

Sustained, Autonomous Coastal Nutrient Observations aboard Moorings and Vertical Profilers

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Abstract—Recent technological advances in autonomous submersible (*in situ*) chemical analyzers have made the real-time determination and reporting of multiple nutrient concentrations possible. Through the use of continuous flow injection analysis, SubChem Systems, Inc.'s Autonomous Profiling Nutrient Analyzer (APNA) is capable of sustained, autonomous deployment aboard coastal moorings, vertical profiling moorings, and other sampling platforms – enabling the determination of coastal nutrient concentrations, spatial distributions, and temporal variability. A series of technological hurdles have been addressed to accomplish this: (1) a more compact size, (2) reduced reagent and power consumption, (3) enhanced biofouling suppression, and (4) ease of use by non-chemists. Advances in micro-fluidics enable a reduction in sample volumes leading, therefore, to a reduction in reagent and power consumption. This, ultimately, extends the duration of remote field deployments. The suppression of bio-fouling, the simplification of wet chemical techniques for easier user operation, and the automation of data analysis into engineering units have also been addressed.

Currently, the performance of the APNA analyzer is being rigorously tested at a variety of highly dynamic field sites that have strong vertical, horizontal, and temporal nutrient gradients as well as substantial biofouling burden caused by episodic phytoplankton blooms. Through extended and ongoing deployments in Narragansett Bay on the URI-GSO Pier, automated data collection, analysis, and quality control routines have been designed and implemented to assess the data integrity, verify *in situ* calibration parameters, and create near real-time plots which can be posted and made accessible via the internet. With funding from the ONR DRI “Layered Organization in the Coastal Ocean (LOCO)”, the APNA was deployed – in a vertical profiling capacity – in Monterey Bay during the summer of 2005 and 2006. In 2005, a time series of high-resolution vertical nutrient profiles were obtained during the deployment of the APNA on a shipboard high resolution vertical profiling package. In 2006, a time series of high-resolution vertical nutrient profiles were obtained during the deployment of the APNA on an autonomous vertical profiler. The profiler was programmed to power the APNA so it would continuously acquire nutrient concentration data while the profiler ascended through the water column. The real-time analytical results indicated that the nutrient gradients were highly correlated with gradients in chlorophyll, salinity, and temperature.

The primary objective for the development of the APNA is to provide accurate, real-time nutrient distributions aboard a variety of ocean observing platforms in order to fulfill the needs of water quality managers as well as the oceanographic community. This is accomplished by using cutting edge technology combined with accepted standard analysis methods and rigorous QA/QC procedures. Long-term deployments in challenging coastal environments allow us to identify, scrutinize, and overcome the real-world obstacles encountered by *in situ* nutrient observing systems.

I. INTRODUCTION

With the vast growth in technology over the past two decades, observational oceanography has been able to move its primary focus from shipboard observations toward autonomous ocean observing systems. This redirect has allowed research in areas such as biogeochemical cycling in the coastal environment, the validation of remote sensing products, and the data collection and validation of global climate models to become more cost effective. Nutrients play a key role in the biogeochemical cycles of the coastal and open ocean environment. Dissolved Inorganic Nitrate (NO_3^-), Nitrite (NO_2^-), Ammonia (NH_3^+), Phosphate (HPO_4^{2-}), and Silicate ($\text{Si}(\text{OH})_4$) are biologically essential chemical species that may significantly enhance or limit phytoplankton growth in the coastal environment. Water column stratification can inhibit the diapycnal transfer of nutrients from deeper, darker, generally nutrient-rich waters to the well-lit, nutrient depleted surface layer. The highly dynamic physical mixing and transport processes intrinsic to the coastal environment require that these chemical species be monitored at high temporal and spatial (horizontal and vertical) resolution in order to fully understand the biogeochemical cycling of these nutrients at ecologically critical scales [1].

Ongoing research and instrument development at SubChem Systems Inc. is moving nutrient analyses from shipboard or ground-based laboratory measurements toward the long-term autonomous *in situ* measurements required for the global ocean observing system. The Autonomous Profiling Nutrient Analyzer™ (APNA) is a submersible chemical analyzer designed to rapidly measure inorganic nutrients and other chemicals in lakes, rivers, estuaries, and coastal marine waters, in real-time. The APNA utilizes a novel continuous flow analysis technique and standard spectrophotometric and/or fluorometric detection methodologies that are optimized for rapid, continuous, *in situ* determinations of several dissolved nutrients (Table I) at trace

| Nutrients | Nitrite | Nitrate | Phosphate | Silicate | Iron(II) | Ammonia |
|---------------------------|-----------|-----------|--------------|------------|----------|-----------------|
| Wavelengths (nm) | A 540 | A 540 | A 880 or 820 | A 820 | A 560 | F 370/460 ex/em |
| Path lengths (cm) | 1 or 5 | 1 or 5 | 1 or 5 | 1 or 5 | 1 or 5 | N/A |
| Range-1 (μM) | 0.05 - 50 | 0.05 - 50 | 0.05 - 75 | 0.10 - 250 | 0.05-50 | 0.01-15 |
| Range-5 (μM) | 0.02 - 10 | 0.03 - 15 | 0.03 - 16 | 0.05 - 50 | 0.02-10 | 0.1-100 |
| Precision (% range) | 2 | 2 | 2 | 3 | 2 | 1 |
| Method Reference | [1] | [1] | [1] | [1] | [3] | [4] |

concentration levels. The APNA may be deployed alone or co-deployed on a variety of ocean observation platforms and sensor systems for vertical profiling, horizontal mapping, or time series measurements of chemical concentrations.

