PAPER

Developing the First Operational Nutrient Observatory for Ecosystem, Climate, and Hazard Monitoring for NERACOOS

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ABSTRACT

An integrated nutrient observatory is being developed within the Northeastern Regional Association of Coastal Ocean Observing Systems (NERACOOS), capable of monitoring nutrient dynamics year-round at temporal and spatial scales necessary to address critical needs of stakeholders throughout the Northeast region. Nutrient levels and fluxes drive total biological productivity throughout the region, from phytoplankton to commercially exploited fish stocks. Nitrate sensors (Satlantic SUNAs) are being installed on existing mooring assets in western Long Island Sound, Narragansett Bay (Prudence Island), Great Bay in New Hampshire, Massachusetts Bay, three sites along the coastal shelf of the Gulf of Maine (GOM), at five depths in Jordan Basin in the interior GOM, and at two depths in the GOM Northeast Channel. Phosphate and ammonium sensors (WET Labs Cycle-PO_4 and Cycle-NH_4) are also being deployed at the three nearshore sites. The measurements from these sensors will extend the current sparse, long-term records of nutrients from discretely collected samples in the Northeast region and will dramatically improve temporal resolution and continuity of the data for use in studying potential impacts of climate change. Nearshore measurements will be used by NERACOOS stakeholders to help assess, regulate, and mitigate the adverse impacts on water quality associated with excessive pollutant loadings. Measurements throughout the GOM will be used to assess basin-wide nutrient variability and to initialize harmful algal bloom (*Alexandrium fundyense*) forecast models.

Keywords: nutrients, observatory, autonomous

Background

Coastal and offshore shelf waters of the Northeast United States are undergoing changes in fluxes and dynamics of dissolved inorganic nutrients, driven principally by anthropogenic nutrient loadings nearshore, and natural oceanographic processes farther offshore. Recent studies have documented changes in the last few decades in both of these nutrient sources, yet supportive data to wisely manage our coastal waters and their natural resources remain lacking. Data and information at the needed time scales can only be delivered by an effective coastal nutrient observatory. Recent advances in nutrient sensor technologies, coupled with leverage from ongoing coastal ocean observing programs, now make this possible.

Anthropogenic Pollutant Loading

The Northeast coastal region faces numerous human and environmental stressors that are representative of the challenges impacting large portions of the United States and the world. A critical stressor is anthropogenic inputs of nutrients, leading to eutrophication, habitat loss, and degraded aesthetic value. Apparent causative links have been established between anthropogenic modification to nutrient levels and increased frequency and intensity of various types of algal blooms (including harmful/toxic species) (e.g., Smayda, 1990; Bricker et al., 2008; Anderson, 2009; Glibert et al., 2010; LaPointe et al., 2015) that sometimes produce severely oxygen-depleted (hypoxic or even anoxic) deep and bottom waters (Rabalais et al., 2002). In the last 40 years, the number of hypoxic/anoxic zones in coastal waters around the world has doubled each decade, and while many of these "dead zones" are seasonal, some low-oxygen areas have begun to persist year-round (Larsen, 2004; Rabalais et al., 2002). The Northeast region spans the range of hypoxia impact: western Long Island Sound experiences chronic hypoxia with a fully collapsed ecosystem (Diaz & Rosenberg, 2008); locations within Narragansett Bay, RI, experience seasonal hypoxia with associated fish kills (Codiga et al., 2009; Vadeboncoeur et al., 2010); Great Bay, NH, has been described as being at a "tipping point," on the brink of hypoxia with an increase in total nitrogen runoff of 42% from 2004 to 2009 (McDowell, 2012); northern Massachusetts Bay copes with increased nutrient loading from sewage flows piped from the Boston metropolitan area (Massachusetts Water Resources Authority); and at the other extreme, Penobscot Bay on the coast of still sparsely populated Maine experiences near pristine nutrient loads (Anderson et al. 2008). In many of these environments, conditions are only expected to worsen in the future (Bricker et al., 2008).

