JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 102, NO. C3, PAGES 5851-5855, MARCH 15, 1997

Reducing the effects of fouling on chlorophyll estimates derived from long-term deployments of optical instruments

R.F. Davis,[1,2] C.C. Moore,[3] J.R.V. Zaneveld,[1] and J.M. Napp[4]

Abstract. Two methods to alleviate the problem of fouling of moored flow tube optical instruments are presented. A chemical method diffuses a concentrated solution of bromine into the flow tube between sampling periods, creating a toxic environment for microorganisms. An optical method removes a baseline value from the red peak of chlorophyll *a*. Three spectral absorption meters equipped with the chemical system were deployed in the southeastern Bering Sea from March to September 1993. For a 40-m instrument the system prevented biofouling for the entire deployment, while an 11-m instrument was free of contamination for approximately 3.5 months. Reasonable estimates of in situ chlorophyll *a* were obtained from all three instruments by the subtraction of the baseline.

1. Introduction

Moored optical sensors provide valuable information about marine ecological processes. However, optical instruments are sensitive to biofouling of light sources and photodetectors. Useful lifetimes of deployment of transmissometers and fluorometers without antifoulant protection are often limited to several weeks. To provide accurate estimates of phytoplankton biomass, the light source and detector windows of the optical instruments must remain free from growth of microorganisms or the effects of biofouling on the collected data must be correctable. Various strategies have been implemented to prevent biofouling, ranging from bronze rings impregnated with tributyl tin oxide [*Butman and Folger*, 1979] to employing divers to periodically clean windows [*Martini and Strahle*, 1993]. While these methods have met with some success, they remain far from ideal. Most biocides, usually heavy metals whose use in the future is to be prohibited [*Evans et al.*, 1995], are biohazards for humans. Moorings in remote and rugged regions are not amenable to frequent servicing. Other researchers have attempted to remove fouling bias via statistical methods [*Stramska and Dickey*, 1992a,b].

As part of the National Oceanic and Atmospheric Administration's Fisheries Oceanography Coordinated Investigations in the southeastern Bering Sea, a mooring was deployed for approximately 6 months during the 1993 field season. This mooring was equipped with first-generation optical instrumentation for the detection of spectral absorption and attenuation of light. In 1992 a mooring without optical instruments was deployed at the same site, and observations of instruments recovered at that time showed extensive biofouling. We describe two methods to alleviate the effects of biofouling. In the first method we used a concentrated solution of bromine to create a toxic environment in the flow tube of the spectral absorption meter and prevent the growth of microorganisms. Bromine is much less of a biohazard than other commonly used biocides and, in fact, is approved for use in swimming pools. This method allows the deployment of optical instruments for periods up to 5 months. Our second method utilizes synoptically collected spectral absorption data from the meter to form a baseline as described below which is subsequently subtracted from the absorption value for the red peak of chlorophyll *a* at 676 nm. This method results in reasonable chlorophyll *a* estimates from absorption data, even after noticeable contamination.

2. Materials And Methods

A mooring was deployed in the southeastern Bering Sea at 54° 47' N, 168° 33' W in 2195 m of water on March 29 and recovered on September 2 1993. The mooring consisted of a modified PROTEUS (PROfile TElemetry of Upper ocean currentS) surface toroid [*McPhaden et al*, 1991; E.D. Cokelet and P.J. Stabeno, Mooring observations of the thermal structure, density stratification, and currents in the SE Bering Sea, submitted to *Journal of Geophysical Research*, 1995; hereafter referred to as Cokelet and Stabeno, submitted manuscript, 1995] with meteorological sensors and a suite of in-water instruments for measuring hydrographic and biological parameters. Among those were three flow tube optical instruments [*Zaneveld et al.*, 1990] manufactured by Western Environmental Technology Laboratories Inc. (WET Labs, Philomath, Oregon). (Reference to trade names does not imply endorsement by the National Marine Fisheries Service, NOAA.) Two of the three instruments were three-wavelength chlorophyll *a*

[1]College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, Oregon.

[2] Now at Dept. of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada.

[3]Western Environmental Technology Laboratories Inc., Philomath, Oregon.

[4]National Oceanic and Atmospheric Administration, Alaska Fisheries Science Centre, Seattle, Washington.