II. METHODOLOGY

A. Technical Description

The APNA relies on a novel electro-fluidic design and sampling technique coupled with a suite of specially-designed ChemStar™ electro-optical detectors (WETLabs Inc.). The instrument is comprised of a) a submersible, multichannel reagent delivery module b) a deck box and cable for power, communication, and configuration c) instrument control software and graphical user interface operating on a host computer (MS Windows compliant) and d) a flooded reservoir for reagents and standards. The reagent delivery module is comprised of a cylindrical pressure housing that contains the electro-fluidics, electro-optical detectors, analog-digital conversion, data acquisition, instrument control, and power regulation systems. The electro-fluidic components of the APNA include a main sample pump, pressure and temperature sensors, a flow-through heater, and several miniature pumps for reagents and calibration standards. Analyzers for operations in deeper waters (>15 - 200 meters) are configured with a pressure compensation system. The continuous flow of filtered (<10 μM pore size) sample water (~5-6 ml/min) is split and directed to multiple fluidic channels (~1 ml/min each) for chemical analysis. The ChemStar™ detectors are flow-through optical cells that are custom manufactured for SubChem Systems Inc. by WET Labs, Inc. (Philomath, OR) for integrated use with the SubChem Analyzers (Fig. 1). The small volume flow-through absorption cells typically have path lengths of 1cm or 5cm – depending on the desired analyte concentration range. A small volume (< 0.5ml) dual-channel fluorometer detector is included if the instrument is configured for ammonia determination. The individual optical cells are fabricated to measure light absorption or fluorescence at the specific wavelengths (Table I) that are required for the selected analytes.

The APNA comes with a deck box capable of supplying 48V/40W power from a standard 120VAC 50/60Hz outlet; however, DC powered options are also available on request. A multi-conductor cable connects the APNA to the deck box that provides DC power and a data

communications interface with the host computer (MS Windows). The software for the APNA – ChemView™ – is a stand-alone executable (developed with National Instruments LabView™) and graphical user interface (GUI) that facilitates user-friendly remote control of all analyzer functions with a data acquisition rate of 1Hz. Communication is accomplished either by RS232 or RS485 with the user laptop or host platform. Internal DC-DC converters convert any unregulated underwater DC supply into

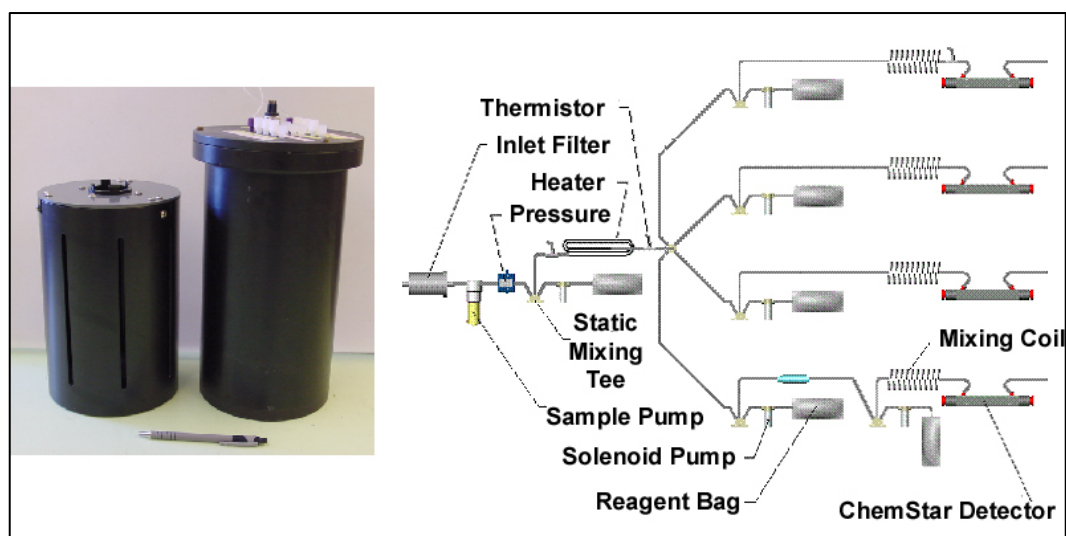


Fig. 1 Fluid Schematic of a 4-Channel Autonomous Profiling Nutrient Analyzer (APNA) – pictured to the left with submersible reagent reservoir.

stabilized power within the APNA. Ancillary instruments and sensors such as CTDs, Chlorophyll fluorometers, or dissolved oxygen sensors can be readily integrated with the APNA.

B. Analytical Methodology

The APNA utilizes the standard spectrophotometric and/or fluorometric analytical methodologies [2] which have optimized for rapid, continuous, in situ determinations at trace concentration levels [1] (see Table I). The APNA includes an internal calibration feature which allows for the analyzer to be routinely calibrated *in situ* via the method of standard additions. The reagents and *in situ* calibration standard are initially prepared in the laboratory and then stored in flexible plastic IV bags in the reagent reservoir – a separate, opaque cylindrical housing that is exposed to ambient underwater pressures. Reagents and standards have been rigorously tested and shown to last ~ 3 months without any significant degradation. Several reagent bags are typically required for deployment – 0.5 or 1.0 liter bags for the analytical reagents and calibration standard. The 1 liter reagent quantities may be sufficient for continuous analyzer operation for about seven days or intermittent operation for longer time periods.

