

# Quantum fluorescence efficiencies of fulvic and humic acids: effects on ocean color and fluorometric detection

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## ABSTRACT

The spectral fluorescence efficiency function ( $\eta(\lambda_x, \lambda_m)$  = quanta fluoresced per nm interval of  $\lambda_m$  per quanta absorbed at  $\lambda_x$ ,  $\lambda_x$  = excitation wavelength,  $\lambda_m$  = emission wavelength) has been determined for several different fulvic and humic acid samples, and the 3-dimensional surfaces have been described mathematically. These data are used along with a published two-flow irradiance model to calculate the effect of solar-stimulated fluorescence due to colored dissolved organic matter (CDOM; also gelbstoff) on irradiance reflectance just below the sea surface along a transect taken on the West Florida Shelf. In addition, a strategy is suggested for using  $\eta(\lambda_x, \lambda_m)$  and mass-specific absorption coefficient measurements of CDOM to determine CDOM concentrations from remotely sensed fluorescence measurements.

## 1. INTRODUCTION

Fluorescence due to colored dissolved organic matter (CDOM; also gelbstoff) has many important effects and consequences in natural waters. For instance, solar-stimulated CDOM fluorescence may contribute significantly to the water-leaving radiance signal<sup>1</sup>, or actively induced CDOM fluorescence may be used to map mixing regimes<sup>2,3</sup>, or to detect CDOM itself<sup>4,5</sup>. To quantitatively model any of these processes, the spectral fluorescence efficiency function,  $\eta$ , of CDOM must be known.  $\eta$  for a compound is a function of both excitation wavelength ( $\lambda_x$ ) and emission wavelength ( $\lambda_m$ ) and it is equal to the quanta fluoresced per nm interval of  $\lambda_m$  per quanta absorbed at  $\lambda_x$ . In a previous report<sup>6</sup>,  $\eta(\lambda_x, \lambda_m)$  was measured for a number of different fulvic acid (FA) and humic acid (HA) samples and the 3-dimensional surfaces were mathematically modeled. CDOM in the marine environment can be accounted for by FA and HA in combination<sup>7,8</sup>.

Two applications of these data are investigated here. First, the effect of solar-stimulated CDOM fluorescence on the irradiance reflectance just below the sea surface is estimated for 4 stations along a transect off Tampa Bay using a two-flow (upwelling and downwelling) irradiance model developed by Spitzer and Dirks<sup>1</sup>. Second, a scheme is described that utilizes  $\eta(\lambda_x, \lambda_m)$  and mass-specific absorption coefficient data for CDOM to measure CDOM concentrations from remotely sensed fluorescence signals.

and  $a_{\text{CDOM}}$  were measured on the cruise, and  $b_{\text{bp}}$  was estimated using a published model<sup>12</sup>.  $D_d = 1.14-1.22$ , calculated according to the solar zenith angle,  $D_u = 2.5^{13}$ ,  $F_d = 1.09-1.18$ , calculated from published volume scattering functions<sup>14</sup> and the solar zenith angle, and  $F_u = 2.02$ , calculated from the volume scattering functions<sup>14</sup> and a published upwelling radiance distribution<sup>15</sup>.  $E_{\text{d}0}$  was calculated using the RADTRAN irradiance model<sup>16</sup>.

$\eta(\lambda_x, \lambda_m)$  for CDOM was calculated by combining the measured  $\eta(\lambda_x, \lambda_m)$  values for FA and HA according to

$$\eta_{\text{CDOM}} = \frac{C_F a_F^* \eta_F + C_H a_H^* \eta_H}{a_{\text{CDOM}}} \quad (4)$$

where  $C_x a_x^* = a_x$ ,  $C_x$  = concentration ( $\text{g}/\text{m}^3$ ) of substance 'x,'  $a_x^*$  = mass-specific absorption coefficient ( $\text{m}^2/\text{g}$ ) of substance 'x,' and the subscript 'x' = 'CDOM', 'F', or 'H.' It is assumed that  $C_F + C_H = C_{\text{CDOM}}$ , and that  $C_F:C_H = 9:1^8$ .  $\eta_{\text{CDOM}}(\lambda_x, \lambda_m)$  for both Station 2 and Station 3 was taken to be an average of that for Stations 1 and 4.

