Transitioning Submersible Chemical Analyzer Technologies for Sustained, Autonomous Observations from Profiling Moorings, Gliders and other AUVs

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LONG-TERM GOALS

To transition existing prototype autonomous profiling nutrient analyzers into commercial products that can be readily deployed on autonomous profiling moorings, coastal gliders and propeller driven unmanned underwater vehicles and used for sustained, autonomous ocean observations of chemical distributions and variability. A series of issues have been identified that that need to be addressed to convert prototype nutrient analyzers into commercial units that can be widely used by the community for sustained and accurate, stable, autonomous operation in the ocean. These issues are; (1) a more compact size, (2) reduced reagent and power consumption, (3) enhanced biofouling suppression, (4) ease of use by non-chemists, and (5) documented performance when deployed on different platforms.

Our plan to address those issues involved using recent advances in micro-fluidics and optical detectors (new SubChem and WET Labs technologies) to reduce sample flow rates and volumes and thus reagent and power consumption; (2) extend the length of field deployments by periodically isolating sensitive components so that back-flushing and chemical techniques can be used to suppress bio-fouling, (3) increase the ease of use by simplifying operation, pre-packaging reagents and outputting the data in engineering units, and (4) thoroughly documenting the performance by conducting demonstration experiments at field sites that have strong vertical and horizontal nutrient gradients and episodic phytoplankton blooms.

We are achieving these goals through this NOPP partnership. The industry partners have taken the lead in developing the commercial versions of the nutrient analyzers while the university and government partners are providing guidance defining the initial performance criteria for the nutrient analyzers and in providing the deployment platforms and conducting the field testing and demonstration experiments.

OBJECTIVES

The primary objectives of this collaborative NOPP project are the technological advancement, verification, demonstration and commercialization of two autonomous profiling nutrient analyzers and a third analyzer, designed for extended moored observations of phosphate, that have been developed to their present status with government and private funding. The Autonomous Profiling Nutrient Analyzer **(**APNA), the Micro-AUV Ready Chemical Analyzer (MARCHEM) and Cycle-P Analyzer are being improved so that they are capable of deployment from profiling and fixed moorings, coastal gliders and other AUVs for sustained, autonomous ocean observations of nutrient concentrations, spatial distributions and temporal variability.

APPROACH AND WORKPLAN

Our general approach to achieve these objectives involves a collaborative partnership between industry (Alfred Hanson, SubChem Systems, Inc., and Casey Moore, WET Labs, Inc.), university (Percy Donaghay, University of Rhode Island) and government (Richard Arrieta & Brian Granger, SPAWAR Systems Center - San Diego). An existing APNA prototype is being modified by SubChem Systems and WET Labs to be a more compact, resource-efficient, autonomous profiling multi-nutrient analyzer (now referred to as APNA II and III), particularly suited for sustained deployments on autonomous moored profiling systems like the IOPC profiler, and other AUVs. The MARCHEM analyzer prototype will be similarly developed, but as a very compact single channel analyzer designed for ready deployment on autonomous underwater vehicles that have more stringent space and power limitations (i.e. coastal gliders and small UUVs). The Cycle-P analyzer is being co-designed by WET Labs and SubChem for long-term monitoring of phosphate in coastal and oceanic environment. The Cycle-P combines a custom optical detector with novel reagent delivery fluidics to perform stop-flow analyses of natural water. All of these analyzers will utilize similar miniaturized electro fluidic, optical detection and instrument communication and control components to accomplish the autonomous chemical analysis with minimal utilization of power and reagents. The academic and government partners, URI-GSO and SPAWAR-SSC, will contribute to the further development of these nutrient analyzers by providing advice and guidance on the analyzer design and specifications for the purpose of integration onto specific oceanographic platforms and accomplishing specific scientific and ocean observation goals. As they are developed, the MARCHEM and APNA analyzers will be tested and demonstrated in the field by integrating and deploying them on various autonomous underwater vehicle test platforms, such as the ORCAS IOPC profiler (URI), REMUS AUV, and Slocum coastal gliders (SPAWAR-SSC).

WORK COMPLETED

Progress was made on multiple objectives during the last fiscal year of NOPP funding.

Transitioning of the APNA into a Commercial Product. SubChem's Autonomous Profiling Nutrient Analyzer (APNA) was commercially released during the past year The APNA (Figure 1) is a five channel autonomous profiling nutrient analyzer (nitrate, nitrite, phosphate, silicate and ammonia) In addition to real-time profiling, the APNA is also configurable for multi-nutrient, time-series measurements for longer-term deployments on fixed moorings (cabled or battery). The APNA analyzers were designed and fabricated by SubChem Systems and WET Labs provided the optical detectors and detector electronics.