Nitrite (NO_2^-) is determined by a spectrophotometric method that is based upon the formation of a colored azo dye. Nitrite reacts with sulfanilamide to form a diazonium ion that is subsequently coupled with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored product (molar absorptivity = ~46,000 at 532 nm). The method is generally considered to be free from interferences and is commonly used in limnology and oceanography. The determination Total Nitrate + Nitrite ($\text{NO}_3^- + \text{NO}_2^-$) is based on the quantitative reduction (>95%) of nitrate to nitrite which is then determined colorimetrically – as described above. The reduction is made with high and stable efficiency when a sample is run through a reducing column containing cadmium coated with copper. The determination of orthophosphate in seawater relies on the formation of phosphomolybdate complex obtained by interaction between the molybdate ion and orthophosphate (primarily HPO_4^{2-} and PO_4^{3-}) in presence of antimony. This complex is then reduced with *L*-ascorbic acid to form a blue compound which has a maximum absorbency at 885 nm. The analytical determination of dissolved inorganic silicate – in the form of silicic acid – relies on the formation of silico-molybdate complex obtained by the addition of molybdic acid which reacts with the silicic acid found in natural waters. Oxalic acid is then added in order to limit potential interference from phosphate. Then the silicomolybdic acid is reduced to silicomolybdous acid, or “molybdenum blue”, using *L*-ascorbic acid as the reductant. The maximum absorbance of the product occurs at 820nm. Iron(II) (reduced iron species) is determined using the classical Ferrozine methodology (molar absorptivity = ~26,500 at 560 nm, slightly less at 540 nm) [3]. For the determination of Ammonia (NH_3), the ion is reacted with o-phthalaldehyde (OPA) and sulfite to yield a product molecule that can be detected fluorometrically. The fluorophore has an excitation spectrum maxima @ 365 nm and an emission spectrum maxima at 420 nm. Sulfite is used as a nucleophilic reagent that forms a bond to the NH_4^+ – OPA reaction partner (the electrophile) by donating both bonding electrons [4]. To prevent precipitate formation within the flow stream, Ethylenediaminetetraacetic acid tetrasodium salt tetrahydrate (EDTA) is added as a chelator. Analytical methodologies for copper, urea, and other chemicals are also being developed.

C. Sampling Capabilities

The APNA has two operational modes – real-time and autonomous mode – either of which can be used for moored sampling or vertical profiling. Real-time mode requires a full-time cabled, communication link to the instrument; therefore, it is most applicable to cabled observatories, shipboard vertical profiling, or mapping with an undulating tow-body. This mode allows for continuous monitoring as well as adaptive sampling during critical periods such as storm events or harmful algal blooms. In autonomous mode, the APNA can be remotely powered (battery pack, etc.) and configured via a script file to periodically sample as well as perform *in situ* calibrations either at a fixed location or onboard an autonomous sampling platform. The resultant data is collected and stored on a 2 GB internal memory card for future analysis using automated analysis routines. The inclusion of file transfer capabilities via radio telemetry allow for near real-time multi-nutrient concentrations from remote ocean observing systems.

III. CASE STUDIES

A. Narragansett Bay Deployment on the University of Rhode Island Graduate School of Oceanography (URI-GSO) Pier

Narragansett Bay is a highly productive, temperate, well-mixed estuary with significant freshwater input from the Seekonk, Providence, Pawtuxet, and Taunton Rivers as well as multiple wastewater treatment facilities in the Upper Bay. Residence times for Narragansett Bay vary from 10 to 40 days – due primarily to variation in freshwater input. The distributions, temporal variability and ecological roles of nutrients have been well studied in Narragansett Bay. Nutrient distributions in the Bay show a distinct seasonal pattern that covaries with the seasonal cycle of freshwater input [5]. Lower Narragansett Bay is dominated by strong advective fluxes with significant outflow on the western side of the West Passage – coinciding with the location of the URI-GSO Pier. The URI-GSO Pier has many advantages for the continued testing of new chemical sensor technology intended for the long-term, unattended monitoring of nutrients (Fig. 2A-C). These advantages include 1) easy access for deployment and recovery 2) unlimited regulated power 3) internet access along with line-of-sight visibility for data telemetry, 4) close proximity

to laboratory auto-analyzers at URI-GSO for nearly immediate verification of nutrient concentrations and 5) decades of historical nutrient data [5].

On September 9, 2008 (JD 253), an APNA was deployed at ~ 1.5m depth off of the GSO Pier. The APNA was configured to sample for 5 minutes (total cycle run time = 16 minutes) every 2 hours. This sampling regime included one calibration cycle (total calibration cycle run time = 26 minutes) per day. The APNA was recovered on September 30, 2008 (JD 274) after a successful deployment – totaling 229 samples (including 22 calibration cycles) over the course of three weeks (Fig. 4). All data was retrieved remotely via GoToMyPC.com™ and quickly batched processed via Matlab™. Upon retrieval, heavy biofouling was evident (See Fig. 3A-D) but did not hinder the overall APNA performance or inhibit further sampling. However, the Total (NO₃ + NO₂) raw data indicated that the input of the buffer reagent ceased on September 14th at ~ 15:00 EST (JD 258) – causing incomplete Nitrate reduction. Upon retrieval, a broken stopcock and empty reagent bag confirmed this suspicion. The APNA was deployed with a 4-filter sampling head with copper mesh surrounding each filter (See Fig. 3B). Despite significant sediment accumulation as well as hydroid, mussel, and barnacle growth, the APNA continued to effectively filter and analyze sample water even after a total throughput of ~ 18.7 Liters of seawater. Unfortunately, the sample pump of the co-deployed Sea-Bird Electronics Inc.’s SBE 911 CTD package intermittently failed during deployment resulting in unreliable dissolved oxygen concentration data as well as WET Labs Inc.’s WetStar™ fluorometer [Chlorophyll a (µg/L)] data.

