Methods for Reducing Biofouling of Moored Optical Sensors

DEREK V. MANOV, GRACE C. CHANG, AND TOMMY D. DICKEY

Ocean Physics Laboratory, University of California, Santa Barbara, Santa Barbara, California

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ABSTRACT

Biofouling is one of the primary limiting factors in terms of measurement accuracy and deployment longevity for oceanographic studies involving autonomous sampling. Copper can significantly reduce marine fouling for long-term optical sensor deployments in coastal and open-ocean environments. Copper can effectively replace previously used highly toxic chemical antifoulant methods. Copper-based antifouling systems can be employed with three types of optical sensors: 1) open, 2) enclosed or semienclosed, and 3) shuttered. Copper plates on open-faced backscattering sensors can enable deployment periods of longer than 60 days in coastal waters without biofouling. In addition, copper tubing on nine-wavelength absorption-attenuation meters (ac-9s) has extended measurement capabilities from about 10 days to greater than 60 days with no signs of biofouling in coastal waters. Implementation of copper shutters on optical sensors in open-ocean waters off Japan has resulted in extended deployment periods (410 days and possibly longer) for optical measurements whereas previous optical measurements in the open ocean were typically degraded within several weeks to at most a few months due to biofouling.

1. Introduction

a. Motivation

New observational approaches are needed for advancing fundamental understanding, monitoring, modeling, and management of the ocean environment. The ocean is tremendously complex, with its large range of scales of variability [over 10 orders of magnitude in space and time; see Dickey (1991)], and its interdisciplinary nature. Scientific data need to be sampled at relatively high frequencies and accuracies for long periods of time, with minimal drift from predeployment calibrations. Further, many of the in situ platforms need to be capable of unmanned or autonomous sampling and real-time or near-real-time data telemetry in order to provide oceanographers with nearly continuous observations regionally and ultimately globally (Dickey 2001a; Clark 2002). The infrastructures for such observations are developing rapidly and will include dedicated ocean observatories and observational systems that will capitalize on moorings, autonomous underwater vehicles (AUVs), gliders, drifters, profiling floats, fiber-optic and electromagnetic cabled platforms, and satellites to facilitate studies of high-frequency, episodic, seasonal, interannual, decadal, and climate-scale phenomena (e.g., Dickey 1991, 2001a; Glenn et al. 2000a,b; Koblinsky and Smith 2001; Clark 2002).

Many scientific advances have been driven by sampling from moorings and other autonomous platforms. These include discoveries of new interdisciplinary processes such as primary production variability associated with El Niño–Southern Oscillation (ENSO) and equatorial long waves (Foley et al. 1997; Chavez et al. 1999; Turk et al. 2001), sediment resuspension forced by internal solitary waves and storms (Bogucki et al. 1997; Dickey et al. 1998; Chang et al. 2001), cloud-induced and diel fluctuations in phytoplankton biomass (Stramska and Dickey 1992, 1998), phytoplankton blooms associated with incipient seasonal stratification (Dickey et al. 1994), frontal- and eddy-trapped inertial waves (Granata et al. 1995), and mesoscale variability (e.g., reviews by Dickey 2001a; Dickey and Chang 2001; Lewis 2002; Dickey and Falkowski 2002; Conte et al. 2003). Study regions have encompassed both open-ocean and coastal settings and have ranged from the equatorial Pacific to high-latitude areas off Iceland and in the Southern Ocean. Despite these major accomplishments, biofouling (marine growth) of sensors still limits data quality and effective deployment periods of optical instrumentation on autonomous sampling platforms.

b. Objectives

The present paper focuses on the biofouling problem and some potential solutions for commercially available and future optical instrumentation. We first introduce

Corresponding author address: Derek V. Manov, Ocean Physics Laboratory, University of California, Santa Barbara, 6487 Calle Real, Suite A, Goleta, CA 93117.
E-mail: derek.manov@opl.ucsb.edu

some of the more commonly used optical instruments and then describe previous work directed toward minimizing biofouling effects. Next, results derived from field testing of chemical- and copper-based antifoulant methods for optical systems are presented. Finally, we summarize the implications of our findings.

2. Optical sensors

There are basically three types of sampling systems that are widely used for moored optical oceanographic measurements: open, closed or semienclosed, and shuttered. The sensing elements of ''open'' instruments are freely exposed to the surrounding water environment. Water is pumped through ''closed'' or ''semienclosed'' instruments, whose sensor elements are enclosed by flow tubes. The third system type consists of ''shuttered'' instruments whose sensing elements are covered between measurement cycles.

Light-sensing devices need unobstructed light paths; the slightest roughness on optical windows, either light source or receiver, can cause erroneous measurements (McLean et al. 1997). Through the mid-1980s, most optical instruments were designed for shipboard profiling systems. Thus, scientists were able to clean optical surfaces after each cast and minimize deleterious buildup of biofouling materials on optical windows. However, the need for improved temporal and spatial resolution to resolve a broader spectrum of oceanic processes and for measurements during adverse weather conditions led oceanographers to refit optical systems for deployments from moorings and drifters (reviews by Dickey 1991, 2001b), and more recently from autonomous underwater vehicles (e.g., Griffiths et al. 1999, 2001; Yu et al. 2002), profiling floats (Bishop et al. 2002), and gliders (Perry 2002). Many of these platforms are not recovered and redeployed, and thus not cleaned, for months to a year or more. Therefore, degradation of data through the natural process of biofouling, or more explicitly the colonization of organisms on sensors and optical windows, is a major concern. Marine growth can be caused by microorganisms such as bacteria that create thin biofilms to larger organisms such as barnacles. The severity of the problem varies spatially and temporally.