Nutrient Dynamics, Climate Change, and Harmful Algal Blooms in the Gulf of Maine (GOM)

Recent work in the GOM region has shown that initiation of *Alexandrium fundyense* blooms, toxic dinoflagellates that cause paralytic shellfish poisoning, are dependent on natural nitrate (Townsend et al., 2001, 2005). Annual blooms begin in areas of tidal mixing and pumping of deep water nutrients into surface waters (He et al., 2008; McGillicuddy et al., 2013; Townsend et al., 2014). The GOM receives negligible anthropogenic fluxes of dissolved inorganic nitrogen (so far —isolated nearshore waters just mentioned notwithstanding; an exception is the annual bloom of *A. fundyense* in the upper reaches of Casco Bay, ME, reported in Anderson, 1997). Typically, however, the source of nutrients that stimulates these toxic blooms is overwhelmingly dominated by the ocean end member (Townsend, 1998; Anderson et al., 2008). Most critical for this project is that there have been significant changes in recent years to the water properties and inorganic nutrient loads of the deep offshore-derived water masses in the GOM (e.g., Pettigrew et al., 2008; Townsend et al., 2010; Rebuck, 2011; Smith et al., 2012; Townsend et al., submitted) that need to be better understood and monitored. Townsend et al. (2010) showed that deep waters in the GOM (>100 m) have become slightly fresher and cooler since the 1970s, with lower nitrate (by ~2–4 μM) but higher silicate (also by ~2–4 μM). This altered nutrient regime in the GOM is the result of a greater proportion of shelf water influxes of Labrador Sea origin. Increased freshwater discharges from Arctic rivers and melting of the Arctic ice cap since the 1970s (reviewed in Perovich & Richter-Menge, 2009) are thought to play an important role in the intensified southward transport of shelf and slope waters in the Labrador Sea and along the coasts of Maritime Canada and the Northeast United States. As those shelf and slope waters mix and flow along the continental shelf, nutrient fluxes are altered (Christensen et al., 1996; Townsend et al., 2010), potentially forcing changes in the structure of the planktonic ecosystem, including lowered primary production throughout the GOM, and either a delayed *A. fundyense* bloom or the absence of a bloom altogether (McGillicuddy et al., 2011; Townsend et al., 2014). It is important to note that these results are based on shipboard surveys conducted exclusively during the warmer months of the year. Improved analyses of the frequency and duration of altered water mass/nutrient fluxes requires year-round nutrient observations. Only then can scientists draw more accurate conclusions about the impacts on planktonic ecosystems, including harmful algal blooms of *A. fundyense*, and effects that may eventually influence the species composition of higher trophic levels, including commercially exploited fish stocks.

Technology and Approach

Autonomous, accurate nutrient sensors with high sampling frequency are emerging technologies that in some cases have recently become commercially available. WET Labs (Philomath, OR) Cycle-PO4 and Cycle-NH4 sensors employ "wet chemistry" methods, with reagent analytes to initiate a colorimetric (PO_4) or fluorometric (NH_4) reaction, similar to bench top autoanalyzers. The standard molybdate blue method is used for phosphate (e.g. Grasshoff et al., 1999). Ammonium is measured based on the method of Kerouel and Aminot (1997), where the sample is reacted with o-phthalaldehyde (OPA) in the presence of sodium sulfite to form a fluorescence species. The Satlantic (Halifax, Canada) SUNA v2

(Submersible Ultraviolet Nitrate [NO_3] Analyzer) uses the spectral absorption signature of nitrate in the ultraviolet for quantification, employing a technique developed at the Monterey Bay Aquarium Research Institute (Johnson & Coletti, 2002; Sakamoto et al., 2009). These platforms are highly amenable to autonomous observatory application, with calibrated analyte concentrations in user-defined concentration units, simple field service protocols, and intuitive software. Both the Cycle-PO4 and SUNA are commercially available with a Technology Readiness Level (TRL) of 8–9, depending on application. The Cycle-NH4 is an emerging commercial product at WET Labs at TRL 7, with several demonstration units that have now been in service for up to 2 years. Technical specifications are provided in Table 1.

