

## **Autonomous Profilers for Carbon System and Biological Observations**

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### **LONG-TERM GOALS**

Our long-term goal is to understand the biogeochemical dynamics of the upper kilometers of the water column. Such an understanding is fundamental to the prediction of the processes partitioning carbon between atmosphere and ocean and to the redistribution of carbon and associated elements within the water column. Key to predictability is understanding day-to-day to seasonal variability of processes governing carbon species (dissolved and particulate, inorganic and organic) in the water column.

### **OBJECTIVES**

Our objective is to demonstrate the concept of low-cost autonomous profiling vehicles, outfitted with a suite of low-power optical, physical and chemical sensors. When widely deployed, these will permit high frequency four-dimensional observations of the variability of ocean biological processes, carbon biomass, upper ocean physics, and parameters of the carbon system in the upper 1000-2000 m. It is envisioned that once proven, such vehicles can be widely deployed to explore carbon variability on global scales. An immediate objective is to demonstrate that we can explore carbon biomass variability in the water column on daily to seasonal time-scales in remote and extreme environments.

# Report Documentation Page

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## APPROACH

*Platform.* The Sounding Oceanographic Lagrangian Observer (SOLO; Davis et al., 2001), a low-cost, long-lived autonomous profiling float is used to profile sensors vertically through the upper kilometer. SOLO is well-proven platform for physical measurements. We are augmenting this well-proven ocean physics platform with new optical sensors for biogeochemistry that will permit the rapid and precise determination of two important products of photosynthesis, particulate organic carbon (POC) and particulate inorganic carbon (PIC), along with physical data (T, S and derived density stratification) relevant to understanding the variability of these products. In order to achieve this aim, and to accommodate the bandwidth required by the additional sensors, SOLO has been modified with ORB-COMM transceivers for bi-directional telemetry of data at much higher data rates than the previously used System Argos.

Implementation of the faster telemetry permits transmission of data from the expanded sensor suite while significantly reducing the time (and hence susceptibility to biofouling) of the float in the surface layer. SIO has lead the modification of SOLO and preparation of floats for sea. Testing of the integrated float/sensor package is a joint effort of LBNL and SIO.

*POC sensor.* Bishop (1999) and Bishop et al. (1999) demonstrated that beam attenuation coefficient at 660 nm is strongly correlated with particulate organic carbon (POC) in open ocean waters. WETLabs has been responsible for providing a stable and precise transmissometer (beam attenuation stable to better than 0.001 m<sup>-1</sup>) for accurate long-term high-frequency measurement of POC in the upper kilometer.

*PIC sensor.* Particulate inorganic carbon occurs mostly as the mineral calcite. Calcite particles dominate all other minerals in most oceanic regimes. LBNL has investigated optical properties (e.g. refractive index, birefringence...) specific to calcite in the laboratory and has worked with WETLabs to develop and implement a transmission type sensor to quantify calcite suspensions.

## WORK COMPLETED

*POC sensor.* LBNL (in cooperation with WETLabs, Inc.) completed work on the design and implementation of sensors for particulate organic carbon (POC) on SOLO. The new sensors are stable to approximately 0.001 m<sup>-1</sup>. Our testing program at sea did show that improved absolute calibration procedures were required in order to achieve this stated accuracy. WETLabs, Inc. is addressing this issue.

*PIC sensor development and proof of concept.* We have proven the concept of an optical particulate inorganic carbon (PIC) sensor and demonstrated methodology which shows a linear response from <0.1 μM to >30 μM PIC levels and has little interference from other non-birefringent particles (Guay and Bishop, in-press). Abstract for this paper follows in the results section. The concept was evaluated at sea in August 2001 with the aim of validating the method with 'real world' samples.

LBNL and WETLabs have cooperated on the development of a profiling PIC sensor. Three prototypes have been tested at sea to date. The task has been daunting since birefringence signals are smaller than 0.1% of the power of the light incident to the sample cell.

*At Sea.* LBNL participated in 4 research cruises during the last year under this project (Bishop, chief scientist on 3). Two (Nov. 2000 and Feb. 2001) were 2 day test cruises aboard R/V Sproul out of San Diego to local waters. The goals to evaluate optics performance and to test SOLO programming were fully met. This led to our April 2001 participation on a transit leg of the US Coast Guard ice breaker, Polar Star (Dutch Harbour, AK to Victoria, BC, Canada) during which two SOLO's were deployed near 50N 145W (station PAPA). The aim was to evaluate POC sensors on SOLO in a water column

that had been optically well characterized (Bishop et al. 1999). In August, LBNL lead a 2 week cruise aboard R/V New Horizon to obtain size fractionated particulate matter samples using the Multiple Unit Large Volume in-situ Filtration System (MULVFS) and compare results of sample analysis with optical signals from simultaneously deployed, transmissometer, scattering, and fluorescence sensors. MULVFS filters 10's of thousands of liters through a series of filters at 12 depths from surface waters to 1000m and was the basis for the calibration of the POC sensor (Bishop et al., 1999).

