

OPTICAL PROPERTIES OF MISSISSIPPI RIVER PLUME AND ADJACENT WATERS DURING MARCH 1991

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Abstract

Variations in attenuation of irradiance (total photosynthetically active radiation and downwelling spectral irradiance) were related to other optical measurements (beam c , solar-stimulated fluorescence) and to concentrations of particulate and dissolved materials determined from analyses of discrete samples. Four sampling locations were studied representative of conditions ranging from very turbid low salinity plume water to very oligotrophic water over the slope. Highest values of K_{par} (over 2.5 m^{-1}) were observed at the surface in a low salinity plume station, although there was considerable scatter in the values. Lowest values were observed at a slope water station ($< 0.8 \text{ m}^{-1}$). The utility of measurements of L_{683} as an index of chlorophyll concentrations was found to be limited. Extracted chlorophyll concentrations tended to be overestimated in near surface waters and underestimated at depth. Profiles of beam c revealed high values ($> 3 \text{ m}^{-1}$) in surface waters of the shelf stations. Spectral attenuation minima at shelf stations were in the vicinity of 540-580 nm. Lowest values of attenuation were observed at the slope water station where the attenuation minimum was around 490 nm. A spectral attenuation model reproduced measured spectra remarkably well considering variations in attenuation spanned over an order of magnitude. It was evident that in shelf waters during this period, absorption and scattering were dominated by dissolved organic carbon and suspended particulate matter.

Introduction

Light is known to be a critical parameter regulating primary production in turbid waters of the Mississippi River plume (Lohrenz et al., 1990). Optical properties in coastal waters are complex and variable, due to the high levels of terrestrially derived constituents that contribute to absorption and scattering of irradiance. Information about the irradiance field can be obtained by direct measurements with irradiance sensors. Spectral resolution of irradiance can provide an indication of the type of constituents that contribute to attenuation of irradiance. In addition, other optical instrumentation (transmissometer, fluorometers) can provide information about distributions of optically active materials with greater spatial resolution than is possible using discrete sampling techniques. Such information may be useful in the development of models (e.g., Gallegos et al., 1990) that permit the characterization of irradiance field on the basis of selected input variables.

Here we describe a series of data collected in conjunction with the NOAA Nutrient Enhanced Coastal Ocean Program (NECOP) during March 1991 in the vicinity of the Mississippi River plume. Our efforts focused on the description of variations in attenuation of irradiance as related to other optical measurements (beam c , solar-stimulated fluorescence) and as related to concentrations of particulate and dissolved materials determined from analyses of discrete samples. The

objectives of this research included the following: 1) to understand the predominate factors that mediate attenuation of irradiance in coastal waters of the northern Gulf of Mexico, and 2) to develop predictive models for irradiance attenuation as input in photosynthesis-irradiance models.

Methods

Data from four general locations occupied during the 4-17 March 1991 cruise aboard the *N/S Malcolm Baldrige* were examined. Locations of stations along with the type of measurement profile were given in Table 1.

Profiles of the diffuse attenuation coefficient of photosynthetically active radiation, K_{par} (400-700 nm), and temperature were determined using a Biospherical Instruments PNF300. This instrument also measured upwelling radiance at 683 nm, L_{683} . Based on assumed values of the absorption coefficient of light at 683 nm ($a(683)$, 0.48 m^{-1}), spectrally averaged pigment-specific absorption (a^*_{pb} , 0.04 m^{-1}) and quantum yield of fluorescence (ϕ_p , $0.045 \text{ (mol quanta)}^{-1}$), an estimate of chlorophyll concentration can be derived from L_{683} (Chamberlin et al., 1990).

An instrument system was used to provide profiles of conductivity, temperature, pressure/depth (Neil Brown CTD) and beam attenuation coefficient (beam c , m^{-1}) (SeaTech 10 cm path transmissometer). Data were provided courtesy of T. Nelsen. Beam c data were not available at Station D.

