

## Project Title

*Carbon transport in the bottom boundary layer*

**#DE-FG02-92ER61443**

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### Objective

Our objective was to characterize distributions of chloropigment fluorescence in relation to physical processes in the benthic boundary layer in support of the Department of Energy (DOE) Ocean Margins Program's (OMP) goal of quantifying carbon transport across the continental shelf.

### Approach

Our approach involved participation in the Ocean Margins Program (OMP) field experiment on the continental shelf off Cape Hatteras by conducting multi-sensor fluorescence measurements of photosynthetic pigments. Specific tasks included 1) pre- and post deployment calibration of multiple fluorescence sensors in conjunction with J. Churchill and A. Williams of Woods Hole Oceanographic Institution (WHOI); 2) collection and analysis of photosynthetic pigment concentrations and total particulate carbon in water column samples to aid in interpretation of the fluorescence time-series during the field experiment; 3) collaboration in the analysis and interpretation of 1994 and 1996 time-series data in support of efforts to quantify pigment and particulate organic carbon transport on the continental shelf off Cape Hatteras. This third component included analysis of data obtained with a multi-sensor fiber-optic fluorometer in the benthic boundary layer of the inner shelf off Cape Hatteras during summer 1994. A manuscript is in preparation for submission for publication.

### Results to Date

#### *Pre- and Post-deployment Calibration of Fluorometers*

Fluorometers were calibrated in the laboratory by sequentially adding portions of phytoplankton cultures into artificial seawater (after Guillard, 1975) that was circulated through the WETLabs WETStar Miniature Fluorometers. Flow rates ranged between 0.002-0.020 L s<sup>-1</sup>. Based on the manufacturer's specifications, this range of flow could result in a 10-15% variation in fluorometer response. No attempt was made to adjust for flow-rate dependence of the response. The fluorometers were powered by a 12V DC power supply and output voltage was monitored with a series of voltmeters. Cultures of the diatom, *Thalassiosira weissfloggi* (Carolina Biological Supply) and the chlorophyte, *Nannochloris atomis* Butcher (clone GSB Nano, Culture Collection

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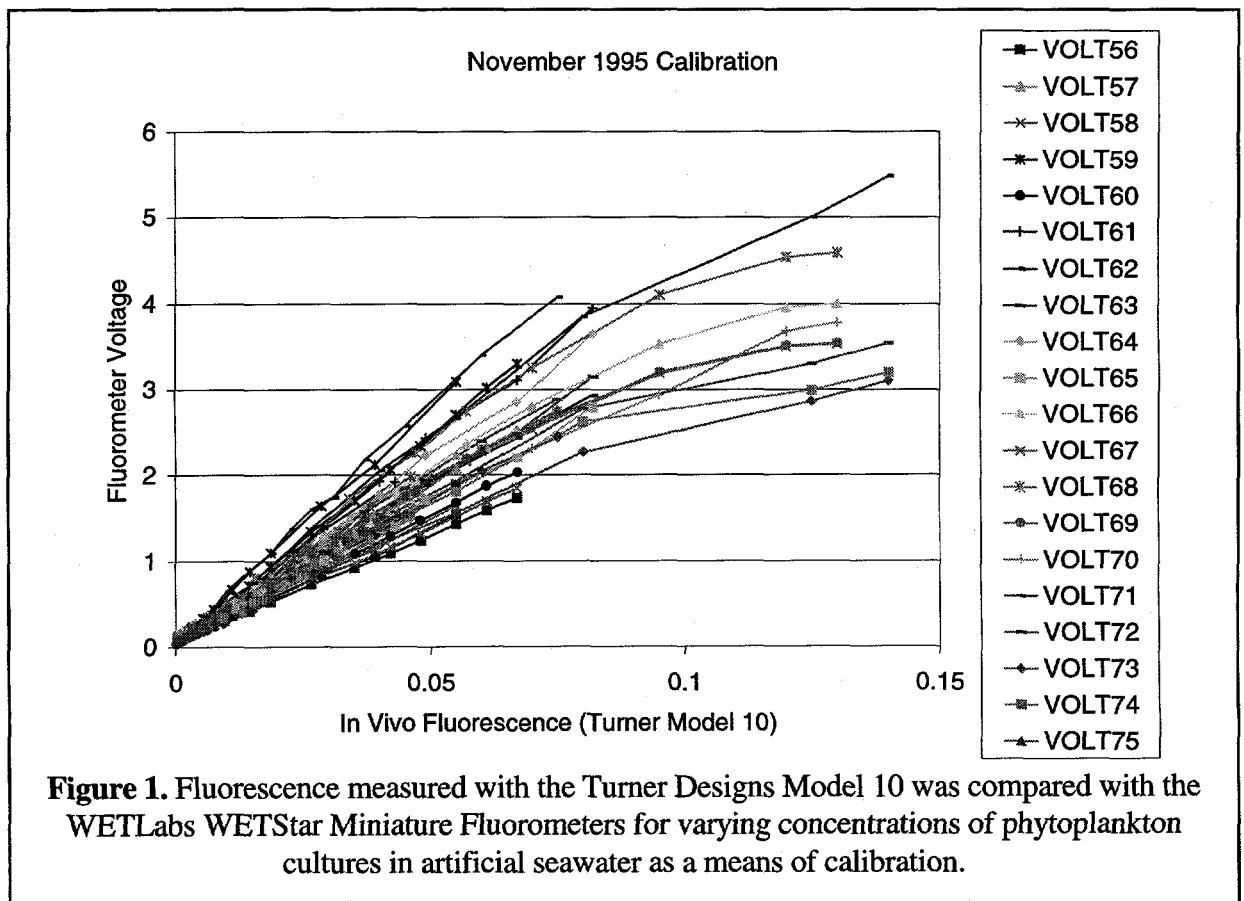
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of Marine Phytoplankton, Bigelow Laboratory) were used for calibration. For each dilution, a sample was filtered onto a 2.5 cm glass fiber filter (Whatman GFF) for chlorophyll analysis. Filters were ground in 90% acetone/Milli-Q water with a teflon pestle and subsequently analyzed by the fluorometric method (Smith et al., 1981). The *in vivo* fluorescence of a 10 mL aliquot of the seawater-algae mixture was read in a 13x100mm cuvette on a Turner Designs Model 10 fluorometer. The latter instrument was equipped with an F4T5 blue lamp, Corning color specification (c/s) 5-60 excitation filter and a c/s 2-64 emission filter and c/s 3-66 reference filter. Calibration was performed with pure chlorophyll *a* (Sigma), and provided a stable reference for comparison between the different instruments. The average door factor (i.e., ratio of chlorophyll *a* concentration in mg L<sup>-1</sup> in 90% acetone to fluorescence) for the Turner Designs fluorometer was 0.069.