Until a few years ago, in situ measurements of inherent optical properties [IOPs; which depend only on the seawater medium and are independent of the ambient light field; Kirk (1994); Mobley (1994)] were generally limited to the beam attenuation coefficient (beam c) at a single wavelength. The beam transmissometer is an open sensor that measures the attenuation of a collimated light beam passing through a fixed pathlength (Bartz et al. 1978). More recently, similar instruments called absorption-attenuation meters (ac meters) have been developed to simultaneously measure the spectral beam attenuation coefficient, $c(\lambda)$, and the spectral absorption coefficient, $a(\lambda)$, at several wavelengths [units of m^{-1}; Zaneveld et al. (1990); Moore et al. (1992)]. The spectral absorption coefficient is determined using a measurement of light passage through a shiny tube, opposed to a flat black tube for beam attenuation. The spectral scattering coefficient, $b(\lambda)$, is obtained by the difference, $b(\lambda) = c(\lambda) - a(\lambda)$. Both absorption and attenuation measurements of the ac meter are made using closed, pumped systems.

One of the more commonly used instruments for measuring apparent optical properties [AOPs; which depend on both the IOPs and the geometric structure of the subsurface ambient light field; Kirk (1994); Mobley (1994)] is a relatively simple broadband (400–700 nm) scalar irradiance (E_0 in units of mol photons m^{-2} s^{-1} or einsteins m^{-2} s^{-1}), or photosynthetically available radiation (PAR) sensor (same units as E_0). A spherical light collector made of diffusing plastic or opal glass receives light from approximately 4π steradians and a photodetector records the output voltage. Analogous AOP sensors use flat-plate cosine or hemispherical collectors. Spectroradiometers are radiance or irradiance meters that use a variable monochromator (color filters or gratings for spectral light operation) placed between a light collector and a photodetector (Smith et al. 1984) and are calibrated using well-characterized, standard light sources. Spectroradiometers can be open or shuttered systems.

In situ fluorometers can be open, closed, or shuttered systems that are used to infer chlorophyll *a*; they emit blue light and measure the fluoresced red light (Bartz et al. 1988). Fluorometers can be calibrated in the laboratory with phytoplankton culture dilution procedures or in the field with concurrently collected ship bottle data. Biofouling of all of the instruments described here has been a serious concern since the inception of autonomous deployments.

3. Antibiofouling approaches

A wide variety of antifoulant approaches have been utilized in an attempt to solve the ongoing problem of biofouling of optical sensors (e.g., Spinrad 1987; Strahle et al. 1994; Davis et al. 1997; McLean et al. 1997). Various forms of tributyl tin- (TBT-) based products have traditionally been used for long-term oceanographic instrumentation antifouling techniques with mixed results (described below). TBT-based antifoulant wax (Aquatek) and Clear-Choice aerosol spray, a polymer-based tributyltin metharcrylate (ITW Philadelphia Resins), have been applied to areas surrounding, but not on, the optical windows of optical instruments. McLean et al. (1997) performed several comprehensive laboratory and field tests of several forms of TBT-based, antifungal agents, and low-friction silicon-based compounds on coated glass and acrylic surfaces as well as uncoated surfaces. They found that although these products were somewhat effective against algal growth, generally it was best not to apply any coating to optical surfaces since coatings introduce surface roughness that is deleterious to measurements of collimated light. Also, coatings may provide better environments for microfauna than smooth surfaces (Spinrad 1987; McLean et al. 1997). Additional problems include perturbed spectral transmission (window clouding) and flaking off of coatings caused by ablation. This results in nonsteady light transmission and, thus, erroneous optical measurements. TBT compounds also have a direct negative environmental impact, as TBT is perhaps the most toxic chemical that has ever been deliberately placed in natural waters. The toxic effects of TBT on mammals and the bioaccumulation of TBT in fish, oysters, and crustaceans have severely limited its long-term usefulness in marine applications. Generally, biocides using heavy metals will likely be prohibited in the future (Evans et al. 1995).

Slowly dissolving chlorine (trichlorisocyanuric acid) and bromine tablets have been utilized in closed optical systems (e.g., Davis et al. 1997). These chemicals act as a toxic agent for microorganisms, preventing growth in the optical tubes. Alconox, a powdered cleaning compound (homogeneous blend of sodium linear alkylaryl sulfonate, alcohol sulfate, phosphates, and carbonates anionic in nature), has also been used in this manner to prohibit algal growth on optical windows.

We have tried several other antifoulant methods for general nonoptical purposes with some limited success. A mixture of cayenne pepper with silicone-based grease applied to the heads of an acoustic Doppler current profiler (ADCP) has shown to help inhibit biological growth on a bottom-mounted tripod. Upon recovery of the ADCP, it was noted that bryozoans had grown on all exposed areas of the ADCP except for the acoustic heads. This method is not recommended for optical sensors as cayenne pepper is red in color and can directly affect the measured optical signals. The grease and pepper coating also forms an undesirable rough surface on optical windows (see above description of the disadvantages of coatings). Zinc anodes on stainless steel instrument cages inhibit growth while surrounding areas have significant marine fouling and accordingly may be used in certain antifouling applications.