Table 1. Times and locations of optical stations. UT=universal time, Op# is an event identification number

Station	UT	Op#	Lat(N)	Lon(W)	Remarks
A	1608	91067238	28.881	89.620	Spectroradiometer
	1630	91067239	28.883	89.619	PNF-300
	1707	91067240	28.886	89.631	CTD 82
B	1720	91069296	28.750	90.129	PNF-300
	2043	91069302	28.791	90.156	Spectroradiometer
	2303	91069308	28.755	90.138	CTD 104
C	1624	91073380	28.909	89.490	Spectroradiometer
	1650	91073381	28.909	89.491	PNF-300
	1708	91073382	28.909	89.491	CTD 119
D	1557	91074405	28.244	88.812	PNF-300
	1631	91074406	28.240	88.822	Spectroradiometer
	1644	91074407	28.238	88.824	CTD 124

Samples for analysis of suspended particulate matter and photosynthetic pigments were collected in conjunction with CTD profiling using a rosette sampler (General Oceanics) fitted with 10 L Niskin bottles. Total suspended particulate material was determined by passing a known volume through a pre-rinsed, pre-weighed 47 mm GF/F filter followed by rinsing, drying and re-weighing the filter. Chlorophyll *a* and pbacopigment analyses were performed on board ship using an extraction technique modified from Shoaf and Liem (1976). Samples were filtered on Whatman GF/F glass fiber filters, which were then immersed in 5 ml of DMSO/acetone (40/60) and allowed to extract in darkness for 1 h. After extraction, samples were centrifuged and fluorescence was measured before and after acidification using a Turner Model 10 fluorometer (Holm-Hansen et al., 1965). Calibrations were made using a Sigma chlorophyll *a* standard.

Downwelling spectral irradiance was determined using a Li-Cor LI-1800-UW underwater spectroradiometer. The instrument was deployed at times and locations given in Table 1. A series of scans (2 nm resolution) were made at selected depths in the upper mixed layer and spectral attenuation at each wavelength band was calculated as follows:

$$(1) \quad k(\lambda, z) = \ln [I(\lambda, z_{i+1}) / I(\lambda, z_i)] / (z_i - z_{i+1})$$

where $I(\lambda, z_i)$ is the irradiance at wavelength λ and depth z_i .

Measurements of diffuse spectral attenuation were compared to estimates derived from a spectral

attenuation model. The diffuse spectral attenuation coefficient, k , was calculated for all wavebands using the relation of Kirk (1984) as described in Gallegos et al. (1990). The model required that total spectral absorption ($a_t(\lambda)$, m^{-1}) and scattering coefficients ($b(\lambda)$, m^{-1}) be determined. The total spectral absorption coefficient, $a_t(\lambda)$, was estimated by summation of absorption due to individual constituents. The spectral absorption coefficient for particulate matter, $a_p(\lambda)$, was estimated by substituting the suspended particulate matter concentration for total suspended solids in Eq. 6 of Gallegos et al. (1990). The coefficient for absorption due to phytoplankton was determined by multiplying the chlorophyll-specific absorption coefficient, $a_{ph}^*(\lambda)$, that was obtained from Table 4 of Gallegos et al. (1990) by the measured chlorophyll *a* concentration. Values of spectral absorption of dissolved matter were estimated by substituting dissolved organic carbon concentrations (DOC) into Eq. 5 from Gallegos et al. (1990). DOC concentrations at our sampling locations were estimated from salinity based on a salinity-concentration relationship determined by R. Benner (unpublished) on the cruise leg immediately preceding ours. Estimated values were 1.2 mg l⁻¹ (Station A), 1.1 mg l⁻¹ (Station B), and 1.9 mg l⁻¹ (Station C). The absorption by dissolved organic matter at the slope water Station D was taken as zero because Eq. 5 from Gallegos et al. (1990) was applicable only for higher concentrations as encountered in shelf waters. The scattering coefficient, $b(\lambda)$, was assumed to be invariant with wavelength and was calculated by assuming that the only significant absorbing substance in the 720 nm waveband was due

Table 2. Water sample data from optical stations. Symbols: Chl=chlorophyll, Phaeo=phaeopigments, SPM=suspended particulate matter, Sal=salinity, n.d.=no data available due to high salt blank, absorption due to suspended matter at Station D was assumed to be negligible.

