INVERSION OF THE INHERENT OPTICAL PROPERTIES AND THEIR UTILITY FOR DELINEATION OF WATER MASSES IN TURBID COASTAL WATERS

Schofield, O.[1], T. Bergmann[1], W. P. Bissett[2], G. Kirkpatrick[3], M. Oliver[1], C. Orrico[4], M. A. Moline[4], S. Glenn[1]

[1]Coastal Ocean Observation Laboratory, Institute of Marine and Coastal Sciences Rutgers University, New Brunswick, NJ 08901

[2]Florida Environmental Research Institute, 4807 Bayshore Blvd. Suite 101, Tampa, FL 33611

[3]Mote Marine Laboratory, 1600 Ken Thompson Parkway, Sarasota, Florida 34236

[4]Biological Sciences Department, California Polytechnic State University, San Luis Obispo, CA 93407

INTRODUCTION

Significant effort over the last decade has focused on developing instrumentation to measure the spectral dependency of the in situ inherent optical properties (IOPs). A major goal is to invert the bulk IOPs to provide "optical" weights for optically active components [e.g. water, colored dissolved organic matter (CDOM), phytoplankton, detritus, sediment, etc.], which are proportional to component concentration (Roelser et al. 1989, Chang and Dickey 1999, Schofield et al. 1999). With the ability to estimate the magnitudes of the individual optical constituents, the derived products can be used to calibrate/tune satellite algorithms, differentiate water masses, and potentially feed optically-based ecosystem models. These models, while rapidly maturing, are still under development but will be a key tool in providing a means to optimally interpolate to regions where in situ data is sparse (in both space and time) and will provide the central component to any ecosystem forecasting network. Developing such a forecasting system is one long-term goal of this group and developing the means to initialize such a system is a vexing issue.

Data from submersible instrumentation reflect bulk absorption, which represents the additive absorption of the specific in situ constituents. The instrument signal can be deconvolved into the contributions by all absorbing components according to:

$$a(\lambda) = \sum_{i=1}^{n} x_i \bullet a_i(\lambda) \qquad (1)$$

where $a_i(\lambda)$ refers to absorption at wavelength λ for component i. The particulate material can be further partitioned into phytoplankton, sediments, and detritus. If there is sufficient variability in the phytoplankton signal, it can be further partitioned into the three major spectral classes of phytoplankton (chlorophytes, chromophytes, and phycobilin-containing algae). These inversion techniques are based on estimating the volumetric absorption using generalized absorption spectral shapes for one or more of the individual absorbing components or using absorption ratios of different wavelengths that vary in a predictable way according to the components present.

Given this, we wanted to develop an optical inversion method using an ac-9 that was robust in optically-complex coastal waters. Secondarily, our goal was to assess which optical parameters could be derived and assess their utility in differentiating water masses for the nearshore coastal ocean.

METHODS

Field data

The field efforts were conducted at the Long tem Ecosystem observatory off the coast of New Jersey. This is a highly instrumented site (Fig. 1) uses real-time data from multiple field assets (satellites, aircraft, ships, and AUVs) to coordinate the adaptive sampling of coastal processes. For the HyCODE project this real-time capacity provided the means to optimize the calibration of multiple hyperspectral aircraft and the international suite of ocean color satellites. Another advantage of the field site was that it provided a wide optical gradient (from very turbid estuarine waters to clear Case 1 offshore waters) that could be sampled by numerous vessels simultaneously during any specific aircraft or satellite pass. Secondarily the optical gradient reflected the variable contributions of many optically-active constituents (phytoplankton, sediments, Colored Dissolved Organic Matter). During the three year HyCODE program a large optical database was collected by both ships and moored profiling systems.