Historically, copper was used extensively to protect wooden-hulled vessels from shipworms (mollusks, genus *Teredo*) and wood-boring crustaceans (genus *Limnoria*) in the age of sailing ships. In 1803, patriot Paul Revere succeeded in rolling enough American copper plates to sheath the hull of the newly built USS *Constitution* to protect her from marine fouling. Copper-based paints have also been used for many years, especially as an antifoulant for boat hulls (Strahle et al. 1994). There are two basic types of antibiofouling paints. The first type works through the slow dissolution of water-soluble portions of the paint film releasing (leaching) cuprous oxide into the surrounding water. A buildup of paint, like a tiny sponge, is left on the surface. The second type, ablative antifouling paints, functions by controlled erosion, or ablation, of the paint film resulting in a continuously renewed surface with fresh toxicant. Brasses, which are essentially alloys of copper and zinc (i.e., naval bronzes), also have a long history of use in nautical applications, primarily as corrosion-resistant elements for structural and decorative purposes. Chavez et al. (2000) have summarized the attributes of copper-based antifoulant systems for ocean instrumentation. Copper interferes with enzymes on cell membranes and prevents cell division. As copper corrodes in seawater, oxidized molecules release into the water rather than remaining on the metal surface. Importantly, while copper is toxic at high concentrations for microbial (e.g., bacteria) and other larger organisms, it is not toxic to humans as opposed to the aforementioned TBTs.

An ultraviolet irradiation technique has been recently developed by Wheaton, Inc., for an in situ oceanographic fluorometer and shows promise as an effective method for inhibiting marine growth on sensors. One of the most interesting future alternatives to TBT and copper-based antibiofouling approaches is the use of enzymes and bacterium as active antibiofouling components in coating systems. Their effectiveness for biooptical sensors is yet to be determined.

Testing of several different antifoulant methods has been conducted during mooring deployments in the Sargasso Sea, equatorial Pacific, Arabian Sea, Mediterranean Sea, Middle Atlantic Bight, Gulf of California; in deep sea waters off Japan; Ocean Weather Station Papa; and in Monterey Bay, California. Several of these experiments and results are summarized below. Here, we quantify the extent of biofouling for all data (except those collected by radiometers) by the minimum number of sections required to linearly best fit the time series from beginning to end. Prior to analysis, the time series are filtered to remove high-frequency variability. We define level 0 biofouling as a nonbiofouled time series. Level 1 biofouling is defined as a time series needing one linear section above the baseline (baseline is defined as the time series itself), level 2 requires a minimum of two, etc. Level n biofouling defines data that require infinite linear sections to fit the time series. Note: we compare all time series with complementary data to test for increases in values caused by environmental variability (e.g., phytoplankton blooms or sediment resuspension) or instrument drift.

a. Experiments using open systems

Fluorometers and beam transmissometers (both open systems) were deployed on an array of moorings off the east coast of the United States (Middle Atlantic Bight) in 1988 in order to resolve cross-shelf exchange of phytoplankton and by inference carbon as part of the Shelf Edge Exchange Processes program (SEEP II; Wirick 1994). The fluorometers (designed by Whitledge and Wirick 1986) were equipped with an automatic scrubbing device that cleaned the optical window of each fluorometer once per day. Wirick (1994) reported that the fluorometers were relatively immune to biofouling for the 4-month experiment (early February–early June 1988). To mitigate biofouling of moored transmissometers, Wirick (1994) utilized plastic support rings painted with Aquatek for the optical windows. Aquatek was enriched with OMP-8, a TBT-based clear optical coating. The optical windows of the beam transmissometers were also cleaned with a dilute solution of Alconox cleanser and then rinsed with distilled water before each deployment. Wirick (1994) suggested that this methodology may have inhibited biofouling of the transmissometers, but stated that thin biological films coated the optical windows by the end of the deployment. Butman and Folger (1979) had earlier employed bronze rings impregnated with tributyl tin oxide to reduce biofouling effects on moored transmissometers. Strahle et al. (1994) used a similar methodology with porous plastic antifouling rings with some success. Results showed increased lengths of useable time series data.

Our group deployed transmissometers and fluorometers equipped with TBT brackets in the Arabian Sea with some limited benefit. Beam c and fluorescence data showed level 1–3 biofouling effects after 3–4 months as opposed to 3 weeks for instruments without TBT brackets, which exhibited level n biofouling. We also applied a thin coating of OMP-8 on the optical lenses of several transmissometers for experiments in the Sargasso Sea and the North Atlantic Ocean south of Iceland. This method had some detrimental effects. Following the recovery of the transmissometers, we found flaking (ablation) and loss of the OMP-8 coating. As mentioned earlier, others have noted a similar effect: OMP-8 can become slightly opaque, thus adversely affecting the optical measurements in long-term applications (Spinrad 1987; McLean et al. 1997). We have also coated an entire transmissometer, except for the windows, with copper-based antifouling paint. The disadvantage of this method for optical systems was in the difficulty of removing the paint for subsequent redeployments and calibrations and its relative ineffectiveness in keeping the windows clear of fouling.

Passive (or static) copper antifoulant devices have also been deployed with a high degree of success in coastal applications. A machined cupronickel plate was created by HOBI Labs, Inc., for use on their optical backscatter sensor, Hydroscat-6 (Fig. 1). A thin (0.0127 cm) Teflon film and nylon screws were utilized to mount the plate to the sensor head, effectively isolating the plate from the aluminum. The copper plate must be electrically isolated from the anodized aluminum pressure case to prevent electrolysis from occurring around the sensor ports if these dissimilar metals are in direct physical contact. During a 60-day deployment in shallow coastal waters, no biological growth was discernible on the sensor ports (Fig. 1; level 0 biofouling).