Station	Depth (m)	Chl (mg m ⁻³)	Phaeo (g m ⁻³)	SPM	Sal	REMARKS
A	2	1.37	0.28	0.540	25.4	cloudy skies, variable light some wind and waves plume water
	5	1.53	0.36			
	8	0.69	0.49			
B	2	3.37	1.79	1.4	26.3	clear skies, some wind and waves good ship angle shelf water
	8	3.78	2.36			
	14	2.60	2.35			
	16	2.09	1.28			
	27	0.34	0.81			
	32	0.54	0.92			
C	2	3.30	4.14	16.1	19.5	cloudy skies, some light variation, calm seas with some ship roll plume water
	4	2.76	5.69			
	6	0.70	0.68			
	9	0.26	0.34			
	17	0.23	0.50			
	26	0.35	0.67			
D	2	0.31	0.26	n.d.	36	cloudy gray skies, seas 1-2 m offshore, blue water
	20	0.36	0.16			
	34	0.57	0.29			
	50	0.56	0.29			
	95	0.08	0.13			

to water (i.e., $a(720)=a_w(720)=1.002 \text{ m}^{-1}$, cf. Gallegos et al., 1990). The scattering coefficient, $b(720)$, was then calculated from measured values of $k(720)$ by rearranging Eq. 2 in Gallegos et al. (1990) and the resulting value was used for all wavebands. In the case of Station D, detection limits of the spectroradiometer did not permit an assessment of $k(720)$. Instead, $b(550)$ was estimated from chlorophyll *a* concentrations using Eq. 18 of Morel (1988). This equation was derived for case I waters. The resulting values of b were 2.19, 2.56, 33.7 and 0.152 m^{-1} for Stations A, B, C and D respectively. The diffuse spectral attenuation, k , was calculated for all wavebands using the relation of Kirk (1984) as described in Gallegos et al. (1990).

Results

The four sampling locations (Fig. 1) included conditions ranging from very turbid low salinity plume water (Station C) to very oligotrophic water over the slope (Station D). Extracted chlorophyll *a* concentrations

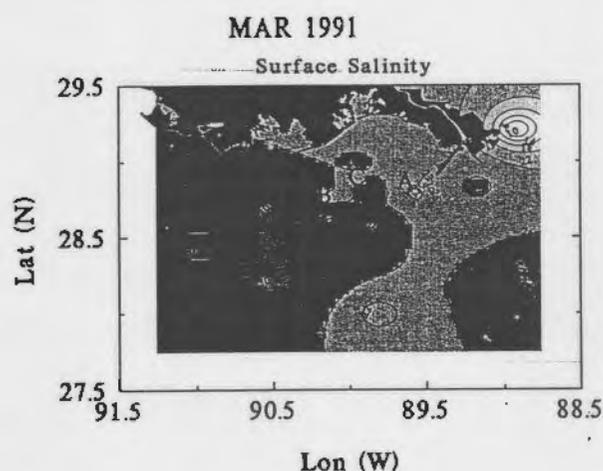


Fig. 1. Location of optical stations in relation to surface salinity based on available data collected during the 4-17 March 1991 cruise aboard the N/S *Malcolm Baldrige*.