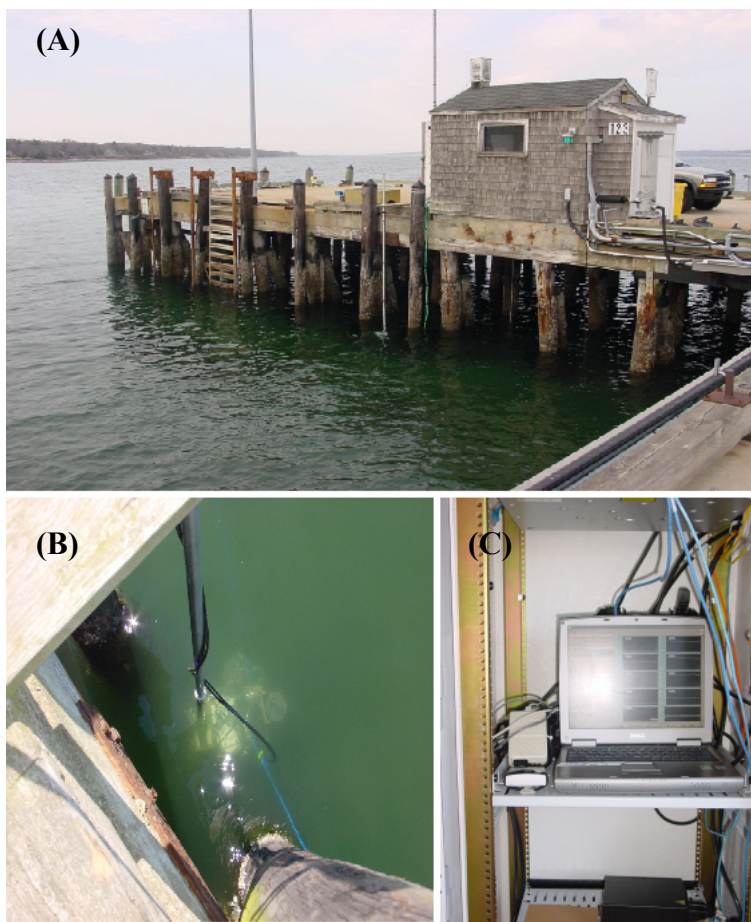


Fig. 2 (A) University of Rhode Island’s Graduate School of Oceanography (URI-GSO) Pier Sampling Station. (B) Photograph of the deployed APNA and CTD package. (C) GSO Pier Environmental Electronics Chamber containing the APNA power source, host laptop, and network internet connection.

The data collected over this three-week deployment period showed high frequency temporal variability in nutrient concentrations intrinsic to the dynamic coastal margin (Fig. 4). This variability, caused by tidal oscillations and passing storm events, is typically under-sampled by traditional water sample collection methods [1]. In general, nutrient concentrations were



Fig. 3 (A) URI-GSO Pier Sampling Package during 9/9/2008 pre-deployment. Package includes the APNA with reagent reservoir, Sea-Bird SBE 911 CTD with DO and pH probe, and WET Labs’ WetStar [Chl a] Fluorometer and AStar Transmissometer. (B) 4-Filter (10µm) Sampling Head and copper mesh during 9/9/2008 pre-deployment. (C) 4-Filter Sampling Head upon 9/30/2008 retrieval. (D) GSO Pier Sampling Package upon 9/30/2008 retrieval.