b. Experiments using closed systems

Closed systems have an advantage in mitigating biofouling, as the sample volume is not exposed to the light field, thus inhibiting photosynthesis within the instruments. Spectral ac meters are closed systems, but are still subject to biofouling of the source and receiver windows as well as the inside surfaces of the optical tubes. The shiny tube for the absorption measurements (absorption or a tube) is especially vulnerable. Davis et al. (1997) developed a chemical method to reduce biofouling effects for two three-wavelength (650, 676, and 710 nm) a meters (deployed at 9- and 40-m depths) and one six-wavelength (440, 540, 600, 650, 676, and 694 nm) ac meter (deployed at 11-m depth). All instruments were deployed in the Bering Sea from March to September 1993. A bromine solution was introduced into the a tubes of the instruments through an inner-perforated canister filled with solid bromine tablets placed within an outer-vented canister. The sizes of the holes in the inner canister serve to control the rate of bromine dissolution. The a tube was flushed (using a pump) sufficiently with seawater prior to measurements to avoid contamination by the bromine solution. Davis et al. (1997) reported that the 40-m instrument was essentially free of biofouling effects for the entire 8 months of deployment and that the 11-m instrument was uncontaminated for about 3.5 months. Typically, biofouling is less problematic at depth as the light field decays exponentially with depth and primary production is likewise reduced. The primary measure of success for these antibiofouling experiments was the return of measured values to values close in magnitude to the initial measurements. Davis et al. (1997) suggest that the fouling that they observed for one of their instruments may have been due to corrosion by the bromine solution. Our group has similarly utilized a chlorine solution in nine-wavelength ac meters (ac-9s) deployed in the Sargasso Sea. Recovered optical data revealed that spectral absorption signals at the beginning of the deployment (first 20 days) were similar to those of the absorption signal of chlorine itself. After 20 days, the absorption and attenuation data were severely biofouled (level N).

We also conducted several antibiofouling tests with ac-9s during the first mooring deployment of the Coastal Mixing and Optics (CMO) experiment. The first CMO mooring was deployed in the Middle Atlantic Bight in 70-m water depth from 8 July through 26 September 1996 (Chang and Dickey 2001). Four ac-9s were deployed at different depths on the mooring, at 13, 37, 52, and 68 m. We utilized TBT porous plastic antifoulant rings in the Tygon tubing of an ac-9 at 13-m water depth. Slowly dissolving chlorine tablets (trichlorisocyanuric acid) were placed in a plastic canister and allowed to seep through the 37-m ac-9 during periods when no measurements were taken. Alconox was placed into a similar plastic canister on the 52-m ac-9 and allowed to slowly dissolve. No antifoulant was used for the ac-

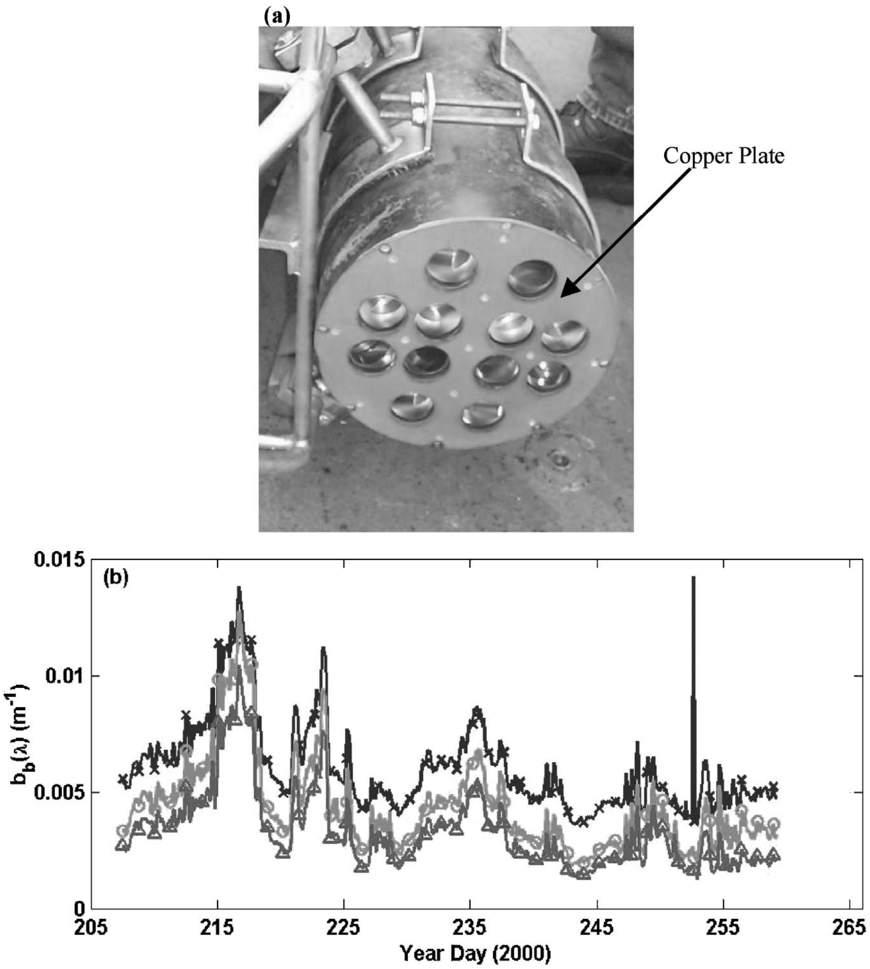

FIG. 1. (a) Photograph of the cupronickel endplate mounted on a HOBI Labs Hydroscat-6 backscattering instrument and (b) a 60-day, level 0 (nonbiofouled) time series of backscattering data at three wavelengths measured by the copper-plated Hydroscat-6 (xs, 442 nm; circles, 510 nm; triangles, 620 nm). The instrument was deployed at 5 m in 25-m water depth off of the coast of NJ during HyCODE.

9 at 68-m water depth. None of the antifoulant methods were shown to have been particularly effective in inhibiting growth on the optical sensors of the ac-9s. The 13-m ac-9 data were visibly biofouled after only 10 days following deployment (Fig. 2). Our biofouling quantification method shows that the 13-m ac-9 data exhibited level 8 biofouling. Chlorine precipitate tended to coat the optical windows of the 37-m ac-9 and degraded the optical measurements, resulting in level 5 biofouling. For the 52-m and ac-9, the Alconox powder in the plastic canister solidified immediately and did not seep into the pumped system as planned and, thus, was ineffective as an antifoulant. Low biomass at the 52- and 68-m depths resulted in level 2 and 1 biofouling, respectively.