Results of the November 1995 fluorometer calibration data (Fig. 1) showed that the responses of the fluorometers were linear for concentrations exhibiting up to a fluorescence of 0.1 on the Turner Designs Model 10. This was equivalent to a chlorophyll concentration of 5-15 mg Chl m<sup>-3</sup>. Regression analysis of the data for the linear region was performed for each fluorometers (Fig. 2a-d). A post-deployment calibration was made for a subset of the fluorometers that were available.



**Figure 1.** Fluorescence measured with the Turner Designs Model 10 was compared with the WETLabs WETStar Miniature Fluorometers for varying concentrations of phytoplankton cultures in artificial seawater as a means of calibration.

In all, a post-deployment calibration was performed for five of the fluorometers in September 1997 (prior to cleaning of the instruments). Flow rates for this calibration were 0.010-0.015 L s<sup>-1</sup>. A comparison of results demonstrated only minor deviations from the initial calibration (Fig. 3). Instrument #56 did display an elevated baseline, probably the result of accumulation of material in

the flow cell. This was consistent with some field data showing increases in baseline fluorescence between peak events (see below). The comparison supported the view that time-series data could be corrected by correcting for baseline elevation as has been done for optical backscatter sensors in other studies (Sherwood et al., 1994). A decrease in fluorescence response of the instrument is to be expected, however, as fouling progresses.

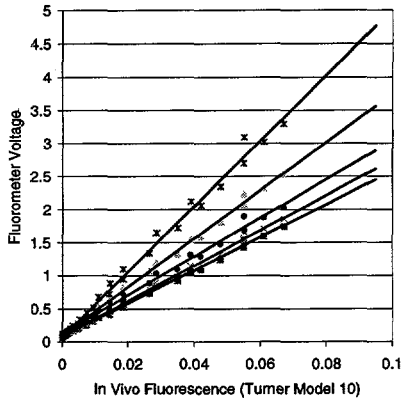


Fig. 2a

|          |  |
|----------|--|
| ■ VOLT56 | $y = 24.87x + 0.0826$<br>$R^2 = 0.9979$  |
| △ VOLT57 | $y = 36.46x + 0.0999$<br>$R^2 = 0.9981$  |
| × VOLT58 | $y = 26.569x + 0.0844$<br>$R^2 = 0.9977$ |
| ✱ VOLT59 | $y = 49.476x + 0.0692$<br>$R^2 = 0.994$  |
| ● VOLT60 | $y = 29.15x + 0.1219$<br>$R^2 = 0.9952$  |

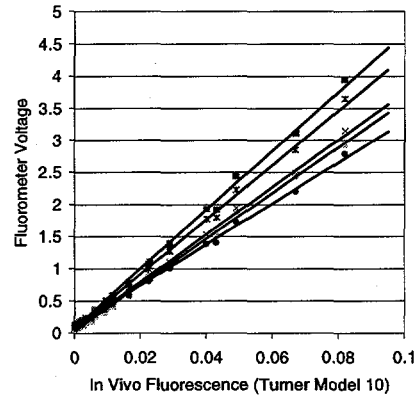


Fig. 2b

|          |  |
|----------|--|
| ■ VOLT61 | $y = 45.875x + 0.0806$<br>$R^2 = 0.9977$ |
| △ VOLT62 | $y = 35.648x + 0.0408$<br>$R^2 = 0.9987$ |
| × VOLT63 | $y = 36.845x + 0.0597$<br>$R^2 = 0.9985$ |
| ✱ VOLT64 | $y = 42.442x + 0.0661$<br>$R^2 = 0.9981$ |
| ● VOLT65 | $y = 31.918x + 0.1005$<br>$R^2 = 0.9984$ |

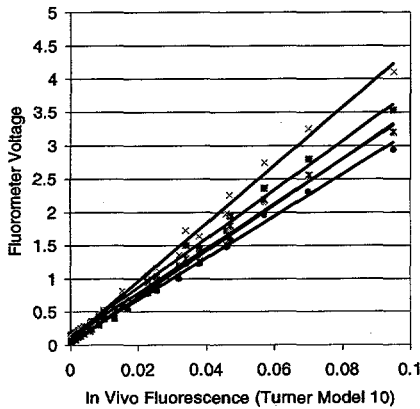


Fig. 2c

|          |  |
|----------|--|
| ■ VOLT66 | $y = 36.678x + 0.1346$<br>$R^2 = 0.9955$ |
| △ VOLT67 | $y = 33.575x + 0.1096$<br>$R^2 = 0.996$  |
| × VOLT68 | $y = 43.569x + 0.087$<br>$R^2 = 0.9949$  |
| ✱ VOLT69 | $y = 34.654x + 0.028$<br>$R^2 = 0.9929$  |
| ● VOLT70 | $y = 31.571x + 0.0478$<br>$R^2 = 0.9965$ |