Develop the capability for real-time environmental data products. The NOPP project partners have also successfully collaborated with Applied Science Associates (ASA) to develop and demonstrate the technology to autonomously acquire and communicate real-time environmental data from the ORCAS profilers, gliders, and AUVs, and to seamlessly interface this data collection system with COASTMAP™ to generate useful real-time data products. COASTMAP is ASA's web-based integrated undersea data collection, management, and visualization system. This integration effort was also partially funded by the Rhode Island Science Technology Advisory Council and by the URI-NUWC Center of Excellence in Undersea Technology (COEUT).

Testing of APNA capabilities on cabled-moorings in collaboration with researchers at the University of Hawaii and the Woods Hole Oceanographic Institute. An APNA submersible nutrient analyzer was deployed on UH's Kilo Nalu ocean observatory during 2008 in collaboration with Drs. Eric DeCarlo and Geno Pawlak. An APNA was also deployed via undersea cable on the Martha's Vineyard Coastal Observatory, in collaboration with Dr. Heidi Sosik. The APNA complements a suite of observational instruments already in place that resolve waves, tides, currents and near-shore water quality in both the Waikiki – Ala Moana and Martha's Vineyard regions.

Development of ChemFIN™ – Design work was continued by SubChem Systems on a new submersible chemical analyzer. ChemFIN™ (Figure 2) is a small independent sensor payload, utilizing microfluidics, and is particularly designed for "low-power" underway measurements on gliders, propeller-driven AUVs and autonomous profilers. Design work and info-exchange discussions with

SPAWAR and WET Labs focused on integrating the "ChemFIN" Chemical Sensor onto the Slocum Glider and the WET Labs AMP-100 profiler. Further progress was made this fiscal year to work with SPAWAR to define an integration path and specification for a ChemFIN prototype to be hosted on the Webb Research SLOCOM Glider. Collaboration with engineering students at UMASS/Dartmouth was also completed to develop a wireless communication system for ChemFIN. The development of ChemFIN is nearly complete, so it will be ready for field testing on the SPAWAR's glider and WET Labs commercial profiler during late 2008.

Development and testing of the Cycle-P Analyzer. These efforts culminated in the development of a production prototype sensor for long-term monitoring of phosphate in coastal and oceanic environments. The instrument combines a custom optical sensor with reagent delivery fluidics to perform stop-flow analyses of natural water. This sensor was tested in various environments (Figure 3) and its performance was demonstrated and evaluated by the Alliance of Coastal Technologies (2008). Important steps in developing these longer-term chemical measurement systems included: reduction of size and power requirements of the electro-fluidic components to match the electro-optical detectors, extension of reagent preservation time scales to enable multi-month deployments, and development and validation of anti-biofouling strategies for multi-month deployments.

RESULTS

The nutrient analyzer development efforts of the NOPP partners continued to be collectively focused on developing improved fluidic pumping technologies, integrated optical sensing and mixing capabilities, advancing sensor technologies, and solving integration issues for autonomous profiling platforms. The development of new fluidic and integrated fluidic-detection technologies is required for the successful adaptation of APNA, MARCHEM, CYCLE, and ChemFIN technologies for sustained autonomous deployments on profiling and fixed moorings and gliders.

Automated Software for Processing Nutrient Data and Generating Useful Data Products: The APNA-IOPC was deployed in Monterey Bay during a field effort sponsored by the ONR directed research initiative "Layered Organization in the Coastal Ocean (LOCO)" during July 2006. The APNA II is a four channel autonomous profiling nutrient analyzer (nitrate, nitrite, phosphate, ammonia) that was designed for deployment on URI's ORCAS IOPC profiler (Figure 1). It was programmed to collect hourly nutrient profiles for a two week time period. The large data set, comprised of over two hundred vertical profiles, was used as the initial test data for the newly developed automated software for processing large collections of APNA nutrient profiles. An initial effort was also made to integrate the output of the automated nutrient data processing software with ASA's COASTMAP software to produce useful data products (i.e. 2D and 3D time series plots).

Developing ChemFIN for AUVs, Gliders and Profilers: During 2006 it was decided to shift the integration path from MARCHEM to a micro-fluidic based analyzer that would allow for a design of an externally mounted UUV/Instrumentation package called ChemFIN™ (Figure 2). A ChemFIN design review meeting, held in San Diego with partners from SPAWAR (Arrieta, Granger, et al.) in late January 2007 led to an improved specification for the best means of integrating the ChemFIN single channel analyzer on to the SPAWAR SLOCOM Glider. The on-going ChemFIN development effort has included additional design reviews for integration with the SPAWAR Glider, the initial design of a specialized, user-friendly, reagent cartridge, and the testing/evaluation of the efficacy of multiple designs for ChemFIN's the micro-fluidic manifold.

