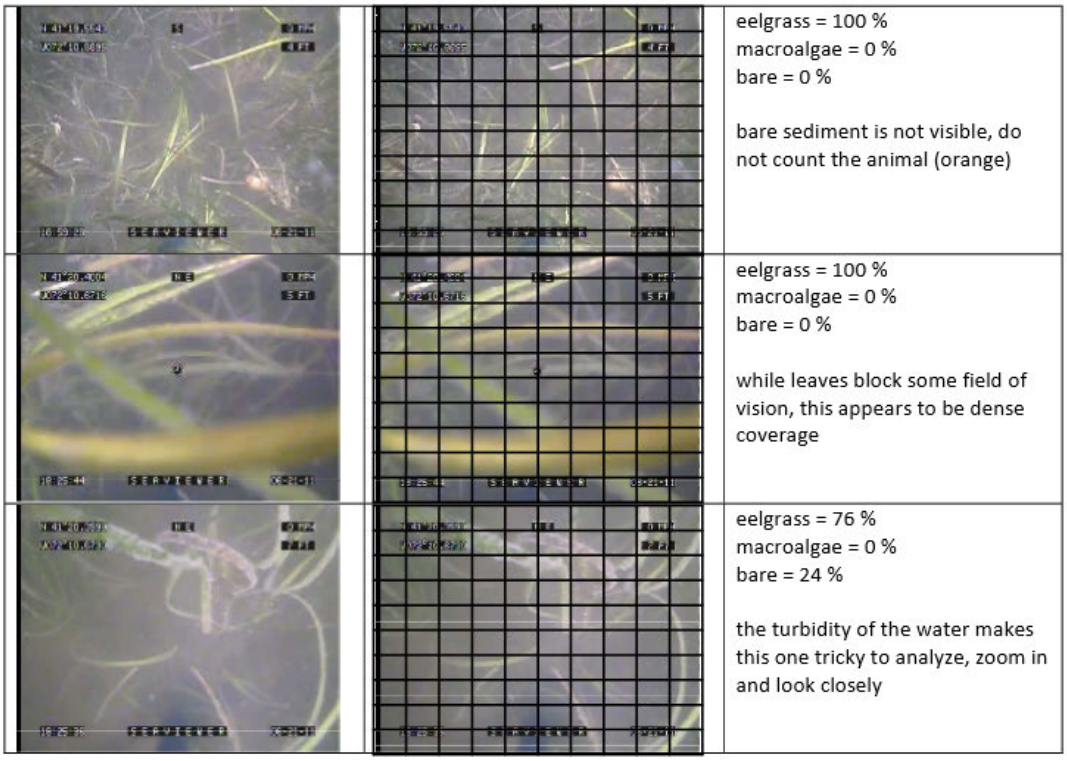
Figure 1: Image of the bottom captured using the video camera system. Note that the black circular disc on the end of the pole keeps the pole from sinking into the sediment and provides a size reference (diameter of disc = 10 cm).



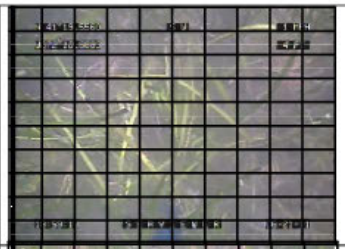
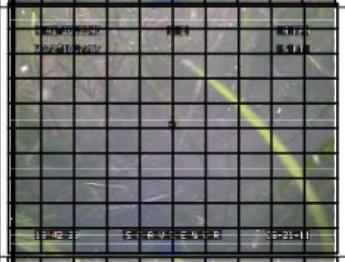
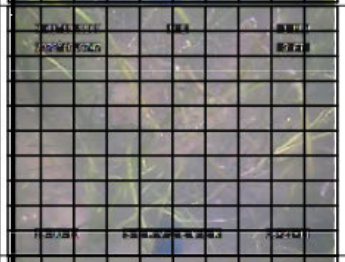
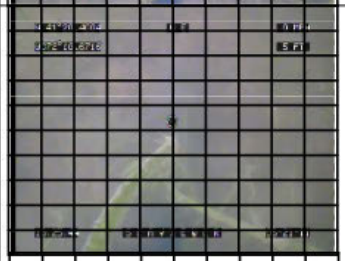
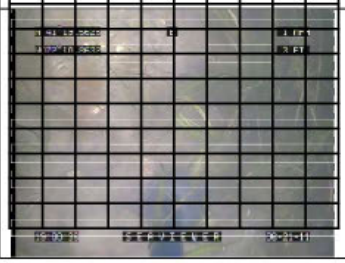
rmat > column > hide)	B								
Photo	NR 062120011 stn 6	41 N	72 W	MM eelgrass	MM macroalgae	MM bare	Christophe eelgrass	Christopher macroalgae	Christophe bare
		20.26750	10.81180	15	0	85	15	0	85

Figure 2: The image from Figure 1 has been entered into the data template and overlaid with the 100-cell grid.

Figure 3: Examples and tips for estimating coverage.



	eelgrass = 100 % macroalgae = 0 % bare = 0 % bare sediment is not visible, do not count the animal (orange)
	eelgrass = 100 % macroalgae = 0 % bare = 0 % while leaves block some field of vision, this appears to be dense coverage
	eelgrass = 76 % macroalgae = 0 % bare = 24 % the turbidity of the water makes this one tricky to analyze, zoom in and look closely

 	eelgrass = 89 % macroalgae = 0 % bare = 11 % harder to estimate – take care counting – you will have to estimate partial grid cells to compute bare area
 	eelgrass = 73 % macroalgae = 0 % bare = 27 % harder to estimate – take care counting – you will have to estimate partial grid cells to compute bare area
 	eelgrass = 69 % macroalgae = 0 % bare = 31 % harder to estimate – take care counting – you will have to estimate partial grid cells to compute bare area
 	eelgrass = 66 % macroalgae = 21 % bare = 13 % note what appears to be Ulva on the left (comment entry with any ?'s) - you will sometimes need to count more than once… (I counted macroalgae, then bare)
 	eelgrass = 43 % macroalgae = 3 % bare = 54 % you can calculate the % coverage for two types, then calculate the third: 100 - 43 - 3 = 54

eelgrass = 16 %
macroalgae = 1 %
bare = 83 %

in a sparse eelgrass area, do not count the leaves that extend across the frame as area – look for the base of the plants

eelgrass = 0 %
macroalgae = 13 %
bare = 87 %

count shells as bare area, unless colonized by macroalgae

VIII. REFERENCES:

IX. QUICK SHEET

Refer to the SOP for details, this list is only a reminder!!

FIELD

collect 20 – 40 images

Camera How-To

- Connect camera and GPS cables
- Turn power switch to "BAT"
- Push power button on Sea-Trak
- Press and hold power button on remote until first green light is steady and second green light is blinking on video recorder.
- To record press and hold record button until last yellow light is steady and red light is blinking.
- To stop recording press the stop button, message will appear on screen to confirm, press OK button.
- Switch power button to "OFF"

STORAGE

Download images ASAP, at least by the day following field work

ANALYSIS

- three analysts check
- record to the nearest 1% of coverage
- Any questions go in the comments column

Appendix B-1
Calibration Datasheet

UWS Sonde Calibration Datasheet
YSI

• Calibrations to be completed **DAY BEFORE** or **MORNING OF** Field Sampling Date •
• Post-Readings to be completed the **AFTERNOON OF** or **DAY AFTER** Field Sampling Date •

Calibrations • Person: _____ **Date:** _____ **Time:** _____

Post-Readings • Person: _____ **Date:** _____ **Time:** _____

Handheld S/N:_____ **Sonde S/N:**_____

◊ COMPLETE **BEFORE** SAMPLING ◊

① Calibrate **DISSOLVED OXYGEN (ODO % sat)**

Barometric Pressure (mmHg) ....

Temperature ....

Pre-Cal Value | Post-Cal Value

ODO Gain ....

② Calibrate **CHLOROPHYLL (µg/L) • 1-Point Calibration**

Pre-Cal Value | Post-Cal Value

③ Calibrate **CHLOROPHYLL (RFU) • 1-Point Calibration**

Pre-Cal Value | Post-Cal Value

④ Calibrate **TURBIDITY • 2-Point Calibration**

→1st Cal Value: 0 NTU (Reagent Grade Water)

Pre-Cal Value | Post-Cal Value

→2nd Cal Value: 124 NTU (Turbidity Standard)

Pre-Cal Value | Post-Cal Value

⑤ Calibrate **Specific Conductance (50,000 µS/cm)**

Pre-Cal Value | Post-Cal Value

Cell Constant ....

⑥ Calibrate **DEPTH (0 m)**

Pre-Cal Value | Post-Cal Value

◊ COMPLETE **AFTER** SAMPLING ◊

① Post-reading for **DISSOLVED OXYGEN (% sat)**
② Post-reading for **CHLOROPHYLL (µg/L)**
③ Post-reading for **CHLOROPHYLL (RFU)**
④ Post-reading for **TURBIDITY (0 NTU)**
⑤ Post-reading for **TURBIDITY (124 NTU)**
⑥ Post-reading for **SP COND (50,000 µS/cm)**
⑦ Post-reading for **DEPTH**

	Reagent Grade Water	Turbidity Standard 124 NTU	Conductivity Standard 50,000 µS/cm
Manufacturer			
Lot Number			
Expiration			

Accuracy Range Table	
DO% (100%)	97 – 103
Chl *a* (0 µg/L)	-0.30 – 0.30
Turbidity (0 NTU)	-3.00 – 3.00
Turbidity (124 NTU)	121.0 – 127.0
SpCond (50,000 µS/cm)	48,500 – 51,500
Depth (0 m)	-0.1 – 0.1

GPS of reference station: (circle one) NAD-83 WGS-84

• within 2 days of sampling day • in decimal degrees •

Lat.:	Long.:

Appendix B-2

Field Datasheet

UWS Field Datasheet

EMBAYMENT NAME(S): _____ **SAMPLE DATE:** _____

PEOPLE: _____ **TIME:** _____

• Tides nearest time of sampling, use NOAA Tide Tables •

Low Tide: _____ **High Tide:** _____

APPROX. EXPECTED RANGE	
Salinity (ppt/PSS)	5 – 30 ppt/PSS
Dissolved Oxygen (mg/L)	0 – 14 mg/L
Dissolved Oxygen (% Sat.)	0 – 120 %
Chlorophyll a (µg/L)	0 – 30 µg/L
Turbidity (NTU)	0 – 30 NTU

WEATHER CONDITIONS

• 24 hours preceding time of sampling •

High Air Temperature (˚C)	
Low Air Temperature (˚C)	

Cloud Cover (%)	
Precipitation State (mist, drizzle, rain, etc.)	
Wind at Embayment (use Beafort scale)	

Daily Precipitation	
Date	Inches

NOTES: _____

Appendix B-3

Sample Event Datasheet

Embayment Name	
Sample Date	
People	

GPS units (circle one):
decimal degree (40.772240°)
degree minutes (40° 46.334')
degree min. sec. (40° 46' 20.06")

Station ID									
Time									
Station Depth (m)									
GPS N									
GPS W									
	bottom (0.5 m off bottom)	mid-depth (if total depth > 10m)	surface (0.5m below surface)	bottom (0.5 m off bottom)	mid-depth (if total depth > 10m)	surface (0.5m below surface)	bottom (0.5 m off bottom)	mid-depth (if total depth > 10m)	surface (0.5m below surface)
Sample Depth (m)									
Temperature (°C)									
Salinity (ppt)									
Dissolved Oxygen (%)									
Dissolved Oxygen (mg/L)									
Fluroescence (RFU)									
Chl-a (µg/L)									
Turbidity (NTU)									

Enter additional field notes on back of sheet
If using a different method than usual, make a note!

At 1 station per embayment,do a second profile (usually at last station).

If total depth < 1.5m, do only mid-depth.

Chlorophyll Reference Check in Bucket (do once per day per embayment)

date & time	Vol Fit.	Vol. Fit.	sonde reading
			RFU
	ID	ID	ug/L

data entry _____ person checking _____

Appendix B-4

Chlorophyll Chain of Custody Form

UWS Chlorophyll Chain of Custody **Organization:**_____

Sample ID	Sample Date	Collection Time	Sample Volume

Relinquished by: _____ Date/Time:_____

Received by:_____ Date/Time:_____

Received by:_____ Date/Time:_____

Received by:_____ Date/Time:_____

Laboratory_____

Appendix B-5

Qualitative Macrophyte Sampling Datasheet

Site Name (short identifier) _____ Date _____

People (full names) _____

_____

Time of Low Tide _____ Time of Sampling (now) _____

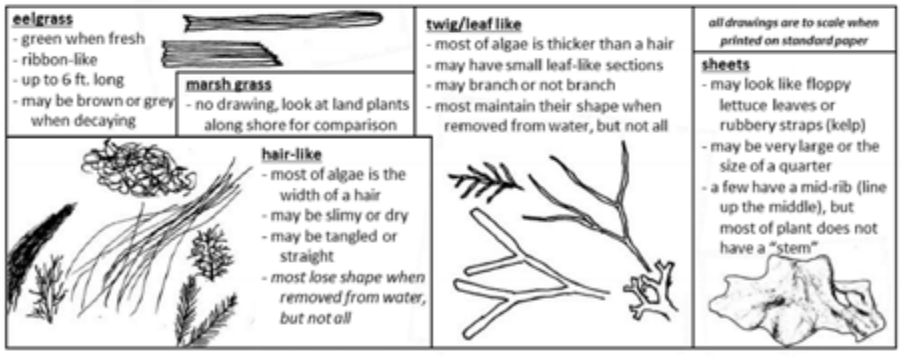
Site Description / Notes (optional) _____

_____

GPS location (in decimal degrees) _____N _____W

For rake toss, complete 6 tosses. For soft shoreline, provide an overview photo and close-up photos of algae types. Remember to include something for a size reference in soft shoreline close-up photos (shoe, keys, ruler, etc.).

Select one: ◯ soft shoreline ◯ rake toss photo ID	*NONE*	*SOME*	*LOTS*	*green hair-like*	*green twig/leaf-like*	*green sheets*	*non-green hair-like*	*non-green twig/leaf-like*	*non-green sheets*	*marsh grass*	*eelgrass*



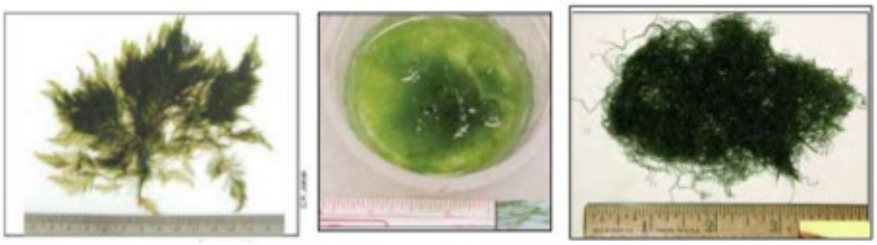
Appendix B-6

Macrophyte Field Guide

Long Island Sound Unified Water Study Algae Guide PAGE 1 of 2

All photos with permission from: Van Patten, Marguerite (Peg). (2009) Seaweeds of Long Island Sound, 2nd ed. Connecticut Sea Grant College Program. 104 pp.
photographer is P. Van Patten, unless otherwise indicated.

green hair-like = very thin filaments, as thick as hair; may branch



non-green hair-like = very thin filaments, as thick as hair; may branch

C. Yarish

sheets = most of plant is sheet form, may have a small holdfast

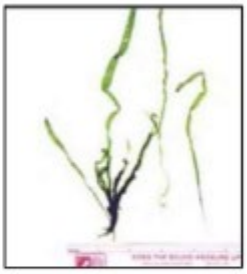
green

non-green

Long Island Sound Unified Water Study Algae Guide PAGE 2 of 2

All photos with permission from: Van Patten, Marguerite (Peg). (2009) Seaweeds of Long Island Sound, 2nd ed. Connecticut Sea Grant College Program. 104 pp.
photographer is P. Van Patten, unless otherwise indicated.