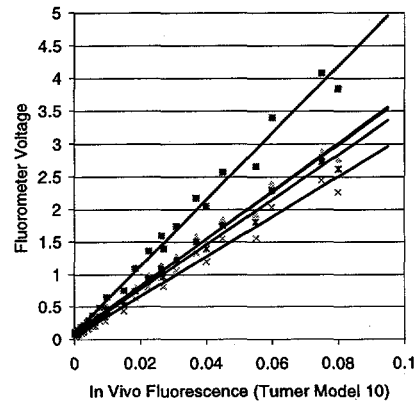
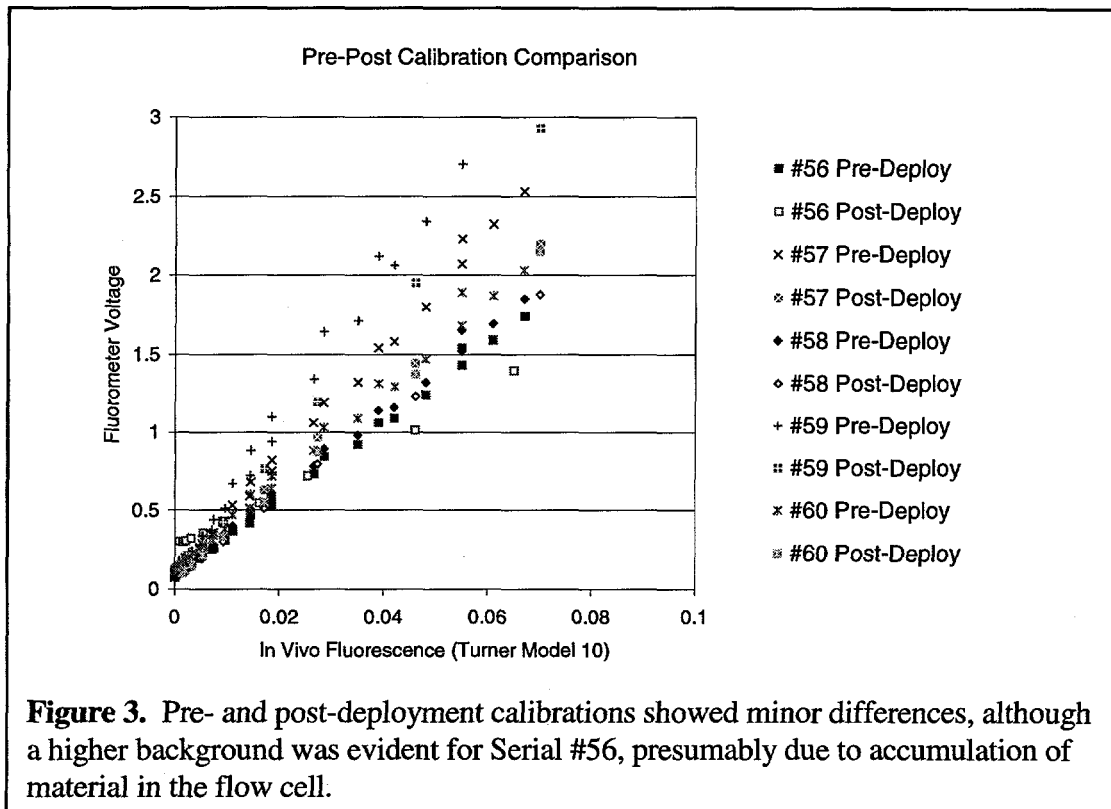


Fig. 2d

|          |  |
|----------|--|
| ■ VOLT71 | $y = 51.169x + 0.0958$<br>$R^2 = 0.9911$ |
| △ VOLT72 | $y = 36.145x + 0.0967$<br>$R^2 = 0.9926$ |
| × VOLT73 | $y = 30.728x + 0.044$<br>$R^2 = 0.9881$  |
| ✱ VOLT74 | $y = 34.429x + 0.081$<br>$R^2 = 0.9914$  |
| ● VOLT75 | $y = 36.581x + 0.0815$<br>$R^2 = 0.9986$ |

**Figure 2.** A regression analysis of Turner Designs vs. WETLabs WETStar fluorescence was performed for the portion of the data exhibiting a linear relationship.



*Relationships among in vivo fluorescence, chlorophyll concentrations and total particulate carbon concentrations in water column and sediments*

Samples were collected during a series of cruises in continental shelf waters off Cape Hatteras, NC. The cruise information is given in Table 1. Water column samples were generally collected using the ships' CTD profiling packages with Niskin bottles mounted on a General Oceanics Rosette®. Chlorophyll and phaeopigment (chlorophyll) content of these samples were determined by filtration onto 2.5 cm glass fiber (Whatman GFF) filters, extraction in 90% acetone/Milli-Q water for a minimum of 12 h at  $-20^{\circ}$  C and subsequent fluorometric analysis (Smith et al., 1981). Samples for total particulate carbon (TPC) were filtered onto Poretics 2.5 cm diameter 0.45  $\mu$ m silver filters and dried in a dessicator. The carbon and nitrogen content on the silver filters was determined using a Carlo-ERBA NA1500 Carbon/Nitrogen Analyzer with sulfanilamide as a primary standard. Total suspended matter (TSM) concentrations were determined by in-line filtration onto tared 0.45  $\mu$ m polycarbonate filters (Poretics). Filters were rinsed with 10 mL ammonium formate (1 M) to remove salts, rinsed with Milli-Q water, dried in dessicators and re-weighed until a consistent weight was achieved. Fluorescence of whole water samples was determined by reading a 10 mL sample in a 13x100 mm glass cuvette in the Turner Designs Model 10 Fluorometer calibrated using pure chlorophyll *a* as described above. Sediment samples collected from several locations on the continental shelf off Cape Hatteras, NC. Locations and dates of collection are given in Table 2. , Mooring Station 17 ( $36^{\circ} 7.455' N$ ,  $74^{\circ} 54.458' W$ ) and Mooring Station 22 ( $35^{\circ} 38.285' N$ ,  $74^{\circ} 51.495' W$ ). Sediment was taken from the footpads of bottom moored instrument tripods after their recovery. The samples were frozen in

plastic bags and returned to the laboratory for analysis. For sediment samples, a portion of the sediment sample was resuspended in artificial seawater. Aliquots of this suspension were used for analysis of chloropigments, total particulate carbon and total suspended matter as described above. The fluorescence of the sediment suspension was determined for a series of dilutions with artificial seawater.

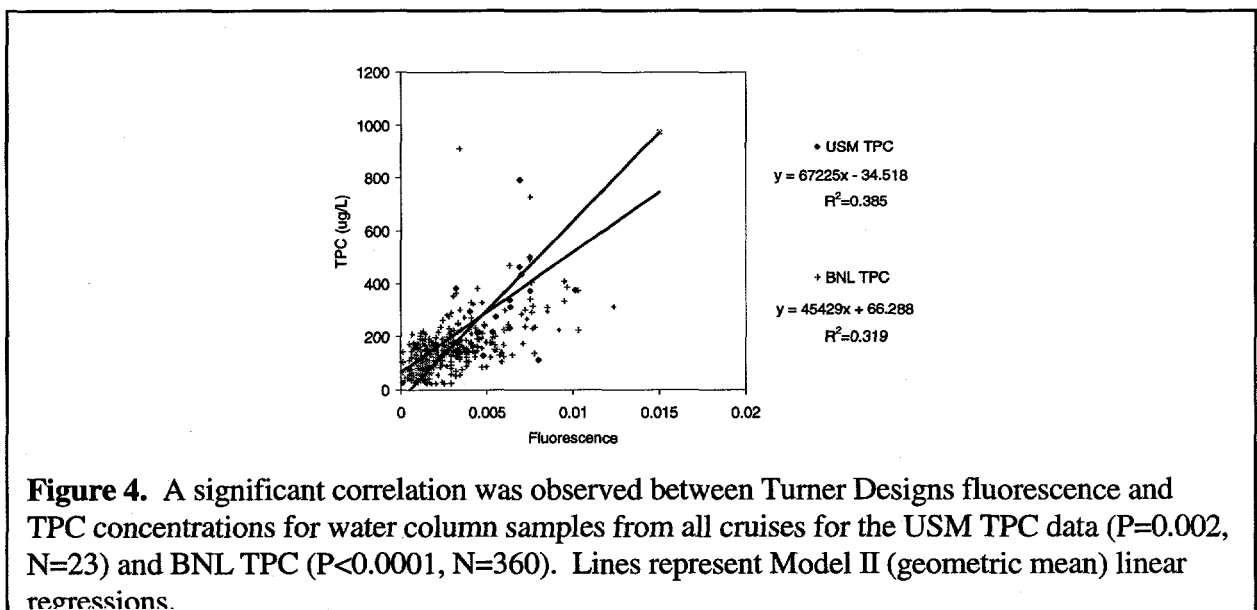
**Table 1. Cruise information for collection of fluorescence, chloropigment (Chl), total particulate carbon (TPC) and total suspended matter (TSM) data for the water column**