The standard shipboard transects consisted of several 15-25 km cross-shelf transects. Specific transect lines and the locations of the stations were determined by the real-time data from ships and satellites. At each station a vertical profile of optical and physical data were collected (see below). Profiles were measured with an integrated bio-optical package consisting of a Wetlabs ac-9, a Falmoth CTD, a profiling Satlantic spectroradiometer, a Sequoia LISST, and a HOBI Hydroscat-6. The measurements of the inherent optical properties used in this study were collected using the standard nine-wavelengths of the Wetlabs ac-9. The instruments were factory calibrated prior to the field season. Manufacturer recommended protocols were used to track instrument calibration throughout the field season. This included clean

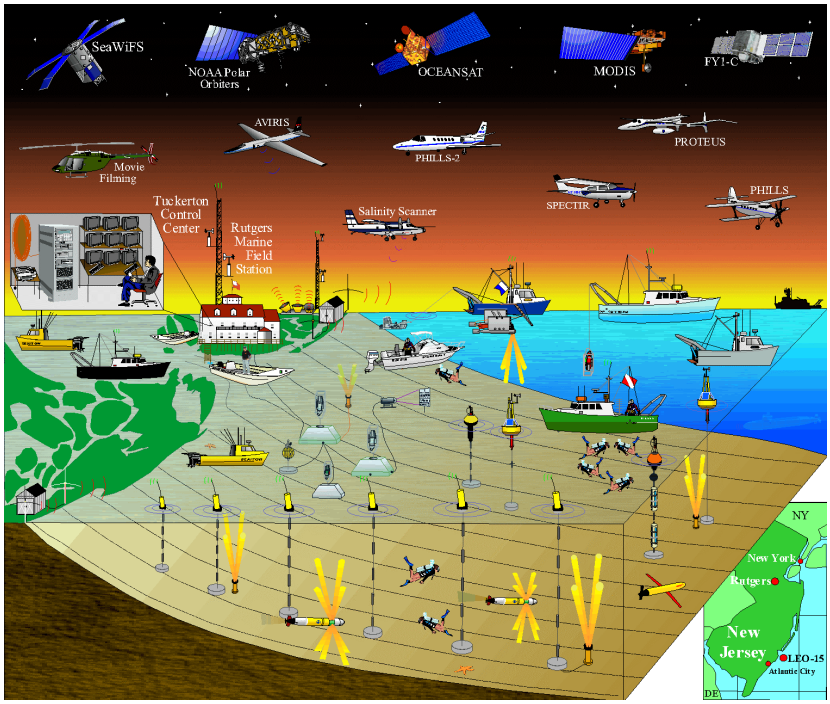

Fig. 1. The experimental infrastructure coordinated through the HyCODE. The inset shows the location of the HyCODE experiment.

water, temperature, and salinity calibrations. Whenever possible daily water calibrations were conducted; however sampling schedules did not always allow for a daily calibration. Under these circumstances the most recent water calibration was used. At each station, the instrument was lowered to depth to remove air bubbles and the instrument was allowed to come to temperature before the data was collected. Only data from the upcast were utilized.

Discrete samples

At each station water was collected with a Niskin bottle for both the surface and bottom water. Aliquots were filtered, under low vacuum (<10 cm Hg), through GF/F (Whatman) glass-fiber filters to concentrate the particles for pigment and absorption determinations. Filters were placed into the snap top vials and quick frozen in liquid nitrogen. Samples were stored at –80 ˚C until later analysis. Photosynthetic and photoprotective pigment complements were determined using high-performance liquid chromatography (HPLC) according to procedures of Wright et al. (1991). Filter pad absorption was measured on a laboratory spectrophotometer in split beam mode outfitted with opal glass using a blank wet filter as a blank. Spectra were corrected for the pathlength amplification factor. The filters were then extracted in methanol. The extraction consisted of both a cold extraction in the dark at –20 ˚C for at least 24 hours, which was then followed by an extraction in boiling methanol under a gentle vacuum filtration. Particulate material was then retained on the filter was used as an estimate of detrital material. The detrital absorption was subtracted from the particulate absorption to provide an estimate of the phytoplankton absorption.