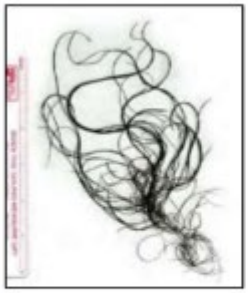
green twig/leaf-like = thicker than a hair, may branch, typically maintains shape when removed form water

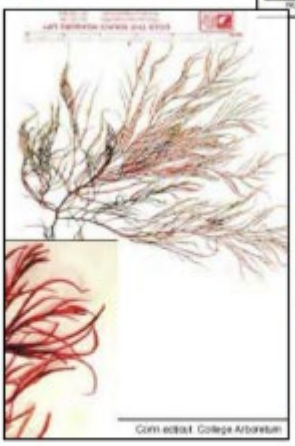


eelgrass

J. Vaudrey

non-green twig/leaf-like = thicker than a hair, may branch, typically maintains shape when removed form water





"beneficial brown"

Appendix B-7

Nutrients Chain of Custody

UWS Nutrients Chain of Custody **Organization:**_____

Sample ID	Sample Date	Collection Time	Salinity (ppt)

Relinquished by: _____ Date/Time: _____

Received by: _____ Date/Time: _____

Received by: _____ Date/Time: _____

Received by: _____ Date/Time: _____

Laboratory_____

Appendix B-8

Nutrients Sampling Event Datasheet

UWS Tier II - Surface Nutrients

Date: ____________________ Embayment: ______________________________

People: ____

collect sample 0.5 m below surface			Notes
station (number, letter)			
GPS N			
GPS W			
time (24 hour)			
total station depth (m)			
salinity (ppt)			
	Unfiltered	Filtered	
60 mL bottle ID	_______ - _______ - U (a thru C)	_______ - _______ - F (a thru C)	

collect sample 0.5 m below surface			Notes
station (number, letter)			
GPS N			
GPS W			
time (24 hour)			
total station depth (m)			
salinity (ppt)			
	Unfiltered	Filtered	
60 mL bottle ID	_______ - _______ - U (a thru C)	_______ - _______ - F (a thru C)	

collect sample 0.5 m below surface			Notes
station (number, letter)			
GPS N			
GPS W			
time (24 hour)			
total station depth (m)			
salinity (ppt)			
	Unfiltered	Filtered	
60 mL bottle ID	_______ - _______ - U (a thru C)	_______ - _______ - F (a thru C)	

Appendix B-9

Logger Retrieval Sample Event Datasheet

UWS Logger Retrieval Data Sheet

Embayment Name:________________ Station ID:__________ GPS N ________

Date:__________ People:______________________ GPS W ________

Barometric Pressure Unit
Serial#:______________
Time of Retrieval:______________

Light Logger Bottom
____
____

Dissolved Oxygen Logger
Serial#:______________
Time of Retrieval:______________
Time of Re-deployment:______________

Light Logger Above
____
____
____

Sonde Readings	Pre-retrieval	Post-retrieval
Time		
Temperature (°C)		
Salinity (ppt)		
Dissolved Oxygen (%)		
Dissolved Oxygen (mg/L)		

Notes:

Embayment Name:________________ Station ID:__________ GPS N ________

Date:__________ People:______________________ GPS W ________

Barometric Pressure Unit
Serial#:______________
Time of Retrieval:______________

Light Logger Bottom
____
____

Dissolved Oxygen Logger
Serial#:______________
Time of Retrieval:______________
Time of Re-deployment:______________

Light Logger Above
____
____
____

Sonde Readings	Pre-retrieval	Post-retrieval
Time		
Temperature (°C)		
Salinity (ppt)		
Dissolved Oxygen (%)		
Dissolved Oxygen (mg/L)		

Notes:

Embayment Name:________________ Station ID:__________ GPS N ________

Date:__________ People:______________________ GPS W ________

Barometric Pressure Unit
Serial#:______________
Time of Retrieval:______________

Light Logger Bottom
____
____

Dissolved Oxygen Logger
Serial#:______________
Time of Retrieval:______________
Time of Re-deployment:______________

Light Logger Above
____
____
____

Sonde Readings	Pre-retrieval	Post-retrieval
Time		
Temperature (°C)		
Salinity (ppt)		
Dissolved Oxygen (%)		
Dissolved Oxygen (mg/L)		

Notes:

Appendix B-10

Macrophyte Percentage Coverage Datasheet

Camera Sampling

People:

Date ____________________

Location ____________________

Site Code ____________________

Sta	video time	ID on White Board	Notes
	start		
	stop		
Sta	video time	ID on White Board	Notes
	start		
	stop		
Sta	video time	ID on White Board	Notes
	start		
	stop		
Sta	video time	ID on White Board	Notes
	start		
	stop		
Sta	video time	ID on White Board	Notes
	start		
	stop		
Sta	video time	ID on White Board	Notes
	start		
	stop		
Sta	video time	ID on White Board	Notes
	start		
	stop		
Sta	video time	ID on White Board	Notes
	start		
	stop		
Sta	video time	ID on White Board	Notes
	start		
	stop		
Sta	video time	ID on White Board	Notes
	start		
	stop		
Sta	video time	ID on White Board	Notes
	start		
	stop		
Sta	video time	ID on White Board	Notes
	start		
	stop		
Sta	video time	ID on White Board	Notes
	start		
	stop		

Appendix C-1

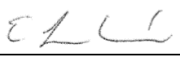
STS Standard Operating Procedure – Determination of Chlorophyll *a* and Pheophytin *a* in Water, Rev.3

Revised by E. Colón
Revision Date: 5/7/2024

Reviewed and Approved By:

Date: 5/7/2024

Peter Linderoth, Director of Water Quality (Technical Director)
Save the Sound



Date: 5/7/2024

Elena Colón, Laboratory Manager (Quality Assurance Officer)
Save the Sound

Table of Contents

1 POINT OF CONTACT

NAME: Peter Linderoth, Save the Sound, Director of Water Quality
ADDRESS: 1385 Boston Post Rd, 2nd Fl, Larchmont, NY 10538
EMAIL: plinderoth@savethesound.org
PHONE: 914-381-3140 ext. 200

2 OBJECTIVE

Determine the concentration of chlorophyll *a* (chl *a*) and pheophytin *a* (pheo *a*) in marine or freshwater phytoplankton using fluorescence detection.

3 OVERVIEW

Fluorescence detection is used to determine the concentration of chlorophyll *a* and pheophytin *a* in the water. Samples are collected from a measured volume of water and filtered through a glass fiber filter (GF/F). The field collection method is detailed in the UWS SOP Filtered Chlorophyll *a*.

Using 90% acetone, the chlorophyll present on the GF/F is extracted for a period of no less than 18 h, but not to exceed 24 h. The acidification method will be used whereby the fluorescence is measured before and after the addition of 0.1 N HCl.

The Method Detection Limit (MDL) for chl *a* is 0.10 µg/L and 0.08 µg/L for pheo *a*.

4 SOURCES

EPA Method 445.0, "*In Vitro* Determination of Chlorophyll *a* and Pheophytin *a* in Marine and Freshwater Algae by Fluorescence."

5 MATERIALS AND EQUIPMENT

5.1 Field Collection

See UWS SOP Filtered Chlorophyll. The field team will need all equipment and materials listed to collect chl *a* samples. Four samples (two of which will be analyzed and two saved as back-up) are to be filtered per field day for verification of sonde readings.

5.2 Lab Analysis

- Trilogy Laboratory Fluorometer
  - Chlorophyll *a* Acidification Module
- HPLC Grade Acetone, diluted to 90%
- Hydrochloric Acid, concentrated, diluted to 0.1 N
- Chlorophyll *a* Standards
- Solid Secondary Standard, Red
- 50 mL Centrifuge Tubes

- ASTM Type I Reagent Grade Water (for diluting acetone)
- Borosilicate Glass Tubes, 12x75mm
- Snap Caps for 12mm Glass Tubes
- Benchtop Centrifuge
- Variable Volume Pipette and Pipette Tips
- Teasing Needle Hook
- Shade Boxes (appropriately labeled with safety warning labels for acetone)
- Kimwipes

6 QUALITY CONTROL

6.1 Initial Demonstration of Performance

An initial demonstration of performance must be conducted to characterize the fluorometer's performance:

- Instrumental Detection Limit (IDL): Pure chlorophyll *a* in 90% acetone solution is serially diluted until it is no longer detected on a maximum sensitivity setting.
- Linear Dynamic Range (LDR): The LDR is determined analyzing a laboratory reagent blank and five calibration standards with concentrations ranging between 0.2 µg/L and 200 µg/L.
- Estimated Detection Limit (EDL): Pure chlorophyll *a* in 90% acetone solution is serially diluted until it yields a respond 3 times the average response of blank filters.
- Method Detection Limit (MDL): Using low-level ambient water, analyze seven replicate samples following the Laboratory Analyses Procedure in Section 7.3. After determining the concentration values, calculate the MDL as follows:

$$\mathrm{MDL} = \mathrm{S}t_{(\mathrm{n}-1,1-\alpha=0.99)}$$

Where,

$t_{(\mathrm{n}\text{-}1,1\text{-}\alpha=0.99)}$ = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom

n = number of replicates

S = Standard Deviation of the replicate analyses

In addition to establishing the initial performance capabilities, laboratory reagent blanks and quality control samples will be used to continually check on performance. All quality control records will be maintained by the laboratory.

6.2 Calibration and Standardization

Calibration of the Turner Fluorometer should be performed on a quarterly basis using Turner Designs chlorophyll *a* standards. The Turner Designs chl a standards package comes with two 20 mL ampoules of known concentration of chl a in a 90% acetone solution. Using the Turner Designs standards, a low and high concentration will be used for a two-point calibration.

6.3 Continuing Calibration Checks

A calibration standard check using Turner Designs Adjustable Solid Secondary Standard should be conducted pre- and post-readings for every batch of samples (30-40 samples) being processed.

If at any time the calibration standard check fails to meet acceptance criteria (± 10% of known value) the fluorometer must be re-calibrated. In the event chlorophyll *a* standards are not immediately available to perform a two-point calibration a post-correction on the RFU readings may be applied to the samples once a calibration has been able to be conducted.

7 METHODS

7.1 Reagents and Standards Preparation

7.1.1 Aqueous Acetone Solution, 1 L

Measure out 100 mL of ASTM Type I Water using a graduated cylinder or 100 mL volumetric flask. Deliver the 100 mL of water into the 90% acetone storage bottle. Measure out 900 mL of acetone in a graduated cylinder and deliver into the 90% acetone storage bottle. Cap and swirl to mix. Be sure to keep acetone solution well sealed to avoid evaporation.

Due to the resulting properties of mixing water and acetone impacting volumetric readings, it is important measure each independently and then mix the known volumes together.

7.1.2 0.1 N Hydrochloric Acid Solution, 500 mL

Add ~350 mL of ASTM Type I Water into a 500 mL volumetric flask. Add in 50 mL of 1N Hydrochloric Acid Concentrate to the water. Swirl flask gently to mix. Add ASTM Type I Water to the volumetric flask to bring the volume to 500 mL. Cap and mix the water and HCl.

7.1.3 Chlorophyll Stock Standard Solutions (SSS)

Chlorophyll *a* standard with a known concentration of chl *a* can be purchased by Turner Designs and must be kept frozen (-20°C) until ready for use. The Turner Designs standard provides two ampoules, one with a high concentration of chl *a* and the other a low concentration.

7.1.4 Laboratory Reagent Blank (LRB)

Place unused GF/F filter in glass tube and fill with 5 mL of 90% Acetone. One LRB per batch of samples should be prepared and handled in the same method as the field samples being analyzed.

7.2 Sample Collection and Storage

7.2.1 Sample Collection

Method of sample collection is detailed in the UWS SOP Filtered Chlorophyll. A measured volume of water is filtered through a 2.5 cm filter holder loaded with a circle GF/F filter (with a nominal pore size of 0.7 µm). Air is expelled through the filter several times to remove excess water. The filter is then removed from the holder, folded inward in half, placed in an unbleached coffee filter and wrapped in aluminum foil.

7.2.2 Storage

For long term storage, unprocessed filters must be kept frozen (-20°C) in the dark until extraction. Short term storage on ice for no more than 12 hours immediately after collecting the sample is acceptable.

7.2.3 Holding Time

Filters must be analyzed within 28 days from date of collection to avoid degradation of the sample material.

7.3 Laboratory Analysis Procedure

7.3.1 Extraction

IMPORTANT - Sample analyses should always be performed in a shaded and cool area of the lab with limited amount of light. Do not expose samples to direct light.

a. Place filter in a 6 mL (12 x 75 mm) glass tube.
b. Add 5 mL of 90% Acetone solution and seal with a snap cap.
c. Swirl tube several times or vortex, mixing filter in acetone very well.
d. Allow filter to steep in acetone for 18-20 hours in a dark freezer (-20°C). There must be no light exposure to the samples.

7.3.2 Sample Analysis

a. Several hours (on the day of) before reading of the sample is to be conducted, it is recommended to mix the sample in the glass once more. Allow to continue to steep in the freezer.
b. Remove sample from the freezer after allowing filter to steep the appropriate number of hours. Ensure light exposure is limited and wait for sample to reach room temperature before proceeding.
c. Taking care to not expose the sample to light for too long, use the teasing needle to remove the filter within the tube. Place the snap cap back on the tube. The filter should be allowed to dry out in the fume hood and thereafter may be disposed of in the regular trash. Make sure to always rinse the teasing needle before using on the next sample by

dipping in 90% Acetone solution.

d. Centrifuge the sample for 5 min at 1000 g or 15 min at 675 g.
e. When not actively handling the sample glass tube (either to remove the filter or centrifuge), it should be covered (shade box) so as to prevent exposure to light as much as possible. Once ready to read the tube, wipe the glass tube with a kimwipe. Place in the fluorometer, close the lid and read. Record the value on your lab datasheet. This is your **F1 value** (before acid).
f. Once the first reading is recorded, add 0.15 µL of 0.1N HCl to the sample tube. Swirl or vortex to distribute the acid. Once acid is added to the sample tube it may be safely exposed to light without concern of compromising the sample. After adding the acid, wait for at least 90 seconds before proceeding to the next step.
g. Centrifuge the sample for 5 minutes at 1000 g or 15 minutes at 675 g.
h. Place the now acidified sample tube in the fluorometer and read. Record the value on your datasheet as your **F2 value** (after acid).

8 TROUBLESHOOTING / HINTS

- Exact volume of water filtered through the GF/F filter sample is required.
- Every attempt should be made to limit light exposure to the sample (pre-acidification) throughout the procedure.

9 DATA PROCESSING AND STORAGE

9.1 Sample Data Handling

The UWS Monitoring Program Coordinator will be the custodian of the finalized data files and final sample analysis results will be shared with the monitoring groups.

The monitoring group is responsible for recording the field sample data (date, time and filtered water volume) and providing the data to the lab via a chain-of-custody at the time the sample is transferred over.

9.2 Data Analysis and Calculations

F_s = Calibration Response Factor = $\frac{C_a}{R_s}$

Where:

C_a = Concentration of chl *a* Standard
R_s = Fluorometer reading of chl *a* Standard

F_m = Acidification Ratio = $\frac{F_b}{F_a}$

Where:

F_b = Fluorometer reading BEFORE acidification of chl *a* Standard
F_a = Fluorometer reading AFTER acidification of chl *a* Standard

V_1: Volume (mL) of acetone used to extract sample
V_2: Volume (L) of water filtered
F1: Fluorescence reading of sample before acidification
F2: Fluorescence reading of sample after acidification

$$\frac{\mu g}{L}\text{ Chlorophyll } a = \frac{F_s \bullet \frac{F_m}{(F_m - 1)} \bullet (F1 - F2) \bullet V_1}{V_2}$$

$$\frac{\mu g}{L}\text{ Pheophytin } a = \frac{F_s \bullet \frac{F_m}{(F_m - 1)} \bullet (F_m \bullet F2 - F1) \bullet V_1}{V_2}$$

10 REFERENCES

EPA, U.S. 1997. Method 445.0: *In Vitro* Determination of Chlorophyll *a* and Pheophytin *a* in Marine and Freshwater Algae by Fluorescence.

Vaudrey, J. Department of Marine Sciences, UCONN. 2018. Chlorophyll – Fluorescence, Acidification and Non-acidification Methods.