| Vessel                      | Dates        | Type of Samples |
|-----------------------------|--------------|-----------------|
| N/S Oregon II               | 17-23 Feb 96 | Chl, TPC, TSM   |
| R/V Endeavour (EN280)       | 12-19 Mar 96 | Chl, TPC, TSM   |
| R/V Seward Johnson (SJ9607) | 19-27 Jul 96 | Chl, TPC, TSM   |
| R/V Oceanus                 | 9-13 Oct 96  | Chl, TPC        |

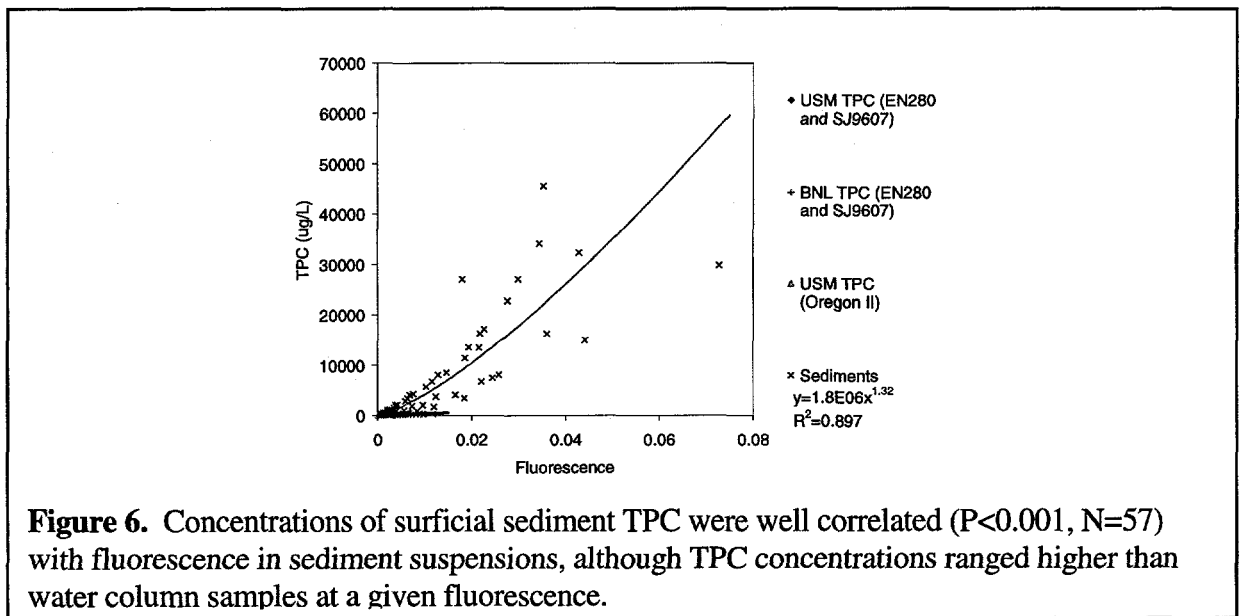
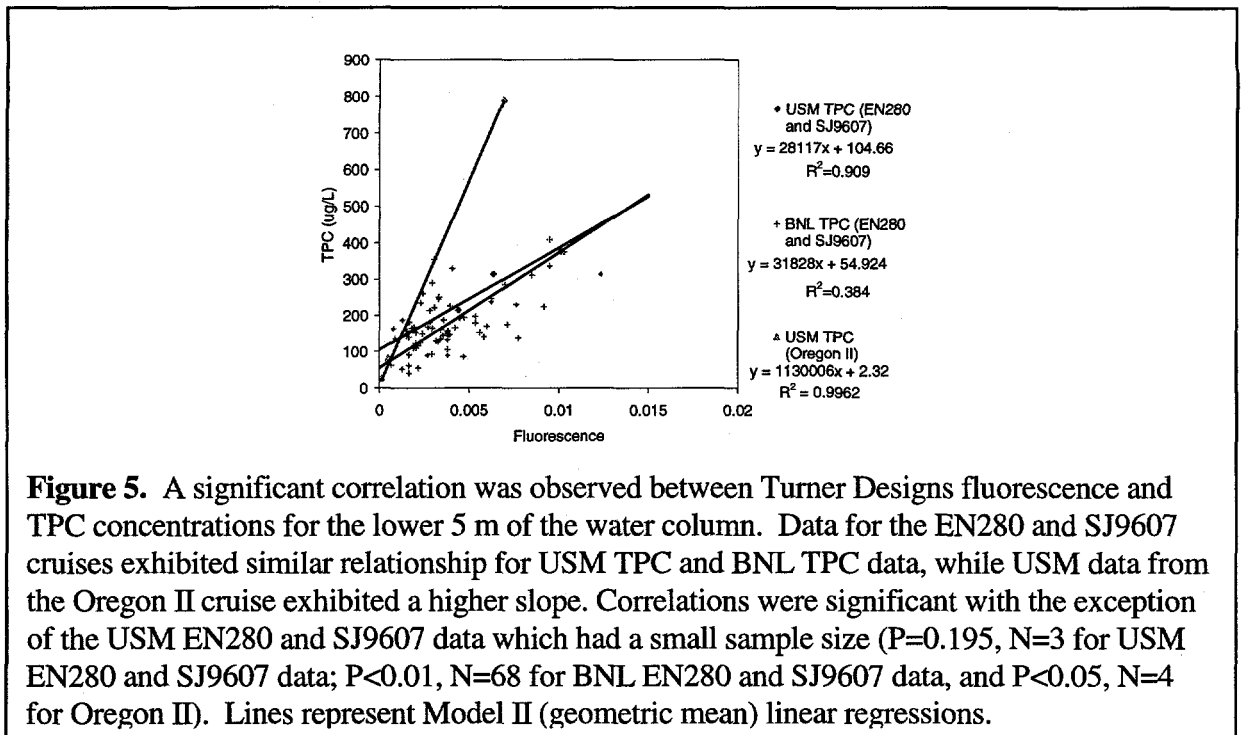
**Table 2. Dates and locations of sediment sample collection.**