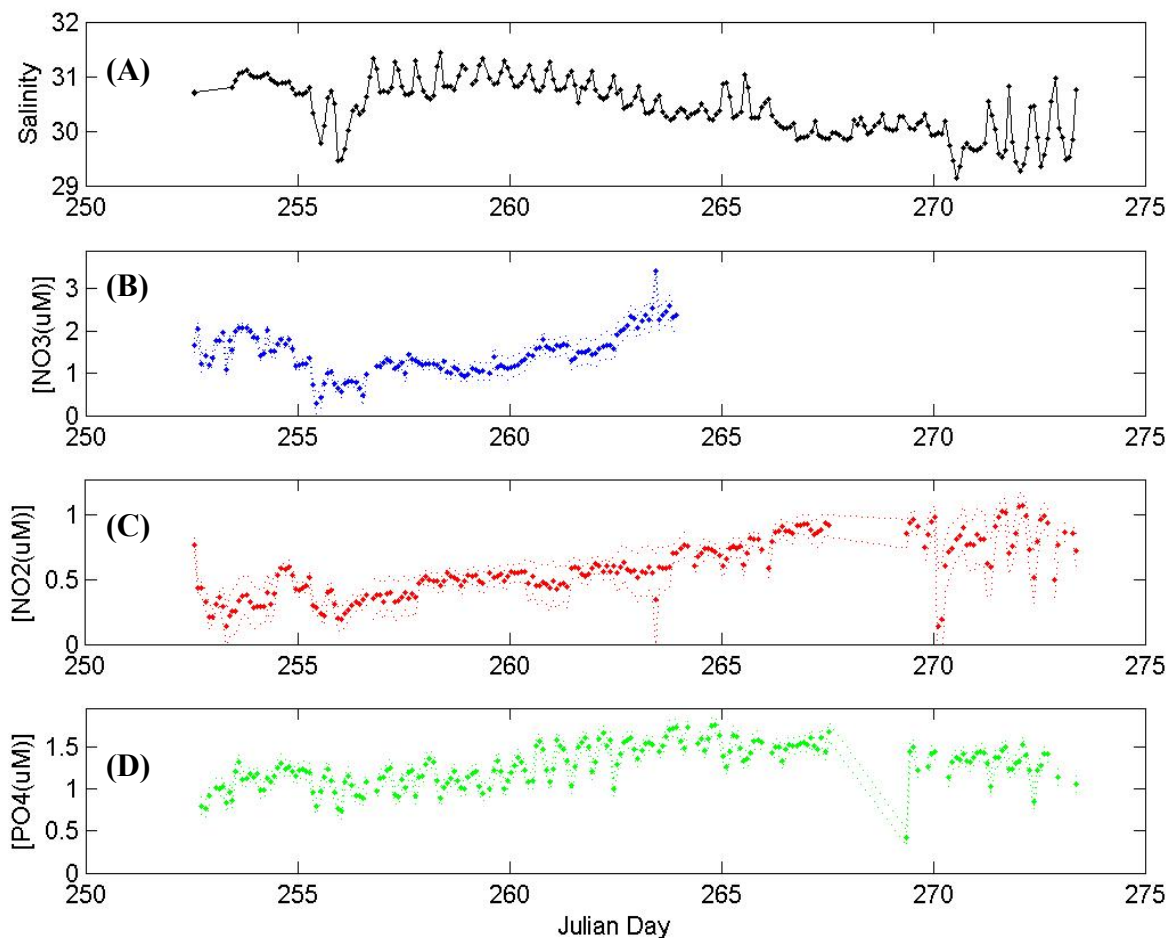


Fig. 4 Oceanographic data collected 9/9/2008 – 9/30/2008 at the URI-GSO Pier Sampling Station. (A) Sea-Bird SBE 911 Salinity (psu) vs. Julian Day (B) APNA [Nitrate (NO_3^-) (μM)] vs. Julian Day. The dotted lines represent \pm measurement error ($\sim 0.100 \mu\text{M}$). (C) APNA [Nitrite (NO_2^-) (μM)] vs. Julian Day. The dotted lines represent \pm measurement error ($\sim 0.100 \mu\text{M}$). (D) APNA [Phosphate (HPO_4^{2-}) (μM)] vs. Julian Day. The dotted lines represent \pm measurement error ($\sim 0.100 \mu\text{M}$).

very low ($< 2\mu\text{M}$) and inversely correlated with salinity which is quite characteristic of a temperate estuary during late summer. Changes in nutrient concentration – sometimes by as much as 50% – caused by tidal advective fluxes as well as lunar oscillations are clearly evident. The passage of two coastal storms and subsequent freshwater run-off – as evidenced by the intrusion of low salinity waters on JD 256 and JD 271 – also greatly influenced the nutrient distributions on timescales as short as hours. The influence of these storm events lasted for 1-2 days with nutrient concentrations gradually returning to average values.

B. LOCO 2005: Monterey Bay Shipboard Vertical Profiles

The objective of the ONR funded “Layered Organization in the Coastal Ocean (LOCO)” program is to further our understanding of the oceanographic processes and mechanisms which influence the dynamics of thin plankton layers in the coastal ocean. Nutrients may significantly influence the formation, persistence, and behavior of plankton blooms in the coastal environment. The position and intensity of the nutracline – an important region for new production – is thought to play a significant role in the episodic formation and maintenance of these thin plankton layers in coastal waters. During August/September 2005 and July 2006, multi-institutional LOCO field surveys were performed along the 20m isobath in the northeast corner of Monterey Bay National Marine Sanctuary $\sim 3.75\text{km}$ offshore from Aptos, CA (centered $\sim 36.937^\circ \text{N}$, 121.919°W) aboard the *R/V Shana Rae*. This region of Monterey Bay is of significant interest because of its role as an “incubator” of harmful algal blooms (HABs) – many species of which have been shown to form thin layers [6][7]. In 2005, oceanographic conditions were characterized by 1) no upwelling, 2) nutrient depleted surface waters, 3) a vertical separation between the pycnocline and nutricline and 4) vertical migrating dinoflagellate layers. In 2006, an upwelling relaxation event was

sampled with rapidly changing nutrient concentrations and a highly complex phytoplankton assemblage. Thin layers were frequently observed in both oceanographic regimes.

In 2005, the APNA was deployed aboard the URI (P.L. Donaghay) shipboard high resolution vertical profiling package which also included a Sea-Bird SBE-25 CTD with DO and PAR sensor PAR as well as a suite of WET Labs bio-optical sensors – chlorophyll and CDOM fluorometers, two AC-9s and two AC-Ss, an Eco-VSF volume scattering function sensor, and a BB-3 backscatter sensor [8]. Vertical high-resolution (cm-m scale) physical, hydrodynamic, bio-optical, and nutrient distributions were periodically collected in the region of the 20 meter isobath from August 15th – September 2nd. Oceanographic conditions became increasingly stratified and nutrient depleted. Thin plankton layers – dominated by the harmful dinoflagellate *Akashiwo Sanguinea* – were frequently observed in the euphotic zone during the day and in deeper water during the nighttime [8][9][10]. For example, during the daytime on 8/31/05, very high chlorophyll concentrations were observed dispersed between 4 and 12 meters depth – with the highest concentrations contained within a very thin layer just below the turbulent surface mixed layer. These thin layers were located within a stratified region of the water column characterized by extremely depleted nutrient concentrations yet supersaturated dissolved oxygen concentrations which is indicative of active primary production. The nutricline was observed several meters deeper than the pycnocline suggesting that vertical distribution of nutrients was not controlled primarily by hydrodynamic mixing processes (Fig.5). Devoid of any significant replenishment from regional upwelling, it was hypothesized that the photosynthetic uptake of nutrients by the abundant dinoflagellate population had pushed the nutricline deeper than the pycnocline – leaving non-motile diatom species in unfavorable growth conditions [9][10].