Several problems exist with the various chemical solution antifoulant methods for ac meters. We found that it was difficult to effectively deliver steady and uniform concentrations of chlorine and other chemicals during the course of a deployment. In some cases, the solution was expended in too high concentrations too early (possibly leading to etching of the shiny surface of the a tube and the direct measurement of chlorine rather than seawater and its constituents), leaving no solution for later periods of the deployment. This was also the case for one of the instruments of Davis et al. (1997). In others, the delivery of antifoulant chemicals was too slow and likely ineffective, with unused chemical (bromine or chlorine tablets or Alconox powder remaining) at the end of the deployment. Dissolution and diffusion rates are dependent upon ambient flow conditions (e.g., from nearly laminar to highly turbulent), which naturally vary in space and time. Thus, the effectiveness and utility of the chemical delivery method of combating biofouling will likely always be unpredictable.

As an alternative to chemical methods, we have developed an antifoulant copper tubing flowthrough system for the ac-9 and HiSTAR (100-wavelength ac meter) as well as for closed system fluorometers (WET Labs,

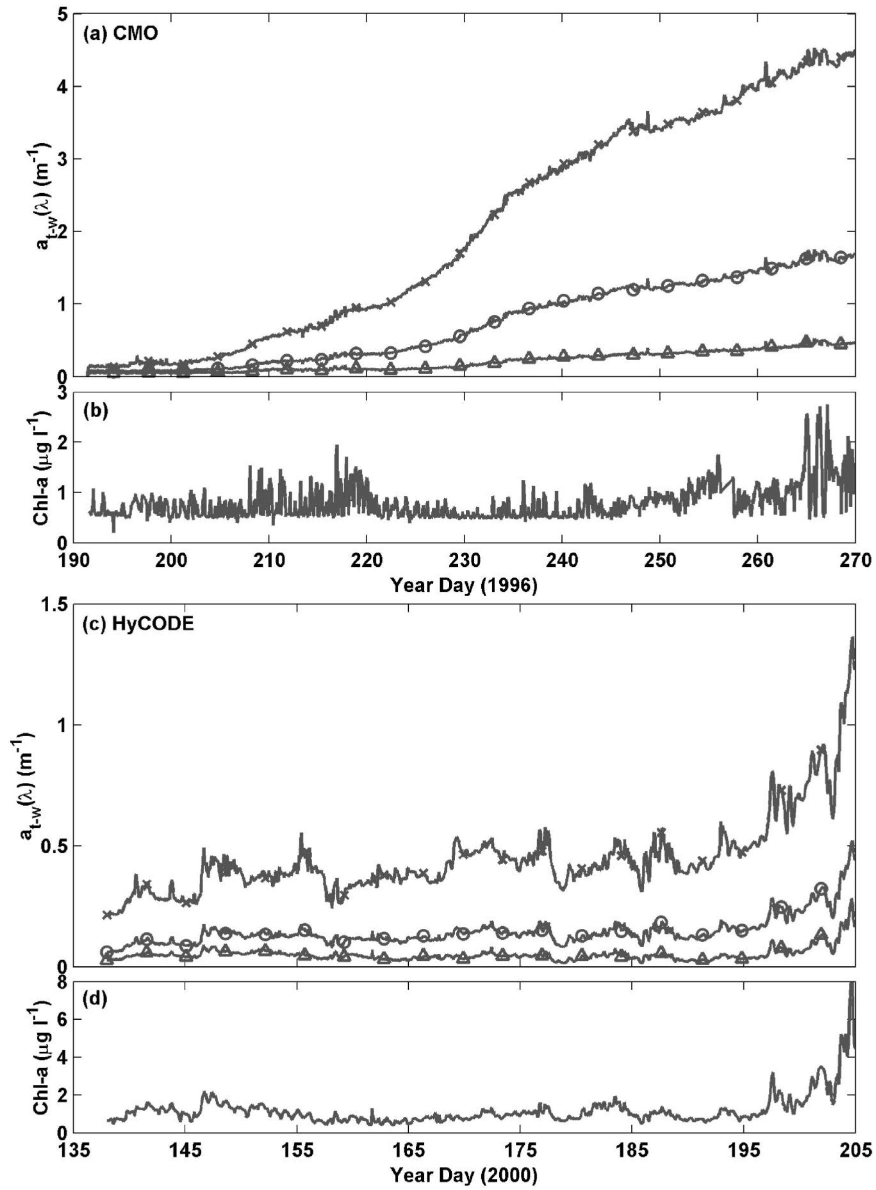

FIG. 2. Time series of hourly averaged (a) absorption coefficient at three wavelengths measured by the ac-9 (xs, 412 nm; circles, 510 nm; triangles, 676 nm), (b) chlorophyll-*a* concentration derived from a fluorometer; (a), (b) measured at 13 m (within the mixed layer) during the stratified period of summer during CMO (note the heavy biofouling in ac-9 data starting 10 days after deployment; level 8); (c) absorption coefficient at three wavelengths measured by the ac-9 (xs, 412 nm; circles, 510 nm; triangles, 676 nm), and (d) chlorophyll-*a* concentration derived from a fluorometer; (c), (d) measured at 5 m (within the mixed layer) during the HyCODE (no visible biofouling in ac-9 or chlorophyll-*a* data; level 0). The increases in absorption and chlorophyll-*a* concentration toward the end of the deployment were due to a phytoplankton bloom, also evidenced in bottle sample data (not shown). Chlorophyll-*a* concentrations illustrate the relative amount of biomass in the water column.