#### 4.3 Model results

$R_0(\lambda_m)$  was calculated according to Eq. 2, and  $R_f(\lambda_m)$  was calculated by taking only the second term in Eq. 2. The ratio  $R_f(\lambda)/R_0(\lambda)$  is plotted in Fig. 4 for all four stations. The maximum effect for these waters is at 520 nm where  $R_f(\lambda)/R_0(\lambda)$  is about 0.085 for Station 1 and about 0.065 for Stations 2, 3, and 4.  $R_f(\lambda)/R_0(\lambda)$  is at least 0.020 for most of the visible range. Spitzer and Dirks<sup>1</sup> found more of a fluorescent contribution in the blue than in the green because their fluorescence emission curves had maxima at 450 nm, while the measured  $\eta(\lambda_x, \lambda_m)$  curves used here have maxima as far out as 550 nm for  $\lambda_x = 490$  nm.

The maximum effect that this added reflectance can have on CZCS-type pigment algorithms<sup>17</sup> was estimated by the ratio  $P/P'$ , where  $P = 1.71 [R_0(440)/R_0(560)]^{-1.82}$ ,  $P' = 1.71 [R_0'(440)/R_0'(560)]^{-1.82}$ ,  $R_0'(\lambda) = R_0(\lambda) - R_f(\lambda)$ , and  $P$  is in  $\text{mg}/\text{m}^3$ . In other words,  $P/P'$  is the ratio of the calculated pigment concentrations for modeled reflectance that includes CDOM fluorescence versus modeled reflectance that does not. For Stations 1, 2, 3, and 4,  $P/P' = 1.048, 1.057, 1.056,$  and  $1.065$ , and  $P = 3.77, 2.21, 1.99,$  and  $1.52$ , respectively. This fluorescence contamination will only affect the accuracy of CZCS-type pigment estimates to the extent that the CDOM fluorescence signal does not covary with actual pigments, so the error in  $P$  due to this effect for these waters is probably  $< 5\%$ . In addition, the ratio  $P/P'$  will be much less for the  $R(520)/R(550)$  spectral ratio algorithm<sup>17</sup>.

Thus, even for these moderately colored waters ( $a_{\text{CDOM}}(350) = 0.3-0.6 \text{ 1/m}$ ), solar-stimulated CDOM fluorescence appears to contaminate the upwelling irradiance significantly at wavelengths important to ocean color remote sensing. Potential errors in CZCS-type pigment estimates will depend on the covariance (or lack thereof) of CDOM fluorescence with pigment concentration. If additional modeling (eg. by Monte Carlo simulation<sup>18</sup>) and/or

Spitzer and Dirks<sup>1</sup> developed a two-flow irradiance model to calculate the fraction of the irradiance reflectance just below the sea surface ( $R_0(\lambda)$ ) that is due to solar-stimulated CDOM fluorescence ( $R_f(\lambda)$ ). They assumed that  $\Phi_f(\lambda_x) = 0.0045^{10}$  and that the emission was a Gaussian curve centered at 450 nm with wavelength on the abscissa. For a phytoplankton pigment concentration of 1 mg/m<sup>3</sup>, they calculated that  $R_f/R_0$  at  $\lambda = 450$  nm was about 10%, 30%, and 70% for waters with CDOM absorption coefficients at 350 nm ( $a_{\text{CDOM}}(350)$ ) of 1.5, 4.5, and 10.5 1/m, respectively, and that  $R_f(\lambda)$  was generally < 10% of  $R_0(\lambda)$  at 520 nm and 550 nm.

Their model has been modified by replacing the Gaussian fluorescence emission curves with the measured  $\eta(\lambda_x, \lambda_m)$  function. The resulting model equation is given by:

$$R_0(\lambda_m) = \frac{c_d(\lambda_m) + \rho_d(\lambda_m)}{b_{bu}(\lambda_m)} + \frac{1}{2 E_{d0}(\lambda_m)} \times \int_{\lambda_x} \frac{a_{\text{CDOM}}(\lambda_x) E_{d0}(\lambda_x) \eta(\lambda_x, \lambda_m)}{\rho_u(\lambda_m) - \rho_d(\lambda_x)} \left[ D_u \frac{c_d(\lambda_x) + \rho_d(\lambda_x)}{b_{bu}(\lambda_x)} + D_d \right] d\lambda_x \quad (2)$$