Inversion of in situ absorption data

The inversion method estimates the coefficients (w_i) and exponential slopes (*s, r*) using a non-linear constrained least-squares regression according to

$$a_{total}(\lambda) = w_1 a_{Phyto1}(\lambda) + w_2 a_{Phyto2}(\lambda) + w_3 a_{Phyto3}(\lambda) + w_4 a_{CDOM}(\lambda, s) + w_5 a_{Detritus}(\lambda, r) \quad (2)$$

where $a_{total}(\lambda)$ is the total spectral absorption measured with the ac-9 (minus the absorption of water), $a_{Phyto1}(\lambda)$, $a_{Phyto2}(\lambda)$ and $a_{Phyto3}(\lambda)$ are generalized spectral absorption of chlorophyll *a-c*, phycobilin and chlorophyll *a-b* containing phytoplankton respectively, $a_{CDOM}(\lambda, s)$ and $a_{Detritus}(\lambda, r)$ are the generalized spectral absorption of CDOM and detritus which are a function of the exponential slopes *s* and *r* respectively, and w_1, w_2, w_3, w_4 and w_5 are non-spectrally dependant scalar coefficients of these spectra. This method requires initial guesses of phytoplankton, CDOM and detrital spectral curves. Spectral phytoplankton curves are averages of high-light and low-light adapted phytoplankton spectra normalized to absorption at 676 nm from Johnsen et al 1994. CDOM and detrital input are idealized and normalized to absorption at 412 nm with initial exponential slopes of 0.010 and 0.008. The constraints on this regression are:

$$w_1 a_{Phyto1}(\lambda), w_2 a_{Phyto2}(\lambda), w_3 a_{Phyto3}(\lambda), w_4 a_{CDOM}(\lambda, s), w_5 a_{Detritus}(\lambda, r) \geq 0 \quad (3)$$

$$w_1 a_{Phyto1}(\lambda) \geq w_3 a_{Phyto3}(\lambda) \quad (4)$$

$$w_2 a_{Phyto2}(\lambda) \geq w_3 a_{Phyto3}(\lambda) \quad (5)$$

$$w_4 a_{CDOM}(555nm, s) \geq w_5 a_{Detritus}(555nm, r) \quad (6)$$

$$w_1 a_{Phyto1}(650nm) \geq w_4 a_{CDOM}(676nm, s) + w_5 a_{Detritus}(676nm, r) \geq 0 \quad (7)$$

$$w_2 a_{Phyto2}(650nm) \geq w_4 a_{CDOM}(676nm, s) + w_5 a_{Detritus}(676nm, r) \geq 0 \quad (8)$$

$$w_4 a_{CDOM}(676nm, s) = w_5 a_{Detritus}(676nm, r) \quad (9)$$

$$s \geq r \quad (10)$$

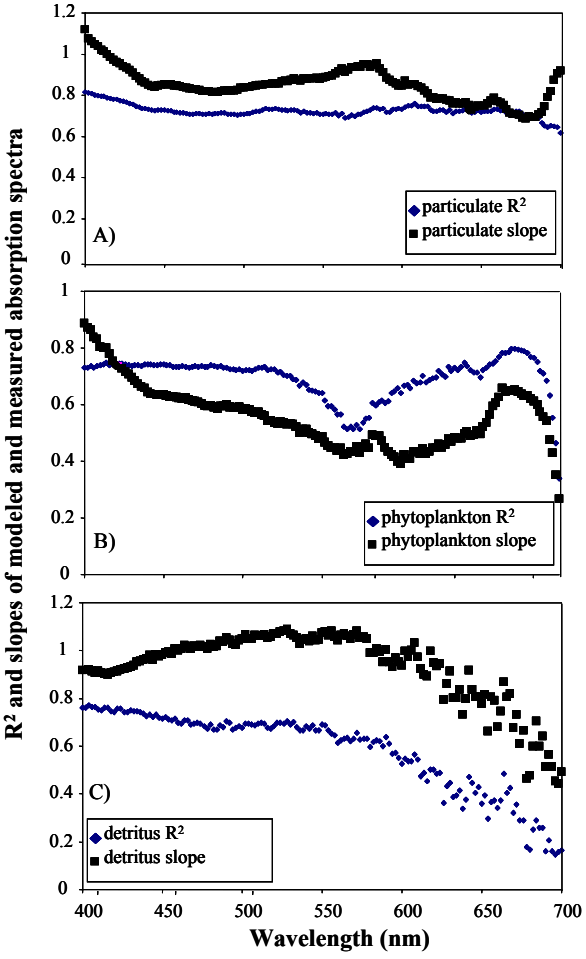

Fig. 2. Comparison of measured and modeled particulate, phytoplankton and detritus absorption. Measured data was discrete samples measured on laboratory spectrophotometer.