Interstate Environmental Commission. 2017. Chlorophyll *a*.

Turner Designs. 2019. Trilogy Laboratory Fluorometer User's Manual, Version 1.7.

UMCES, Chesapeake Biological Laboratory. 2019. Fluorometric Determination of Chlorophyll *a* in waters and sediments of Fresh/Estuarine/Coastal Areas.

Appendix C-2

Standard Operating Procedure
Ammonia
EPA 350.1
SM 4500-NH3 G
Nutrients Laboratory

Prepared by:
Name: Steph Kexel **Signature**: _____ **Title**: _____ **Date**: _____

Approved by:
Name: Chris Perkins **Signature**: _____ **Title**: _____ **Date**: _____

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State of CT: PH-0778 – EPA: CT01022

Ammonia EPA 350.1
SM4500-NH3 G

Scope and Application

- EPA Method 350.1 is the reference method for measuring ammonia in water and seawater by automated colorimetric determination with phenate. This section provides a stepwise procedure for bench use by laboratory personnel.

- This method (Lachat ammonia method number 31-107-06-1-B) was developed for the quantitative analysis of ammonia in water and seawater. The applicable range is 0 to 0.5mg/L of ammonia as nitrogen (NH_3-N). Samples higher in range may be diluted and re-run or analyzed using the same method.

- This method does not perform a distillation step prior to analysis; therefore, it cannot be used for compliance sample analysis or NPDES wastewater sample analysis.

- Method Detection Limits will be developed for all CTDPH approved methods according to the process and procedures detailed in the CESE Laboratory Quality Assurance Plan Section 7.4 (Method Detection Limit Studies).

- Contamination of samples with ammonia is a problem of great concern. Ammonia is ubiquitous in the environment. Ammoniated floor strippers and waxes are strictly prohibited in the laboratory.

- This method is based on automated colorimetric determinations and is restricted to the use by, or under the supervision of, analysts experienced in the use of auto analyzer equipment.

Summary of Method

- The whole water sample may be filtered though a 47mm GF/F glass-fiber filter in the field. The filtrate is then frozen at or below –10°C until analysis can be completed. Analysis is completed within 28 days from arrival date at the laboratory. Samples for ammonia are analyzed by an automated procedure, on a Lachat, utilizing the Berthelot reaction.

- Ammonia in the sample reacts with alkaline sodium phenolate and then sodium hypochlorite to form indophenol blue. A solution of EDTA is added to the sample stream to eliminate the precipitation of the hydroxides of calcium and magnesium. Sodium nitroprusside is added to intensify the blue color.

- The Lachat is calibrated with a minimum of a six-point curve (including the blank) at the time of analysis. The calibration curve is then verified by an external quality control sample from Fisher (an independent supplier). Fisher supply guidelines are used for making up the quality control solutions, as well as for information on the true value and acceptable value range for the analytes being measured in each quality control sample.

- An initial calibration check along with an initial calibration blank, demonstrate that the instrument is capable of acceptable performance at the beginning of the sample analysis. In order to ensure continuing acceptable performance a continuing calibration check and continuing calibration blank are run every 20 samples. Additionally, a laboratory spike and a laboratory duplicate analysis is performed every 20 samples.

- See the Laboratory QAP (Quality Assurance Plan) for definitions of common laboratory terms.

Definitions

- See the Laboratory QAP (Quality Assurance Plan) for definitions of common laboratory terms.

Interferences

- Calcium and magnesium ions could precipitate if present in sufficient concentration. EDTA is added to the sample stream to rectify this problem.

- Color (as well as certain organic species) can cause interference.

- Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that may bias analyte response.

References

31-107-06-1-B, August 2003. Determination of Ammonia in Brackish or Seawater by Flow Injection Analysis. Lachat Instruments, Loveland, CO.

EPA Method 350.1. Determination of Ammonia Nitrogen by Semi-Automated Colorimetry. Revision 2.0, August 1993. Environmental Monitoring Systems

Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.

Standard Method 4500-NH3 G Ammonia by Automated Phenate. Page 4-103—4-112, 20th Edition, 1998, Standard Methods for the Examination of Water and Wastewater.

Associated SOP's

Refer to "SOP" titled "Hazardous Waste SOP" for proper waste disposal.

Refer to the notebook titled "SOPs" located in the Nutrients laboratory.

Safety

Reagents are hazardous and are made in the hood. Protective gear is worn when making reagents.

Phenol is a known carcinogen and is hazardous. Read MSDS before using Phenol. Use caution when making this reagent. There are special gloves in the Phenol cabinet. Be sure to wear them when using this reagent.

Ensure that waste lines from the Lachat are going to the proper hazardous waste jug located under the instrument.

Refer to the University of Connecticut's Environmental Health and Safety Chemical Health and Safety web page at:

http://www.ehs.uconn.edu/ppp/index.php

A hard copy of the Chemical Hygiene Plan can be found on the notebook rack located on the lab bench. Also refer to the Hazardous Waste SOP.

Materials

Lachat QuickChem 8500

Procedure

Reagent Preparation

- Unless otherwise specified, all chemicals should be ACS grade or equivalent. DI water refers to high quality reagent water, TYPE I or TYPE II as defined in

ASTM Standards, Part 31, D1193-74. When making reagents, date the container in which the reagent is stored, initial it, and write out the entire name of the reagent.

❖ Phenol

We are currently using Fisher Scientific phenol crystals (catalog no. A92-100) and Fisher sodium hydroxide (catalog no. S318-3).

CAUTION: Phenol is very poisonous, causes severe burn, and is rapidly absorbed into the skin. Wear gloves and safety glasses.

Phenol, Crystals	83g
Sodium Hydroxide	32g
DI Water, q.s.	1000mL final vol.

In a volumetric flask, fill ¾ with deionized water and dissolve 32g of sodium hydroxide in approximately 600mL of water, dissolve and cool under cold tap water, being sure not to introduce tap water into the volumetric flask. Add 83g of phenol crystals and dilute to one liter with DI water and mix thoroughly. Store the reagent in an amber poly bottle. This material is corrosive and is stable for about 2 weeks or until brown.

❖ Sodium Hypochlorite Solution

We are currently using Fisher sodium hypochlorite (Cat # SS290-1) that contains 5.65% NaOCl and no additives.

Sodium Hypochlorite Solution, 5.65%	50mL
DI water, q.s.	50mL

Dilute 50mL of hypochlorite to 50mL with DI water and mix thoroughly. Prepare fresh daily.

❖ Sodium Nitroprusside

We are currently using Fisher sodium nitroferricyanide dehydrates, 99% (sodium nitroprusside, catalog no. S350-100).

Sodium Nitroprusside	1.75g
DI Water, q.s.	1000mL final vol.

Fill a volumetric flask ¾ with deionized water and add 1.75g of sodium nitroprusside in 1000mL of water and mix thoroughly. Store the solution in an amber poly bottle. Degas with helium for 5 minutes. Solution is stable for 2 weeks.

❖ Buffer Chelating Reagent

We are currently using Fisher EDTA (catalog no. S311-500) and Fisher sodium hydroxide (S399-212).

EDTA	50g
Sodium Hydroxide	11g
DI Water, q.s.	1000mL final vol.

In a 1L volumetric flask, fill ¾ with DI water, and add 50g of EDTA and 11g sodium hydroxide. Dilute to one liter and mix well. Store the solution in a clear poly bottle. Degas for 5 minutes with helium. Solution is stable for one month.

Standard Preparation

- Working standards can be made by weight or volume. Standards are made using a 1000µg/mL stock certified from AccuStandard or another source different from the QC.

❖ Stock Standard, 10.0mg/L N

AccuStandard Stock (Ammonia)	1mL
DI water, q.s.	100mL final vol.

In a 100mL volumetric flask containing about 80mL of DI add 1mL of Stock AccuStandard Ammonia Standard. Dilute to 100mL with DI and mix thoroughly. Record the standard information in the stock standard logbook. Standard must be made fresh weekly.

❖ Preparation of working standards:

Transfer aliquots of Stock 10mg/L stock as noted below to individual 100mL volumetric flasks. Dilute to volume with DI water and mix thoroughly. Record the information in working standard logbook. Prepare fresh weekly.

▪ Working Standard Solutions for Low Range Analysis

mL(g) 10mg/L Stock	mg/L as N
5.0	0.500
3.0	0.300
1.0	0.100
0.5	0.050
0.25	0.025
0.1	0.010

Sample Preparation

- Sample turbidity may be removed by filtration though a 47mm GF/F filter prior to analysis. Turbidity absorbance in the range of 660 nanometers (nm) will present a positive bias.

- The filtrate is then preserved in the field by adding H_2SO_4 to a pH of <2 at the time of collection and freezing at or below -10°C until analysis is performed. The client may decide to solely freeze samples without preservation to eliminate variability, and to minimize potential safety issues associated with field acidification. The client will notify/discuss these procedures with CESE staff prior to sample acceptance.

- Sample containers are to be rinsed with 1:1 hydrochloric acid, followed by DI water and finally by an aliquot of the sample itself. Disposable plastic sample tubes are used during analysis to avoid contamination from improper washing of glass tubes.

- Generally, spiked samples are spiked with 100µL of the 10ppm stock standard, yielding a spike concentration of 0.196ppm.

- The Quality Control Sample (QC) is made up in 100mL volumes per every 60 or so samples. Larger quantities are necessary if running large batches of samples. Generally, the concentration of the QC is 0.3ppm and is made fresh daily.

Instrumental Analysis

- It is assumed that the user is basically familiar with the appearance and location of the various parts of the Lachat QuickChem Autoanalyzer. It is also assumed that a method for running ammonia analysis has already been created, and that the user is familiar with basic system operations. For a physical description of the instrument and any related software information, see the “Running Lachat” SOP.

- The pH of the final reaction solution must lie within certain limits. Collect the solution from the flowcell waste line to verify the pH is between 11.5 and 11.9.

- **It is very important to introduce the reagent lines in this order: buffer, phenol, nitroprusside then bleach. When removing reagent lines when shutting down the instrument, do so in reverse order to prevent calcium precipitate from forming on the inside of the manifold.**

- Ensure that the pump tubes are pumping reagents and that the sample line is hooked up to port 6 of the switching valve.

Calculations

- Percent Recovery for the QC is calculated by the following formula:

$$\%Recovery = \frac{Observed\ QC\ Value}{Expected\ QC\ Value} \times 100$$

- Percent recovery for the spike is determined using the following formula:

$$\%Recovery = \frac{(A - B)}{C} \times 100$$

Where: A = measured value in mg/L for the sample + spike
B = measured value in mg/L for the original sample
C = concentration of the spike in mg/L

- Relative percent difference for the duplicate is calculated by the following formula:

$$RPD = \frac{(A - B)}{[(A + B) \div 2]} \times 100$$

Where: A = The value in mg/L for the first run of the sample
B = The value in mg/L for the second run of the sample

Quality Control

- A certified second source quality control sample (purchased from Fisher) is analyzed for every delivery group (or every 20 samples). The value must be within 90-110% recovery, or as per client request, to be considered acceptable. Prepare fresh daily.

- A spike is analyzed for every delivery group (or every 20 samples). The percent recovery must fall within the 85-115% recovery to be considered acceptable.

- A duplicate is analyzed for every delivery group (or every 20 samples). The duplicate relative percent difference (RPD) must be below 20% or as per client request.

- A blank is analyzed every delivery group, or every 20 samples and the value must fall below the PQL to be considered acceptable.

- A second quality control concentration is analyzed every batch and at the end of the run and is the PQL, or the practical quantitation limit. Acceptable ranges for the PQL are 50-150 % recovery.

Other System Notes

- Chemistry Manifold 1
- Light interference filter: 660nm
- Special instructions: The reaction module for ammonia determinations comes equipped with a heating coil that heats the sample stream (after the addition of the reagents) to 37°C, which promotes better color development. This coil should be given 15 minutes to warm up before any samples are run.

Appendix C-3

Standard Operating Procedure
Nitrate, Nitrite, and Organic Nitrogen
EPA 353.2
SM 4500 NO_2^-, NO_3^-, and N_{org}
Nutrients Laboratory

Prepared by:
Name: Steph Kexel **Signature**: _____ **Title**: _____ **Date**: _____

Approved by:
Name: Chris Perkins **Signature**: _____ **Title**: _____ **Date**: _____

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State of CT: PH-0778 – EPA: CT01022

Nitrate and Nitrite EPA 353.2
SM 4500 NO_2^-, NO_3^-, and N_{org}

Scope and Application

- EPA Method 353.2 is the reference method for measuring nitrate + nitrite in water and seawater by automated colorimetric determination. This section provides a stepwise procedure for bench use by laboratory personnel.

.

- This method (Lachat method number 31-107-04-1-A) was developed for the quantitative analysis of nitrates in water and seawater. The applicable range is 0 to 0.5mg/L as nitrogen. Samples higher in range may be diluted and re-run.

- This method is based on automated colorimetric determination and is restricted to the use by or under the supervision of analysts experienced in the use of auto analyzers.

- This method may be used for analysis of NO_X (nitrate + nitrite) or nitrite alone. NO_X-N values are obtained by activating the cadmium column and calibrating with NO_3^--N standards. Nitrite (NO_2^--N) is calibrated with NO_2^--N standards and the cadmium column is not activated. Reagents remain the same. The nitrate (NO_3^--N) value is calculated by subtracting the nitrite (NO_2^--N) value from the nitrate + nitrite (NO_X-N) value.

- Organic nitrogen may be calculated by subtracting the sum of the NO_x-N and NH_3-N from the TN value.

Summary of Method

- The whole water sample may be filtered through a 47mm GF/F filter in the field. The filtrate is frozen at –10°C or below until analysis can be completed (samples must not be preserved with mercuric chloride or thiosulfate, as these degrade the copper-cadmium column used in this analysis). Analysis is completed within 28 days from arrival date at the laboratory. Samples for nitrate + nitrite are analyzed using flow injection on the Lachat. Nitrate is reduced to nitrite at pH 7.5 in a copperized cadmium column. The nitrate reduced to nitrite, plus any free nitrite present, reacts under acidic conditions with sulfanilamide to form a diazo compound that couples with N-1-Naphthylethylenediamine dihydrochloride to form a reddish-purple azo dye that is measured at 520nm. For nitrite analyses the cadmium column is not used.

- Method Detection Limits will be developed for all CTDPH approved methods according to the process and procedures detailed in the CESE Laboratory Quality Assurance Plan Section 7.4 (Method Detection Limit Studies).

- This method is based on automated colorimetric determinations and is restricted to the use by, or under the supervision of, analysts experienced in the use of auto analyzer equipment.

- The instruments are calibrated with a minimum of a six-point curve (including the blank) at the time of analysis. The calibration curve is then verified by an external quality control sample from Fisher, an independent supplier. Fisher supply guidelines are used for making up the quality control solutions, as well as for information on the true value and acceptable value range for the analytes being measured in each quality control sample.

- An initial calibration check along with an initial calibration blank, demonstrate that the instrument is capable of acceptable performance at the beginning of the sample analysis. To ensure continuing acceptable performance continuing calibration verification and continuing calibration blank are run every tenth sample. For every 20 samples, a laboratory spike analysis and a laboratory duplicate analysis are performed. For every delivery group of samples and at the end of the run a PQL (Practical Quantitation Limit) is run for further quality control verification. This is the lowest standard.

Definitions

- See the Laboratory QAP (Quality Assurance Plan) for definitions of common laboratory terms.

Interferences

- Build up of suspended matter in the cadmium column will restrict flow. Look for a "jerking" action in one or several of the pump tube lines as evidence of such a blockage. Nitrate nitrogen is, however, found in a soluble state, so pre-filtering of samples should be sufficient to keep lines clear.

- Low results are possible for samples high in metals concentrations such as iron or copper. (1.0g per liter) $Na_2EDTA{\cdot}2H_2O$ can be added to the buffer to reduce this interference.

- Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. Pre-extracting the sample with an organic solvent eliminates this interference.

References

31-107-04-1-A, August 19, 2003. Determination of Nitrate/Nitrite in Brackish or Seawater by Flow Injection Analysis. Lachat Applications Group, Lachat Instruments, Loveland CO.