Inc., WETStars) and transmissometers (WET Labs, Inc., C-Stars). These copper tubing systems were tested on a mooring (instruments at 5-, 11-, and 20-m depths) during the Hyperspectral Coastal Ocean Dynamics Experiment (HyCODE) in productive inland waters off of New Jersey (Chang et al. 2002). One-half-inch- (1.26 cm) diameter copper tubing was utilized to connect the intakes of the ac-9 to a pump (Fig. 3). Between 1-h measurement cycles, copper from the tubing was allowed to leach into the water contained in the tubes of the instrumentation system. Prior to taking the absorption and attenuation measurements, the pump was turned

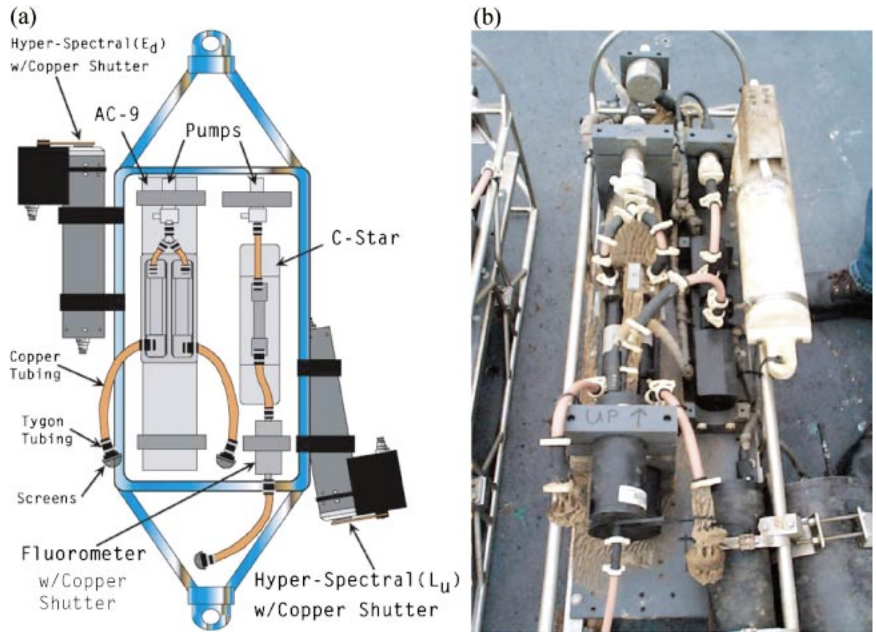

FIG. 3. (a) Schematic diagram of a biooptical system package illustrating the copper tubing used for the flowthrough optical instruments and copper shutters and (b) photograph of a biooptical system recovered after a 2-month deployment. Note the growth of macroalgae on the components of the instrument package while the copper tubing remained free of biofouling. Also note that (a) and (b) are not the same instrument package.

on for 10 s to clear the system of the leached copper and to pump uncontaminated water into the intake port for sampling. The pump was then left on during the 70-s measurement period. Stainless steel screen filters were used to remove large particles, for example, seaweed, macroorganisms, and large detritus, from the sensor elements (Fig. 3). Separate pumped water systems were utilized for the plumbing of the WETStars and C-Stars. One-quarter-inch- (0.13 cm) diameter copper tubing was utilized to connect the two instruments together and to a pump (Fig. 3). Isolation of the copper by Tygon tubing (black tubing is used to reduce ambient light levels) was made in order to avoid dissimilar metal corrosion effects (differing metals for the sensors pressure cases, mounting brackets, and stainless steel instrumentation cages).

Results from HyCODE indicate that biofouling is not present in the HyCODE ac-9 data, likely due to the addition of copper elements mounted on the instruments. Biofouling is apparent in CMO ac-9 data, collected during comparable environmental conditions, which did not use the copper tubing. Figure 2 shows an exponential increase in spectral absorption during CMO while chlorophyll-*a* concentrations remained relatively low. This is an indicator of biofouling in optical measurements (level 8). Comparable HyCODE data exhibited steady values until day 200 (level 0 biofouling), when a phytoplankton bloom was detected in chlorophyll-*a* concentration time series data, shipboard profiles, and whole water samples [Fig. 2; O. Schofield (2000, personal communication)]. Conditions for biofouling were actually greater during HyCODE as compared to CMO. For example, chlorophyll-*a* concentrations are slightly higher during HyCODE, indicating that primary productivity was greater. In addition, HyCODE data presented in Fig. 2 were from 5-m water depth, with more biological growth expected than at the 13-m depth of ac-9 deployment during CMO.

c. Experiments using shutter systems

A copper-shutter system for spectroradiometers was developed by Chavez et al. (2000). The system was designed to prevent biofouling on a spectroradiometer that measures downwelling irradiance at six wavelengths and upwelling radiance at seven wavelengths, as well as PAR. A motor drives the mechanism for shutters that open for data collection and close for window protection over the optical windows. The timing sequence is preprogrammed with samples being collected every 10 min during daylight hours. The shutter system was tested in the equatorial Pacific (20-m depth) in late 1997–early 1998 over a 5-month deployment. Shutters have the advantage of keeping the optical window in the dark and in very close proximity to a copper plate that is releasing toxic copper; both effects reduce the opportunity for the formation of biofilms that attract other fouling organisms. Data collected from the 20-m radiometer system with the copper-shutter system showed no apparent signs of degradation. However, nearby instruments (at 10- and 30-m depths) without