Paper number 96JC02430.
0148-0227/96/96JC-02430$09.00

absorption meters (a-3) that measured in situ absorption at 650, 676, and 710 nm. The other instrument was a six-wavelength absorption and attenuation meter (ac-6) that measured in situ absorption and attenuation at 440, 540, 600, 650, 676, and 694 nm. Only absorption data ($a(\lambda)$; m^{-1}) will be considered here. The first a-3 was deployed at 9 m, the ac-6 at 11 m, and the second a-3 at 40 m. A miniature temperature recorder (MTR) [*Milburn and McLain,* 1991] was deployed at 10 m between the upper a-3 and ac-6, and two SeaCat (Sea-Bird Electronics) thermosalinographs were placed at 17 m and 42 m. The optical instruments were programmed to collect data every 2 hours, while the MTR and SeaCats collected data every 10 min.

To prevent biofouling in the sample chamber of the absorption meters, a novel system was implemented that utilized the enclosed flow tube of the instruments (Figure 1). A perforated inner canister was filled with solid bromine tablets (BioGuard Brominating Tablets, Bio-Lab, Inc., Decatur, Georgia) and then placed into a vented outer canister. The holes in the inner canister allow the slow dissolution of the bromine tablets into the seawater within the outer canister, with the rate of bromine dissolution being determined by the size of the holes. We chose a dissolution such that a concentration of ~30 parts per million (ppm) built up in the enclosed flow tube of the optical instrument within 15 min after a sampling period, a concentration about 10 times the minimum toxic level determined from tests on natural waters from Newport, Oregon (C.S. Roesler, personal communication, 1993). The sample chamber was flushed for 5 s prior to data collection using a Sea-Bird pump model 5T, which provided more than three full volume exchanges in the flow tube. This flushing insured that the bromine did not compromise absorption measurements.

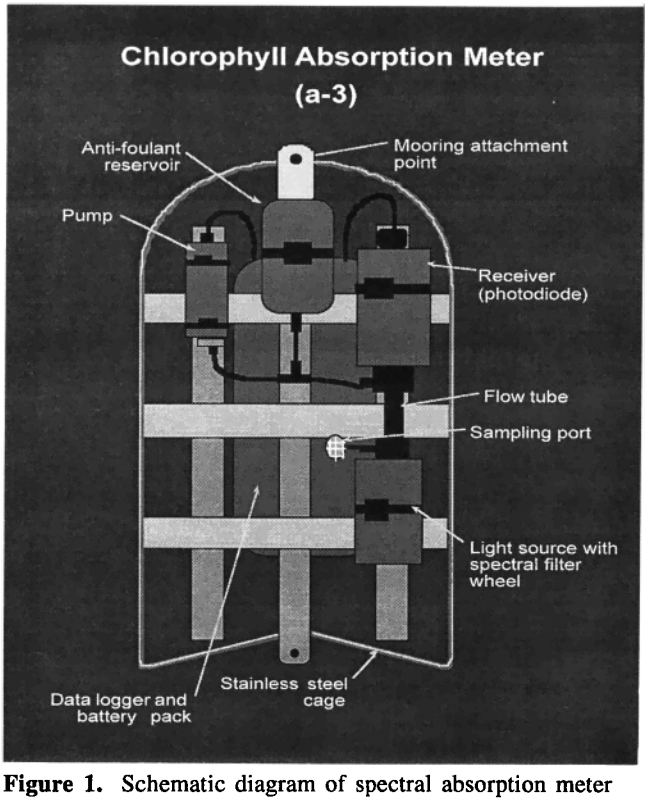

Figure 1. Schematic diagram of spectral absorption meter deployed on mooring.

Digital counts from the absorption meters were converted into engineering units by referencing them to clean water counts:

$$a(\lambda,t) = \frac{-\ln\left[S_{sig}(\lambda,t)/S_{wat}(\lambda)\right]}{x} \quad (1)$$

where $S_{sig}(\lambda,t)$ are sample counts for wavelength λ and time t, $S_{wat}(\lambda)$ is clean-water count for wavelength λ, and x is the path length of the instrument (0.10 m for the a-3s, 0.25 m for the a-6). For the ac-6 both $S_{sig}(\lambda,t)$ and $S_{wat}(\lambda)$ were normalized to an internal reference used to detect degradation of the lamp or the photodetector. Although the a-3s did not possess an internal reference, the reference data from the three red channels of the ac-6 changed < 1% over the deployment. In some instances the a-3s initial in situ counts were higher (i.e., greater transmissivity) than those obtained during factory calibrations using distilled waters (all three channels of the 9-m instrument, one channel of the 40-m instrument). When this occurred, the higher in situ counts were used as reference values to avoid negative absorption values. The higher in situ counts of the a-3 may be a function of not having an internal reference since the normalized ac-6 data did not have in situ counts higher than lab counts. By referencing to clean water, absorption values reported here have already had absorption due to water removed. Absorption values from the far red channel on all three instruments were corrected to take into account differential effects of temperature on absorption by water [*Pegau and Zaneveld,* 1993].