EPA Method 353.2. Determination of Nitrate-Nitrite Nitrogen by Automated Colorimetry. Revision 2.0, August 1993. Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.

Standard Method 4500-N. Nitrogen. Page 4-99—4-123, 20th Edition, 1998, Standard Methods for the Examination of Water and Wastewater.

Associated SOP's

Refer to "SOP" titled "Hazardous Waste SOP" for proper waste disposal.

Refer to the notebook titled "SOP's" located in the nutrients laboratory.

Safety

Cadmium crystals are a known carcinogen; use caution when reactivating the cadmium for column repacking.

Reagents are hazardous and are made in the hood. Protective gear is worn when making reagents.

Ensure that waste lines from the detector are going to the proper hazardous waste jug located under the instrument.

The following chemicals have the potential to be highly toxic or hazardous, consult MSDS:

- Phosphoric acid
- Hydrochloric acid
- Sulfuric acid

Refer to the University of Connecticut's Environmental Health and Safety Chemical Health and Safety web page at:

http://www.ehs.uconn.edu/ppp/index.php

A hard copy of the Chemical Hygiene Plan can be found on the notebook rack located on the lab bench. Also refer to the Hazardous Waste SOP.

Materials

Lachat QuickChem 8500 Auto Analyzer
Cadmium column

Procedure

Reagent Preparation

- Unless otherwise specified, all chemicals should be ACS grade or equivalent. DI water refers to high quality reagent water, TYPE I or TYPE II as defined in ASTM Standards, Part 31, D1193-74. When making reagents, date the container in which the reagent is stored, initial it, and write out the entire name of the reagent.

❖ Ammonium Chloride Buffer

We are currently using Fisher hydrochloric acid (catalog no. A144S-212), Fisher disodium EDTA (catalog no. S311-500), and Fisher ammonium hydroxide (catalog no. A669S-212).

Hydrochloric Acid (concentrated)	105mL
Ammonium Hydroxide	95mL
Disodium EDTA	1.0g

Be sure to make this reagent in the hood. Wear all protective gear! Add about 500mL DI water to a 1000mL volumetric flask. Carefully pour in 105mL concentrated hydrochloric acid and rinse cylinder and volumetric well before proceeding. With a new graduated cylinder, pour in 95mL ammonium hydroxide. Again, rinse graduated cylinder and flask well before proceeding. Add 1.0g disodium EDTA, dissolve and dilute to the mark. Add stir bar and mix. Adjust the pH to 8.5 with 2N HCl solution. Store in clear poly bottle. Solution is stable for 2 months.

❖ Sulfanilimide Color Reagent

We are currently using Fisher sulfanilamide (catalog no. AC132855000), Acros NED (catalog no. AC42399-0250), and Fisher phosphoric acid (catalog no. A242-212).

Phosphoric Acid (85% soln. by wt.)	100mL
Sulfanilamide	40.0g
NED (N-(1-napthyl)ethylenediamine dihydrochloride	1.0g

To a 1L volumetric flask, add about 600mL DI water then add 100mL 85% phosphoric acid, 40g sulfanilamide and 1.0g NED. Dilute to the mark, add stir bar and stir to

dissolve for 30 minutes or until completely dissolved over medium heat. Store in a dark bottle and discard when the solution turns pink, about one month.

❖ Cadmium-Copper Reduction Column

Pre-packed cadmium columns are available from Lachat/HACH (Lachat part/order no. 50237A). Instructions for repacking columns in the laboratory are at the end of this SOP.

Standard Preparation

Working standards can be made by weight or volume. Standards are made using a 1000µg/mL stock certified from AccuStandard or another source different from the QC. Prepare fresh weekly.

❖ Stock Standard, 10.0mg/L N

AccuStandard Stock (NO_3^- or NO_2^-)	1mL
DI water, q.s.	100mL final vol.

In a 100mL volumetric flask containing about 80mL of DI add 1mL of Stock AccuStandard NO_3^--N or NO_2^--N Standard. Dilute to 100mL with DI and mix thoroughly. Record the information in the stock standard logbook.

❖ Preparation of working standards:

Transfer aliquots of Stock 10mg/L stock as noted above to individual 100mL volumetric flasks. Dilute to volume with DI water and mix thoroughly. Record the information in working standard logbook. Prepare fresh weekly.

- Working Standard Solutions for Low Range Analysis

mL(g) 10mg/L Stock	mg/L N
5.0	0.500
3.0	0.300
1.0	0.100
0.5	0.050
0.25	0.025
0.1	0.010

Transfer aliquots of Stock 10mg/L stock as noted above to individual 100mL volumetric flasks. Dilute to volume with DI water and mix thoroughly. Record the information in working standard logbook. Prepare fresh weekly.

- A NO_2^--N QC of the same concentration as the NO_3^--N QC must also be made when running with the cadmium column to ensure that the cadmium column is working efficiently. A recovery greater than 90% is considered acceptable by Lachat instruments. Anything lower than this value indicates that the cadmium column must be replaced. Prepare fresh daily.

Sample Preparation

- Sample turbidity may be removed by filtration though a 47mm GF/F filter prior to analysis. Turbidity absorbing in the range of 550 nanometers (nm) will present a positive bias.

- Sample containers are to be rinsed with 1:1 Hydrochloric Acid, followed by DI water and finally by an aliquot of the sample itself. Disposable plastic sample tubes are used during analysis to avoid contamination from improper washing of glass tubes.

- The sample is preserved in the field by adding H_2SO_4 to a pH of <2 at the time of collection and freezing at or below -10°C until analysis is performed. The client may decide to solely freeze samples without preservation to eliminate variability, and to minimize potential safety issues associated with field acidification. The client will notify/discuss these procedures with CESE staff prior to sample acceptance.

- Generally, 7.5mL of sample is spiked with 150µL of the 10ppm stock standard, yielding a spike concentration of 0.196ppm.

- The quality control sample (QC) is made up in 100mL volumes per every 60 or so samples. Larger quantities are necessary if running large batches of samples. Generally, a QC concentration of 0.3ppm is used and is made fresh daily.

Instrumental Analysis

- It is assumed that the user is basically familiar with the appearance and location of the various parts of the Lachat. It is also assumed that a method for running NO_3^--N or NO_2^--N analyses has already been created, and that the user is familiar with basic system operations. For a physical description of the instrument and any related software information, see “Running the Lachat”.

- Ensure that the correct size sample loop (22.5cm) is attached at the manifold valve between ports 1 and 4.

- Ensure that the 520nm wavelength filter is in the detector.

- Ensure that the sample line is attached to port 6 of the switching valve and that the reagents are all pumping properly.

General Analyzer Information

- The nitrite value can be determined by eliminating the cadmium reduction column and standardizing with a certified nitrite solution.

- To determine the nitrate values, the nitrite alone must be subtracted from the NO_X (nitrate + nitrite). Run the instrument with cadmium column active and calibrate with NO_3-N standards, then run with NO_2^--N standards and subtract this value from the NO_X-N value.

- When using the cadmium column, check the efficiency of the column daily by analyzing equal concentrations of nitrate and nitrite standards. The efficiency should be >90%.

- Introduce the ammonium chloride reagent into the chemistry manifold first, allow the system to flow for about a minute, and then introduce the Sulfanilimide.

- **When using the cadmium column, ALWAYS ensure that the column is activated when ALL reagents are pumping through the system. Likewise, make sure the column is in the "off" position at the end of the run before taking reagent lines out of solution for the wash step.**

- Cadmium columns are purchased from Lachat instruments (CAT # 50237A), however cadmium may be regenerated in the laboratory according to Lachat publication WI#J20008. Publication included at the end of this SOP.

- Ensure that the proper method has been selected, either for freshwater analysis or one that utilizes the refractive index correction for seawater samples.

Calculations

- Percent Recovery for the QC is calculated by the following formula:

$$\%Recovery = \frac{Observed\ QC\ Value}{Expected\ QC\ Value} \times 100$$

- Percent recovery for the spike is determined using the following formula:

$$\%Recovery = \frac{(A - B)}{C} \times 100$$

Where: A = measured value in mg/L for the sample + spike
B = measured value in mg/L for the original sample
C = concentration of the spike in mg/L

- Relative percent difference for the duplicate is calculated by the following formula:

$$RPD = \frac{(A - B)}{[(A + B) \div 2]} \times 100$$

Where: A = The value in mg/L for the first run of the sample
B = The value in mg/L for the second run of the sample

- To determine the column efficiency, use the following formula:

$$E = \frac{(NO_3^- - N)}{NO_2^- - N} \times 100$$

Where: E = column efficiency
NO_3^--N = concentration of nitrate standard
NO_2^--N = concentration of nitrite standard

Quality Control

- A certified second source quality control sample (purchased from Fisher) is analyzed for every delivery group (or every 20 samples) and the value must be within 90-110% recovery, or as per client request, to be considered acceptable. Prepare fresh daily.

- A spike is analyzed for every delivery group (or every 20 samples). The percent recovery must fall within the 85-115% recovery to be considered acceptable.

- A duplicate is analyzed for every delivery group (or every 20 samples) and the relative percent difference must be below 20%, or as per client request.

- A blank is analyzed every delivery group, or every 20 samples and the value must fall below the PQL to be considered acceptable.

- A second quality control sample is analyzed for every delivery group and at the end of the run and is the concentration of the PQL, or the lowest standard. Acceptable ranges for the PQL are 50-150% recovery.

- Cadmium column efficiency is analyzed with every calibration.

Other System Notes

- Light interference filter: 520nm
- Sample Loop Size: 22.5cm

WI #: J20008	Date Issued: 10Jun96
Title: Copperizing and Packing Cadmium Reductor Columns	Revision Date: 21Feb 02
Author: David Diamond	
Purpose: To provide instruction on how to copperize and pack cadmium columns. Section 3 explains how to remove cadmium from a used glass column.	
Scope: These guidelines and requirements apply to Cadmium columns prepared at Lachat Instruments.	

1. Special Instructions

1.1. Use cadmium granules (Lachat Part no. 50231), which have been sieved to pass a 14-mesh screen and retain on a 40-mesh screen. Lack of uniformity in the granule size may cause flow problems.

1.2. While packing the column observe the pump tube on the inlet side of the pump for pulsing. This is an indication that the column tubing is plugged or the pump tubing is plugged. Also, observe the flow of ammonia buffer from the column just prior to disconnecting it from the peristaltic pump. Look for pulsing or lack of flow.

1.3. New cadmium granules will give a more uniform color and will results in longer lifetimes than recycled granules.

2. Equipment Needed

2.1. 0.2% Copper Sulfate Pentahydrate ($CuSO_4 \cdot 5H_2O$) – In a 1 L volumetric flask, dissolve 2 g $CuSO_4 \cdot 5H_2O$ in about 250 mL of deionized (DI) water. Dilute to the mark with DI water. If packing more than 4 columns, increase concentration of copper sulfate to 2%.

2.2. 1M Hydrochloric Acid – In a 1 L volumetric flask, slowly add 82.5 mL of hydrochloric acid (HCl) to approximately 500 mL of DI water. Dilute with to the mark with DI water. Recipe by weight: In a 1 L container, add 917 g DI water and 100 g conc. HCl.

2.3. Acetone, Lab grade

2.4. Packing Funnel, plastic, for 12.5 cm diameter paper, VWR cat. No. 30246-021, 6.5 mm O.D. at top. With a scissors, cut about 1.5 cm from the tip of the funnel. Cut a 2 cm piece of 3/8" (5 mm) PVC tubing. Sleeve the PVC tubing over the end of the funnel.

2.5. Wash Basin, approx. 12" X 14" X 6" deep.

2.6. Peristaltic Pump, set at 35.

2.7. Pump tube, green/green, Lachat Part No.53214, attached to large PVC transmission tubing with a glass line weight attached. On the other end of the pump tubing attach a pump tube adapter with a large collar.

2.8. Dissecting Probe, Lachat part No. 50060

2.9. Sample Probe

2.10. Foam Plugs (2 per column). Plugs should be cut with a scissors to 5 mm^3. Foam Part No: 50229

2.11. Ammonia Buffer – CAUTION: Fumes! To a 10 L container add, 8442 g DI water, 765 g Ammonium Chloride (NH4Cl),and 9.0 g disodium ethylenediamine tetraacetate (Na2EDTA·2H2O). Stir until dissolved. The pH of this solution must be 8.5. Adjust if necessary with 15 N sodium hydroxide (NaOH) before use. Store in a tightly sealed container. This reagent is good for at least 2 months.

2.12. Check pH of buffer before use, and adjust if necessary!!!!

2.13. 30 – 125 mL containers and 30 labels (front and back) for cadmium granules.

3. Column Preparation Procedure – Removal of Used Cadmium

3.1. Fill a 1 L container about one third full with DI water.

3.2. Gather used columns, dissecting probe and sample probe. Unscrew both the end fittings and the end caps on each side of the column.

3.3. While holding the column over the container, start to disassemble the column. First remove the end fittings from both ends. Lay these pieces aside. Remove one end cap and use the dissecting probe to remove the old foam plug. Then turn the column over (make sure that the open end is over the container). Remove the other end cap and foam piece using the dissecting probe. Then tap the column ends on the sides of the container. The cadmium should fall out the lower end. If they do not, use a squirt bottle filled with DI water and put water through the column. The cadmium may come out by doing this, if not, then use the dissecting probe or sample probe to remove the rest of the cadmium. If necessary to dislodge the cadmium, use a sonicator to loosen the cadmium. Then try to remove the cadmium with the dissecting probe and DI water. If the cadmium cannot be removed, the column is considered broken and needs to be placed aside for the next lab pack.

3.4. Once the cadmium has been removed, clean and inspect all of the parts. The parts include two end fittings, two end caps, two unions, two Teflon 15 cm lengths of tubing with gripper assemblies attached, and a 10 cm length of .032" id. Teflon tubing. The tubing used with the grippers is special in that the dimensions and tolerances are specific for the gripper fittings. (See Figure A). If glass columns are chipped on the ends, they will leak when reassembled.

3.4.1. For end fittings, look at the threads for wear. If the threads are turned over, discard the end fitting.

3.4.2. For end caps, look at the threads on the inside. If there are strands of plastic or the threads are bad, discard the end cap. Make sure there is still the white frit in the end.

3.4.3. For unions, make sure that there are two unions. If the unions are not properly assembled, replace.

3.4.4. For the grippers, make sure that there are no crimps in the tubing. If there are, discard the gripper.

3.4.5. For glass columns, make sure that the inside of the column is clean. DI water can be used to rinse them out. Look at the threads on each end of the column. If there is a chip in just one thread, it can be deemed as okay. If the chip is in the same spot along more than one thread, then the column may leak. Look at the end of the glass column. The end is opaque. If there is a chip that does not extend across then entire bottom, the column may be okay. If it is across the entire bottom, the column will most likely leak. If there is doubt as to whether the column may leak, use a Sharpie marker and mark the end of concern. This column may be repacked. When finished, if it leaks, then the column needs to be replaced.

3.5. Once the parts have been inspected, place them in a bucket that contains DI water. This allows the parts to be cleaned of debris.

3.6. Clean and dry the glass column and place a foam plug in one end. Screw a end cap finger tight on the end with the foam plug. Then add a end fitting with gripper to the tightened end cap. Do not place a foam plug in the other end yet. Set the column aside. Assemble the rest of the assembly by connecting two unions by 8.5 cm of 0.032" i.d. tubing. Then add the other gripper, end fitting, and end cap to the union assembly. Set this aside.

3.7. Continue step 3.1.6 until all cadmium columns are assembled. Additional parts may be needed from inventory to replace the damaged parts from the QC steps.

4. Cadmium Preparation Procedure

4.1. Use about four and a half grams of cadmium for each column to be packed. This can be weighed into a 250 mL beaker. First, add 30 - 80 mL of acetone to the cadmium granules and swirl. Swirl for 5 -10 seconds and then decant the acetone to organic waste. This step is to remove any organic residue from the granules. This step may be repeated.

4.2. Second, add 100 - 150 mL of DI water to the beaker and swirl for 5 - 10 seconds and gently pour off the waste. During both of these two rinse steps the solution will become cloudy but the color of the cadmium granules will not change.