Motile phytoplankton can overcome nutrient limitation by migrating vertically through the water column – often forming thin layers within the region most conducive for growth. On the evening of September 2, 2005, the diurnal migration of *Akashiwo Sanguinea* from the well-lit, nutrient depleted surface layer to deeper, nutrient-rich waters was observed and extensively sampled with the shipboard high-resolution vertical profiling package aboard the *R/V Shana Rae*. Within a 2-hour time period beginning around sunset (~ 8:00PM Local Time), a thin plankton layer began to vertically compress and migrate downward through the pycnoclinic barrier into a region of elevated ($> 2\mu\text{M NO}_3^- + \text{NO}_2^-$) nutrient concentrations (Fig. 6). This region of the water column just above the bottom mixed layer was characterized by a sharp nutrient gradient and a marked increase in upward nitrate flux. It is apparent that the motile plankton layer migrated just deep enough to take advantage of the more favorable nutrient conditions without venturing into deeper yet more nutrient rich and turbulent waters.

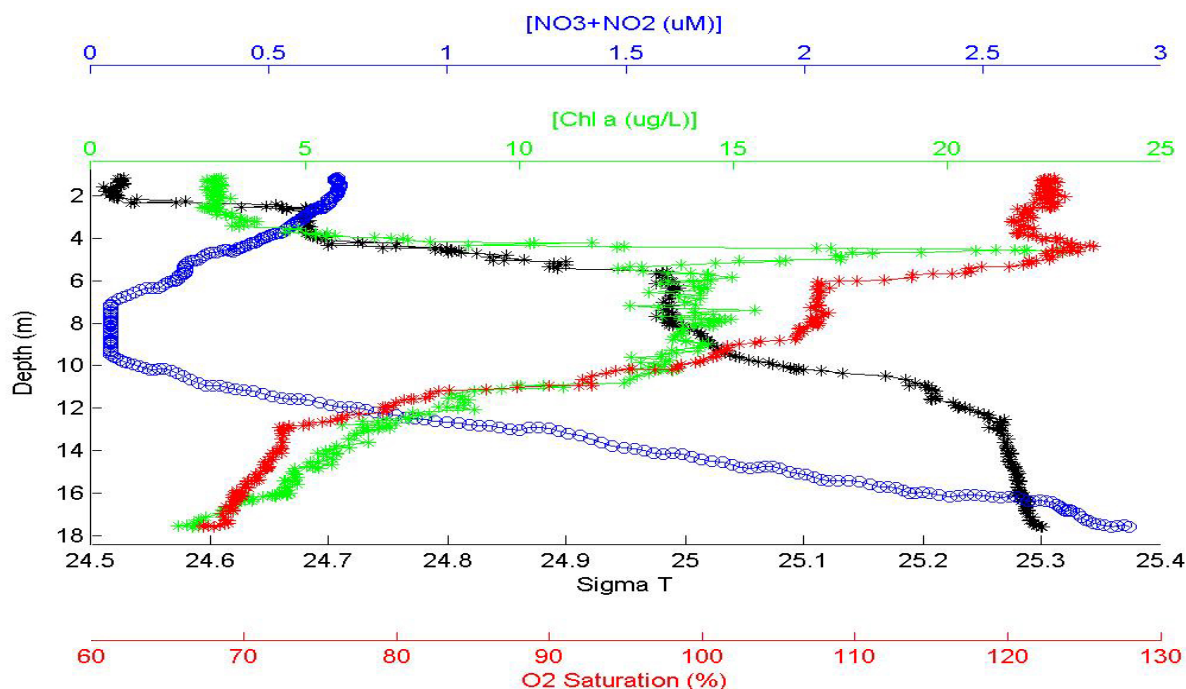


Fig. 5 Vertical Distribution of Density (black), [Total ($\text{NO}_3^- + \text{NO}_2^-$) (μM)] (blue), [Chlorophyll a ($\mu\text{g/L}$)] (green), and Dissolved O_2 %Saturation (red) with Depth on August 31, 2005 @ 13:30 PCT in Monterey Bay, CA ~ 36.937° N, 121.920° W.