Over the last several years, the SUNA has been deployed autonomously in environments ranging from upland forest streams to open ocean moorings for periods of several months (Pellerin et al., 2012; Johnson, 2010). The SUNA has been independently vetted by the Alliance for Coastal Technologies (2009a) and the United States Geological Survey (USGS) (Pellerin et al., 2013), with the latter detailing recommended protocols for use and data quality assurance and quality control (QA/QC). An example of nitrate data collected at 100 m at Buoy M in the Jordan Basin of the GOM in the summer to winter period of 2013–2014 with a Satlantic ISUS (In Situ Ultraviolet Spectroscopy), the sensor precursor to the SUNA, is shown in Figure 1. An unusual intrusion was observed of Gulf Stream Water (warm, salty, low nitrate), which, without nitrate as a third conservative water mass tracer, would have been mistaken for Warm Slope Water (WSW) (warm, salty, high nitrate). Apart from that short-lived event, the data record also shows a gradual replacement of deep waters in the GOM with a greater proportion of nutrient rich WSW, setting the stage perhaps for a productive spring diatom bloom and follow-on *A. fundyense* bloom.

While wet chemistry, *in situ* autoanalyzer-type sensors have met with limited successes in the past, the family of Cycle sensors has overcome limitations of earlier technologies. Cycle sensors have now been deployed for months at a time in hypereutrophic freshwater environments, riverine systems including under ice in high mountain streams, a multitude of different coastal sites, and oligotrophic open ocean moorings. Several organizations building observational programs are beginning to integrate Cycles. Domestically these include the Great Lakes Environmental Research Lab (GLERL), USGS, state water management districts, the NSF-STC Center for Coastal Margin Observation & Prediction (CMOP), and (sporadically to date) the National Oceanic and Atmospheric Administration's Integrated Ocean Observing System (NOAA IOOS). Internationally these include Australia's Commonwealth Scientific and Industrial Research Organization (CSIRO) and the national Integrated Marine Observing System (IMOS) program, France's National Center for Scientific Research (CNRS), and the UK's Centre for Environment, Fisheries and Aquaculture Science (CEFAS). New insights into the high-frequency dynamics of nutrient cycling resolved with the Cycles in coastal waters have been remarkable, bringing into question the interpretation of numerous collection programs throughout the United States, where a discrete sample for lab analysis is collected typically once per week at best. Nutrients can exhibit twofold variability through a single tidal cycle (Figure 2). Academic researchers are publishing novel biogeochemical findings using Cycle

TABLE 1

Specifications for nutrient sensors.

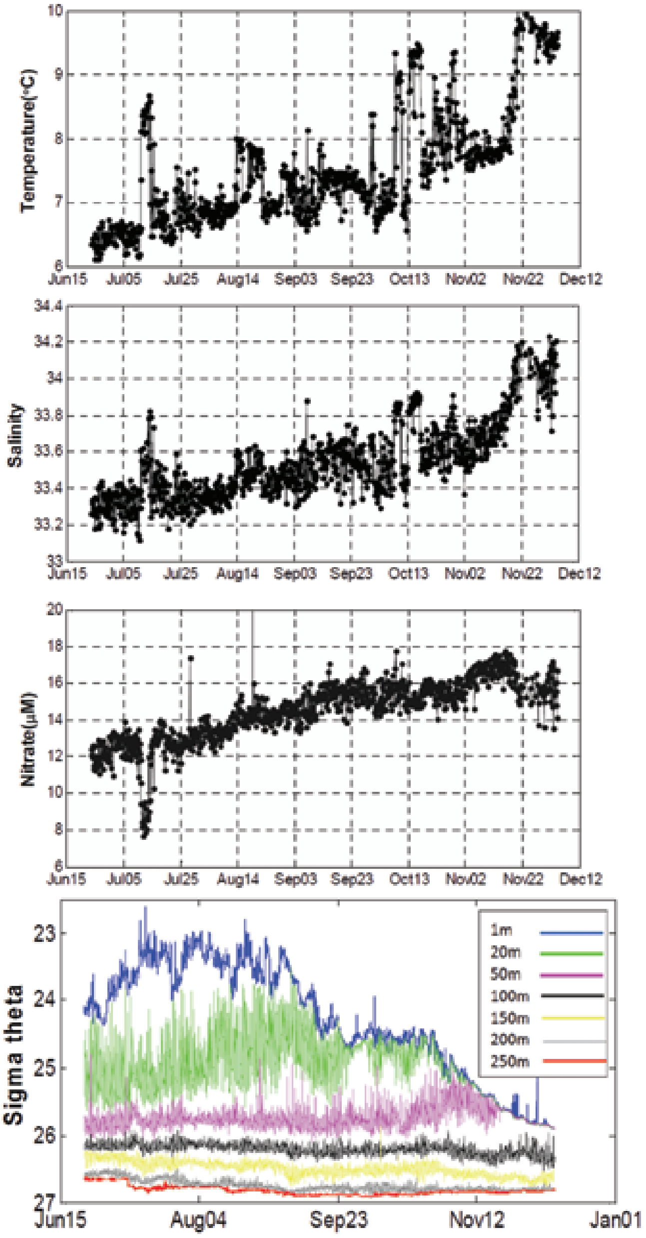
	Detection Limit (µM)	Uncertainty (µM)	Range (µM)	Depth Rating (m)	Current Draw (Ave. mA @12 VDC)
Cycle-PO4	0.1	0.05	0–10	200	125
Cycle-NH4	0.25	0.15	0–20	200	125
SUNA v2	0.5*	0.3*	0–3000	500**	625