Absorption values were converted into estimates of chlorophyll *a* concentration using standard spectrophotometric techniques [*Parsons et al.,* 1984]. Values at the red peak of chlorophyll *a* ($a(676)$) were baseline corrected by fitting a λ^{-n} curve between $a(650)$ and $a(710)$ (for the two a-3 instruments) or between $a(650)$ and $a(694)$ (for the ac-6). The wavelength exponent n was calculated according to (2) and absorption by chlorophyll by (3):

$$n = \frac{\log_{10}[a(710) - \log_{10}(a(650)]}{\log_{10}(650) - \log_{10}(710)} \quad (2)$$

$$a_{chl} = a(676) - \frac{a(650)}{650^{-n}} 676^{-n} \quad (3)$$

Values of a_{chl} (m^{-1}) were divided by the chlorophyll-specific absorption value for phytoplankton at 676 nm (0.017 m^2 (mg chl)$^{-1}$; [*Bricaud et al.,* 1988; *Bricaud and Stramski,* 1990]) to convert into chlorophyll *a* concentration. If the assumption is made that any fouling of the optical windows affects the three red wavelengths equally, then this procedure will also remove the fouling effects.

3. Results

Absorption in the red channels for all three instruments showed similar trends; therefore only absorption at 650 nm ($a(650)$) will be discussed. Absorption at 650 nm for the shal-

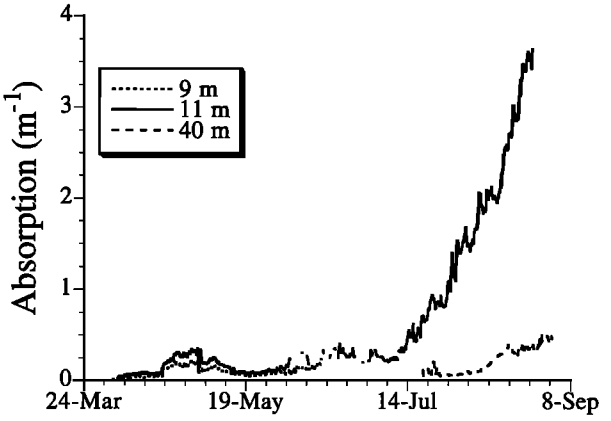

Figure 2. Time series of $a(650)$ (m^{-1}) for three spectral absorption meters deployed on mooring. Data have been smoothed using a three-point running average.

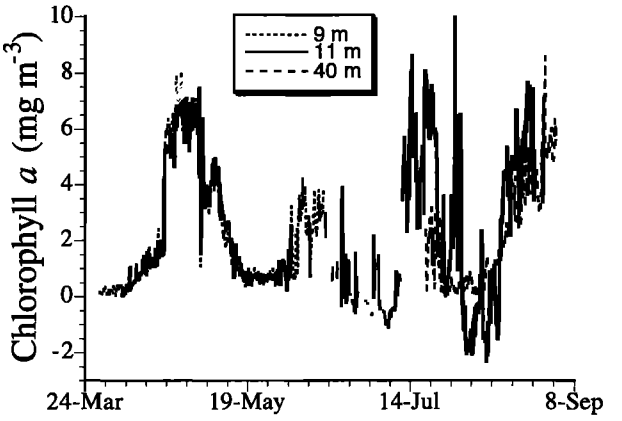

Figure 3. Time series of chlorophyll a concentration (mg m^{-3}) estimated from spectral absorption meters deployed on mooring. Data have been smoothed using a three-point running average.

low two instruments was initially low (~0.02 m^{-1}; Figure 2). The intrusion of a warm surface layer in late April (Cokelet and Stabeno, submitted manuscript, 1995) was accompanied by a threefold increase in $a(650)$ in 8 hours. By mid-May surface $a(650)$ had returned to initial values, indicating that during the first 2 months of deployment, no significant biofouling had occurred. The 9-m a-3 stopped recording data on June 14. From mid-June to mid-July the 11-m ac-6 experienced sporadic data losses, but, in general, $a(650)$ remained constant at ~0.3 m^{-1}. On ~ July 12, $a(650)$ began to increase precipitously, rising to ~3.7 m^{-1} in 6 weeks. The increase in $a(650)$ was not strictly monotonic, with variations about the trend observed.