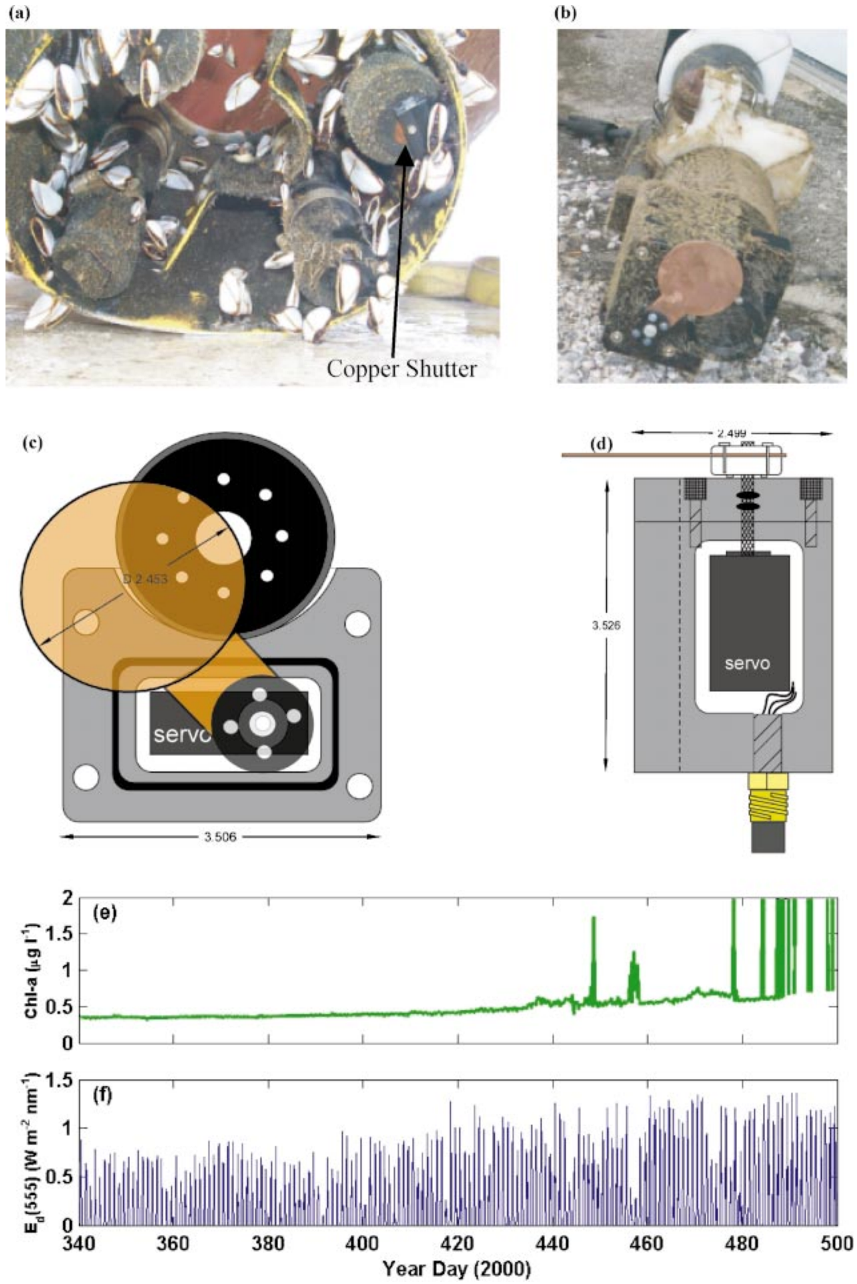

FIG. 4. Photographs of the (a) WET Labs, Inc., copper-shuttered ECO fluorometers and ECO-VSF sensors and (b) Ocean Physics Laboratory (OPL) designed copper-shuttered radiometer system, recovered after 5 months of deployment on the Bermuda Testbed Mooring (BTM). Note the heavy growth of organisms on all components of the instruments except for the copper. Cutaway schematic diagrams of the OPL-designed copper-shuttered radiometer system: (c) top view and (d) side view. Five-month time series of (e) chlorophyll fluorescence data derived from the 2-m copper-shuttered ECO fluorometer, and (f) 7-m downwelling irradiance data at 555 nm collected by a copper-shuttered radiometer data. Both instruments were deployed on BTM. The fluorescence data are slightly biofouled (level 1) until day 490, as seen in the steady increase in fluorescence values over the time series. After day 490, data are heavily biofouled (level *n*). As seen from past deployments, the fluorescence signal would increase exponentially starting ~10 days after deployment without the use of copper shutters.

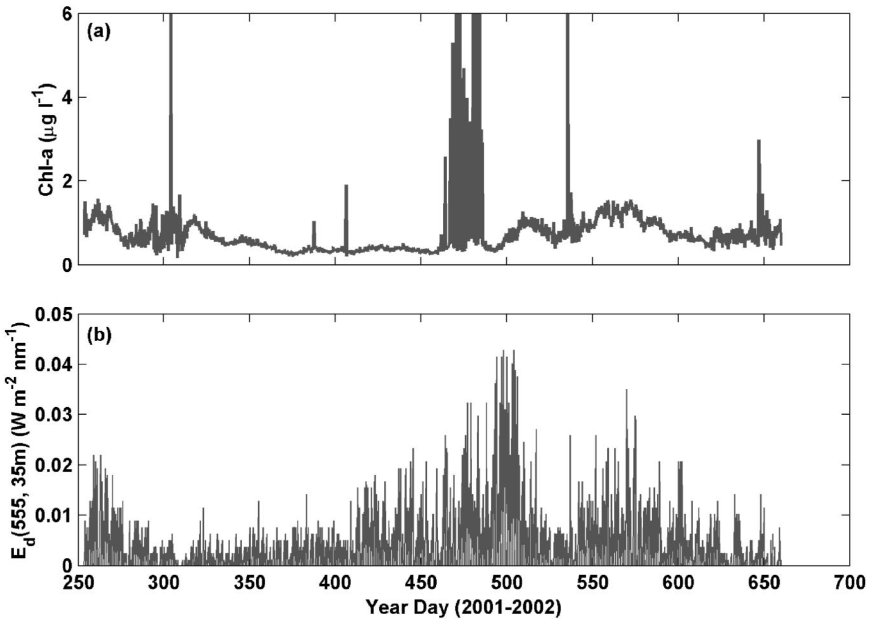

FIG. 5. A 410-day time series of level 0 (nonbiofouled) (a) 6-h-averaged chlorophyll-*a* concentration derived from a copper-shuttered ECO fluorometer and (b) downwelling irradiance at 555 nm measured with a copper-shuttered radiometer. Both instruments were deployed at 35 m in the Japan Sea from Sep 2001 to Oct 2002.

the copper shutters began to show biofouling effects (significantly reduced values) after less than 2 months.