Some of these constraints may seem arbitrary, they were based on five years of experience in these waters; furthermore it should be noted that this inversion method using the same assumptions has been successfully used in both the oligotrophic Gulf of Mexico and the southern basin of Lake Michigan.

RESULTS AND DISCUSSION

Verification of the derived optical products

Derived particulate, detrital and phytoplankton loads were compared to independent in situ and discrete data. The global data-set represents the comparison of ac-9 data and over 200 filter pad measurements made over a range of optical conditions encountered during the HyCODE program (Fig. 2). There was good agreement between measured and modeled particulate spectra, with the R^2 ranging from 0.75 to 0.8 irrespective of wavelength. The slope between the measured and modeled spectra generally ranged from 1.1 to 0.8. Therefore the derived particulate spectra could be quantitatively derived from the ac-9

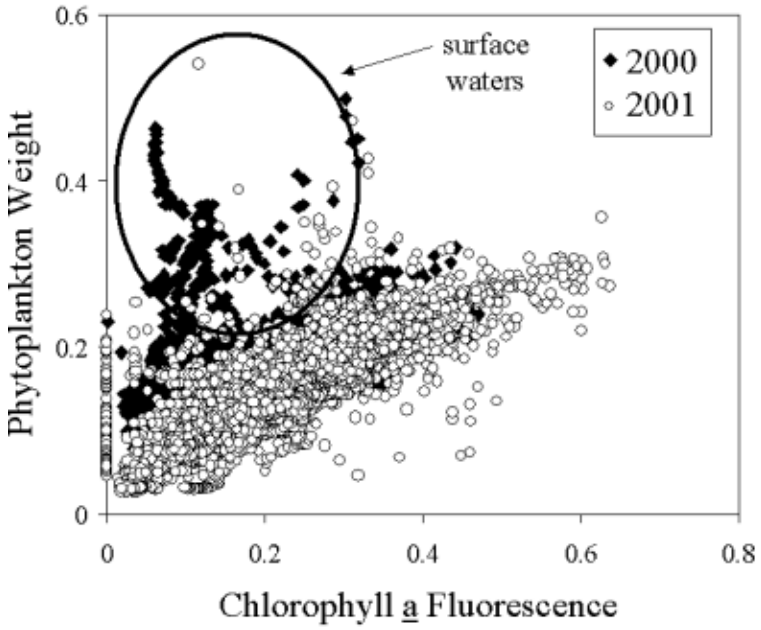

Fig. 3. Correlation between in situ fluorescence and ac-9 derived phytoplankton optical weight for the summer HyCODE experiment in the summers of 2000 and 2001.

with no major bias as a function of wavelength. Quantitative agreement tended to fall off in the red wavelengths of light where signal was low. The partitioning of the particulate spectra into the detrital and phytoplankton absorption generally resulted in an underestimate in the phytoplankton and overestimate in the detrital concentrations. As before quantitative agreement tended to be strongest in the blue wavelengths of light and lower in the red wavelengths of light. For the ac-9 derived phytoplankton spectra, the derived values were lowest in the green and orange wavelengths of light where phytoplankton absorption is lowest. Despite these problems, 70-80% of the variability in the phytoplankton absorption could be explained by the ac-9 derived phytoplankton estimates, with lowest values in the green wavelengths associated with the phycobilin absorption. This reflected the pronounced phycobilin absorption in the inverter input spectra and reflects the distinctive absorption often observed when phytoplankton are grown in the lab compared to nature. Despite these problems, there was good linear agreement between phytoplankton optical load and in situ chlorophyll fluorescence (Fig. 3), despite that the bulk IOPs were dominated by many components other then phytoplankton. In Summer 2000, the field site was impacted by highly turbid low salinity plume of water, which was characterized by particularly high CDOM concentrations. In contrast, summer 2001 was dominated by alternating upwelling/downwelling conditions, which resulted in a dense phytoplankton bloom with high levels of detritus. Despite these differences there was a robust correlation between the pooled ac-9 estimated phytoplankton and fluorescence data (Fig. 3). The exception to this was a series of points, which had low fluorescence despite high phytoplankton biomass. These points were found in the surface waters and reflect the natural variability in the fluorescence yield (fluorescence per chlorophyll; Kiefer 1973, Cullen 1982, Falkowski and Kiefer 1985, Sosik et al. 1989). This decrease in the fluorescence yield reflected either xanthophyll pigment cycling or photoinhibition when the surface population is light saturated (Schofield et al. 1998).