| Vessel      | Date of Collection | Station | Latitude (N) | Longitude (W) | Depth (m) |
|-------------|--------------------|---------|--------------|---------------|-----------|
| R/V Gyre    | 5/24/1993          | 16      | 36° 5.31'    | 75° 21.93'    | 25        |
| R/V Gyre    | 7/2/1994           | 10      | 36° 8.2998'  | 75° 10.5'     | 30        |
| R/V Oceanus | 5/12/96            | 17      | 36° 7.455'   | 74° 54.458'   | 75        |
| R/V Oceanus | 10/14/96           | 22      | 35° 38.285'  | 74° 51.495'   | 77        |

Comparisons of whole water fluorescence (i.e., measured with the Turner Designs Model 10) and TPC concentrations in water samples revealed a significant correlation for the entire water column (Fig. 4) and for the lower 5 m (Fig. 5) although there was considerable scatter in the data. Relationships determined for the TPC data determined by our laboratory (USM TPC) and that determined by Brookhaven National Laboratories (BNL TPC) were similar. The data for fluorescence and TPC in suspended sediment covered a much larger range than the water column data, and TPC values at a given fluorescence were generally higher than observed for the water column data (Fig. 6).



**Figure 4.** A significant correlation was observed between Turner Designs fluorescence and TPC concentrations for water column samples from all cruises for the USM TPC data ( $P=0.002$ ,  $N=23$ ) and BNL TPC ( $P<0.0001$ ,  $N=360$ ). Lines represent Model II (geometric mean) linear regressions.



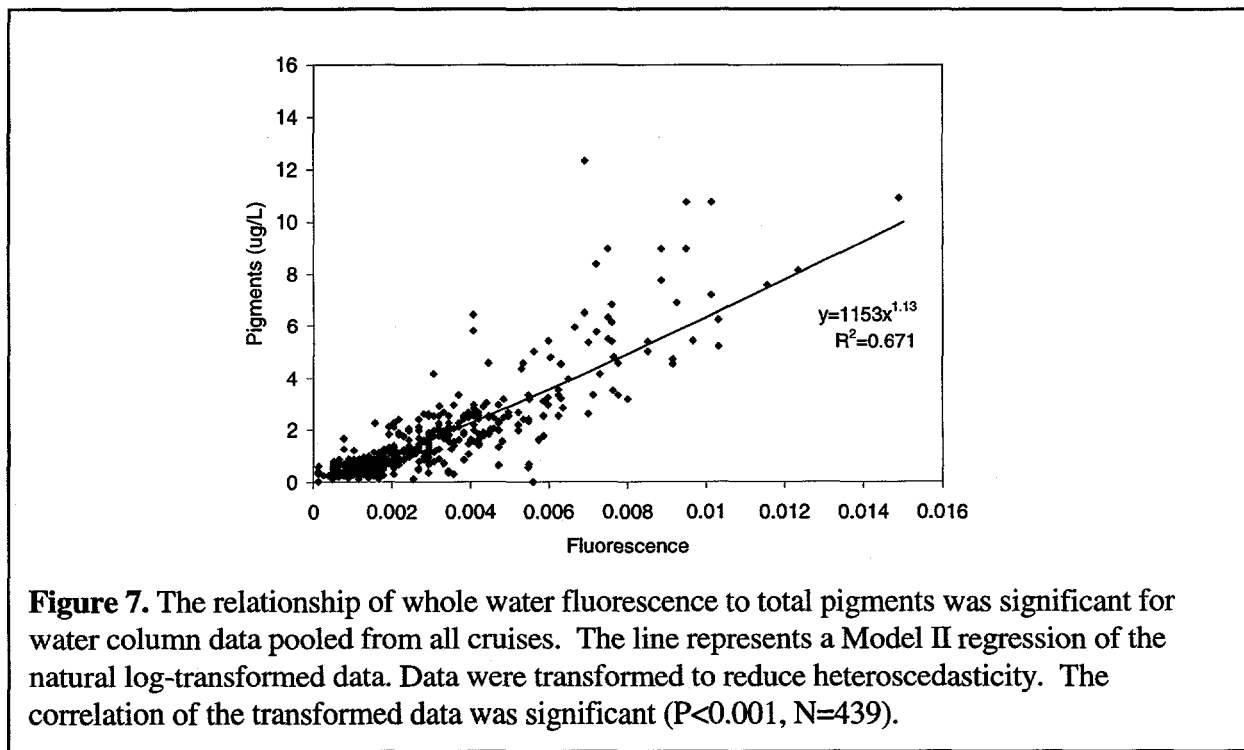
The higher slope in the Oregon II data (Fig. 5) may have been due to increased resuspension of sediment due to severe weather. Consistent with the view that resuspension was important was the fact that the phaeopigments accounted for a larger proportion of total pigments in near-bottom samples during the Oregon II cruise as compared to EN280 and SJ9607 cruises (Table 3). Phaeopigments generally accounted for the majority of pigments in sediment samples (data not shown).



| CRUISE:                               | EN280 and SJ9607 | Oregon II |
|---------------------------------------|------------------|-----------|
| Mean Phaeopigment/Total Pigment Ratio | 0.241            | 0.371     |
| Std. Dev.                             | 0.131            | 0.225     |
| N                                     | 202              | 77        |
| <i>t</i> -statistic                   | -5.96            |           |
| <i>P</i> two tailed ( $T \leq t$ )    | 7.71E-09         |           |