The Performance Demonstration of the CYCLE-P Analyzer. WET Labs tested the CYCLE-P in various environments and a performance demonstration was conducted for the Alliance for Coastal Technologies in 2008. During the performance demonstration the WET Labs Cycle-P was successfully tested in a fixed, surface mooring deployment at three test sites including freshwater, brackish water, and salt water coastal environments. The test instrument functioned continuously for four weeks at each test site measuring a wide-range of phosphate concentrations. There was no apparent degradation of the on-board reagents or standards over the deployment periods.

IMPACT/APPLICATIONS

It is a critical gap that the oceanographic community does not currently have the capability to make routine and sustained nutrient measurements, *in situ* and autonomously, at the same space and time scales that are possible for temperature, salinity, oxygen, and chlorophyll fluorescence. In recent years, though, there has been significant progress in the development and application of reagent-based optical multi-nutrient sensors. The on-going research for this NOPP project is giving us the opportunity to further develop, improve and demonstrate these autonomous chemical profiling technologies. These efforts represent substantial advancements in the development of this technology and bring us much closer to a demonstrated capability for sustained, autonomous ocean observations of nutrient distributions and variability.

TRANSITIONS

The APNA instrumentation is now commercially available from SubChem Systems, Inc and WET Labs, Inc. Eight units were purchased and delivered to government and university laboratories in the USA, China and South Africa. The MARCHEM AUV nutrient sensing payload is slated for integration into HYDROID's REMUS-600 as part of the coastal component of the NSF Ocean Observatories Initiative. A contract is also in place with the Naval Research Laboratory (NRL) to adapt the MARCHEM AUV payload to utilize NRL immunosensor technology for the underwater detection of explosives and other chemicals of interest that may be detected by the successful NRL analytical technology.

SubChem Systems and NRL have been granted a new FY08 NOPP award "Developing ChemFin, a Miniature Biogeochemical Sensor Payload for Gliders, Profilers, and other AUVs". WET Labs, Inc., SubChem Systems, Inc. and other partners have also been granted a new FY08 NOPP award "Long-term in situ chemical sensors for monitoring nutrients: phosphate sensor commercialization and ammonium sensor development".

RELATED PROJECTS

A related project is the ONR sponsored Directed Research Initiative entitled "Layered Organization in the Coastal Ocean (LOCO)". New nutrient monitoring technologies developed in this NOPP project were demonstrated and utilized within the LOCO field research during 2005 and 2006. PIs Hanson (SubChem) and Donaghay (URI) both have LOCO projects.