Our group has designed noncontact servo-controlled copper-shuttered devices for three-wavelength radiometers (Fig. 4) based upon the concept developed by Chavez et al. (2000). This new battery-powered shuttered system uses a commercial high-torque servo with dual ball bearings and metal gears (Fig. 4). The servo is connected by a cable to a microcontroller, datalogger, and battery pack; all of these elements are enclosed within a Delrin pressure housing. A copper plate was attached to the servo arm through a waterproof dynamic O-ring seal. The copper shutter is kept closed over the spectral radiometer sensor's optical elements until a measurement is required. The servo is then powered up and an arm with a copper plate is swung out of the way of the sensor. Data are collected for 5 min and then the copper plate is swung back over the sensor to keep the optical elements protected from biofouling between measurement intervals. Power to the servo is then turned off and the system is put into a dormant state until the next measurement is made. A servo was used because of its direct positive control function, ease of interfacing, reliability, and low power requirement characteristics. A pulse width modulation interface is used with this servo design providing accurate, repeatable shutter control with simple electronic control elements. Some differences between the OPL and the Chavez et al. (2000) copper-shuttered system are 1) our system is battery operated and requires relatively low power; 2) it is self-contained and flexible, easily interfaced and integrated into a complete datalogging system; and 3) a variety of additional sensors may be fitted with this type of copper-shutter system.

WET Labs, Inc., has developed a new series of fluorometers and volume scattering function (VSF) sensors (Environmental Characterization Optics or ECO sensors; ECO fluorometers and ECO-VSF meters) with revolving copper antifouling shutters following the design described above (Fig. 4). Power is applied once per hour to each instrument through a preprogrammed data-collecting sequence. The copper shutter rotates 180° to uncover the sensor's optical windows, a measurement is made, and then the shutter continues around through 360° until the optical windows are once again covered. ECO fluorometers were deployed at 2-m depth on 5 December 1999 in the Sargasso Sea. Copper-shuttered spectral radiometer systems (described above) were deployed at depths of 7 and 20 m. All of these systems were successfully recovered on 26 May 2000 with nearly 5 months of data. The fluorescence data are slightly biofouled (level 1 biofouling) until day 490, as seen in the steady increase in fluorescence values over the time series (Fig. 4). After day 490, data are heavily biofouled (level *n*). In the past, similar measurements have been made without copper antifouling devices and resulted in visibly biofouled data after just 20 days of deployment.

Figure 5 shows the most recent and successful long-term optical data obtained by using copper-based antifoulant methods. Copper shutters were employed with two sets of spectroradiometers and ECO fluorometers for deployment in September 2001 at 35 m in the North Pacific off Japan (K1: 52°N, 165°E; K2: 47°N, 160°E). The instruments were recovered in October 2002, more than a year later. Little to no biofouling was found on the instruments upon recovery, as supported by the data shown in Fig. 5. Fluorometer data remained relatively stable throughout the 410-day time series; beginning and end values were similar, at ~1 μg L^{-1}, suggestive of level 0 biofouling (Fig. 5a). The decreases in irradiance and radiance over the 410-day time series (days 300–460 and 600–650) were due to seasonal cloud cover in the region and not from biofouling, as evidenced in the seasonal cycle of irradiance (Fig. 5b), that is, low irradiance values in winter months.

4. Summary

The antifoulant methods described here are intended for both open and coastal ocean deployments and must be able to facilitate high quality data return. Many open-ocean moorings can only be revisited annually; therefore, our targeted longevity for open-ocean optical measurements is 1 yr. The coastal ocean presents more severe problems of biofouling, because of high biological productivity and coastal pollution in the form of wastewaters, storm runoff, and agricultural fertilizers. Fortunately, access is generally quite easy for coastal moorings. Thus, mooring turnaround intervals of a few months are feasible for most coastal situations. Biofouling remains the primary limiting factor in terms of measurement accuracies and deployment longevity.

Copper has been shown to significantly reduce marine fouling for long-term biooptical sensor deployments in coastal and open-ocean environments and can effectively replace highly toxic TBT and other less benign antifoulants. The three types of copper-based antifouling systems presented here have shown marked improvements in obtaining long-term datasets for acquisition of optical measurements. Copper plates are useful for open systems such as the Hydroscat-6. The passive copper-based tubing is particularly effective for closed systems such as transmissometers and absorption-attenuation sensors. Copper tubing, used with ac-9s, deployed in coastal waters, has extended measurement capabilities from about 10 to greater than 60 days and copper plates on the Hydroscat-6 have resulted in deployment periods of longer than 60 days. Shuttered systems are effective for optical measurements (e.g., chlorophyll fluorescence and spectral radiation) where sensors need clear or open paths to the seawater. Implementation of copper shutters on optical sensor packages has resulted in extended deployment periods (410 days and possibly longer) for optical measurements in the open ocean whereas previous optical measurements were degraded due to biofouling within several weeks.

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