$$\text{where } \rho_u = \frac{1}{2}(c_u - c_d) + \frac{1}{2}[(c_u + c_d)^2 - 4 b_{bu} b_{bd}]^{\frac{1}{2}} \quad (3)$$

$$\rho_d = \frac{1}{2}(c_u - c_d) - \frac{1}{2}[(c_u + c_d)^2 - 4 b_{bu} b_{bd}]^{\frac{1}{2}}$$

and  $c_x = a_x + b_{bx}$ ,  $a_x = aD_x$ ,  $b_{bx} = b_b F_x$ ,  $a$  = absorption coefficient (1/m),  $b_b$  = backscattering coefficient(1/m),  $D$  = distribution coefficient,  $F$  = backscattering distribution coefficient, and the subscript 'x' refers to 'u' for upwelling or 'd' for downwelling.  $E_{d0}$  = subsurface downwelling solar irradiance.

#### 4.2 Model inputs for West Florida Shelf transect

Optical measurements were taken at 4 stations along a transect from the mouth of Tampa Bay to the mid-West Florida Shelf on 4-5 March 1990 (see Fig. 3). FA and HA were extracted from the two endpoints of the transect, Stations 1 and 4. For Stations 1, 2, 3, and 4, pigment concentration ( $P$  = chlorophyll + pheopigments) was 2.43, 1.65, 1.71, and 1.35 mg/m<sup>3</sup>, and  $a_{\text{CDOM}}(350)$  was 0.624, 0.347, 0.329, and 0.267 1/m, respectively.

To apply the irradiance model to these stations, absorption and backscattering were calculated as  $a = a_w + a_p + a_{\text{CDOM}}$ , and  $b_b = b_{bw} + b_{bp}$ , where the subscripts 'w', 'p', and 'CDOM' refer to water, particles, and CDOM.  $a_w$  and  $b_{bw}$  were obtained from Ref. 11,  $a_p$

constant, CDOM concentrations can be overestimated by up to 11% for mid-shelf waters compared to coastal waters when using a 355 nm excitation source. This overestimate is reduced to 3% if a 390 nm excitation source is used.

## 7. ACKNOWLEDGEMENTS

Financial support was provided by NASA through grant NAEW-465 and GSFC contract NAS5-30779, and by ONR through grant N00014-89-J-1091. Ship support was provided by the State of Florida through the Florida Institute of Oceanography. The authors also wish to thank Bob Steward and Bob Chen for computer assistance, Joan Hesler for administrative assistance, Stacie Little for preparing the map, and Zhongping Lee and Tom Peacock for insightful discussions about fluorescence.

## 8. REFERENCES

1. D. Spitzer and R.W.J. Dirks, "Contamination of the reflectance of natural waters by solar-induced fluorescence of dissolved organic matter," *Appl. Opt.*, 24(4), 444-445, 1985.
2. J.D. Willey, "The effect of seawater magnesium on natural fluorescence during estuarine mixing, and implications for tracer applications," *Mar. Chem.*, 15, 19-45, 1984.
3. P. Berger, R.W.P.M. Laane, A.G. Ilahude, M. Ewald, and P. Courtot, "Comparative study of dissolved fluorescent matter in four West-European estuaries," *Oceanol. Acta*, 7, 309-314, 1984.
4. F.E. Hoge and R.N. Swift, "Airborne spectroscopic detection of laser-induced water Raman backscatter and fluorescence from chlorophyll a and other naturally occurring pigments," *Appl. Opt.*, 20, 3197-3205, 1981.
5. P.L. Smart, B.L. Finlayson, W.D. Rylands, and C.M. Ball, "The relation of fluorescence to dissolved organic carbon in surface waters," *Water Res.*, 10, 805-811, 1976.
6. S.K. Hawes, K.L. Carder, and G.R. Harvey, "Quantum fluorescence efficiencies of humic and fulvic acids," Proc. First Thematic Conf. on Remote Sensing for Marine and Coastal Environments, ERIM, New Orleans, LA, 1992.
7. G.R. Harvey, D.A. Boran, L.A. Chesal, and J.M. Tokar, "The structure of marine fulvic and humic acids," *Mar. Chem.*, 12, 119-132, 1983.
8. K.L. Carder, B.G. Steward, G.R. Harvey, and P.B. Ortner, "Marine humic and fulvic acids: their effects on remote sensing of ocean chlorophyll," *Limnol. Oceanogr.*, 34(1), 68-81, 1989.
9. R.A. Velapoldi and K.D. Mielenz, "A fluorescence standard reference material: quinine sulfate dihydrate," NBS special publication 260-64, 1980.
10. R.G. Zepp and P.A. Schlotzhauer, "Comparison of photochemical behavior of various humic substances in water: III. Spectroscopic properties of humic substances," *Chemosphere*, 10(5), 479-486, 1981.
11. R.C. Smith and K.S. Baker, "Optical properties of the clearest natural waters (200-800 nm)," *Appl. Opt.*, 20(2), 177-184, 1981.
12. A. Morel, "Optical modeling of the upper ocean in relation to its biogenous matter content (Case 1 waters)," *J. Geophys. Res.*, 93(C9), 10,749-10,768, 1988.