Another robust test if the phytoplankton inversion is functioning properly is to see whether it is possible to delineate the presence of the three spectral classes of

phytoplankton. With HPLC data we used ChemTax (Millie et al. 2002) to estimate the proportion of total chlorophyll associated with the major bloom-forming taxa. The inverter estimates the total amount of phytoplankton absorption as a combination of chlorophyll c, phycobilin, and chlorophyll b-containing phytoplankton. The inverter did a good job predicting ($p<0.05$) the concentration of chlorophyll c and phycobilin-containing phytoplankton (Fig. 4). There was little success predicting the distribution of

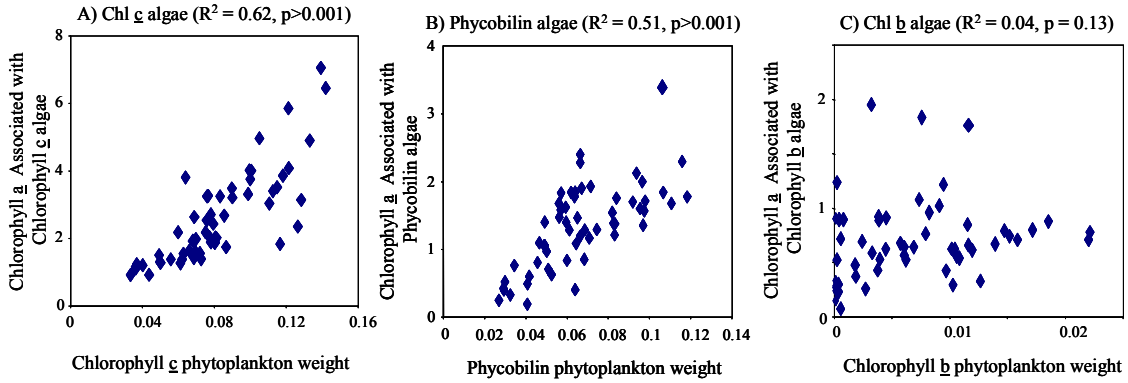

Figure. 4. The correlation between HPLC and ac-9 estimates of the major spectral classes of phytoplankton. The chlorophyll c and phycobilin relationships are significant.

chlorophytes, but this largely reflects that they are minor amount off the total phytoplankton community at LEO. These results demonstrate that the IOP inverter provides reasonable estimates and the spectral absorption of CDOM particles, detritus, and phytoplankton can reasonably be estimated using an ac-9. The inverter thus allows maps to be constructed of the dominant optical components to be constructed (Fig. 5).