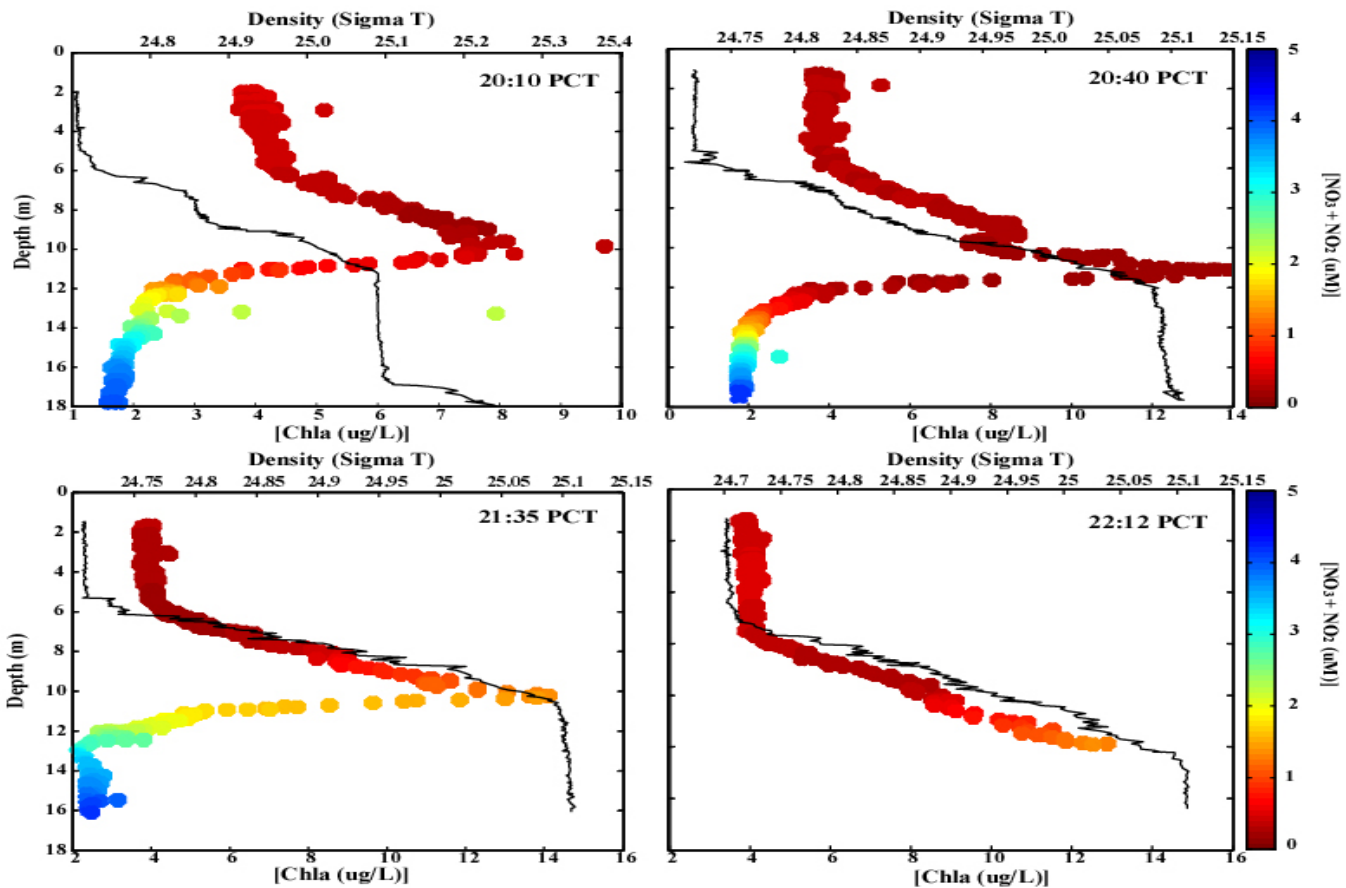


Fig. 6 Vertical Distribution of Density (black line) and [Chlorophyll a ($\mu\text{g/L}$)] (colored circles) vs. Depth with the color bar representing the $[\text{Total } (\text{NO}_3^- + \text{NO}_2^-)]$ (μM). Profiles were collected on September 2, 2005 between 8:00PM – 10:30PM Local Time in Monterey Bay, CA $\sim 36.937^\circ \text{N}$, 121.920°W .

C. LOCO 2006: Monterey Bay Autonomous Vertical Profiles

In 2006, the APNA was deployed aboard the URI (P.L. Donaghay) Ocean Response Coastal Analysis System – Inherent Optical Properties + Chemistry autonomous moored vertical profiler (ORCAS-IOPC)(Fig. 7A) [8][11]. The ORCAS bottom-up autonomous profiler slowly ascends through the water column at 2-3 cm/s collecting extremely fine-resolution physical, hydrodynamic, bio-optical, and chemical data until it reaches the surface where it transfers the data to a shore station via line-of-sight radio telemetry. The ORCAS-IOPC payload included the APNA, a Sea-Bird SBE-49 CTD with DO sensor, a Satlantic OCR4 4-channel downwelling irradiance sensor, and a suite of WET Labs bio-optical sensors including an AC-S, a chlorophyll fluorometer, a CDOM fluorometer, and a BB-3 backscatter sensor. During July 14th – 28th, three ORCAS profilers were programmed to continuously profile once every hour with a service interval occurring approximately every 4 to 5 days. The central ORCAS-IOPC profiler collected continuous hourly nutrient profiles from July 17th to July 25th – totaling 178 high resolution vertical nutrient profiles.

Highly dynamic oceanographic conditions combined with a complex and diverse phytoplankton assemblage were sampled during the 2006 study period [8][10]. Initially, nutrient concentrations relatively high ($> 7\mu\text{M } \text{NO}_3^-$ on 7/15/06) and the water column was weakly stratified – indicative of recent upwelling. As the relaxation of this upwelling event progressed, wind speeds slowed, current velocities subsided, and stratification increased leading to a significant decrease of nutrient concentrations in the euphotic zone. Thin plankton layers were frequently observed in the study region; however, they primarily occurred during daylight hours. One of the dominant species observed in these layers was the paralytic shellfish poisoning (PSP) toxin-producing dinoflagellate *Alexandrium Catenella* [8][10]. On July 24th, a coastal front, including internal breaking wave packets, associated with the incoming spring tide passed through the LOCO study region. The nutrient profiles collected with the ORCAS-IOPC showed very low nitrate concentrations ($< 1\mu\text{M}$) within the surface waters associated with the frontal zone and noticeably different vertical distributions within and on either side of the front (Fig 7B). A phytoplankton thin layer associated with the passage of the tidal front was observed within the nutricline above a region of low current velocities (Fig. 7C). The dinoflagellate