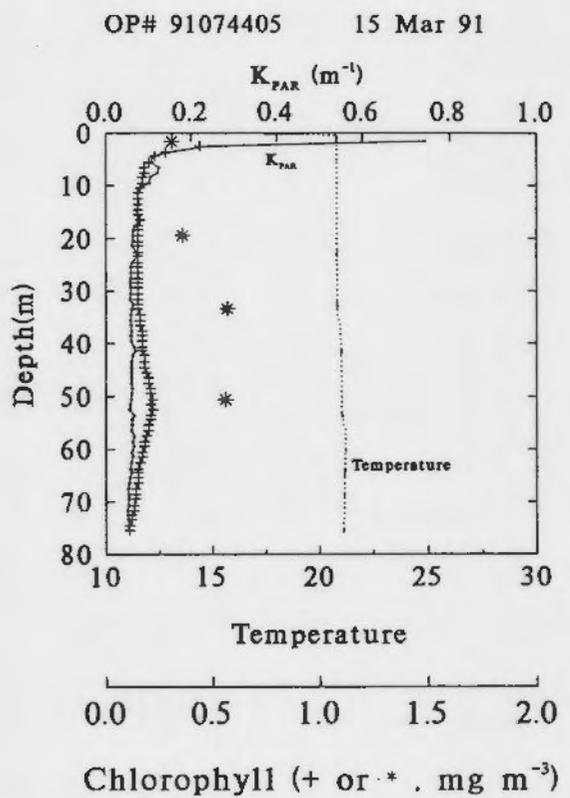
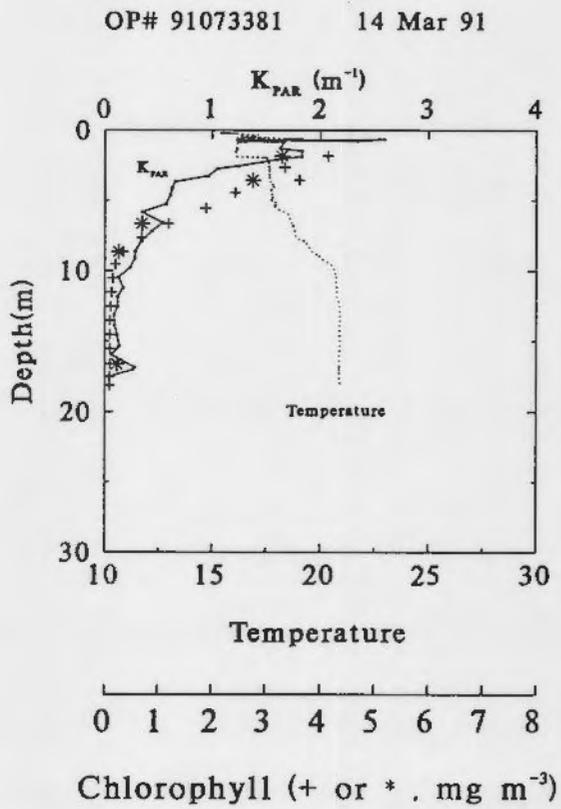
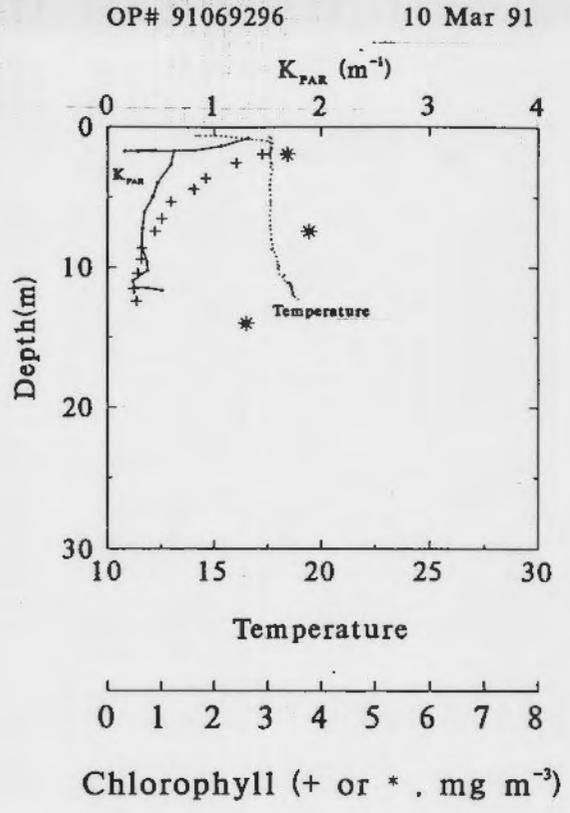
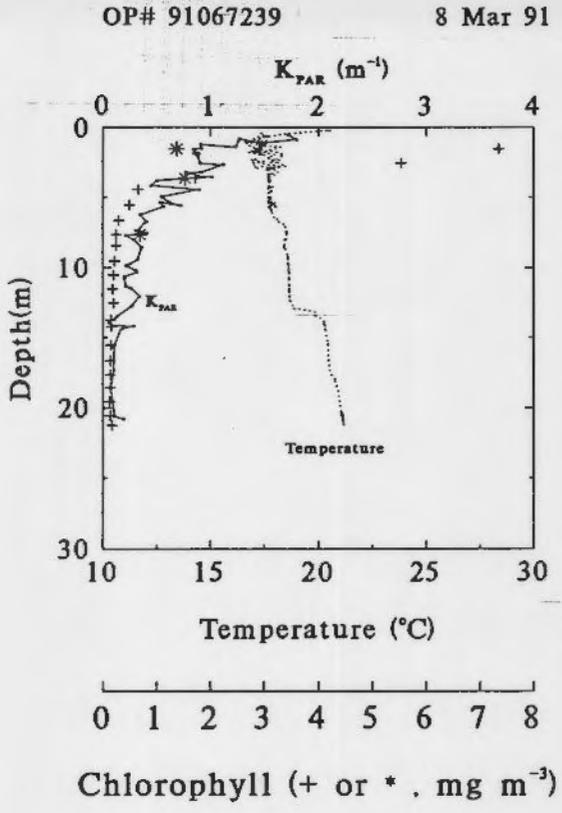