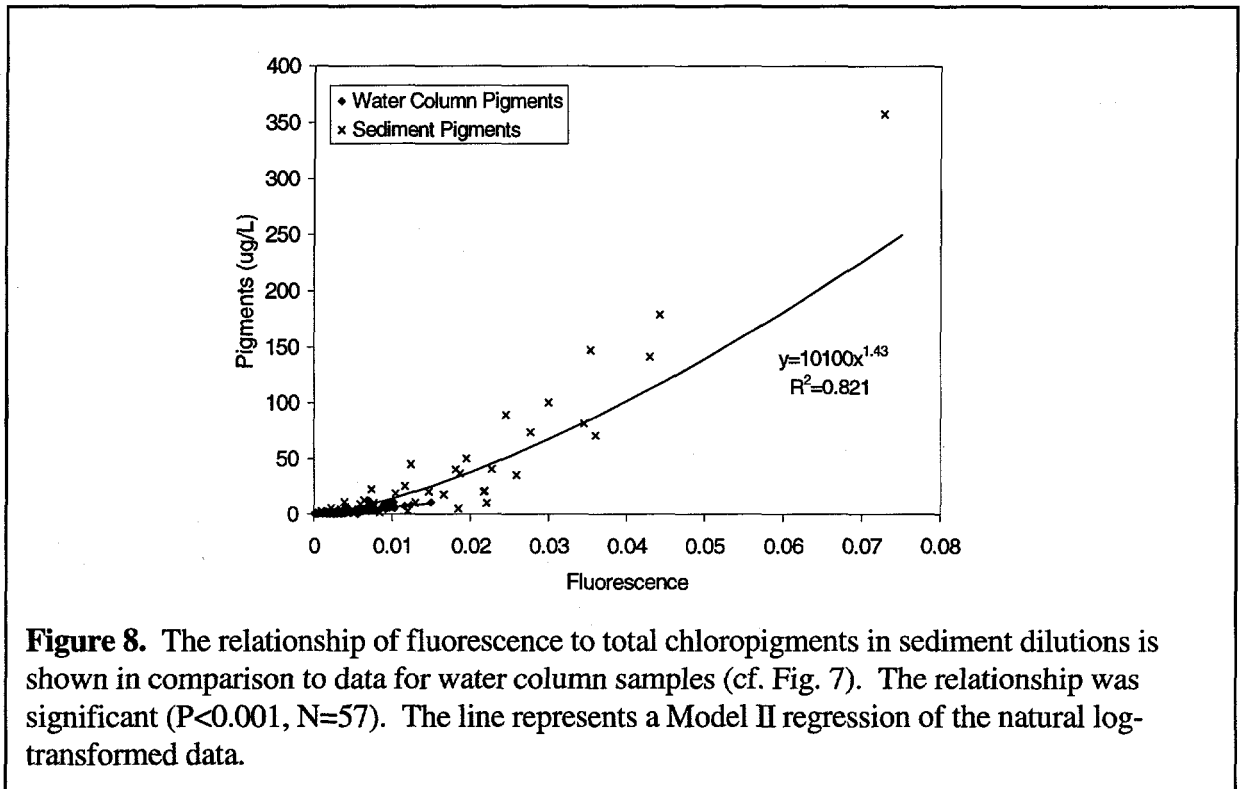
These results are evidence that the calibration of fluorescence to TPC in near-bottom waters was dependent on physical conditions. In conditions when the source of particulate matter was primarily from water column processes (sinking, in situ growth, transport), then a water column calibration (Fig. 5) would be most appropriate. During periods of increased bottom stress that could lead to sediment resuspension, the sediment calibration was probably more appropriate. It follows logically that distance from the bottom would also be a factor that would influence the fluorescence/TPC relationship. Such considerations should be taken into account when attempting to relate fluorescence to TPC concentrations.

The relationship between total chloropigments (chlorophyll + phaeopigments) and whole water fluorescence was highly significant for data pooled from all cruises (Fig. 7). The relationship was quite consistent, despite the fact that data were collected from throughout the water column, various times of the day, and different seasons (Feb-Oct).



**Figure 7.** The relationship of whole water fluorescence to total pigments was significant for water column data pooled from all cruises. The line represents a Model II regression of the natural log-transformed data. Data were transformed to reduce heteroscedasticity. The correlation of the transformed data was significant ( $P < 0.001$ ,  $N = 439$ ).

The relationship of fluorescence to total pigments in sediments was also significant (Fig. 8), and was comparable to that observed for water column pigments for the corresponding range of fluorescence. As for TPC, much higher concentrations of pigments were attained with sediment dilutions than was observed for water column samples. The fluorescence yield of pigments in the water column is known to vary as a result of several factors (e.g., Strass, 1990), and this may have contributed to the scatter observed in fluorescence-pigment relationships. However, despite these sources of variance, fluorescence was a skillful predictor of pigment concentrations over a wide concentration range and for a wide variety of sample types and conditions.



**Figure 8.** The relationship of fluorescence to total chloropigments in sediment dilutions is shown in comparison to data for water column samples (cf. Fig. 7). The relationship was significant ( $P<0.001$ ,  $N=57$ ). The line represents a Model II regression of the natural log-transformed data.

### *In-situ Time Series of Fluorescence*

Initial characterizations of fluorescence variations in the benthic boundary layer have been achieved using a multi-sensor fiber optic fluorometer (D'Sa et al., 1994, 1997) specifically developed for the Department of Energy's Oceans Margins Program. The instrument was used to conduct time-series observations of fluorescence in the bottom 5 m of the water column at a 20 m site near Duck, NC. The instrument was deployed for a 29 d period from July 24 - August 22, 1994, in conjunction with physical observations of currents determined using a BASS (Benthic Acoustic Stress Sensor) tripod in collaboration with Williams and Churchill (Woods Hole Oceanographic Institution). A manuscript is in preparation.

Additional deployments of WETLabs WETStar Miniature Fluorometers were accomplished in conjunction with deployment of other instrumentation during the field component of the Ocean Margins Program 1996 field study. The instruments were mounted on bottom tripods at Mooring

Stations 17 (36° 7.455' N, 74° 54.458' W) and 26 (35° 27.601' N, 74° 51.816' W) at 5 depths within the bottom 5 m from February – July 1996. In July, the instruments were recovered and serviced. Instruments were redeployed only at Mooring Station 22 where they remained until October 1996. Other instrumentation on the tripods included Benthic Acoustic Stress Sensors (BASS, Williams et al., 1987), optical backscatter sensors (OBS, D&A Instruments), thermistors and transmissometers.