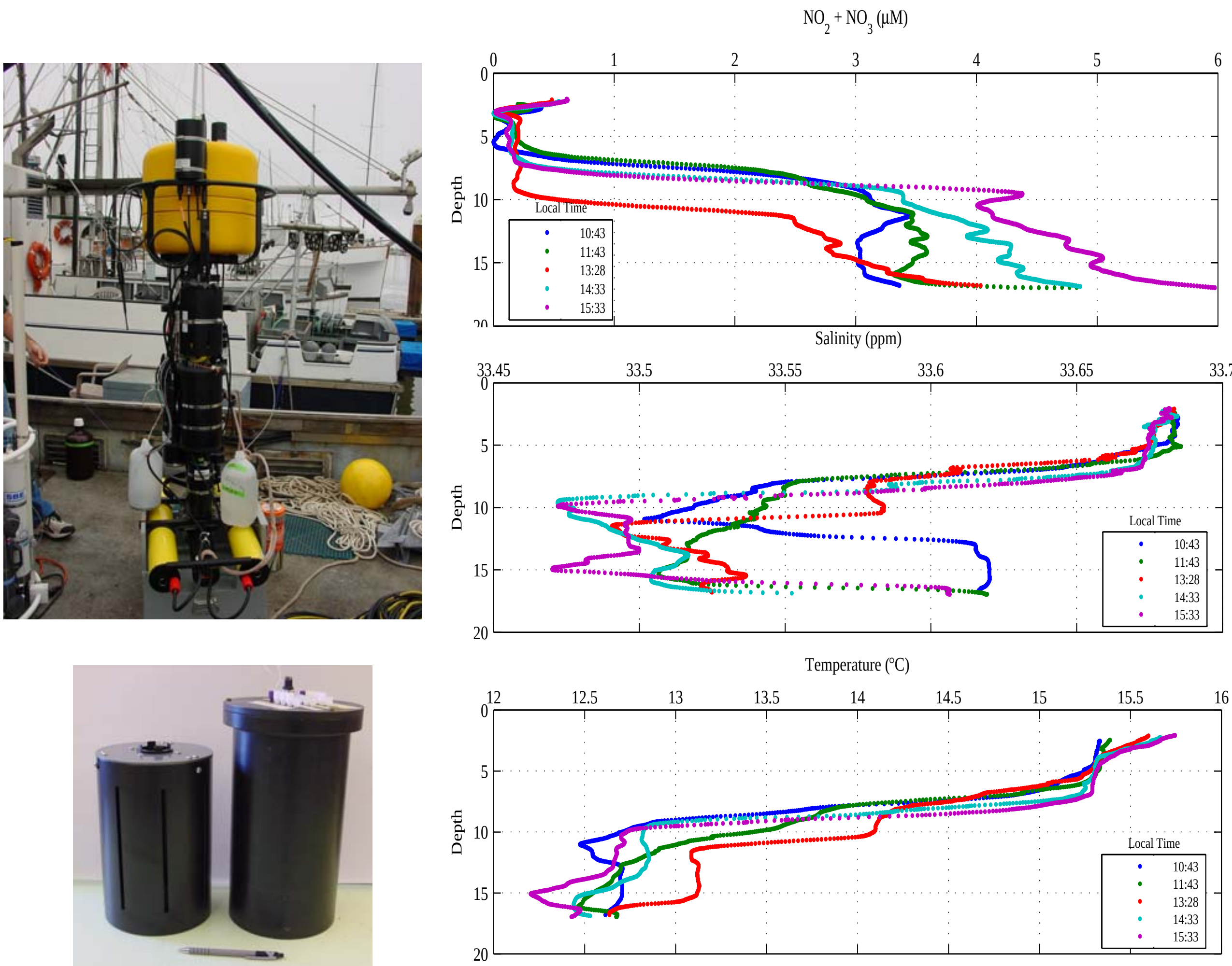

Figure 1. The IOPC profiler with the APNA II nutrient analyzer payload ready for deployment in Monterey Bay from the R/V Shana Rae and examples of hourly profiles for nitrate (top), salinity (middle), and temperature (lower) that were obtained autonomously with the system in Monterey Bay.

[The URI IOPC profiler is an autonomous, battery operated moored-profiler that may be deployed in the coastal ocean for weeks at a time. It contains a full suite of instruments and sensors for monitoring the physical, optical, biological and chemical properties of the water. The profiler can be programmed to make repeated profiles, from the bottom to the surface, on a pre-set time schedule, to send the multi-parametric results by radio telemetry to a shore- or ship-based receiver station, and then return to the bottom to wait for the time to start the next profile.]