*With T-S correction, which will be possible for data from all buoy deployments by leveraging existing NERACOOS assets. Correction will be applied through processing by DMAC GMRI.

**100 m with hydro-wiper.

FIGURE 1

Right: Results of a preliminary deployment, from 6/23/13 to 1/26/14, of a Satlantic ISUS UV optical nitrate sensor at 100 m on Buoy M in Jordan Basin (see Figure 3), with accompanying temperature and salinity at the same depth. An anomalous influx of Gulf Stream Water is evident as a brief (less than 1 week) pulse of warm, salty, and low-nitrate waters in July. A possible second influx in late November is also evident or may indicate a recirculation of the first event. The overall trend in T, S, and NO_3 shows the gradual influx of warm, salty, and high-nitrate Warm Slope Water throughout the summer-to-fall period, followed by a winter period of falling nitrate and variable T and S, possibly the result of winter convective mixing with shelf waters. Bottom: The fall trend of rising T, S, and NO_3 is not the result of fall overturn (convective mixing), as shown in the plot of sigma-t for each of the sample depths on Buoy M; convective mixing did not reach 100 m until mid-December. Then, in January, there is evidence of an influx of low-density shelf waters.



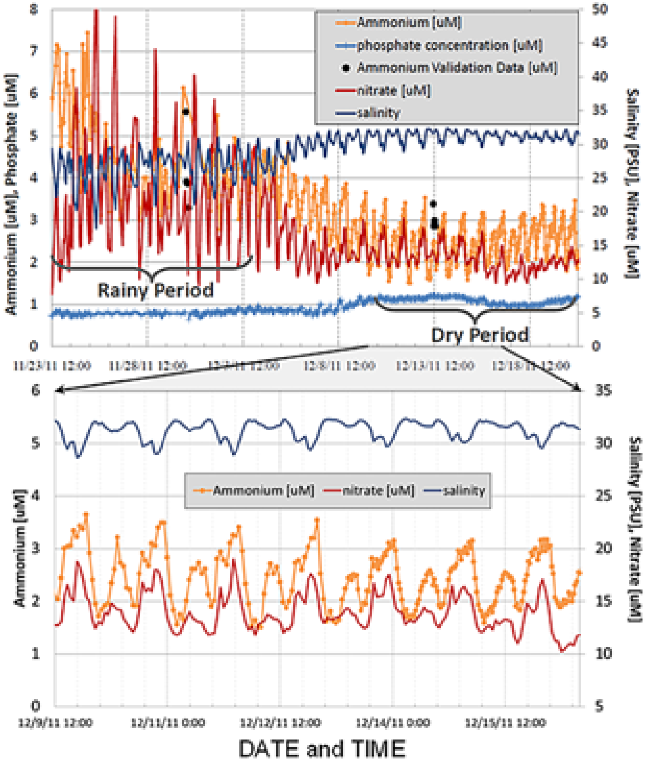
sensors (Cohen et al., 2013; Gilbert et al., 2013; Sherson, 2013). The Cycle-PO4 sensor has also been independently and objectively evaluated by the Alliance for Coastal Technologies (2009b) with favorable results. A 2014 National Oceanographic Partnership Program-sponsored Cycle commercialization project included an intensive validation study with many research and resource management partners and demonstrated that the Cycle-PO4 has accuracy comparable to classic grab sampling and laboratory analysis (Table 1). Cycle-NH4 sensors use the same extreme-environment-tested microfluidics as the Cycle-PO4 and have undergone several successful beta deployments by the University of California, Santa Barbara, CMOP, USGS, and WET Labs in coastal NW waters. The USGS California Water Science Center is currently integrating the Cycle-NH4 into long-term monitoring efforts to better understand the impact of waste-water effluent on nutrient-sensitive ecosystems. In summary, the Cycle is rapidly changing community perception of wet chemistry nutrient sensors, with extensive evidence demonstrating these sensors are now viable for long-term operational deployment.