Thus far only a preliminary analysis of the time-series data has been achieved. Distinct episodic features in bottom fluorescence were observed that corresponded with peaks in beam attenuation and optical backscatterance (Fig. 9). These features appeared to be related to increases in current velocities. These data are being evaluated in a collaborative effort with J. Churchill and A. Williams of Woods Hole Oceanographic Institution and T. Gross of Skidaway Institute of Oceanography. The results presented in this report will provide the basis for estimation of TPC and pigment concentrations from time-series of fluorescence. Such information will then be analyzed in conjunction with physical data to estimate transport.

### Project Impact

Near-bottom transport may represent an important process controlling the fate of organic matter and its availability to benthic ecosystems. Knowledge of lateral transport of organic matter in benthic boundary layers is critical to determining linkages of carbon budgets between inner and outer shelf regions and between shelf and deep ocean environments. A variety of evidence suggests such linkages may be important in the Cape Hatteras shelf and slope regions. Yet little is known about the magnitude of such transport and its relationship to physical processes. Photosynthetic pigments (e.g., chlorophyll and its degradation products) can serve as tracers of organic matter, and concentrations of pigments can be estimated using fluorescence. Previous studies leave many unanswered questions regarding the distribution of chlorophyll in the benthic boundary layer, its resuspension and transport in association with near-bottom flows, and the quantitative significance of carbon export off the shelf via lateral transport along the bottom. This project will provide some of the answers to these questions, which are integral to the DOE Ocean Margins Program's goals to better understand the sources, sinks and fate of carbon in ocean margins so as to evaluate their role in global carbon cycles.

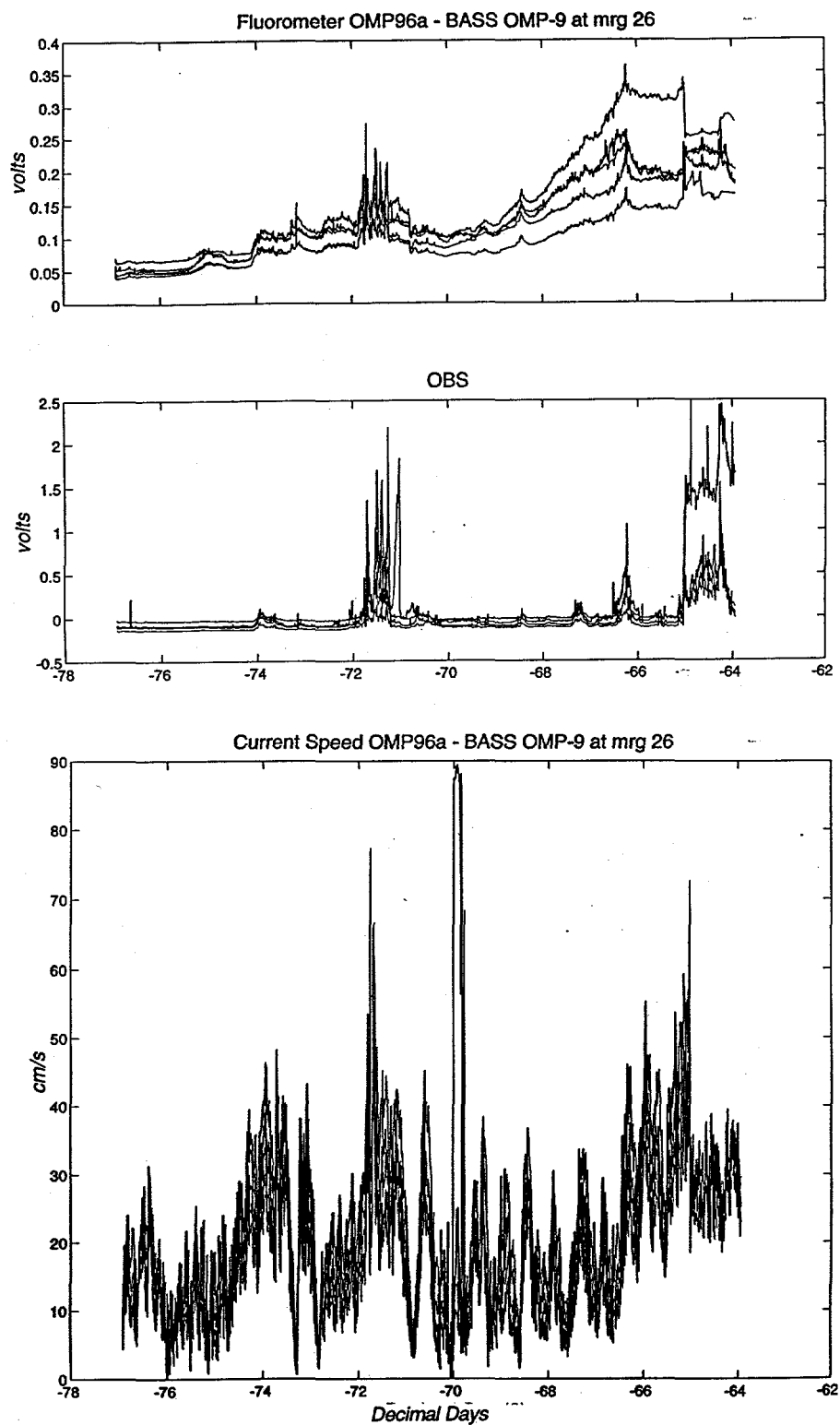
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Sherwood CR, Butman B, Cacchione DA, Drake DE, Gross TF, Sternberg RW, Wiberg PL, Williams AJ III (1994) Sediment-transport events on the northern California continental shelf during the 1990-1991 STRESS experiment. *Cont Shelf Res* 14:1063-1099

Smith RC, Baker KS, Dustan P (1981) Fluorometric techniques for the measurement of oceanic chlorophyll in the support of remote sensing. University of California-San Diego, Scripps Institution of Oceanography, SIO Ref. 81-17, 14 pp.

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**Figure 9.** Uncalibrated time-series of fluorescence and optical backscatter from the BASS tripod at mooring station 26 are shown in relation to current speed.

## Project Outcomes-Deliverables

### Scientific Publications

D'Sa, E. J., Lohrenz, S. E. Asper, V. L., Walters, R. A. (1997): Time series measurements of chlorophyll fluorescence in the oceanic bottom boundary layer with a multi-sensor fiber-optic fluorometer. *J. Atmosph. Ocean. Tech.* 14, 889-896.

D'Sa, E. J., S.E. Lohrenz, J. Churchill, V. L. Asper, J. Largier and A. J. Williams, III  
Chloropigment distribution and transport on the inner shelf off Duck, NC. Manuscript in preparation.