Time series of $a(650)$ for the 40 m a-3 are also shown in Figure 2. Due to a timer malfunction this instrument did not start data collection until July 19. The 40-m $a(650)$ record starts with low absorption values (~0.1 m^{-1}) that tended to increase over time, with high-frequency variability from August 21 until the end of deployment. In comparison, the ac-6 on July 19 recorded $a(650)$ values of ~0.7 m^{-1}. The 40-m a-3 $a(650)$ values never exceeded 0.6 m^{-1}.

Estimates of chlorophyll a concentration (mg m^{-3}) range from -2.4 mg m^{-3} at 11 m during early August to 7.4 mg m^{-3} during the intrusion of the warm surface layer in late April to 11 mg m^{-3} in late August (Figure 3). Negative chlorophyll values derived from the ac-6 were due to baseline values being higher than $a(676)$. Chlorophyll estimates from the 9-m a-3 and the ac-6 were highly coherent ($r = 0.98$, $P < 0.001$). Chlorophyll estimates from the ac-6 were highly variable after ~ June 17 but not, except for the negative chlorophyll, unrealistic. Coherence between the ac-6 and the 40-m a-3 chlorophyll estimates was lower than between the two shallow instruments but still significant ($r = 0.62$, $P < 0.001$). The 40-m a-3 began collecting data in an apparent high chlorophyll period, dropped to baseline levels, and then increased rapidly to over 6 mg m^{-3} chlorophyll a.

4. Discussion

Biofouling was minimized in flow tube optical instruments by the use of a simple dissolution/diffusion system of bromine in seawater during a 5-month deployment in the southeastern Bering Sea. The bromine is equally effective against microbes as well as larger fouling organisms such as barnacle larvae. We interpret the ability of an absorption meter to return data during the deployment that is close in magnitude to initial in situ values as evidence that the optical windows of the instrument were free of contamination. Even after some contamination was evident, as was the case for the 11-m ac-6, estimates of chlorophyll a were computed through the subtraction of a baseline.

The spectral absorption and attenuation meter mounted at 11 m recorded low absorption values for ~3.5 months, after which $a(\lambda)$ increased rapidly. If this increase were attributed solely to growth of phytoplankton in the water column, it would represent a local rate of increase of ~7% per day. While this growth rate is reasonable for subarctic phytoplankton [*Eppley*, 1972], the final yield of chlorophyll necessary to produce these large absorption values (~3.8 m^{-1} at 676 nm) would be over 200 mg m^{-3}, an unreasonable value for these waters [*Sambrotto et al.*, 1986; J.M. Napp, unpublished data,

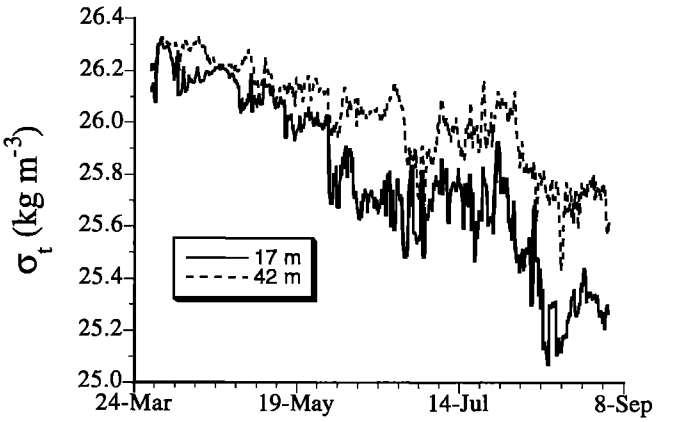

Figure 4. Time series of density (σ_t = (fluid density -1000) kg m^{-3}) from 17 and 42 m. Data collected at 15 min intervals have been hourly averaged and smoothed using a nine-point running average.

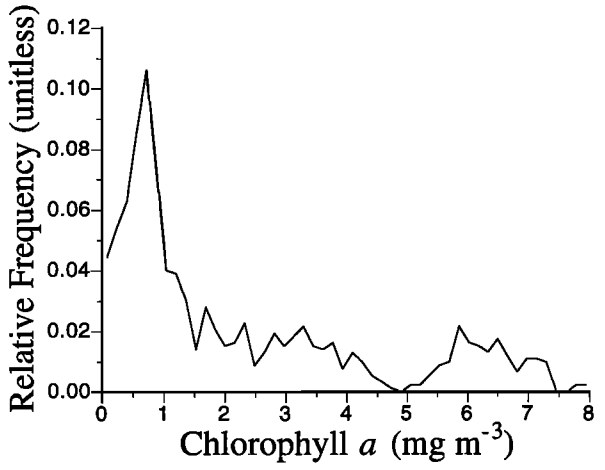

Figure 5. Histogram of relative frequency of chlorophyll *a* concentration estimated from the 9-m a-3. Number of samples is 923; number of bins is 50.