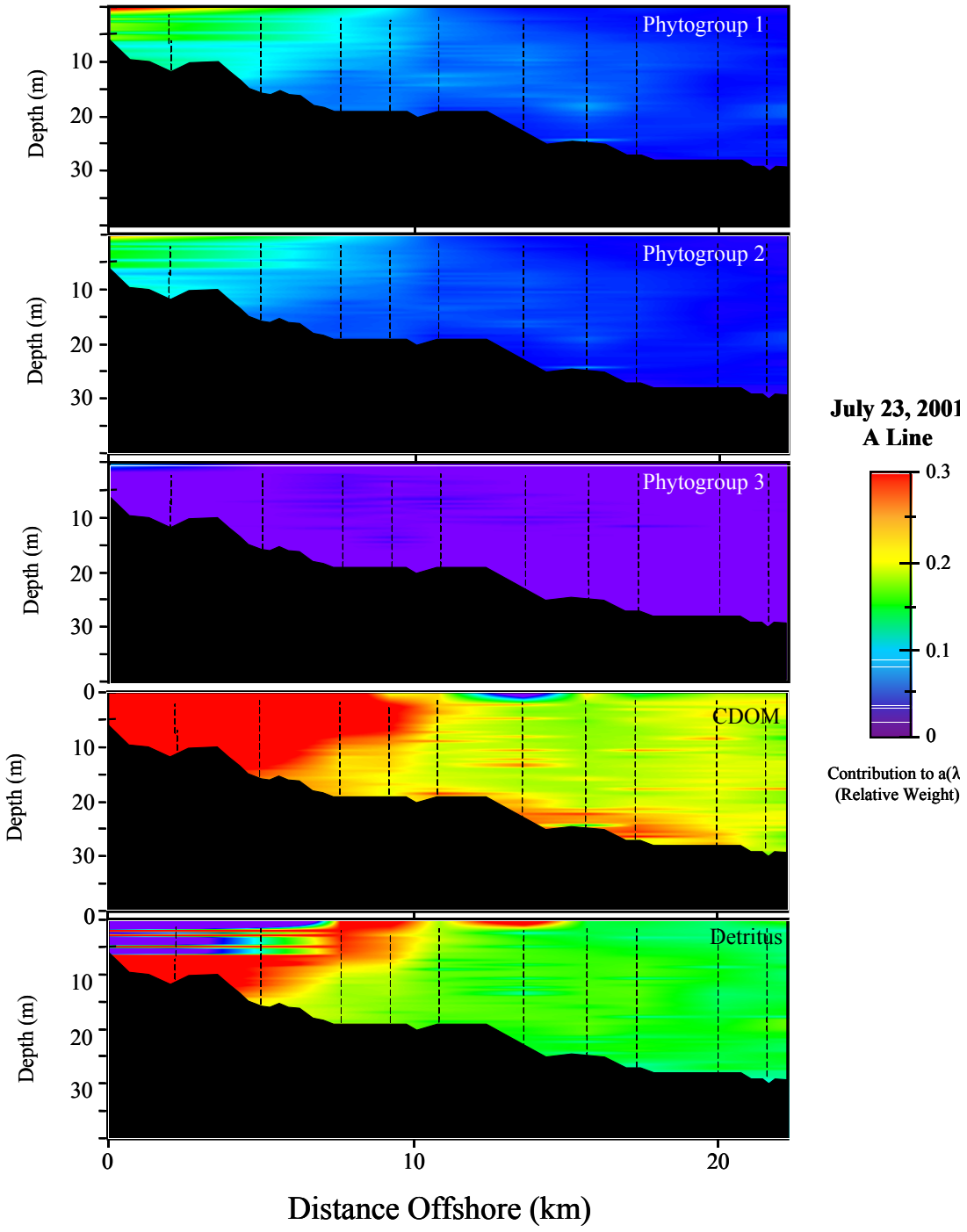

Fig. 5. A typical cross-shore transect and the derived optical products for a day in summer 2001. Phytoplankton 1, 2, and 3 represent the Chromophytes, Phycobilin-algae, and Chlorophytes respectively.

Hydrographic parameters (T-S) have been useful in defining oceanic water masses on a number of spatial scales (Helland-Hansen 1916, Knauss 1996). However, quantification of smaller water masses such, as estuarine plumes, is difficult and it is often useful to include additional parameters such as chemical signatures to extend the analysis into multi-dimensional space (Tomczak 1999). The T-S relationships in this study indicated the presence of significantly different water masses within and between each year, however their boundaries were difficult to resolve from T-S structure alone. Measured and derived optical properties were also highly variable; therefore it may be possible to extend water mass analysis into multi-dimensional space using these parameters. This is consistent with Aarup et al. (1996) and Højerslev et al. (1996), which identified discrete water masses based on apparent optical properties derived from yellow substance concentrations in the Baltic Sea region because it was a quasi-conservative parameter. While these optical parameters are semi-conservative, the relative change of these parameters is longer than many coastal ocean processes enhancing their potential utility. Examples from HyCODE included the Hudson River plume with the high