Fig. 2-5 Profile of K_{par} , temperature, and chlorophyll estimated from Lu683 (+) and discrete analyses (*) at Station A (upper left), Station B (upper right), Station C (lower left) and Station D (lower right).

(Table 2) exceeded 3 mg m^{-3} at Stations B and C, while at Station D values were always less than 1 mg m^{-3} . Highest values of suspended particulate matter and lowest salinities were encountered at Station C, presumably strongly impacted by river outflow.

Profiles of K_{par} (Figs. 2-5) exhibited high values in the upper water column and decreased with depth. This was attributed to both the spectral shift in irradiance with depth (e.g., Kirk, 1983) as well higher turbidity in the surface layer (e.g., Station C, Table 2). Highest values of K_{par} were observed at Station C (Fig. 4), although there was considerable scatter in the values. Lowest values were observed at the slope water Station D (Fig. 5).

Chlorophyll estimated from $L_{\text{c}683}$ (Figs. 2-5) was generally highest near the surface and decreased with depth. At Station A, chlorophyll estimated from $L_{\text{c}683}$ exceeded extracted chlorophyll concentrations in surface waters, but underestimated extracted chlorophyll concentrations at depth (Fig. 2). At Stations B, C and D, chlorophyll estimated from $L_{\text{c}683}$ was similar to

extracted chlorophyll concentrations in surface waters (Figs. 3-5). However, at both Stations B and D, values estimated from $L_{\text{c}683}$ underestimated extracted chlorophyll concentrations at depth. At Station C, both estimated and extracted chlorophyll showed similar decreases with depth (Fig. 4).

Profiles of beam c revealed high values in surface waters at Stations A, B and C (Figs. 6-8 respectively). Highest values of beam c were observed at Stations A and C. Sampling limitations of the instrument package precluded resolution within the upper 2-3 m, and there was a possibility that values were higher there. At Stations B and C, subsurface layers of high turbidity were observed that were apparently associated with a benthic nepheloid layer. Intermediate peaks in beam c were observed at Station C that did not reflect pigment maxima (cf. Fig. 4).

Average attenuation coefficient spectra (solid lines in Fig. 9) were similar at Stations A and B. High attenuation at short wavelengths was evident in the spectrum determined at Station C. Spectral attenuation minima at Stations A, B and C were in the vicinity of 540-580 nm. Lowest values of attenuation were observed at the slope water Station D where the attenuation minimum was around 490 nm. The spectral attenuation model performed well (dashed lines in Fig. 9). At Station D, there was a tendency of the modeled values to underestimate measured attenuation, particularly at either end of the spectrum.

Discussion

A wide range of water conditions were encountered in this study. Evidence of high turbidity in river plume was demonstrated by the high values of K_{par} (Fig. 4) and high spectral attenuation (Fig. 9) at Station C. Sharp vertical changes in optical properties were evident and attributed both to high concentrations of optically active constituents and heterogeneous vertical distributions. Spatial variation in irradiance attenuation characteristics was evident from the comparison of the different sampling locations, and underscored the complex nature of the optical environment in this coastal ecosystem.