Observatory Development

The nutrient sensors are being integrated on existing Northeastern Regional Association of Coastal Ocean Observing Systems (NERACOOS) mooring assets in collaboration with the University of Maine, University of New Hampshire, and University of Connecticut. Fifteen (15) Satlantic SUNA v2 sensors will be integrated on current NERACOOS moorings in western Long Island Sound (LIS), Narragansett Bay National Estuarine

FIGURE 2

Top panel: 1 month autonomous deployment of Cycle-PO_4, Cycle-NH_4, and SUNA sampling hourly in intertidal Yaquina Bay, OR, in 2011. Bottom panel: focus on 1-week period from 12/9 through 12/16. Short-term variability is consistent with tidal forcing; longer-term variability is climatological. More than a factor of two variabilities in a tidal cycle was observed in ammonium and nitrate.



Research Reserve System (NERRS) Prudence Island site, Great Bay in New Hampshire, Massachusetts Bay, three sites along the coastal shelf of the GOM, at five depths in Jordan Basin in the interior GOM, and at two depths in the GOM Northeast Channel, between Georges and Browns Bank (Figure 3). In addition, three WET Labs Cycle-PO4 and three WET Labs Cycle-NH4 sensors will be deployed at the nearshore sites listed above (Long Island Sound, Narragansett Bay, Massachusetts Bay, and Great Bay; Figure 3).

Because of the manner in which NERACOOS has grown over the years, each of the moorings throughout NERACOOS being configured with nutrient sensors has several distinct properties, including existing sensor, data logging, telemetry, mechanical layout, and power capabilities. Different sites also have a wide range of susceptibility to biofouling. Each installation is thus a unique challenge. For example, SUNAs deployed at depth in the GOM will use inductive modems to communicate with a data handling module, will have only an external copper mesh screen to resist biofouling, and will be serviced approximately every 12 months (6 months for Buoy A). Conversely, nutrient sensors deployed at the LIS station will use patch cables, will employ wipers and copper shutters over optical interfaces or toxic solutions to prevent biofouling, and will be serviced every 2–3 weeks. Power for the sensors will be provided by battery packs at some sites and solar panels at others. Data telemetry will generally employ cellular modem communications for the nearshore sites and satellite communications (e.g., Iridium network) for offshore sites.