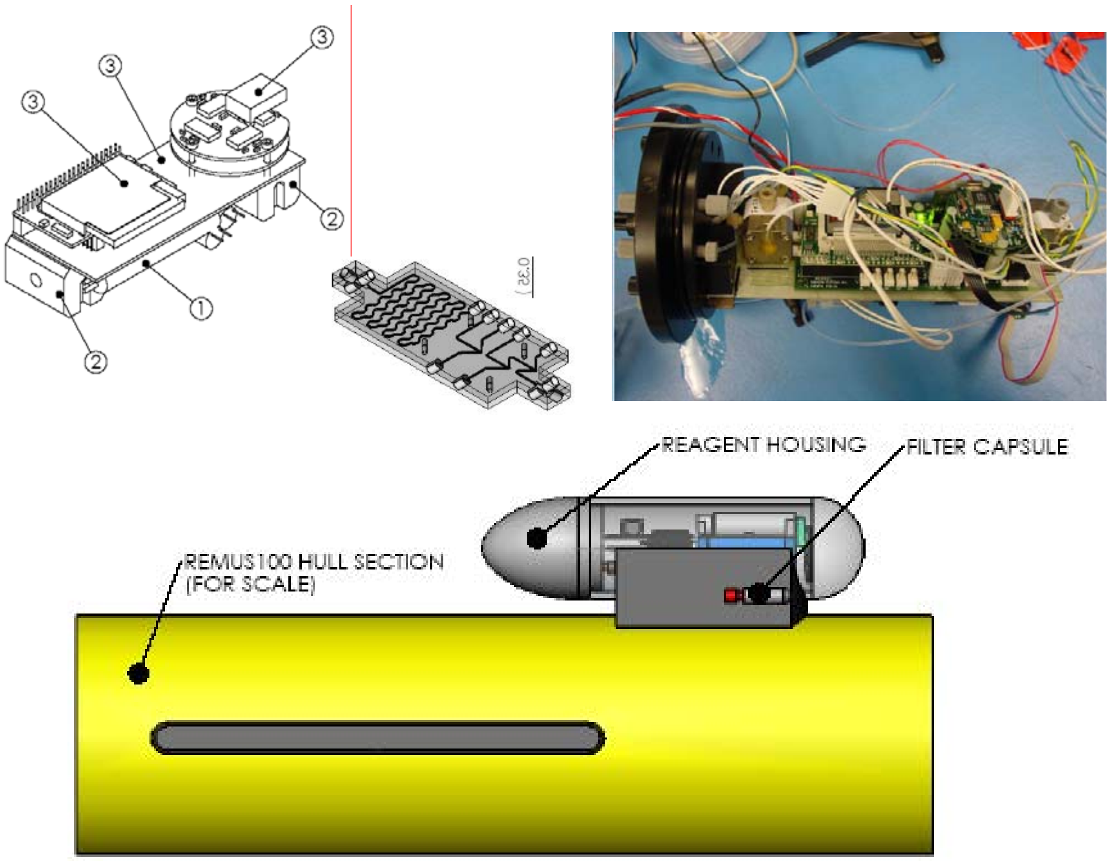

Figure 2. SubChem Systems's compact design for ChemFIN^{TM} the next generation chemical sensing payload for AUVs, Gliders and Profilers. The ChemFIN compact microfluidics(1), optical detection(2) and electronics(3) systems (left) and housing (right) externally mounted onto a REMUS vehicle hull section.

[The ChemFIN^{TM} is designed as an independent compact payload containing a micro-fluidic chemical analyzer that minimizes the power and space demands on the AUV platform.]

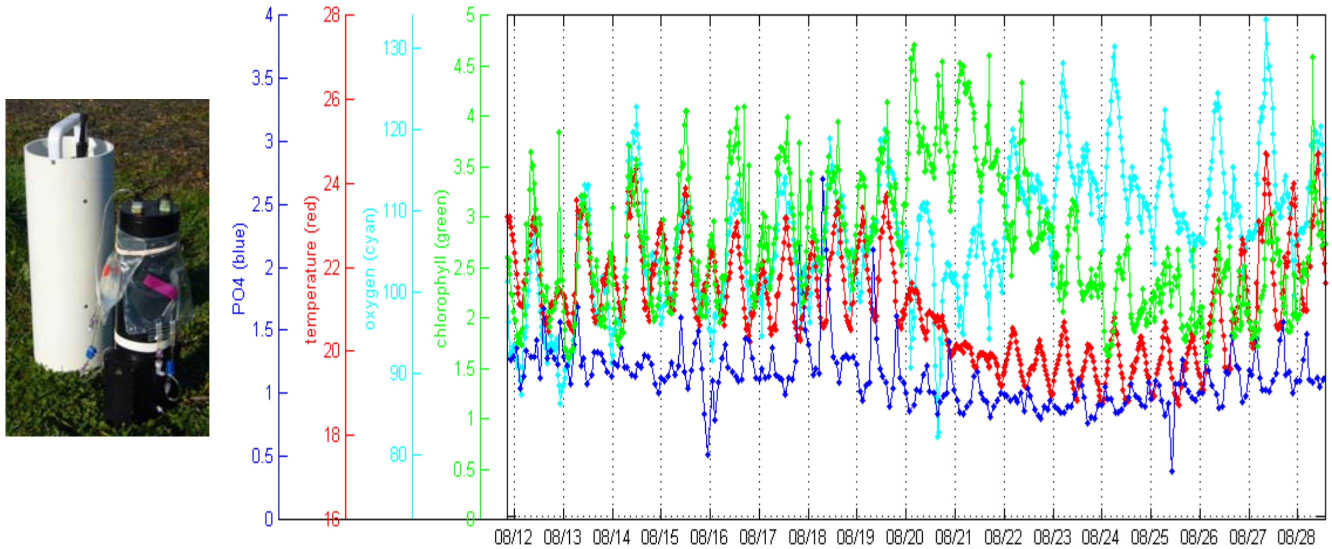

Figure 3. Photograph of WET Labs in situ beta prototype CYCLE-Phosphate analyzer removed from its protective housing (right, black unit with reagent bags), and the sensor installed within the protective deployment housing (left, white cylindrical body).
Also shown is a section of a six week time series of phosphate data (blue; μM) collected using the CYCLE-Phosphate prototype instrument in a West Coast estuary, Yaquina Bay, OR. Chlorophyll concentration (green; μg/l), temperature (red; °C), oxygen concentration (cyan; mg/l) data obtained with a WET Labs WQM are also shown.