The utility of measurements of $L_{\text{c}683}$ as an index of chlorophyll concentrations was found to be limited. Extracted chlorophyll *a* concentrations tended to be overestimated in near surface waters and underestimated at depth. Surprisingly, the station where the best agreement was found was Station C, the most turbid of our sampling locations. The discrepancies observed between estimated and extracted chlorophyll concentrations in the surface waters was likely due to a significant source of scattered $L_{\text{c}683}$ that did not originate from chlorophyll fluorescence. Underestimates

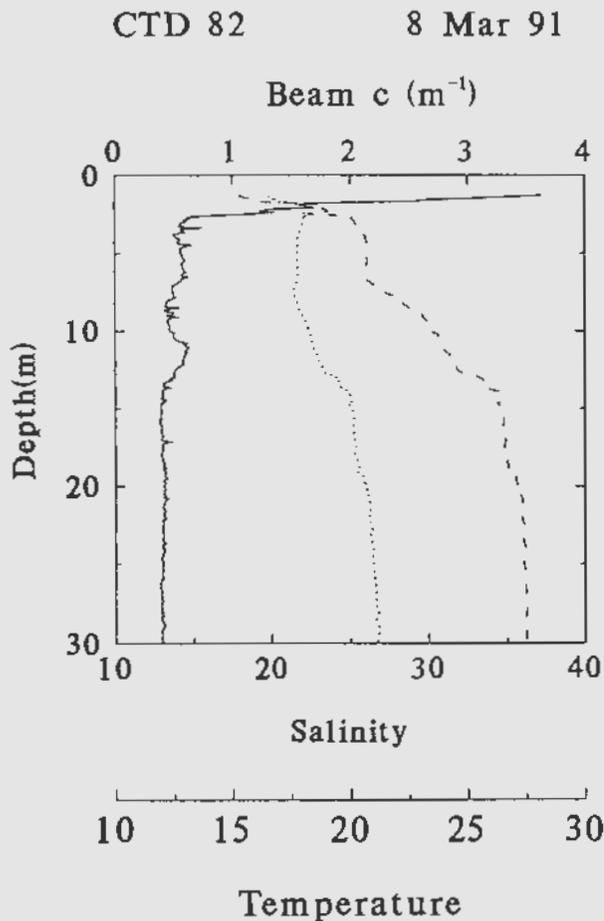


Fig. 6. Profile of salinity (dashed line), temperature (dotted), and beam c (solid) at Station A.

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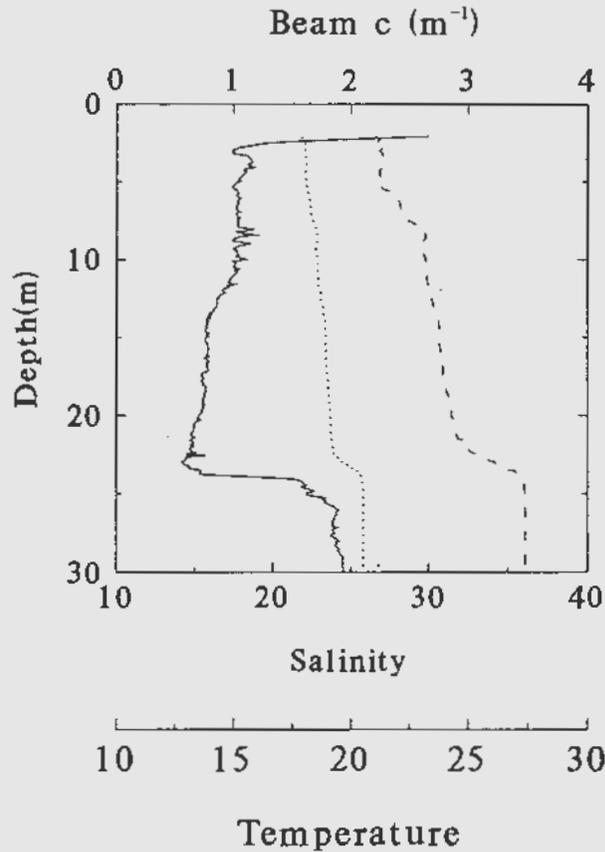


Fig. 7. Profile of salinity (dashed line), temperature (dotted), and beam c (solid) at Station B.