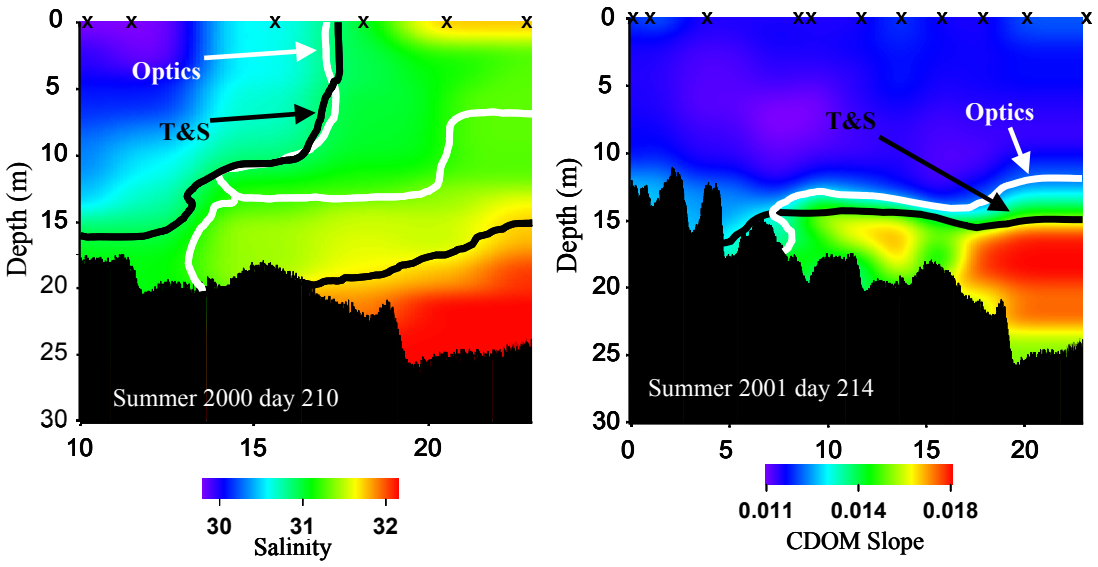

Fig. 6. Crosshore transects from a day in Summer 2000 and 2001. The black lines represent the water mass classification based upon the entire summers temperature and salinity data. The white line represents the water masses identified based on the ac-9 inverter for the entire summers dataset. The water masses were calculated from the different parameters by subtracting the mean of the data set and dividing by the standard deviation of the data set. Based on Euclidian distance, a distance matrix was calculated for the data set, and then hierarchically clustered according to Ward's linkage (Ward 1963). The generated similarity index was used in conjunction with a multivariate analysis of variance (MANOVA) to define the major groupings of temperature and salinity (i.e. water masses). Summer 2000 was dominated by a low salinity plume of Hudson River water that is evident in the cross-shelf transect of salinity. The summer of 2001 was dominated by alternating upwelling/downwelling conditions with high phytoplankton concentrations above the thermocline and cold marine water below the thermocline.

concentration of large particles, phytoplankton, CDOM and detritus during summer 2000. Here the river was dominated with shallow slopes consistent with terrestrially derived materials (Vodacek et al., 1997; Nelson and Guarda 1995, Fig. 6). A second example was dense bottom water, which was easily identified optically (Fig. 6). Associated with the bottom water intrusions are steep CDOM slopes, which is consistent with offshore marine waters in the Mid-Atlantic Bight (Vodacek et al., 1997) where the CDOM has been photo-oxidized and/or degraded by microbial populations (Moran et al., 2000) (Fig. 6). The water mass clusters for the temperature/salinity and the optics (CDOM slope & load, detritus slope and load, and phytoplankton load) generally agreed with each delineating 3 major water masses in summer 2000 and 2 major water masses in summer 2001. These derived products will be key tools in future ocean observation efforts and provides a means for biologists and chemists to collect relevant data over similar spatial/temporal timescales as physical oceanographers.

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