4.3. Next, add 50 - 100 mL of the 1 M hydrochloric acid. The cadmium will turn very light gray in color and there may be a slight effervescence

4.4. Swirl the granules with 1 M hydrochloric acid until they are all uniformly gray in color. If you are using recycled cadmium, it may not wash well enough in the above steps; therefore some of the granules will remain darker than others.

4.5. More than one washing with 1 M hydrochloric acid may provide a more uniform final color. Gently decant the 1 M hydrochloric acid into a waste container.

4.6. The final step is to copperize the granules by adding 50 - 100 mL of copper sulfate solution and swirling to provide solution contact with the granules. The granules will turn dark in color and the copper sulfate solution will become a lighter shade of blue.

4.7. Swirl for 10 - 20 seconds and decant the solution to waste. Add another 50 mL aliquot of copper sulfate solution and continue to swirl the beaker. Repeat this step until colloidal copper begins to appear in the solution above the granules. The colloidal copper has a red/rust color to it. The liquid will also turn a brown color. Decant this liquid and add one more 50 mL aliquot of copper sulfate solution until it turns brown.

4.8. At this point, stop the copperization process. If too much copper sulfate is added, the colloidal copper will plug the column. If too little copper sulfate is used, the efficiency and column lifetime will degrade.

4.9. Last, add 50 mL of ammonia buffer. At this point the solution may become slightly turbid. If so, gently decant the ammonia buffer to waste and continue to rinse until the buffer is clear.

4.10. At this stage the granules can be stored for up to one week by covering the beaker with parafilm. The copperized granules must remain immersed in the buffer. Place this beaker in the fume hood.

5. Column Packing Procedure (See Figure B)

5.1. Place the peristaltic pump to the left of the wash basin. Place the beaker containing copperized granules, both probes, and the funnel in the wash basin.

5.2. Place the green pump tube assembly in the pump, apply tension to the pump cassette and begin pumping ammonia buffer at a speed of 35 into the wash basin.

5.3. On one side of the wash basin you will have the glass columns with one end cap. On the other side, place the other end cap, end fitting and two union assemblies.

5.4. Attach the column to the pump ammonia buffer by attaching the gripper Teflon tubing to the union in the wash basin. Hold the column upright and observe the flow.

5.5. While the column is filling with buffer, use the sample probe to dislodge air bubbles in the foam plug at what is now the bottom of the column chamber. Sleeve the funnel over the top of the column until buffer has risen above the flared section in the funnel.

5.6. Using a weighing spatula, scoop granules from the beaker into the funnel. Using the spatula, gently tap the sides of the column until the column is full. If air bubbles are observed in the column, empty it and start over. Tapping the column helps to avoid gaps in the cadmium. If a gap is seen, the column needs to be emptied and start over.

5.7. Remove the funnel, letting the excess granules drop into the beaker. Using the dissecting probe, insert the top foam plug into the column. Push the plug into the column. (If the plug is over the glass surface at the top of the column it will leak.)

5.8. Pick up the end cap, end fitting, gripper and union assembly from the bench and screw the end cap on finger tight. Completely dry the column and observe it for at least one minute for leaking.

5.9. Disconnect the column from the pump at the outlet of the pump tube adapter. Quickly attach the end of the gripper to the union. After the connections have been made, ensure that the end caps are tight. Place the column in another bucket that contains DI water.

5.10. When all columns are finished being packed, empty the DI water and allow the cadmium columns to dry overnight.

5.11. Check both end caps to be sure they are on tightly and that the end fitting has been backed out far enough for it to be screwed all the way in. Check to be sure there are no air bubbles or gaps. Check the glass column right around the end caps to make sure there has not been any leakage of buffer. If there is, tighten the end caps again and place the column aside for further time to ensure there is not leak.

Figure A

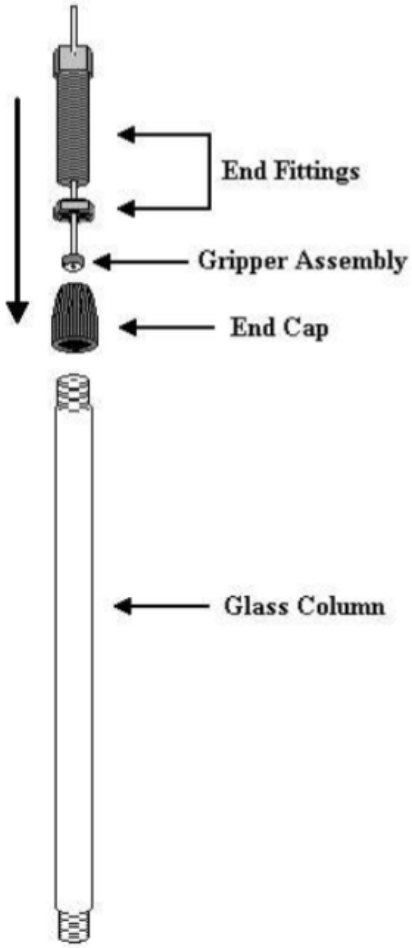
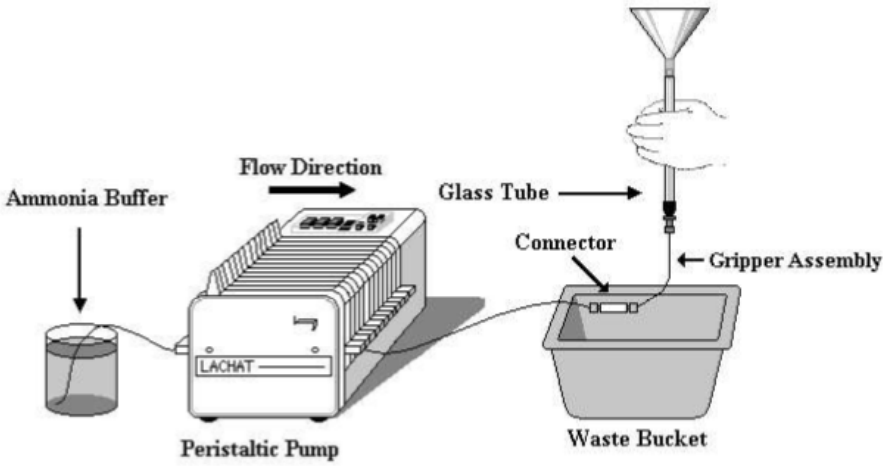


Figure B


Flow Direction
Ammonia Buffer
Glass Tube
Connector
Gripper Assembly
LACHAT
Peristaltic Pump
Waste Bucket

Standard Operating Procedure
Total Dissolved Nitrogen (TN) and Total Nitrogen (TDN)
EPA 353.2 – SM 4500-N C
Nutrients Laboratory

Prepared by:
Name: Steph Kexel **Signature**: _____ **Title**: _____ **Date**: _____

Approved by:
Name: Chris Perkins **Signature**: _____ **Title**: _____ **Date**: _____

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State of CT: PH-0778 – EPA: CT01022

Total Nitrogen and Total Dissolved Nitrogen EPA 353.2
SM 4500 N C

Scope and Application

- This is an alkaline persulfate oxidation method (D'Elia 1977) on water and/or seawater for total nitrogen (TN) and total dissolved nitrogen (TDN). Nitrate is the sole N product of the digestion and is determined by an automated colorimetric procedure. This section provides a stepwise procedure for bench use by laboratory personnel.

- EPA Method 353.2 is the reference method for measuring nitrate + nitrite in water and seawater by automated colorimetric determination, and SM 4500 N C is the digestion. This section provides a stepwise procedure for bench use by laboratory personnel.

- This method is based on automated colorimetric determination and is restricted to the use by or under the supervision of analysts experienced in the use of auto analyzers. The applicable range is from 0.0 to 2.0mg/L.

- Samples are extracted with potassium persulfate and NO_x values are obtained by activating the cadmium column and calibrating with combined NO_3-N + NH_3-N standards as N for the TN/TDN calibration curve.

Summary of Method

- For total nitrogen analysis (TN), the whole water sample is pipetted into test tubes and analyzed. For total dissolved nitrogen (TDN) analysis, the whole water sample is filtered though a 47mm GF/F filter in the field. 10mL of sample is then pipetted into a screw cap test tube. The pipetted sample is then frozen at –10°C or below until digestion can be completed. 5mL of an oxidizing reagent (potassium persulfate) is then added. The tubes are placed in an autoclave at 235°F for 60 minutes. The sample is allowed to sit overnight and then is ready for analysis of TN/TDN. Analysis is completed within 28 days of arrival at the laboratory.

- This method is interchangeable with the Combo digestion method that combines the TN and the TP digestion into one preparation. Comparison studies are available upon request.

- Every 20 samples, a preparation blank, a laboratory spike, and a laboratory duplicate analysis are performed. Samples are analyzed using flow injection on the Lachat. Nitrate is reduced to nitrite at pH 7.5 in a copperized cadmium column. The nitrate reduced to nitrite, plus any free nitrite present, reacts under acidic conditions with sulfanilamide to form a diazo compound that couples with

N-1-Naphthylethylenediamine dihydrochloride to form a reddish-purple azo dye that is measured at 550nm.

- Method Detection Limits will be developed for all CTDPH approved methods according to the process and procedures detailed in the CESE Laboratory Quality Assurance Plan Section 7.4 (Method Detection Limit Studies).

- This method is based on automated colorimetric determinations and is restricted to the use by, or under the supervision of, analysts experienced in the use of auto analyzer equipment.

- The analyzer is calibrated with a minimum of a six-point curve (including the blank) at the time of analysis. The calibration curve is then verified by an external quality control sample from ERA, an independent supplier. ERA supply guidelines are used for making up the quality control solutions, as well as for information on the true value and acceptable value range for the analytes being measured in each quality control sample.

- Initial calibration verification along with an initial calibration blank demonstrate that the instrument is capable of acceptable performance at the beginning of the sample analysis. To ensure continuing acceptable performance, a continuing calibration check and continuing calibration blank are run every twenty samples. For every 20 samples, a laboratory spike analysis and a laboratory duplicate analysis are performed. At the end of the run a PQL (Practical Quantitative Limit) is run for further quality control verification.

Definitions

- See the Laboratory QAP (Quality Assurance Plan) for definitions of common labor

Interferences

- Build up of suspended matter in the cadmium column will restrict flow. Look for a "jerking" action in one or several of the pump tube lines as evidence of such a blockage. Nitrate-nitrogen is, however, found in a soluble state, so pre-filtering of samples should be sufficient to keep lines clear.

- Low results are possible for samples high in metals concentrations such as iron or copper. (1.0g per liter) $Na_2EDTA{\cdot}2H_2O$ can be added to the buffer to reduce this interference.

- Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. Pre-extracting the sample with an organic solvent eliminates this interference.

References

10-107-04-1-C, March 2003. Determination of Nitrate/Nitrite in Surface and Wastewaters by Flow Injection Analysis. Lachat Instruments, Loveland, CO.

31-107-044-A, September 18, 2003. Determination of Total Nitrogen in Brackish or Seawater by Flow Injection Analysis. Lachat Instruments Applications Group, Loveland, CO.

EPA Method 353.2. Determination of Nitrate-Nitrite Nitrogen by Automated Colorimetry. Revision 2.0, August 1993. Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.

Standard Method 4500 –N C. Nitrogen: Persulfate Method. Page 4-102—4-103, 20th Edition, 1998, Standard Methods for the Examination of Water and Wastewater.

Associated SOP's

Refer to "SOP" titled "Hazardous Waste SOP" for proper waste disposal.

Refer to the notebook titled "SOP's" located in the nutrients laboratory.

Safety

Samples are disposed of in a hazardous waste jug and are properly labeled.

Reagents are hazardous and are made in the hood. Protective gear is worn when making reagents.

Ensure that waste lines from the Lachat are going to the proper hazardous waste jug located under the instrument.

The following chemicals have the potential to be highly toxic or hazardous, consult MSDS:

- Phosphoric acid
- Hydrochloric acid
- Sulfuric acid

Refer to the University of Connecticut's Environmental Health and Safety Chemical Health and Safety web page at:

http://www.ehs.uconn.edu/ppp/index.php

A hard copy of the Chemical Hygiene Plan can be found on the notebook rack located on the lab bench. Also refer to the Hazardous Waste SOP.

Materials

Market Forge Autoclave
Lachat Quick Chem 8500
Cadmium column

Procedure

Reagent Preparation

- Unless otherwise specified, all chemicals should be ACS grade or equivalent. DI water refers to high quality reagent water, TYPE I or TYPE II as defined in ASTM Standards, Part 31, D1193-74. When making reagents, date the container in which the reagent is stored, initial it, and write out the entire name of the reagent.

  ❖ Digestion Reagent – Potassium Persulfate

We are currently using Fisher sodium hydroxide (catalog no.S399-212) and Sigma Adlrich potassium persulfate (catalog no. 216224-500). The potassium persulfate should be kept in a desiccator to minimize the possibility of oxidization and may also come from the supplier with nitrogen contamination. Monitor blanks for issues.

Sodium Hydroxide	6g
Potassium Persulfate	40.2g
Boric Acid	12g
DI Water, q.s.	1000mL final vol.

In a 1L volumetric flask, dissolve 6.0g sodium hydroxide in about 600mL of water. When the sodium hydroxide is completely dissolved, add 40.2g potassium persulfate and 12.0g of boric acid and dissolve. Dilute to 1 liter with DI water and mix thoroughly. This solution is unstable and should be made immediately prior to use.

❖ Ammonium Chloride Buffer

We are currently using Fisher hydrochloric acid (catalog no. S318-3) and Fisher ammonium hydroxide (catalog no. A669S-212).

Hydrochloric Acid (concentrated)	210mL
Ammonium Hydroxide	190mL
Disodium EDTA	2.0g
DI Water, g.s.	2000mL final vol.

Be sure to make this reagent in the hood. Wear all protective gear! Add about 1000mL DI water to a 2000mL glass volumetric flask. Carefully pour in 210mL concentrated hydrochloric acid and rinse well. With a new graduated cylinder, pour in 190mL ammonium hydroxide and rinse. Add 2.0g disodium EDTA, dissolve and dilute to the mark. Add stir bar and mix. Adjust the pH to 8.5 with 15N sodium hydroxide solution. Solution is stable for 2 months.

❖ Sulfanilimide Color Reagent

We are currently using Fisher sulfanilamide (catalog no. O4525-100), Acros NED (catalog no. AC42399-0250), and Fisher phosphoric acid (catalog no. A242SK-2212).

Phosphoric Acid (85% soln. by wt.)	200mL
Sulfanilamide	80.0g
NED (N-(1-napthyl)ethylenediamine dihydrochloride	2.0g
DI Water, g.s.	1000mL final vol.

To a 1L volumetric flask, add about 600mL DI water then add 200mL 85% phosphoric acid, 80g sulfanilamide and 2.0g NED. Store in a dark bottle and discard when the solution turns pink in about a month.

❖ 2N Hydrochloric Acid

We are currently using Fisher hydrochloric acid (catalog no. S318-3).

Hydrochloric Acid (concentrated)	16.6mL
DI Water, q.s.	100mL final vol.

Add 50mL DI water to a graduated cylinder. Carefully pour in 16.6mL hydrochloric acid and dilute to 100mL with DI water. Prepare solution quarterly.

❖ Cadmium-Copper Reduction Column

Pre-packed cadmium columns for use with the Lachat nitrate/nitrite manifold and are available from Lachat/HACH (Lachat part/order no. 50237A). Instructions for repacking columns in the laboratory are at the end of this SOP.

Standard Preparation

Working standards can be made by weight or volume. Standards are made using a 1000µg/mL stock certified from AccuStandard or another source different from the QC. Prepare fresh weekly.

❖ Stock Standard, 20.0mg/L N

AccuStandard Stock (NH_3-N and NO_3^--N)	1mL of each
DI water, q.s.	100mL final vol.

In a 100mL volumetric flask containing about 80mL of DI add 1mL each of Stock AccuStandard NH_3-N and NO_3^--N Standards. Dilute to 100mL with DI and mix thoroughly. Record the information in the stock standard logbook.

❖ Preparation of working standards:

Transfer aliquots of Stock 20mg/L stock as noted below to individual 100mL volumetric flasks. Dilute to volume with DI water and mix thoroughly. Record the information in working standard logbook. Prepare fresh weekly.