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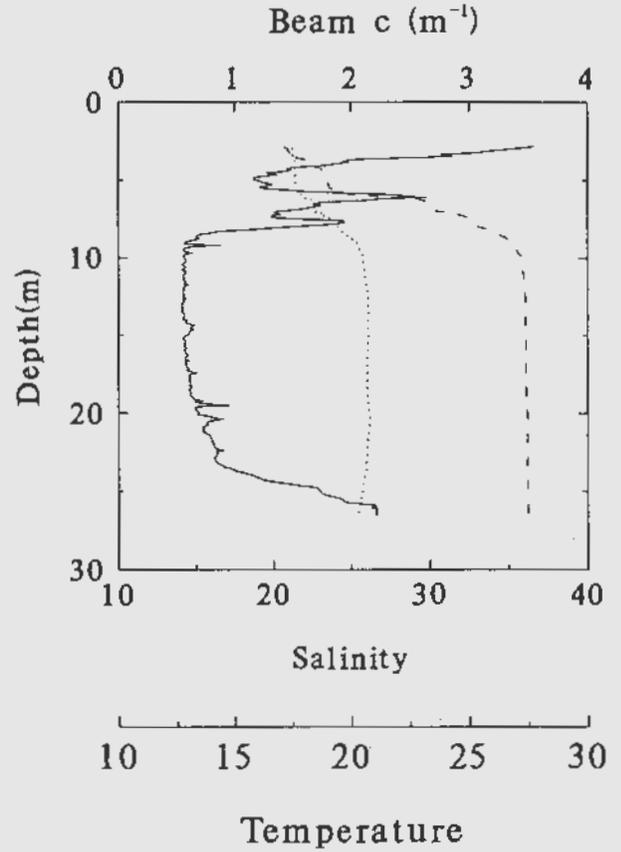


Fig. 8. Profile of salinity (dashed line), temperature (dotted), and beam c (solid) at Station C.

at depth were apparently due to errors in the assumed values of coefficients. For example, decreases in either the spectrally averaged pigment-specific absorption (a^*_{ph}) or the quantum yield of fluorescence (ϕ_f) would increase the estimated chlorophyll (cf. Chamberlin et al., 1990).

The spectral attenuation model performed remarkably well (Fig. 9) considering variations in attenuation spanned over an order of magnitude. Estimates of the relative contribution of individual constituents to total spectral absorption (data not shown) revealed that absorption at wavelengths less than 600 nm was dominated by DOC at Stations A and B, and by DOC and SPM at Station C. It was also evident from consideration of Eq. 18 from Morel (1988) that the scattering coefficients that were derived for Stations A, B and C were substantially higher than could be attributed to the observed chlorophyll *a* concentrations. We thus concluded that attenuation of PAR in shelf

waters during this period was controlled primarily by factors other than pigment concentrations. In slope water (Station D), attenuation was underestimated by the model. This could be attributed to the fact that effects of both SPM and DOC terms were not quantified at this location. SPM estimates were not available at Station D because a high salt blank interfered with the measurement and the empirical relationship to estimate a_s from DOC was applicable only in regions of higher concentrations as encountered in coastal waters. Another factor that may have caused the model to underestimate attenuation at Station D was that the Kirk (1984) relation was intended to provide an average over the euphotic zone (to 1% light level). Our data were from upper 20 m where attenuation may have been slightly higher due to more rapid attenuation of longer wavelengths (cf. Fig. 5).

The spectral attenuation model required input of SPM, DOC, and chlorophyll. In addition, an estimate