1996]. We parsimoniously conclude that the antifoulant became depleted in the ac-6 in early July, permitting contamination of the optical windows. Upon recovery of the mooring, bromine canisters from all of the instruments were empty. The depletion of the antifoulant created an unplanned experiment, where the effects of biofouling on spectral absorption values could be directly observed. The exact nature of the biofouling is unknown but is presumed to be bacteria and not phytoplankton due to the extreme low light environment of the flow tube. Macroscopic examination of the tubes did not reveal any large fouling organisms. Some fouling may not be biological but rather corrosion caused by the bromine solution.

In contrast to the ac-6, the 40-m a-3 did not show any apparent effects from biofouling. Values of $a(\lambda)$ remained low (< 0.75 m^{-1}) until the end of the deployment (Figure 2). An increase in $a(\lambda)$ observed in late August by the a-3 was also evident in the data from the ac-6. This apparent autumn phytoplankton bloom was also observed the following year [R.F. Davis, unpublished data, 1994]. While the difference between the 11-m and 40-m dissolution/diffusion rates could be due to any combination of factors, such as gradients in temperature, pressure, alkalinity, or mooring motion, the most likely reason for the difference is the decreased turbulence at depth relative to the surface. Density estimated from temperature and salinity measurements at 17 and 42 m decreases with time (Figure 4), primarily due to solar heating. Initially, density was similar at both depths and then diverged with time, indicating stratification of the upper water column (Cokelet and Stabeno, submitted manuscript, 1995). This is consistent with vertical sections for the region reported by *Reed and Stabeno* [1989] and *Reed* [1991]. Stratification means that the 11-m ac-6 experienced increased sea surface-generated turbulence relative to the 40-m a-3 [*Dillon and Caldwell,* 1980]. Since dissolution of a solid is a diffusion controlled process, increased turbulent flow past the 11-m bromine tablets would result in increased dissolution.

Even though biofouling occurred in the ac-6, a_{chl} could be calculated by subtracting from $a(676)$ a baseline determined from concurrent spectral measurements at 650 and 694 nm. Both the 11-m and the 40-m instruments recorded high chlorophyll values in mid-July, and both instruments tracked an increase in chlorophyll starting at ~ August 12. There was also a significant degree of correlation between the two instruments. We interpret the 11-m signal's return to low chlorophyll values in early August and the temporal coherence between the two instruments, one of them presumably uncontaminated, as indication that the baseline correction employed was sufficient to remove much of the effects of biofouling.

A calibration of the moored instruments against regularly spaced discrete chlorophyll samples was not possible due to the remote nature of the mooring. However, a comparison of the frequency histogram of chlorophyll estimates from the 9-m instrument (Figure 5) to data published by *Müller-Karger et al.* [1990] from Processes and Resources of the Bering Sea Shelf (PROBES) data and Coastal Zone Color Scanner (CZCS) images for the southeastern Bering Sea shelf shows good agreement, with a sharp mode near or below 1 mg m^{-3}.

The development of a simple, low-cost, low-toxicity antifoulant system has made it possible to collect long-term, high-quality data on in situ light absorption, even in remote environments such as the Bering Sea. The ability to deploy optical instruments for extended periods of time will produce considerable savings in resources since periodic servicing of instruments will no longer be necessary. Absorption data from these instruments can be used to calculate reasonably accurate estimates of chlorophyll concentration by the simple subtraction of a baseline value for background absorption. Time series of phytoplankton biomass and hydrographic properties can be used to validate biophysical algal growth models and investigate ecological processes on several timescales.

Acknowledgments. We would like to thank E.D. Cokelet for physical data from the mooring, C. DeWitt, B. Parker, and the crew of the R/V *Miller Freeman* for field assistance, and L. Britt and C. Roesler for lab assistance. This research is contribution FOCI-B271 to NOAA's Coastal Ocean Program Bering Sea Fisheries-Oceanography Coordinated Investigations.