❖ Working Standard Solutions for Low Range Analysis

mL(g) 20mg/L Stock	mg/L N
10	2.0
5	1.0
3	0.6
1	0.2
0.05	0.1
0.025	0.0

- Cadmium column efficiency is not tested for this analysis because the calibrants are digested in potassium persulfate. Ensure that column efficiency has been tested prior to this run on the most recent NO_x analysis and has fallen within acceptable limits.

Sample Preparation

- Sample turbidity may be removed by filtration though a 47mm GF/F filter prior to analysis and will yield the TDN result. Turbidity absorbing in the range of 550 nanometers (nm) will present a positive bias.

- Preserve the sample by freezing at -10°C or below until the time of analysis. Samples may be stored in test tubes in the freezer until time of analysis. Ensure that test tubes are not cracked after defrosting samples for preparation.

- Sample containers are to be rinsed with 1:1 hydrochloric acid, followed by DI water and finally by an aliquot of the sample itself. Disposable plastic sample tubes are used during analysis to avoid contamination from improper washing of glass tubes.

- Pipette 10mL of sample into a 30mL test tube. 10mL of standards, QC and blanks should also be pipetted. The highest concentration of standard is pipetted 6 times to account for setting the gain on the instrument and running the drift and primer cups. The rest of the standards are pipetted at least 3 times for each concentration.

- The quality control sample (QC) is made up in 100mL volumes per every 60 or so samples. Larger quantities are necessary if running large batches of samples. The QC concentration changes with each new lot # purchased from Environmental Resource Associates. It is made fresh daily.

- Generally, spiked samples are spiked with 250µL of the 20ppm stock standard and are spiked directly into the test tube before digestion yielding a spike concentration of 0.488ppm.

- Add 5mL of digestion reagent and mix thoroughly. Place the samples and standards into the autoclave and heat from 235°F for one hour for a final volume of 15mL in the test tube.

- Allow the autoclave pressure to equalize, and the temperature to decrease before removing the sample. Cool to room temperature overnight.

- If analysis cannot be performed immediately samples can be stored at 4°C after digestion.

Instrumental Analysis

- Transfer the samples to disposable test tubes for automated TN/TDN analysis on the Lachat (method 31-107-04-4-A).

- It is assumed that the user is basically familiar with the appearance and location of the various parts of the Lachat. It is also assumed that a method for running TN/TDN analyses has already been created, and that the user is familiar with basic system operations. For a physical description of the instrument and any related software information, see the Lachat SOP.

- Ensure that the proper sized sample loop is connected between ports 1 and 4 of the inject valve.

- The sample loop is 150cm long and labeled "TN". It can be found in the drawer of Lachat parts.

- The column efficiency should be greater than 90%, as stated by certification from Lachat. When the efficiency falls outside of this range, the cadmium column must be replaced.

- Introduce the ammonium chloride reagent into the chemistry manifold first and let it flow for about a minute before introducing the sulfanilamide.

- **When using the cadmium column, ALWAYS ensure that the column is activated when ALL reagents are pumping through the system. Likewise, make sure the column is in the "off" position at the end of the run before taking reagent lines out of solution for the wash step.**

- Cadmium columns are purchased from Lachat instruments (CAT # 50237A), however cadmium may be regenerated in the laboratory according to Lachat publication WI#J20008. Publication included at the end of this SOP.

Calculations

- Percent Recovery for the QC is calculated by the following formula:

$$\%Recovery = \frac{Observed\ QC\ Value}{Expected\ QC\ Value} \times 100$$

- Percent recovery for the spike is determined using the following formula:

$$\%Recovery = \frac{(A - B)}{C} \times 100$$

Where: A = measured value in mg/L for the sample + spike
B = measured value in mg/L for the original sample
C = concentration of the spike in mg/L

- Relative percent difference for the duplicate is calculated by the following formula:

$$RPD = \frac{(A - B)}{[(A + B) \div 2]} \times 100$$

Where: A = The value in mg/L for the first run of the sample
B = The value in mg/L for the second run of the sample

- To determine the column efficiency, use the following formula:

$$E = \frac{[NO_3^- - N]}{NO_2^- - N} \times 100$$

Where: E = column efficiency
NO_3^--N = concentration of nitrate standard
NO_2^--N = concentration of nitrite standard

Quality Control

- A certified second source quality control sample (purchased from ERA) is analyzed for every delivery group (or every 20 samples) and the value must be within 90-110% recovery, or as per client request, to be considered acceptable. Prepare fresh daily.
- A spike is analyzed for every delivery group (or every 20 samples). The percent recovery must fall within the 85-115% recovery to be considered acceptable.
- A duplicate is analyzed for every delivery group (or every 20 samples). The relative percent difference for the duplicate analysis must fall below 20%, or as per client request.
- A blank is analyzed every delivery group, or every 20 samples and the value must fall below the PQL to be considered acceptable.
- A second quality control sample is analyzed every delivery group and at the end of the run and is the concentration of the PQL, or the lowest standard. Acceptable ranges for the PQL are 50-150% recovery.

Other System Notes

- Light interference filter: 520nm
- Sample Loop Size: 150cm

WI #: J20008	Date Issued: 10Jun96
Title: Copperizing and Packing Cadmium Reductor Columns	Revision Date: 21Feb 02
Author: David Diamond	
Purpose: To provide instruction on how to copperize and pack cadmium columns. Section 3 explains how to remove cadmium from a used glass column.	
Scope: These guidelines and requirements apply to Cadmium columns prepared at Lachat Instruments.	

1. Special Instructions

1.1. Use cadmium granules (Lachat Part no. 50231), which have been sieved to pass a 14-mesh screen and retain on a 40-mesh screen. Lack of uniformity in the granule size may cause flow problems.

1.2. While packing the column observe the pump tube on the inlet side of the pump for pulsing. This is an indication that the column tubing is plugged or the pump tubing is plugged. Also, observe the flow of ammonia buffer from the column just prior to disconnecting it from the peristaltic pump. Look for pulsing or lack of flow.

1.3. New cadmium granules will give a more uniform color and will results in longer lifetimes than recycled granules.

2. Equipment Needed

2.1. 0.2% Copper Sulfate Pentahydrate ($CuSO_4 \cdot 5H_2O$) – In a 1 L volumetric flask, dissolve 2 g $CuSO_4 \cdot 5H_2O$ in about 250 mL of deionized (DI) water. Dilute to the mark with DI water. If packing more than 4 columns, increase concentration of copper sulfate to 2%.

2.2. 1M Hydrochloric Acid – In a 1 L volumetric flask, slowly add 82.5 mL of hydrochloric acid (HCl) to approximately 500 mL of DI water. Dilute to the mark with DI water. Recipe by weight: In a 1 L container, add 917 g DI water and 100 g conc. HCl.

2.3. Acetone, Lab grade

2.4. Packing Funnel, plastic, for 12.5 cm diameter paper, VWR cat. No. 30246-021, 6.5 mm O.D. at top. With a scissors, cut about 1.5 cm from the tip of the funnel. Cut a 2 cm piece of 3/8" (5 mm) PVC tubing. Sleeve the PVC tubing over the end of the funnel.

2.5. Wash Basin, approx. 12" X 14" X 6" deep.

2.6. Peristaltic Pump, set at 35.

2.7. Pump tube, green/green, Lachat Part No.53214, attached to large PVC transmission tubing with a glass line weight attached. On the other end of the pump tubing attach a pump tube adapter with a large collar.

2.8. Dissecting Probe, Lachat part No. 50060

2.9. Sample Probe

2.10. Foam Plugs (2 per column). Plugs should be cut with a scissors to 5 mm^3. Foam Part No: 50229

2.11. Ammonia Buffer – CAUTION: Fumes! To a 10 L container add, 8442 g DI water, 765 g Ammonium Chloride (NH4Cl),and 9.0 g disodium ethylenediamine tetraacetate (Na2EDTA·2H2O). Stir until dissolved. The pH of this solution must be 8.5. Adjust if necessary with 15 N sodium hydroxide (NaOH) before use. Store in a tightly sealed container. This reagent is good for at least 2 months.

2.12. Check pH of buffer before use, and adjust if necessary!!!!

2.13. 30 – 125 mL containers and 30 labels (front and back) for cadmium granules.

3. Column Preparation Procedure – Removal of Used Cadmium

3.1. Fill a 1 L container about one third full with DI water.

3.2. Gather used columns, dissecting probe and sample probe. Unscrew both the end fittings and the end caps on each side of the column.

3.3. While holding the column over the container, start to disassemble the column. First remove the end fittings from both ends. Lay these pieces aside. Remove one end cap and use the dissecting probe to remove the old foam plug. Then turn the column over (make sure that the open end is over the container). Remove the other end cap and foam piece using the dissecting probe. Then tap the column ends on the sides of the container. The cadmium should fall out the lower end. If they do not, use a squirt bottle filled with DI water and put water through the column. The cadmium may come out by doing this, if not, then use the dissecting probe or sample probe to remove the rest of the cadmium. If necessary to dislodge the cadmium, use a sonicator to loosen the cadmium. Then try to remove the cadmium with the dissecting probe and DI water. If the cadmium cannot be removed, the column is considered broken and needs to be placed aside for the next lab pack.

3.4. Once the cadmium has been removed, clean and inspect all of the parts. The parts include two end fittings, two end caps, two unions, two Teflon 15 cm lengths of tubing with gripper assemblies attached, and a 10 cm length of .032" id. Teflon tubing. The tubing used with the grippers is special in that the dimensions and tolerances are specific for the gripper fittings. (See Figure A). If glass columns are chipped on the ends, they will leak when reassembled.

3.4.1. For end fittings, look at the threads for wear. If the threads are turned over, discard the end fitting.

3.4.2. For end caps, look at the threads on the inside. If there are strands of plastic or the threads are bad, discard the end cap. Make sure there is still the white frit in the end.

3.4.3. For unions, make sure that there are two unions. If the unions are not properly assembled, replace.

3.4.4. For the grippers, make sure that there are no crimps in the tubing. If there are, discard the gripper.

3.4.5. For glass columns, make sure that the inside of the column is clean. DI water can be used to rinse them out. Look at the threads on each end of the column. If there is a chip in just one thread, it can be deemed as okay. If the chip is in the same spot along more than one thread, then the column may leak. Look at the end of the glass column. The end is opaque. If there is a chip that does not extend across then entire bottom, the column may be okay. If it is across the entire bottom, the column will most likely leak. If there is doubt as to whether the column may leak, use a Sharpie marker and mark the end of concern. This column may be repacked. When finished, if it leaks, then the column needs to be replaced.

3.5. Once the parts have been inspected, place them in a bucket that contains DI water. This allows the parts to be cleaned of debris.

3.6. Clean and dry the glass column and place a foam plug in one end. Screw an end cap finger tight on the end with the foam plug. Then add an end fitting with gripper to the tightened end cap. Do not place a foam plug in the other end yet. Set the column aside. Assemble the rest of the assembly by connecting two unions by 8.5 cm of 0.032" i.d. tubing. Then add the other gripper, end fitting, and end cap to the union assembly. Set this aside.

3.7. Continue step 3.1.6 until all cadmium columns are assembled. Additional parts may be needed from inventory to replace the damaged parts from the QC steps.

4. Cadmium Preparation Procedure

4.1. Use about four and a half grams of cadmium for each column to be packed. This can be weighed into a 250 mL beaker. First, add 30 - 80 mL of acetone to the cadmium granules and swirl. Swirl for 5 -10 seconds and then decant the acetone to organic waste. This step is to remove any organic residue from the granules. This step may be repeated.

4.2. Second, add 100 - 150 mL of DI water to the beaker and swirl for 5 - 10 seconds and gently pour off the waste. During both of these two rinse steps the solution will become cloudy but the color of the cadmium granules will not change.

4.3. Next, add 50 - 100 mL of the 1 M hydrochloric acid. The cadmium will turn very light gray in color and there may be a slight effervescence

4.4. Swirl the granules with 1 M hydrochloric acid until they are all uniformly gray in color. If you are using recycled cadmium, it may not wash well enough in the above steps; therefore some of the granules will remain darker than others.

4.5. More than one washing with 1 M hydrochloric acid may provide a more uniform final color. Gently decant the 1 M hydrochloric acid into a waste container.

4.6. The final step is to copperize the granules by adding 50 - 100 mL of copper sulfate solution and swirling to provide solution contact with the granules. The granules will turn dark in color and the copper sulfate solution will become a lighter shade of blue.

4.7. Swirl for 10 - 20 seconds and decant the solution to waste. Add another 50 mL aliquot of copper sulfate solution and continue to swirl the beaker. Repeat this step until colloidal copper begins to appear in the solution above the granules. The colloidal copper has a red/rust color to it. The liquid will also turn a brown color. Decant this liquid and add one more 50 mL aliquot of copper sulfate solution until it turns brown.

4.8. At this point, stop the copperization process. If too much copper sulfate is added, the colloidal copper will plug the column. If too little copper sulfate is used, the efficiency and column lifetime will degrade.

4.9. Last, add 50 mL of ammonia buffer. At this point the solution may become slightly turbid. If so, gently decant the ammonia buffer to waste and continue to rinse until the buffer is clear.

4.10. At this stage the granules can be stored for up to one week by covering the beaker with parafilm. The copperized granules must remain immersed in the buffer. Place this beaker in the fume hood.

5. Column Packing Procedure (See Figure B)

5.1. Place the peristaltic pump to the left of the wash basin. Place the beaker containing copperized granules, both probes, and the funnel in the wash basin.

5.2. Place the green pump tube assembly in the pump, apply tension to the pump cassette and begin pumping ammonia buffer at a speed of 35 into the wash basin.

5.3. On one side of the wash basin you will have the glass columns with one end cap. On the other side, place the other end cap, end fitting and two union assemblies.

5.4. Attach the column to the pump ammonia buffer by attaching the gripper Teflon tubing to the union in the wash basin. Hold the column upright and observe the flow.

5.5. While the column is filling with buffer, use the sample probe to dislodge air bubbles in the foam plug at what is now the bottom of the column chamber. Sleeve the funnel over the top of the column until buffer has risen above the flared section in the funnel.

5.6. Using a weighing spatula, scoop granules from the beaker into the funnel. Using the spatula, gently tap the sides of the column until the column is full. If air bubbles are observed in the column, empty it and start over. Tapping the column helps to avoid gaps in the cadmium. If a gap is seen, the column needs to be emptied and start over.

5.7. Remove the funnel, letting the excess granules drop into the beaker. Using the dissecting probe, insert the top foam plug into the column. Push the plug into the column. (If the plug is over the glass surface at the top of the column it will leak.)

5.8. Pick up the end cap, end fitting, gripper and union assembly from the bench and screw the end cap on finger tight. Completely dry the column and observe it for at least one minute for leaking.

5.9. Disconnect the column from the pump at the outlet of the pump tube adapter. Quickly attach the end of the gripper to the union. After the connections have been made, ensure that the end caps are tight. Place the column in another bucket that contains DI water.

5.10. When all columns are finished being packed, empty the DI water and allow the cadmium columns to dry overnight.

5.11. Check both end caps to be sure they are on tightly and that the end fitting has been backed out far enough for it to be screwed all the way in. Check to be sure there are no air bubbles or gaps. Check the glass column right around the end caps to make sure there has not been any leakage of buffer. If there is, tighten the end caps again and place the column aside for further time to ensure there is no leak.