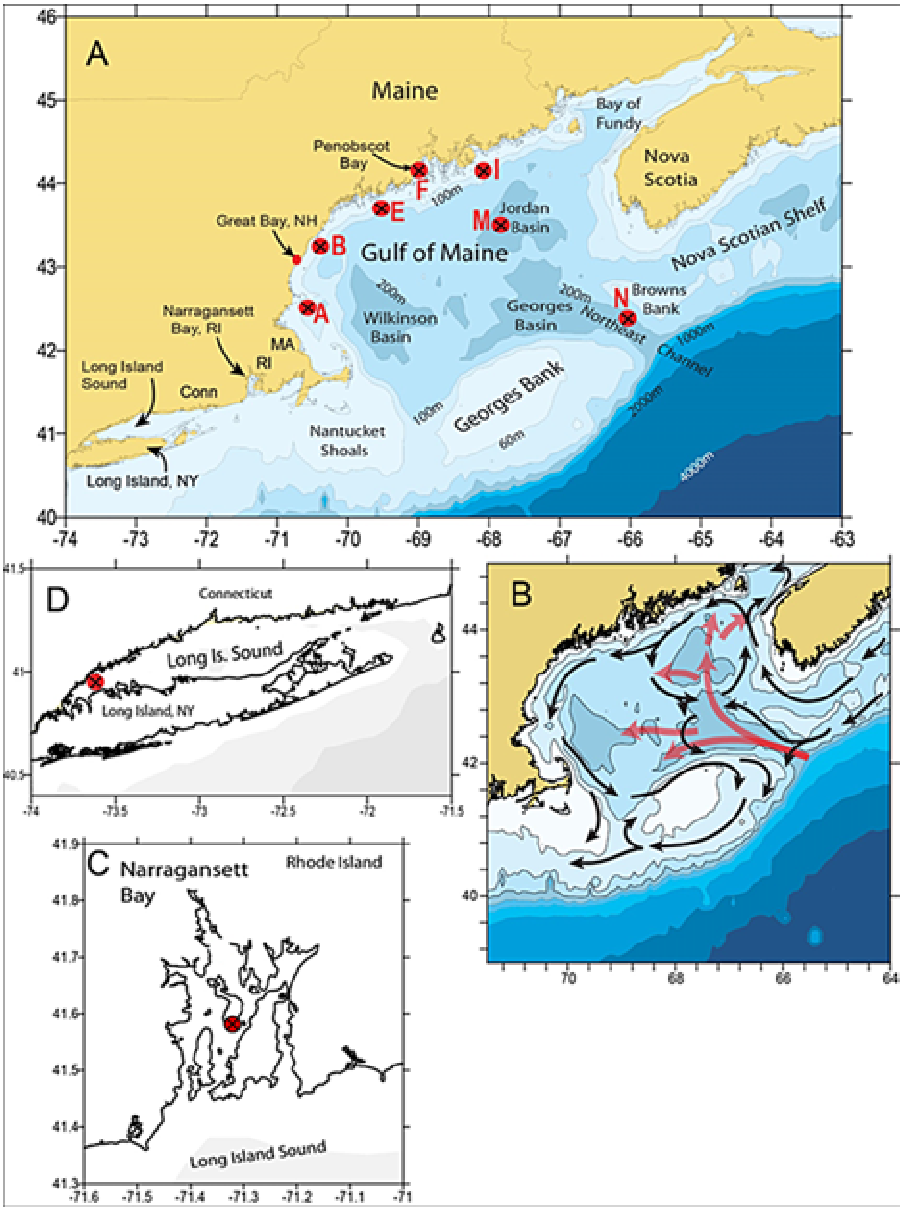
Nutrient sensors at the western LIS, Narragansett Bay, Great Bay, and GOM sites will sample hourly to adequately resolve variability over tidal cycles (and serviced every 2–4 weeks). A measurement will be taken every 48 min for the SUNAs on the deeper GOM buoys to conserve battery life for a 12-month duty cycle. During servicing, samples will be collected for independent lab verification of nutrient levels.

Quality Assurance

Data management for the observatory is being carried out through existing NERACOOS infrastructure, with additional checks for QA/QC. Continuous monitoring provides high-resolution data sets, but with this richness comes extremely large amounts of data. Manually sifting through real-time data to ensure quality is rapidly becoming resource prohibitive. Cycle and SUNA sensors are complex instruments that collect large amounts of raw data to then derive the parameter of interest. Much of these data can be, but typically are not, used for inherent knowledge of data quality. For example, SUNA collects hyperspectral absorption data and can output metadata that a scientist can interpret to determine presence of optical interferences. Likewise, Cycle performs *in situ* standard additions, but quality decisions are left to the researcher when postprocessing data.

FIGURE 3

(A) Map of the Gulf of Maine and New England shelf, showing locations of Buoys A, B, E. I, F, M and N and the mooring site in Great Bay, NH. (B) General diagram of surface currents (black arrows) and deep/bottom water flows (red arrows). (C) Narragansett Bay mooring location. (D) Long Island Sound mooring.