### Technical Publications

D'Sa, E. J., Lohrenz, S. E. Asper, V. L., Walters, R. A., Morris, M. J., Rathbun, C. (1994): A multi-sensor in situ fiber optic fluorometer. *Proc. Soc. Photo-Opt. Instrum. Engineer., Ocean Optics XII* 2258, 33-43.

### Published Abstracts

Lohrenz, S. E., C. E. Rathbun, E. J. D'Sa and V. L. Asper (1996) High concentrations of peridinin in a thin subsurface layer in near shore waters off Cape Hatteras, N.C. *EOS, Transactions, American Geophysical Union*, 76, 3.

Lohrenz, S. E., E. J. D'Sa, V. L. Asper and C. E. Rathbun (1996) Temporal variations in chlorophyll fluorescence in the benthic boundary layer at LEO-15. *Journal of the Mississippi Academy of Sciences*, 41, 1, 64.

D'Sa, E. J., S. E. Lohrenz, J. H. Churchill, A. J. Williams, III, and V. L. Asper (1996) Pigment distribution and transport in the benthic boundary layer at the Cape Hatteras inner shelf, *EOS, Transactions, American Geophysical Union*, 76, 3.

D'Sa, E. J., S. E. Lohrenz, V. L. Asper and J. H. Churchill (1996) Observations of pigments and sediment suspensions in the benthic boundary layer at the Cape Hatteras inner shelf. *Journal of the Mississippi Academy of Sciences*, 40, 1, 65.

Lohrenz, Steven E., C. E. Rathbun, E. J. D'Sa and V. L. Asper (1995) High abundance of dinoflagellates observed in a thin subsurface layer in nearshore waters off Cape Hatteras, N.C., *Journal of the Mississippi Academy of Sciences*, 40, 1, 66.

D'Sa, E. J., Steven E. Lohrenz, and V. L. Asper (1995) Vertical microscale distributions of chlorophyll fluorescence in the benthic boundary layer measured using a fiber optic fluorometer, *Journal of the Mississippi Academy of Sciences*, 40, 1, 67.

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#### *Presentations at National/International Meetings*

Lohrenz, S. E., C. E. Rathbun, E. J. D'Sa and V. L. Asper (1996) High concentrations of peridinin in a thin subsurface layer in nearshore waters off Cape Hatteras, N.C. American Geophysical Union Ocean Sciences Meeting, February 12-16, San Diego, CA.

D'Sa, E. J., S. E. Lohrenz, J. H. Churchill, A. J. Williams, III, and V. L. Asper (1996) Pigment distribution and transport in the benthic boundary layer at the Cape Hatteras inner shelf, American Geophysical Union Ocean Sciences Meeting, February 12-16, San Diego, CA.

Lohrenz, S. E., E. J. D'Sa, V. L. Asper and C. E. Rathbun (1996) Temporal variations in chlorophyll fluorescence in the benthic boundary layer at LEO-15. Mississippi Academy of Sciences, Sixtieth Annual Meeting, February 22-23, Jackson, MS.

D'Sa, E. J., S. E. Lohrenz, V. L. Asper and J. H. Churchill (1996) Observations of pigments and sediment suspensions in the benthic boundary layer at the Cape Hatteras inner shelf," Mississippi Academy of Sciences, Sixtieth Annual Meeting, February 22-23, Jackson, MS.

Lohrenz, Steven E., E. J. D'Sa, V. L. Asper and C. E. Rathbun (1995) Pigment dynamics in coastal benthic boundary layers, The Oceanography Society, Fourth Scientific Meeting, April 18-21, Newport, Rhode Island.

Lohrenz, Steven E., C. E. Rathbun, E. J. D'Sa and V. L. Asper (1995) High abundance of dinoflagellates observed in a thin subsurface layer in nearshore waters off Cape Hatteras, NC, Mississippi Academy of Sciences, Fifty-ninth Annual Meeting, February 9-10, Biloxi, MS.

D'Sa, E. J., Steven E. Lohrenz, and V. L. Asper (1995) Vertical microscale distributions of chlorophyll fluorescence in the benthic boundary layer measured using a fiber optic fluorometer, Mississippi Academy of Sciences, Fifty-ninth Annual Meeting, February 9-10, Biloxi, MS.

D'Sa, E. J., S. E. Lohrenz, and V. L. Asper (1994) A multi-sensor in situ fiber optic fluorometer. Society of Photo-Optical Instrumentation Engineers International Conference on Ocean Optics XII, Bergen, Norway, June.

D'Sa, E. J., S. E. Lohrenz, and V. L. Asper (1994) Multi-sensor in situ fiber optic fluorometer: design and initial results. American Geophysical Union/American Society of Limnology and Oceanography, San Diego, CA, February.

#### *Workshops*

D'Sa, E. J., Steven E. Lohrenz, V. L. Asper, and J. H. Churchill (1995) Observations of pigments and sediment suspensions in the benthic boundary layer at the Cape Hatteras inner shelf, Middle

Atlantic Bight Physical Oceanography and Meteorology Workshop, November 2-3, State University of New York, Stony Brook, NY.

Lohrenz, Steven E., E. J. D'Sa and V. L. Asper (1995) Time series of high resolution observations of gradients in pigment fluorescence at LEO-15 using a multi-sensor fiber optic fluorometer, LEO-15 Workshop, November 28-29, NOAA National Undersea Research Program, Tuckertown, NJ.

Lohrenz, Steven E., J. H. Churchill, E. J. D'Sa, A. J. Williams, III, and V. L. Asper (1995) Episodic transport of pigments and particulate organic carbon in the benthic boundary layer at the Cape Hatteras inner shelf, Department of Energy, Ocean Margins Program Investigators Workshop, September 24-27, Savannah, Georgia.

#### *Invited Presentations*

Lohrenz, Steven E. (1995) Observations of chlorophyll in the benthic boundary layer, Invited lecture, Louisiana Universities Marine Consortium, February 7, Cocodrie, LA.

#### *Ph.D. Dissertation*

D'Sa, E. J. (1996) Pigment dynamics in a coastal bottom boundary layer and its relation to the physical regime: measurements using an *in situ* fiber-optic fluorometer. Ph.D. Dissertation, University of Southern Mississippi.

#### *M.S. Thesis*

Chen, N. The relationship of chloropigment fluorescence to composition of sediments in the Mid-Atlantic Bight. M.S. Thesis, May 1998.

#### *Data submission to Brookhaven National Laboratory Oceanographic Database*

Data for chlorophyll and TPC have been submitted to the Brookhaven National Laboratory Oceanographic Database.