Figure A

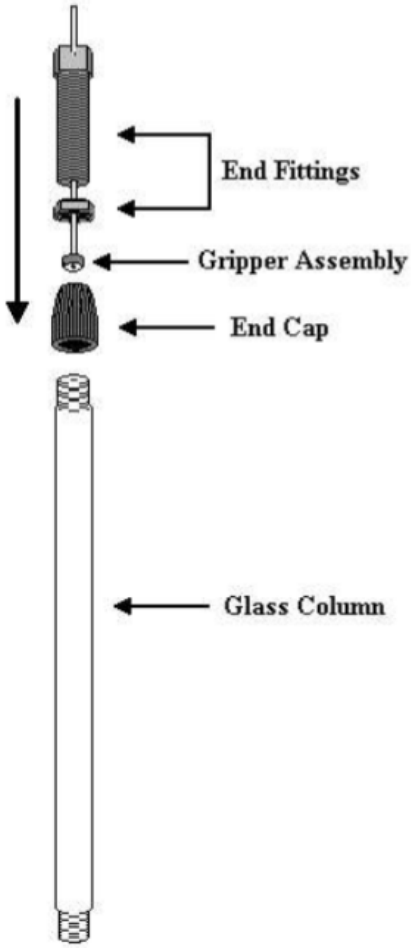
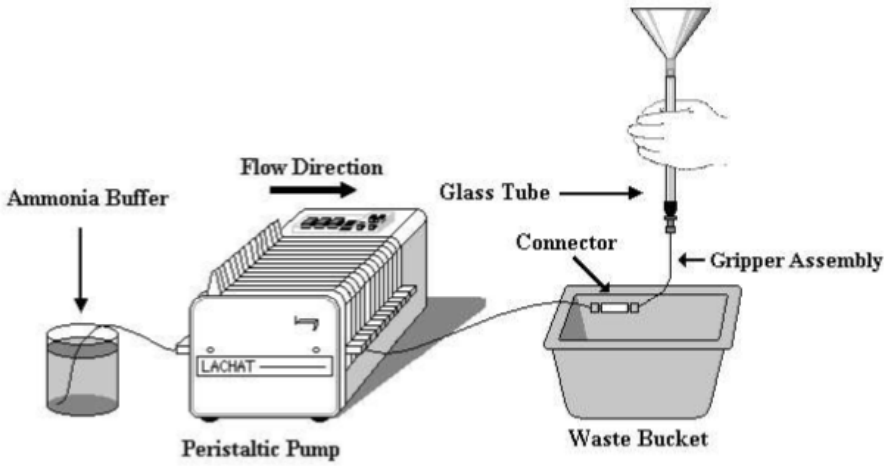


Figure B


Flow Direction
Ammonia Buffer
Glass Tube
Connector
Gripper Assembly
LACHAT
Peristaltic Pump
Waste Bucket

Appendix C-4

Standard Operating Procedure
Ortho-Phosphate and Dissolved Inorganic Phosphorus
EPA 365.1
SM 4500-P A, B, and G
Nutrients Laboratory

Prepared by:
Name: Steph Kexel **Signature**: _____ **Title**: _____ **Date**: _____

Approved by:
Name: Chris Perkins **Signature**: _____ **Title**: _____ **Date**: _____

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State of CT: PH-0778 – EPA: CT01022

Ortho-Phosphate – Dissolved Inorganic Phosphorus EPA 365.1 SM4500-P A, B and G

Scope and Application

- EPA Method 365.1 is the reference method for measuring ortho-phosphate or dissolved inorganic phosphorus in water and seawater by automated colorimetric determination. This section provides a stepwise procedure for bench use by laboratory personnel.

- This method (Lachat ortho-phosphate method number 31-115-01-1-H) was developed for the quantitative analysis of ortho-phosphate in water and seawater. The applicable range is 0.010 to 0.500mg/L of ortho-phosphate as phosphorus. Samples higher in range may be diluted and re-run or analyzed by recalibrating with higher concentration.

- This method is based on automated colorimetric determination and is restricted to the use by or under the supervision of analysts experienced in the use of auto analyzers.

Summary of Method

- For dissolved inorganic phosphorus, the whole water sample is filtered though a 47mm GF/F filter in the field. The filtrate is then preserved in the field by adding H_2SO_4 to a pH of <2 at the time of collection and freezing at or below -10°C until analysis is performed. The client may decide to solely freeze samples without preservation to eliminate variability, and to minimize potential safety issues associated with field acidification. The client will notify/discuss these procedures with CESE staff prior to sample acceptance.

- Samples for ortho-phosphate are analyzed by an automated procedure on the Lachat QuickChem flow injection analyzer. The analysis depends on the formation of a phosphomolybdenum blue complex, which is read colorimetrically at 880nm.

- Method Detection Limits will be developed for all CTDPH approved methods according to the process and procedures detailed in the CESE Laboratory Quality Assurance Plan Section 7.4 (Method Detection Limit Studies).

- This method is based on automated colorimetric determinations and is restricted to the use by, or under the supervision of, analysts experienced in the use of auto analyzer equipment.

- The Lachat is calibrated with a minimum of a six-point curve (including the blank) at the time of analysis. The calibration curve is then verified by an external quality control sample from Fisher, an independent supplier. Fisher supply guidelines are used for making up the quality control solutions, as well as for information on the true value and acceptable value range for the analytes being measured in each quality control sample.

- An initial calibration check along with an initial calibration blank, demonstrate that the instrument is capable of acceptable performance at the beginning of the sample analysis. To ensure continuing acceptable performance a continuing calibration check and continuing calibration blank are run every tenth sample. For every 20 samples, a laboratory spike analysis and a laboratory duplicate analysis are performed. At the end of the run a PQL (Practical Quantitation Limit) is run for further quality control verification.

Definitions

- See the Laboratory QAP (Quality Assurance Plan) for definitions of common laboratory terms.

- **Phosphorus Fraction Definitions --**

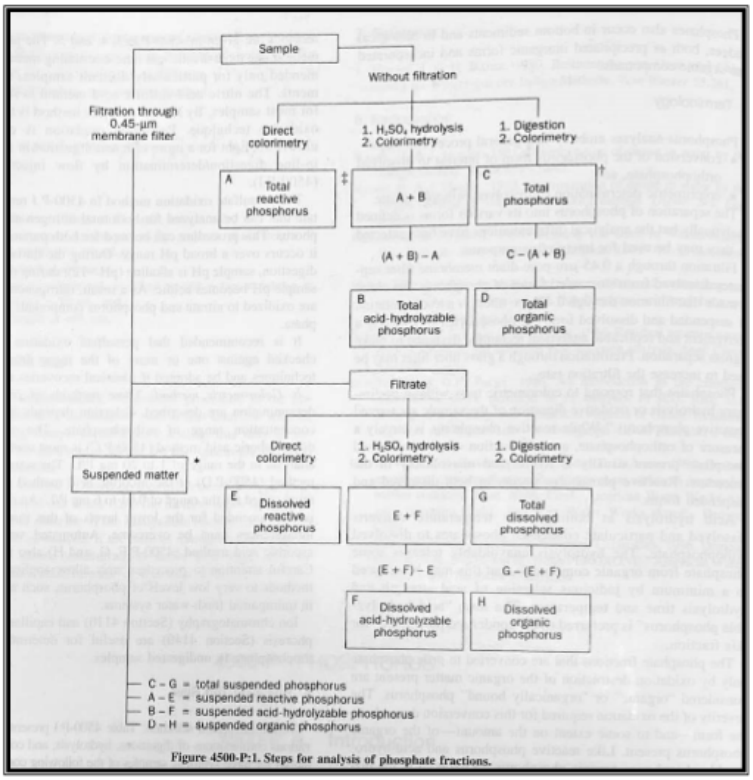

Figure 4500-P:1. Steps for analysis of phosphate fractions.

- In the Nutrient's Laboratory, most of the Phosphorus fractions are analyzed in these main analytical runs:
    - **Total Phosphorus (TP)** – All of the phosphorus present in the sample regardless of forms is digested by the persulfate digestion procedure, then analyzed by direct colorimetry. In the chart above, this is "C".
    - **Total Dissolved Phosphorus (TDP)** – The sample is passed through a 0.45µm filter and then the filtrate is digested with persulfate and analyzed by direct colorimetry. This is also referred to as "Total Dissolved Phosphorus" in the above chart or "G".
    - **Ortho-Phosphate (o-PO_4)** – This is the sample analyzed on the instrument without any filtration or digestion. It is referred to as Total Reactive Phosphorus above in "A".
    - **Dissolved Inorganic Phosphorus (DIP)** – This is the sample filtered through a 0.45µm filter then analyzed colorimetrically without a digestion step. In the above chart, it is referred to as Dissolved or Soluble Reactive Phosphorus or "E".
    - **Particulate Phosphorus (PP)** – This is the suspended matter captured on a 0.45µm filter then digested with 1N Hydrochloric Acid and analyzed colorimetrically. This may be required when greater precision is necessary because the calculations of above fractions to determine the Suspended Phosphorus are less precision.
- All phosphorus forms are reported as P.

Interferences

- Silica forms a pale blue complex that also absorbs at 880nm and is generally insignificant because a silica concentration of approximately 30mg/L would be required to produce a 0.005-P/L positive error in ortho-phosphate.
- Concentrations of ferric iron greater than 50mg/L cause a negative error due to competition with the complex for the reducing agent ascorbic acid. Samples may be treated with sodium bi-sulfite to eliminate this interference, as well as interferences due to arsenates.
- Acidity among samples, standards and blanks should be carefully controlled. Large variations in acidity will affect sample and/or standard peaks.

- Good glassware cleaning procedures should always be used. Phosphorus contamination is a constant problem. Proper glassware washing protocol should eliminate this problem.

References

31-115-01-1-H, August 2003. Determination of Orthophosphate by Flow Injection Analysis. Lachat Instruments, Loveland, CO.

EPA Method 365.1. Determination of Phosphorus by Semi-Automated Colorimetry. Revision 2.0, August 1993. Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.

Standard Method 4500-P A, B, G, H and J. Phosphorous: Flow Injection Method. Page 4-139 – 4-153, 20th Edition, 1998, Standard Methods for the Examination of Water and Wastewater.

Associated SOP's

Refer to "SOP" titled "Hazardous Waste SOP" for proper waste disposal.

Refer to the notebook titled "SOP's" located in the nutrients laboratory.

Safety

Reagents are hazardous and are made in the hood. Protective gear is worn when making reagents.

Ensure that waste lines from the Lachat are going to the proper hazardous waste jug located under the instrument.

Refer to the University of Connecticut's Environmental Health and Safety Chemical Health and Safety web page at:

http://www.ehs.uconn.edu/ppp/index.php

A hard copy of the Chemical Hygiene Plan can be found on the notebook rack located on the lab bench. Also refer to the Hazardous Waste SOP.

Materials

Lachat QuickChem Auto-Analyzer

Procedure

Reagent Preparation

- Unless otherwise specified, all chemicals should be ACS grade or equivalent. DI water refers to high quality reagent water, TYPE I or TYPE II as defined in ASTM Standards, Part 31, D1193-74. When making reagents, date the container in which the reagent is stored, initial it, and write out the entire name of the reagent.

❖ Stock Antimony Potassium Tartrate

We are currently using Fisher antimony potassium tartrate (catalog no. A867-250).

Antimony Potassium Tartrate	1.61g
DI Water, q.s.	500mL final vol.

Dissolve 1.61g of antimony potassium tartrate in about 400mL of DI water in 500mL volumetric flask. Dilute to 100mL with DI water and mix thoroughly. Store the solution in a dark plastic container. Solution is stable for one month.

❖ Stock Ammonium Molybdate

We are currently using Fisher ammonium molybdate (catalog no. A674-500).

Ammonium Molybdate	20g
DI Water, q.s.	500mL final vol.

Fill amber poly bottle ¾ with DI water and add 20g of ammonium molybdate. Dilute to 500mL with DI water and mix thoroughly. Solution is stable for one month.

❖ Molybdate Color Reagent

We are currently using Fisher sulfuric acid (catalog no. SA176-4).

Stock Antimony Potassium Tartrate Solution	72mL
Stock Ammonium Molybdate	213mL
Sulfuric Acid	35mL
DI Water, q.s.	1000mL final vol.

To a 1L volumetric flask add about 500mL of DI water, then 35mL of concentrated sulfuric acid. Swirl to mix. Add 213mL of stock ammonium molybdate solution and 72mL of stock antimony potassium tartrate solution. Dilute to 1000mL with DI water and mix thoroughly. Degas with helium for at least 5 minutes. Store in a dark plastic container. This solution is stable for one month.

❖ Ascorbic Acid

We are currently using Fisher, L-ascorbic acid (catalog no. BP351-500) and Fisher SDS (catalog no. BP166-100).

Ascorbic Acid	60g
SDS	1g
DI Water, q.s.	1000mL final vol.

In a 1L volumetric add 60g of ascorbic acid in approximately 800mL DI water. Dilute to 1000mL with DI water and mix thoroughly. Degas for a minimum of 5 minutes. Pour into clear plastic bottle and add 1g of SDS and swirl gently. This solution is stable for 5 days. Store the solution in a clear poly container.

Standard Preparation

- Working standards can be made by weight or volume. Standards are made using a 1000µg/mL stock certified from AccuStandard or another source different from the QC. Prepare fresh weekly.

❖ Stock Standard, 10.0mg/L N

AccuStandard Stock (Phosphorus)	1mL
DI Water, q.s.	100mL

In a 100mL volumetric flask containing about 80mL of DI add 1mL of Stock AccuStandard phosphorus standard. Dilute to 100mL with DI and mix thoroughly. Record the information in the stock standard logbook.

❖ Preparation of working standards:

Transfer aliquots of Stock 10mg/L stock as noted below to individual 100mL volumetric flasks. Dilute to volume with DI water and mix thoroughly. Record the information in working standard logbook. Prepare fresh weekly.

- Working Standard Solutions for Low Range Analysis

mL(g) 10mg/L Stock	mg/L P
5.0	0.500
3.0	0.300
1.0	0.100
0.5	0.050
0.25	0.025
0.1	0.010

Sample Preparation

- Turbidity absorbing in the range of 880 nanometers (nm) will present a positive bias.

- For dissolved inorganic phosphorus, the whole water sample is filtered though a 47mm GF/F filter in the field. The filtrate is then preserved in the field by adding H_2SO_4 to a pH of <2 at the time of collection and freezing at or below -10°C until analysis is performed. The client may decide to solely freeze samples without preservation to eliminate variability, and to minimize potential safety issues associated with field acidification. The client will notify/discuss these procedures with CESE staff prior to sample acceptance. Disposable plastic sample tubes are used during analysis to avoid contamination from improper washing of glass tubes.

- Generally, 7.5mL of sample is spiked with 150µL of the 10ppm stock standard, yielding a spike concentration of 0.196ppm.

- The quality control sample (QC) is made up in 100mL volumes per every 60 or so samples. Larger quantities are necessary if running large batches of samples. Generally, the QC concentration is 0.3ppm. QC is made up daily.

Instrumental Analysis

- It is assumed that the user is basically familiar with the appearance and location of the various parts of the Lachat. It is also assumed that a method for running Ortho-Phosphate analysis has already been created, and that the user is familiar with basic system operations. For a physical description of the instrument and any related software information, see the SOP entitled “Running the Lachat”.

- Ensure that reagents are pumping through all pump tubes and that the sample line is connected to port 6 of the switching valve.

- Ensure that the proper method has been selected, either for freshwater analysis or one that utilizes the refractive index correction for seawater samples.

Calculations

- Percent Recovery for the QC is calculated by the following formula:

$$\%Recovery = \frac{Observed\ QC\ Value}{Expected\ QC\ Value} \times 100$$

- Percent recovery for the spike is determined using the following formula:

$$\%Recovery = \frac{(A - B)}{C} \times 100$$

Where: A = measured value in mg/L for the sample + spike
B = measured value in mg/L for the original sample
C = concentration of the spike in mg/L

- Relative percent difference for the duplicate is calculated by the following formula:

$$RPD = \frac{(A - B)}{[(A + B) \div 2]} \times 100$$

Where: A = The value in mg/L for the first run of the sample
B = The value in mg/L for the second run of the sample

Quality Control

- A certified second source quality control sample (purchased from Fisher) is analyzed for every delivery group (or every 20 samples) and the value must be within 90-110% recovery, or as per client request, to be considered acceptable. Prepare fresh daily.

- A spike is analyzed for every delivery group (or every 20 samples). The percent recovery must fall within the 85-115% recovery to be considered acceptable.

- A duplicate is analyzed every delivery group (or every 20 samples) and the relative percent difference must fall below 20%, or as per client request.

- A blank is analyzed every delivery group, or every 20 samples and the value must fall below the PQL to be considered acceptable.

- A second quality control sample is analyzed every sample delivery group and at the end of the run and is the concentration of the PQL, or the lowest standard. Acceptable ranges for the PQL are 50-150% recovery.