Cycle operation is analogous to an autoanalyzer, and determination of signatures of poor-quality analysis from inline bubbles, suspected reaction kinetics, etc., is relatively straightforward from raw collected data. These quality checks are currently being automated to provide real-time flags for suspected problems. Further QA/QC is being developed through a NOAA Quality Assurance of Real-Time Ocean Data (QARTOD) effort being implemented in 2015. All NERACOOS web services are registered in the IOOS Service Registry, which will populate an IOOS Data Catalog where the nutrient datasets will be made available for use by the community.

Application of Nutrient Data

A primary goal of the observatory is to deliver actionable ocean and coastal nutrient information to regional stakeholders to help improve their assessments of nutrient cycling and their ability to develop targeted management plans to improve and/or protect water quality. There are numerous stakeholders throughout the region, including state and federal agencies, industry, academic institutions, and nongovernmental organizations that have all expressed a need for automated *in situ* nutrient monitoring. A running theme is assessment, regulation, and mitigation of the adverse impacts on water quality associated with excessive pollutant loadings. The primary stakeholders and a description of how they will use the observatory data are summarized in Table 2.

Autonomous nutrient sensing capabilities will develop an unprecedented capacity to understand regional ocean nutrient dynamics in a range of ecosystems. The broad benefits of such a capacity are indicated by the number and variety of consumers of the information (Table 2). These benefits include better management decisions with regulatory implications for inland and coastal waters and the ability to directly track the input, distribution, and utilization of nutrients into regional seas. Nutrients are a core ecosystem variable with a potential direct influence on harmful algal bloom events and resulting economic impacts. Also, with the advent of novel, market-based nutrient trading programs, such as that recently embraced

TABLE 2

Stakeholders of nutrient observatory data.

Users	How Observatory Results Will Be Used
Long Island Sound Study	Monitor impact of nutrient reduction management practices
CT Dept. of Energy and Environment	Complement our monthly nutrient monitoring, aid in understanding nutrient dynamics and support development of appropriate numerical nutrient criteria for Long Island Sound
RI Dept. of Environmental Services	Characterize water quality conditions, support calibration of water quality models for Narragansett Bay
Massachusetts Water Resource Authority	Improve the boundary conditions for our permit-required modeling, as well as provide context for the effects of nitrogen discharged from the MWRA outfall
MA Office of Coastal Zone Management	Help to determine what background nutrients are in order for us to then determine any changes in Mass and Cape Cod Bays that might be due to ocean outfalls
WHOI Northeast PSP program	Interpreted nutrient fields incorporated into predictive HAB models
NH Dept. Environmental Services	Monitor permit compliance, support numeric nutrient criteria development, and asses management actions
NH Piscataqua Region Estuaries Partnership	Support research to develop a better understanding of nutrient cycling, geochemistry, and nutrient removal in the Piscataqua Watershed
ME Dept. of Marine Resources	Increase understanding of critical environmental factors that relate to interannual differences in shellfish toxicity
ME Coastal Program	Assist managers in forecasting future HAB events and shed light on past ones
ME Dept. of Environmental Services	Support assessment of water quality standards within state waters and enable better understanding of the variability of nutrient parameters of interest on a tidal cycle basis up to interannual fluctuations
EPA Region 1	Evaluating the response of coastal waters to nutrient reductions from waste water treatment plants and serving as key sentinels sites
EPA's Atlantic Ecology Division	Incorporation of data into tools for diagnosing and predicting the effects of human activity on aquatic resources and wildlife
NOAA's Northeast Fisheries Science Center	Understanding the driving force for regional primary production in the ecosystem, which serves as the foundation for fisheries and marine mammal production
Northeast Regional Ocean Council	Nutrient monitoring would become part of the Integrated Sentinel Monitoring Program being developed by NERACOOS and NROC

by Virginia (Virginia Department of Environmental Quality, Phase I Watershed Implementation Plan), nutrient monitoring must not only be sufficiently accurate but also legally defensible. Such programs are expected to encourage economic investment while reducing nutrient loading to local waterways in order to meet water quality goals and will heavily rely on strategically situated, continuous nutrient monitoring with carefully controlled accuracies.

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