Our April 2001 deployment of two SOLO's has been a great success. The floats were modified by SIO with fast bidirectional ORBCOMM telemetry and data handling systems for extended optical sensors; at present, SOLO's T and S sensors have been augmented with optical sensors for transmission (particulate organic carbon, POC), and light scattering. Two SOLO's deployed in the subarctic north Pacific ocean near 45N 145W in early April 2001 have returned data streams over 5 months (they remain in operation having completed 200+ profiles each with little interruption of observations during stormy weather (the SIO report documents only 0.02% data loss and 6% loss of position information). A major finding has been that biofouling of the untreated transmissometer sensors is small (e.g. <1% over 80 profiles; ~2% at 260 profiles) and has been easily quantified and thus managed. This is a consequence of the varied profiling and fast ORBCOMM telemetry.

The two week August 2001 R/V New Horizon cruise occupied 19 stations across the California Current from biologically productive coastal waters to oligotrophic offshore waters with the aim of sampling a variety of bio-optical environments with a suite CTD mounted optical sensors, including transmissometer (POC sensor), scattering, fluorometer, and a 3rd generation prototype PIC sensor. Major stations were located near Pt Conception (2), Monterey Bay, 35N 130W and at 2 points intermediate between the three locations. At major stations MULVFS casts were completed along with pairs of CTD/rosette casts. Simultaneous optical and particulate matter sampling will allow assessment and calibration of all sensors and a further test of the calibration of the POC sensor (Bishop et al., 1999). A third SOLO was deployed for 10 days in biologically productive waters near Pt. Conception. This SOLO will be redeployed at PAPA next year.

Chris Guay and Todd Wood have contributed substantially to all phases of this project at LBNL.

## RESULTS

PIC sensor development efforts are described in Guay and Bishop (2001; in press - abstract below) and have been presented at the Ocean Optics XV meeting in Monaco and at AGU meetings; a patent disclosure has been filed.

Abstract. The extreme birefringence of calcium carbonate ( $\text{CaCO}_3$ ) relative to other major components of marine particulate matter provides a basis for making optical in situ measurements of particulate inorganic carbon (PIC) in seawater. This concept was tested with a benchtop spectrophotometer equipped with a 1- and 10-cm path length sample cell and modified with linear polarizers to measure the birefringence of suspended particles. Sample suspensions containing 3 to 100%  $\text{CaCO}_3$  (by weight) were prepared from calcareous marine sediment material and varying amounts of non-birefringent diatomaceous earth. The samples ranged in total suspended material from 0.003 to 249  $\text{mg l}^{-1}$  and PIC from 0.03 to 1820  $\mu\text{mol CaCO}_3 \text{ l}^{-1}$ . A positive relationship was observed between birefringence and PIC, with response falling off as the total particle concentration and the relative abundance of non- $\text{CaCO}_3$  particles in the sample increased. Sensitivity increased linearly with optical path length, and absolute detection limits of 0.2 to 0.4 and 0.04 to 0.08  $\mu\text{mol CaCO}_3 \text{ l}^{-1}$ , respectively, were determined for path lengths of 1- and 10-cm based on the intrinsic signal noise of the modified spectrophotometer. Conventional (i.e., non-polarized) transmittance measurements were used to correct the birefringence signal for the sensitivity loss due to interference from scattering and absorption. Without further modi-

fication, this spectrophotometer-based method can be used (with a 10-cm cell) to quantify PIC in most surface ocean waters including those influenced by coccolithophore blooms. The spectrophotometer results determine performance requirements and design parameters for an in situ instrument capable of operating over the oceanic range of PIC.

## **IMPACT/APPLICATIONS**

The sensors and methodology employed in this project can easily migrate to other autonomous platforms; furthermore, the work of this partnership will lay the foundation for expanded sensor suites and their integration onto recoverable autonomous self-navigating platforms designed to quantify both the reactants and products of photosynthesis, and the rates of carbon-system processes.

## **TRANSITIONS**

WETLabs plans to market the stabilized POC sensor as a commercial product in the fall of 2001.

## **RELATED PROJECTS**

Russ Davis and Jeff Sherman (SIO) and Casey Moore (WETLabs) are supported separately by ONR under this National Ocean Partnership Program project.

Greg Mitchell (SIO) and Jeff Sherman are supported through the ocean optics program to instrument SOLO with radiance sensors. This instrument recently successfully completed a 76-cycle time series in the Japan Sea with good results. It will be desirable to eventually integrate these sensors with the POC and PIC sensor suite to make more comprehensive observations of the upper ocean carbon system.

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Bishop, J.K.B., Guay, C.K., Sherman, J.T., Moore, C.C., and R.E. Davis (2001) Prospects for a "C-Argo": A new approach for exploring ocean carbon system variability. Extended Abstract 01-07, International Workshop on Autonomous Measurements of Biogeochemical Parameters in the Ocean, Honolulu, Hawaii. Sponsors: Japan Ministry of Education, Culture, Sports, Science and Technology and Japan: National Institute for Resources and Environment (NIRE). Feb 20-22 2001. 6 pp.

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## **PATENTS**

Patent Disclosure: JIB-1595: Bishop, J.K.B. and C.K. Guay. An in-situ optical sensor for measuring particulate inorganic carbon in seawater.