Other System Notes

- Chemistry manifold 2
- Light interference filter: 880nm
- Special instructions: The reaction module for phosphorus determinations comes equipped with a heating coil that heats the sample stream (after the addition of the reagents) to 37°C, which promotes better color development. This coil should be given 15 minutes to warm up before any samples are run.

SOP No: Nuts-030-13
Date Initiated: 7/20/99
Revision Date: 1/26/23
Page 1 of 11

Standard Operating Procedure
Total Phosphorus (TP) and Total Dissolved Phosphorus (TDP)
EPA 365.1
Standard Methods 4500-P A, B, and H
Nutrients Laboratory

Prepared by:
Name: Steph Kexel **Signature**: _____ **Title**: _____ **Date**: _____

Approved by:
Name: Chris Perkins **Signature**: _____ **Title**: _____ **Date**: _____

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State of CT: PH-0778 – EPA: CT01022

Total Phosphorus and Total Dissolved Phosphorus EPA 365.1
SM4500-P A, B and H

Scope and Application

- EPA Method 365.1 is the reference method for the measurement of total phosphorus in water and seawater after preliminary digestion with sodium persulfate.

- Method Detection Limits will be developed for all CTDPH approved methods according to the process and procedures detailed in the CESE Laboratory Quality Assurance Plan Section 7.4 (Method Detection Limit Studies).

- This section provides a stepwise procedure for bench use by laboratory personnel.

- This method (Lachat method number 31-115-01-1-H) was developed for the quantitative analysis of ortho-phosphate in water and seawater. The applicable range is 0 to 0.5mg/L of ortho-phosphate as phosphorus. Samples higher in range may be diluted and re-run or analyzed calibrating with a higher concentration (usually 1.0ppm).

- This method is based on automated colorimetric determination and is restricted to the use by or under the supervision of analysts experienced in the use of auto analyzers.

Summary of Method

- For total dissolved phosphorus, the whole water sample may be filtered though a 45mm GF/F filter. The filtrate is then preserved by adding H_2SO_4 to a pH of <2 at the time of collection and freezing at or below -10°C until analysis is performed. The client may decide to solely freeze samples without preservation and should notify/discuss these procedures with CESE staff prior to sample acceptance. The filtered sample will yield the total dissolved phosphorus (TDP) value, while the whole water sample will yield a total phosphorus (TP) value. Analysis is completed within 28 days of arrival at the laboratory.

- The sample is digested with sodium persulfate in an autoclave at 235°F for one hour.

- This method is interchangeable with the Combo digestion method that combines the TN and the TP digestion into one preparation. Comparison studies are available upon request.

- Samples for TP/TDP are analyzed by an automated procedure on the Lachat flow analyzer. An aliquot of digested sample is reacted with reagents containing sulfuric acid, antimony tartrate, ammonium molybdate and ascorbic acid, and the resulting molybdenum blue complex is measured photometrically at 880nm.

- This method is based on automated colorimetric determinations and is restricted to the use by, or under the supervision of, analysts experienced in the use of auto analyzer equipment.

- The Lachat QuickChem is calibrated with a minimum of a six-point curve (including the blank) at the time of analysis. The calibration curve is then verified by an external quality control sample from Fisher, an independent supplier. Fisher supply guidelines are used for making up the quality control solutions, as well as for information on the true value and acceptable value range for the analytes being measured in each quality control sample.

- This initial calibration check along with an initial calibration blank, demonstrate that the instrument is capable of acceptable performance at the beginning of the sample analysis. To ensure continuing acceptable performance a continuing calibration check and continuing calibration blank are run every twenty samples. For every 20 samples, a laboratory spike analysis and a laboratory duplicate analysis are performed. At the end of the run a PQL (Practical Quantitative Limit) is run for further quality control verification.

Definitions

- See the Laboratory QAP (Quality Assurance Plan) for definitions of common laboratory terms.

- **Phosphorus Fraction Definitions --**

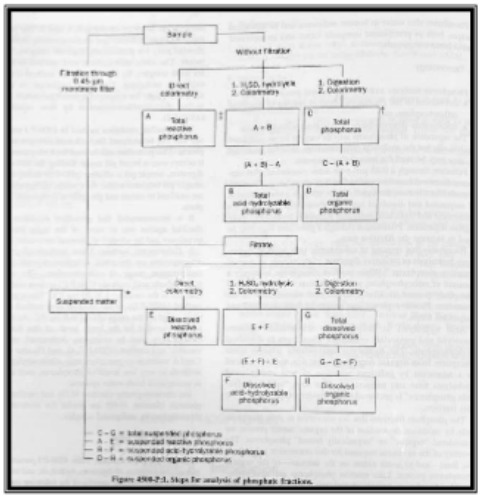

Figure 4500-P.1. Steps for analysis of phosphate fractions.

- In the Nutrient's Laboratory, most of the Phosphorus fractions are analyzed in these main analytical runs:
    - **Total Phosphorus (TP)** – All of the phosphorus present in the sample regardless of forms is digested by the persulfate digestion procedure, then analyzed by direct colorimetry. In the chart above, this is "C".
    - **Total Dissolved Phosphorus (TDP)** – The sample is passed through a 0.45µm filter and then the filtrate is digested with persulfate and analyzed by direct colorimetry. This is also referred to as "Total Dissolved Phosphorus" in the above chart or "G".
    - **Ortho-Phosphate (o-PO_4)** – This is the sample analyzed on the instrument without any filtration or digestion. It is referred to as Total Reactive Phosphorus above in "A".
    - **Dissolved Inorganic Phosphorus (DIP)** – This is the sample filtered through a 0.45µm filter then analyzed colorimetrically without a digestion step. In the above chart, it is referred to as Dissolved or Soluble Reactive Phosphorus or "E".
    - **Particulate Phosphorus (PP)** – This is the suspended matter captured on a 0.45µm filter then digested with 1N Hydrochloric Acid and analyzed colorimetrically. This may be required when greater precision is necessary because the calculations of above fractions to determine the Suspended Phosphorus are less precision.
- All phosphorus forms are reported as P.

Interferences

- Silica forms a pale blue complex that also absorbs at 880nm and is generally insignificant because a silica concentration of approximately 30mg/L would be required to produce a 0.005 P/L positive error in ortho-phosphate.
- Concentrations of ferric iron greater than 50mg/L cause a negative error due to competition with the complex for the reducing agent ascorbic acid. Samples may be treated with sodium bi-sulfite to eliminate this interference, as well as interferences due to arsenates.
- Acidity among samples, standards and blanks should be carefully controlled. Large variations in acidity will affect sample and/or standard peaks.

- Good glassware cleaning procedures should always be used. Phosphorus contamination is a constant problem. Proper glassware washing protocol should elevate this problem.

References

31-115-01-1-H, August 2003. Determination of Orthophosphate by Flow Injection Analysis. Lachat Instruments, Loveland, CO.

EPA Method 365.1. Determination of Phosphorus by Semi-Automated Colorimetry. Revision 2.0, August 1993. Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.

Standard Method 4500-P A, B, G and H Phosphorous: Flow Injection Method. Page 4-139 – 4-153, 20th Edition, 1998, Standard Methods for the Examination of Water and Wastewater.

Associated SOP's

Refer to "SOP" titled "Hazardous Waste SOP" for proper waste disposal.

Refer to the notebook titled "SOP's" located in the nutrients laboratory.

Safety

Samples are disposed in a hazardous waste jug and are appropriately labeled.

Reagents are hazardous and are made in the hood. Protective gear is worn when making reagents.

Ensure that waste lines from the Lachat are going to the proper hazardous waste jug located under the instrument.

Refer to the University of Connecticut's Environmental Health and Safety Chemical Health and Safety web page at:

http://www.ehs.uconn.edu/ppp/index.php

A hard copy of the Chemical Hygiene Plan can be found on the notebook rack located on the lab bench. Also refer to the Hazardous Waste SOP.

Materials

Lachat QuickChem 8500
Market Forge Autoclave

Procedure

Reagent Preparation

- Unless otherwise specified, all chemicals should be ACS grade or equivalent. DI water refers to high quality reagent water, TYPE I or TYPE II as defined in ASTM Standards, Part 31, D1193-74. When making reagents, date the container in which the reagent is stored, initial it, and write out the entire name of the reagent.

❖ Stock Antimony Potassium Tartrate

We are currently using Fisher antimony potassium tartrate (catalog no. A867-250).

Antimony Potassium Tartrate	1.61g
DI Water, q.s.	500mL final vol.

Dissolve 1.61g of antimony potassium tartrate in about 400mL of DI water in 500mL volumetric flask. Dilute to 500mL with DI water and mix thoroughly. Store the solution in a dark plastic container. Solution is stable for one month.

❖ Stock Ammonium Molybdate

We are currently using Fisher ammonium molybdate (catalog no. A674-500).

Ammonium Molybdate	20g
DI Water, q.s.	500mL final vol.

Fill amber poly bottle ¾ with DI water and add 20g of ammonium molybdate. Dilute to 500mL with DI water and mix thoroughly. Solution is stable for one month.

❖ Molybdate Color Reagent

We are currently using Fisher Sulfuric Acid (catalog no. SA176-4).

Stock Antimony Potassium Tartrate Solution	72mL
Stock Ammonium Molybdate	213mL
Sulfuric Acid	35mL
DI Water, q.s.	1000mL final vol.

To a 1L volumetric flask add about 500mL of DI water, then 35mL of concentrated sulfuric acid. Swirl to mix. Add 213mL of stock ammonium molybdate solution and 72mL of stock antimony potassium tartrate solution. Dilute to 1000mL with DI water and mix thoroughly. Degas with helium for at least 5 minutes. Store in a dark plastic container. This solution is stable for one month.

❖ Ascorbic Acid

We are currently using Fisher, L-ascorbic acid (catalog no. BP351-500) and Fisher SDS (catalog no. BP166-100).

Ascorbic Acid	60g
SDS	1g
DI Water, q.s.	1000mL final vol.

In a 1L volumetric add 60g of ascorbic acid in approximately 800mL DI water. Dilute to 1000mL with DI water and mix thoroughly. Degas for a minimum of 5 minutes. Pour into clear plastic bottle and add 1g of SDS and swirl gently. This solution is stable for 5 days. Store the solution in a clear poly container.

❖ Digestion Reagent -- Sodium Persulfate

We are currently using Fisher Acros sodium persulfate (catalog no.AC20202-0010) and Fisher sulfuric acid (catalog no. SA176-4).

Sulfuric Acid	11.4mL
Sodium Persulfate	50g
DI Water, q.s.	1000mL final vol.

Add 11.4mL sulfuric acid in a 1L clear small-mouthed poly bottle and cool under tap water. Dissolve 50g of sodium persulfate and dilute to final volume of 1000mL with DI. The solution is not stable and should be made immediately prior to use.

Standard Preparation

Working standards can be made by weight or volume. Standards are made using a 1000µg/mL stock certified from AccuStandard or another source different from the QC. Prepare fresh weekly.

❖ Stock Standard, 10.0mg/L N

AccuStandard Stock (Phosphorous)	1mL
DI water, q.s.	100mL

In a 100mL volumetric flask containing about 80mL of DI add 1mL of Stock AccuStandard Phosphorus Standard. Dilute to 100mL with DI and mix thoroughly. Record the information in the stock standard logbook.

❖ Preparation of working standards:

Transfer aliquots of stock 10mg/L stock as noted below to individual 100mL volumetric flasks. Dilute to volume with DI water and mix thoroughly. Record the information in working standard logbook. Prepare fresh weekly.

- Working Standard Solutions for Low Range Analysis

mL(g) 10mg/L Stock	mg/L P
5.0	0.500
3.0	0.300
1.0	0.100
0.5	0.050
0.25	0.025
0.1	0.010

Sample Preparation

- Sample turbidity may be removed by filtration though a 47mm GF/F prior to analysis. Turbidity absorbing in the range of 880 nanometers (nm) will present a positive bias. The filtered water sample will yield a total dissolved phosphorus (TDP) result.

- The filtrate is then preserved in the field by adding H_2SO_4 to a pH of <2 at the time of collection and freezing at or below -10°C until analysis is performed. The client may decide to solely freeze samples without preservation to eliminate variability, and to minimize potential safety issues associated with field acidification. The client will notify/discuss these procedures with CESE staff prior to sample acceptance. Disposable plastic sample tubes are used during analysis to avoid contamination from improper washing of glass tubes.

- Sample containers are to be rinsed with 1:1 hydrochloric acid, followed by DI water and finally by an aliquot of the sample itself. Disposable plastic sample tubes are used during analysis to avoid contamination from improper washing of glass tubes.

- Pipette 10mL of sample into a 30mL test tube. 10mL of standards, QC and blanks should also be pipetted. The lowest concentration of standard is pipetted 6 times

to allow for the analysis of PQL throughout the run. The rest of the standards are pipetted at least 3 times for each concentration.

- The Quality Control sample (QC) is made up in 100mL volumes per every 60 or so samples. Larger quantities are necessary if running large batches of samples. The QC concentration changes with each new lot # purchased from Environmental Resource Associates. Prepare fresh daily.

- Generally, spiked samples are spiked with 250µL of the 10ppm stock standard and are spiked directly into the test tube before digestion yielding a spike concentration of 0.244ppm.

- To each test tube add 3mL of digestion reagent and mix thoroughly. Place the samples, QC and standards into the autoclave and heat to 235°F for 1 hour.

- Allow the autoclave pressure to equalize and the temperature to decrease before removing the sample. Cool to room temperature overnight.

- Samples are run the day following preparation, however if analysis cannot be performed immediately samples can be stored at 4°C after the digestion.

- Transfer the samples to disposable glass test tubes for automated ortho-phosphate analysis on the Lachat.

Instrumental Analysis

- Analyze the sample for TP/TDP using Lachat method for phosphate in water and seawater (method 31-115-01-1-H).

- It is assumed that the user is basically familiar with the appearance and location of the various parts of the Lachat. It is also assumed that a method for running TP/TDP analyses has already been created, and that the user is familiar with basic system operations. For a physical description of the instrument and any related software information, see the SOP entitled “Running the Lachat”.

- Ensure that pump tubing is pumping all reagents and proper sample loop is connected to port 1 and 4 of the switching valve.

- Ensure that the sample line from the auto-sampler is connected to port 6 of the valve.

- Ensure that a method is selected that utilizes the refractive index correction as all TP samples have the refractive index dip at the start of the peak. This correction eliminates any issues that would be seen with integration.

Calculations

- Percent Recovery for the QC is calculated by the following formula:

$$\%Recovery = \frac{Observed\ QC\ Value}{Expected\ QC\ Value} \times 100$$

- Percent recovery for the spike is determined using the following formula:

$$\%Recovery = \frac{(A - B)}{C} \times 100$$

Where: A = measured value in mg/L for the sample + spike
B = measured value in mg/L for the original sample
C = concentration of the spike in mg/L

- Relative percent difference for the duplicate is calculated by the following formula:

$$RPD = \frac{(A - B)}{[(A + B) \div 2]} \times 100$$

Where: A = The value in mg/L for the first run of the sample
B = The value in mg/L for the second run of the sample

Quality Control

- A certified second source quality control sample (purchased from Fisher) is analyzed for every delivery group (or every 20 samples) and the value must be within 90-110% recovery to be considered acceptable or as per client requirements.
- A spike is analyzed for every delivery group (or every 20 samples). The percent recovery must fall within the 85-115% recovery to be considered acceptable.
- A duplicate is analyzed for every delivery group (or every 20 samples) and must have a relative percent difference below 20%, or as per client request.
- A blank is analyzed every delivery group, or every 20 samples and the value must fall below the PQL to be considered acceptable.
- A second quality control sample is analyzed with every delivery group or at the end of the run and is the concentration of the PQL, or the lowest standard. Acceptable ranges for the PQL are 50-150% recovery.

Other System Notes

- Chemistry channel 2
- Sample loop 150cm
- Light interference filter: 880nm
- Special instructions: The reaction module for phosphorus determinations comes equipped with a heating coil that heats the sample stream (after the addition of the reagents) to 37°C, which promotes better color development. This coil should be given 15 minutes to warm up before any samples are run.