References

Bricaud, A., and D. Stramski, Spectral absorption coefficients of living phytoplankton and nonalgal biogenous matter: A comparison between the Peru upwelling area and the Sargasso Sea, *Limnol. Oceanogr., 35,* 562-582, 1990.

Bricaud, A., A.L. Bedhomme, and A. Morel, Optical properties of diverse phytoplanktonic species: Experimental results and theoretical interpretation, *J. Plankton Res., 10:*, 851-873, 1988.

Butman, B., and D.W. Folger, An instrument system for long-term sediment transport studies on the continental shelf, *J. Geophys. Res., 84,* 1215-1220, 1979.

Dillon, T.M., and D.R. Caldwell, The Batchelor spectrum and dissipation in the upper ocean,*J. Geophys. Res., 85,* 1910-1916, 1980.

Eppley, R.W., Temperature and phytoplankton growth in the sea, *Fish. Bull., 70,* 1063-1085, 1972.

Evans, S.M., T. Leksono, and P.D. McKinnell, Tributyltin pollution: A diminishing problem following legislation limiting the use of TBT-based anti-fouling paints, *Mar. Pollut. Bull.., 30:*, 14-21, 1995.

Martini, M.A., and W.J.Strahle, Multi-sensor system for coastal environments, *Sea Technol.., 34,* 49-53, 1993.

McPhaden, M.J., H.B. Milburn, A.I. Nakamura, and A.J. Shepherd,

PROTEUS - PROfile TElemetry of Upper ocean currentS, *Sea Technol., 32*, 10-19, 1991.

Milburn, H.B., and P.D. McLain, Miniature temperature recorder owner's manual, 11pp., Pac. Mar. Environ. Lab., NOAA, Seattle, Wash., 1991.

Müller-Karger, F.E., C.R. McClain, R.N. Sambrotto, and G.C. Ray, A comparison of ship and coastal zone color scanner mapped distribution of phytoplankton in the southeastern Bering Sea, *J. Geophys. Res., 95*, 11,483-11,499, 1990.

Parsons, T.R., Y. Maita, and C.M. Lalli, A Manual of Chemical and Biological Methods for Seawater Analysis, 173pp., Pergamon, Tarrytown, N.Y., 1984.

Pegau, W.S., and J.R.V. Zaneveld, Temperature-dependent absorption of water in the red and near-infrared portions of the spectrum, *Limnol. Oceanogr., 38*:, 188-192, 1993.

Reed, R.K., Circulation and water properties in the central Bering Sea during OCSEAP studies, Fall 1989-Fall 1990, *NOAA Tech. Rep. ERL 446*, 13 pp., 1991.

Reed, R.K., and P.J. Stabeno, Circulation and property distributions in the central Bering Sea, Spring 1988, *NOAA Tech. Rep. ERL 439*, 13 pp., 1989.

Sambrotto, R.N., H.J. Niebauer, J.J. Goering, and R.L. Iverson, Relationships among vertical mixing, nitrate uptake, and phytoplankton growth during the spring bloom in the southeast Bering Sea middle shelf, *Cont. Shelf Res.* , *5*, 161-198, 1986.

Stramska, M., and T.D. Dickey, Short-term variations of the bio-optical properties of the ocean in response to cloud-induced irradiance fluctuations, *J. Geophys. Res.* ,*97*, 5713-5721, 1992a.

Stramska, M., and T.D. Dickey, Variability of bio-optical properties of the upper ocean associated with diel cycles in phytoplankton population, *J. Geophys. Res.* ,*97*, 17,873-17,887, 1992b.

Zaneveld, J.R.V., R. Bartz, and J.C. Kitchen, Reflective-tube absorption meter, in*Ocean Optics, 10, Proc. SPIE Int. Soc. Opt. Eng.1302*, 124-136, 1990.

R.F. Davis, Department of Oceanography, Dalhousie University, Halifax, Nova Scotia B3H 4J1, Canada. (e-mail: rfdavis@is.dal.ca)

C.C. Moore, Western Environmental Technology Laboratories Inc., PO Box 518, Philomath, OR 97370. (e-mail: casey@wetlabs.com)

J.M. Napp, National Oceanic and Atmospheric Administration, Alaska Fisheries Science Centre, 7600 Sand Point Way NE, Seattle, WA 98115. (e-mail: jnapp@afsc.noaa.gov)

J.R.V. Zaneveld, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331. (e-mail: zaneveld@oce.orst.edu)

(Received January 5, 1996; revised July 10, 1996; accepted August 5, 1996.)