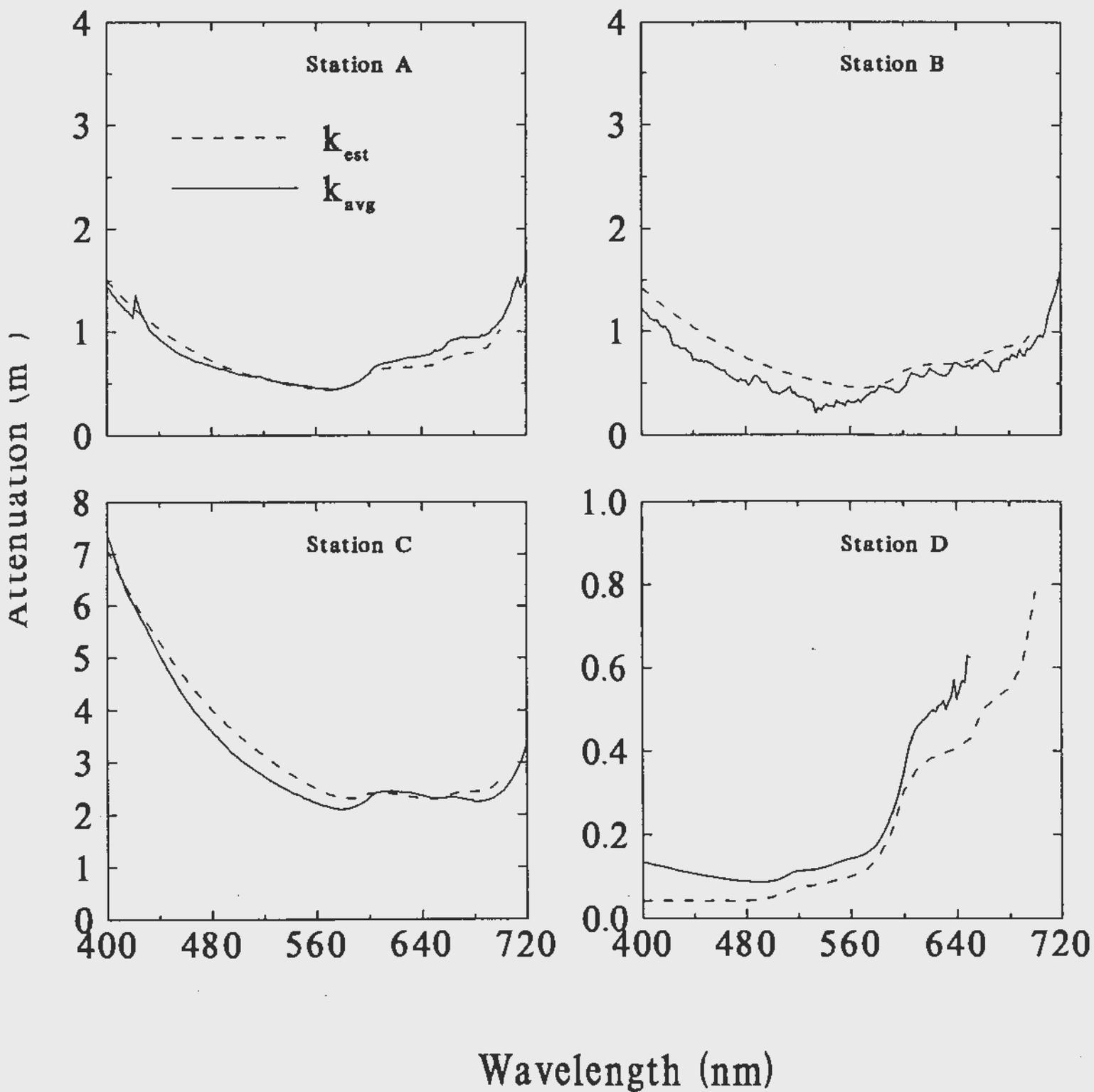


Fig. 9. Attenuation coefficient spectra calculated (Eq. 1) from measured spectral irradiance (solid lines). Scans were averaged from the upper 8 m (Station A), the upper 2 m (Stations B and C) or the upper 20 m (Station D). Dashed lines represent spectral attenuation estimated from a spectral attenuation model as described in Methods.

of $k(720)$ was used to derive the scattering coefficient, b . Ideally, it would be possible to obtain information about these variables using high resolution sampling techniques. For example, empirical relationships have been found to exist between DOC and salinity (Benner, 1994 and unpublished). Thus, a limited set of samples across the salinity gradient may be adequate to characterize DOC on the basis of salinity mapping. It should be noted, however, that the relationship between DOC and salinity has been shown to be nonconservative during periods of high primary production (Benner, 1994). Improved vertical resolution of beam c may provide a convenient means of estimating SPM (cf. Spinrad, 1986). Such estimates would be useful for the assessment of particulate absorption, $a_p(\lambda)$. In addition, empirical relations between SPM and the scattering coefficient, b , may be derived (cf. Gallegos et al., 1990). Such a relation would eliminate the need for determining $k(720)$.

As new instrumentation becomes available, it may be possible to better assess inputs required by this and other spectral models. In view of the strong impact of irradiance on primary production in this ecosystem, advances in the ability to characterize the optical environment should improve our ability to estimate and predict productivity.

Acknowledgements

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