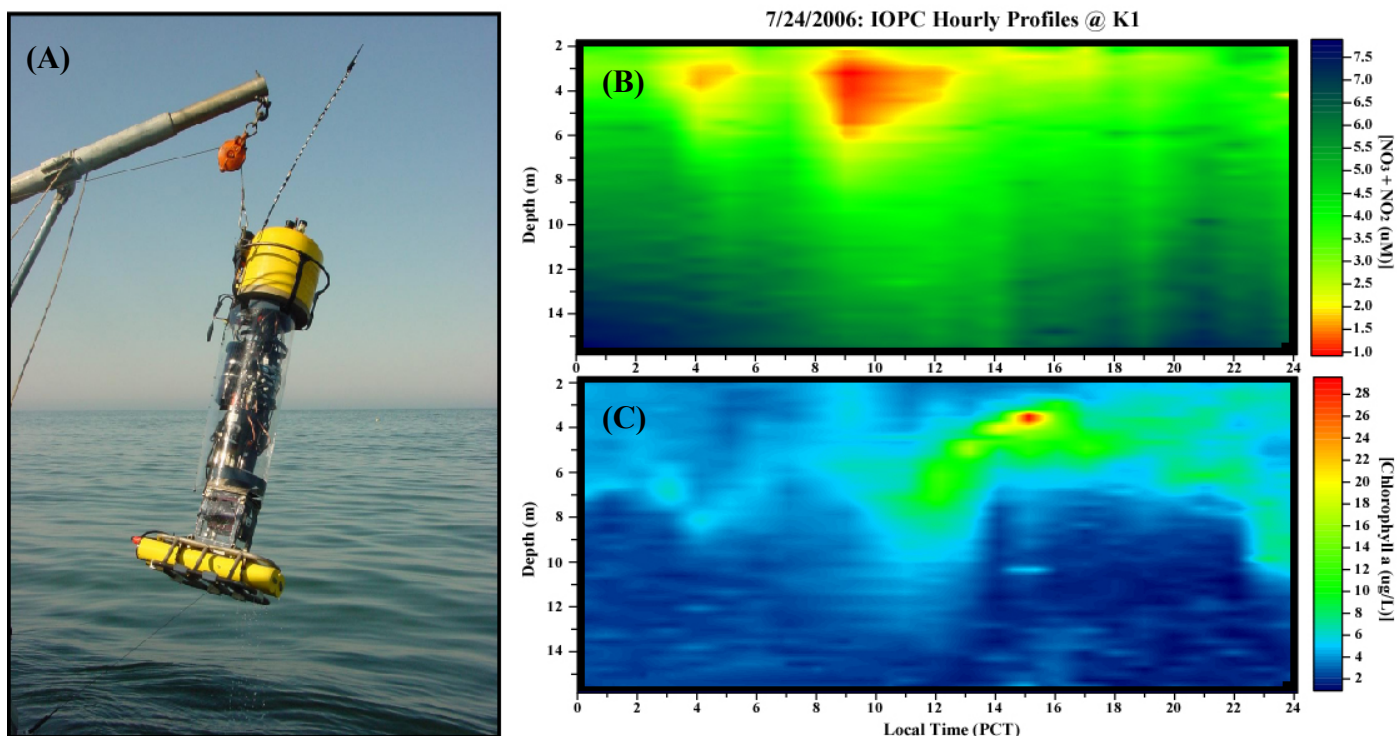


Fig.7 (A) Ocean Response Coastal Analysis System autonomous moored vertical profiler (ORCAS). (B) Contoured distribution of hourly [Total ($\text{NO}_3^- + \text{NO}_2^-$) (μM)] vs. Depth collected on 7/24/06 with the ORCAS-IOPC in Monterey Bay, CA $\sim 36.937^\circ$ N, 121.920° W. (C) Contoured distribution of hourly [Chlorophyll a ($\mu\text{g/L}$)] vs. Depth contoured distribution also collected on 7/24/06 with the ORCAS-IOPC in Monterey Bay, CA $\sim 36.937^\circ$ N, 121.920° W.

Alexandrium Catanella is known to commonly form blooms within frontal regions [12]. Though it appears that the layer forms and intensifies at this sampling station with the incoming tide, it is difficult to ascertain whether this is due to phytoplankton production, motile species aggregation, or simply water mass advection. It is hypothesized, however, that the formation and maintenance of this thin phytoplankton layer is linked to the increased vertical flux of nutrients into the euphotic zone caused by an increase in turbulence and water column mixing associated with the coastal tidal front.

IV. CONCLUSIONS

The long-term deployment of *in situ* instrumentation onboard ocean observing platforms in the challenging coastal environment is plagued by real-world obstacles such as biofouling, power limitation, and technological complexity. The primary objective of SubChem Systems Inc. is to overcome these obstacles and provide accurate, real-time nutrient distributions aboard a variety of ocean observing platforms. This is accomplished with accepted standard analysis methods, cutting edge technology, instrumental automation, and rigorous QA/QC procedures. For unattended, autonomous deployments for long durations (3-6 months), the analytical methods used for *in situ* instrumentation must be optimized in order to conserve reagent and power consumption. The methods must also be fully characterized in order to account for reagent longevity and calibration stability. SubChem Systems Inc. has developed an innovative micro-fluidic analytical design combined with stable reagent constituents and automated *in situ* calibration methodology in order to fulfill the sampling requirements of modern ocean observing systems. Recent technological advances in micro-processors and on-board package controllers have increased our ability to rapidly collect, analyze, and report nutrient concentrations in near real-time via the internet.

Oceanographic parameters, such as nutrient concentrations, must be monitored at very high temporal scales in order to provide an accurate description of the processes which control the biogeochemical cycling of pollutants, harmful algal blooms, coastal eutrophication, and other pertinent topics to water quality managers and the oceanographic community as a whole. Scientific objectives, such as the study of thin plankton layers or the influence of stratification and turbulence on the vertical flux of nutrients, require that parameters be monitored at high temporal and spatial resolution in the dynamic coastal environment. The APNA is specifically designed to accurately measure sub-meter scale nutrient gradients while aboard a moving ocean observing platform. This multi-dimensional, multi-parameter data provides a more descriptive snapshot of the processes that regulate the biogeochemical cycling of nutrients in natural waters compared to traditional water sampling methods.

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