field studies can verify the accuracy of the model used here, then future ocean color models and related algorithms<sup>19</sup> need to account for CDOM fluorescence.

## 5. FLUOROMETRIC DETECTION OF FA AND HA

CDOM fluorescence has frequently been used as a means of assessing dissolved organic carbon (DOC) concentrations with varying degrees of success<sup>5,20,21</sup>. Most of the attempts regress measured fluorescence vs. measured DOC, which may become invalid if there are sources (eg. biological production) or sinks (eg. photo-bleaching) of CDOM, or if the fluorescence efficiency changes over the study area.

As an alternative approach, CDOM concentrations ( $C_{\text{CDOM}}$ ) can be related to remotely sensed fluorescence signals ( $F(\lambda_m)$ ) if both  $a^*(\lambda_x)$  and  $\eta(\lambda_x, \lambda_m)$  for CDOM in the study area are known or if they can be estimated *a priori*. Ignoring other forms of trans-spectral scattering,  $F(\lambda_m)$  is approximately proportional to  $A(\lambda_x, \lambda_m) C_{\text{CDOM}} a^*_{\text{CDOM}}(\lambda_x) \eta(\lambda_x, \lambda_m)$ , where  $A(\lambda_x, \lambda_m)$  is an instrumental constant that can be determined in calibration.  $a^*(\lambda_x)$  and  $\eta(\lambda_x, \lambda_m)$  can be measured at two endpoints of an inshore/offshore transect, with fluorescence measured via either airborne LIDAR or an *in situ* fluorometer towed by a ship. The measured fluorescence signals can then be converted to  $C_{\text{CDOM}}$  if the instruments have been properly calibrated and if the estimated gradients of  $a^*(\lambda_x)$  and  $\eta(\lambda_x, \lambda_m)$  along the flight/ship track are accurate.

We can calculate the error in CDOM concentration estimates induced by variability in  $\eta(\lambda_x, \lambda_m)$  by examining the appropriate wavelength regions of the  $\eta(\lambda_x, \lambda_m)$  surfaces. For example, consider a LIDAR instrument, ground truthed at Station 1, using a 355 nm laser excitation source and a 10 nm bandwidth receiver centered on 490 nm.  $\eta(355, 485-495)$  is 11% higher at Station 4 than at Station 1, which will cause an 11% overestimate of CDOM concentration if variability in  $\eta(\lambda_x, \lambda_m)$  is not accounted for. However, if  $(\lambda_x, \lambda_m)$  for the system can be changed to (390, 440-490), the overestimate can be reduced to about 3%.

## 6. SUMMARY

1.  $\eta(\lambda_x, \lambda_m)$  for several different FA and HA samples has been modeled mathematically and presented here. These data are important in optical models that account for CDOM fluorescence.
2. At the mouth of Tampa Bay, the percent contribution of solar stimulated CDOM fluorescence to the subsurface irradiance reflectance was 8.5% at 520 nm and was  $> 5\%$  for  $450 \text{ nm} < \lambda < 630 \text{ nm}$ . For waters slightly offshore on the West Florida Shelf, the contribution was about 80% that for the inshore station. The potential error in CZCS-type pigment retrievals due to this fluorescence was estimated to be  $< 5\%$  for these waters.
3. Concentrations of CDOM can be calculated by remotely sensed fluorescence signals if the variability of both  $a^*(\lambda_x)$  and  $\eta(\lambda_x, \lambda_m)$  for the CDOM in the study area are known or can be estimated *a priori*. On the West Florida Shelf, if  $\eta(\lambda_x, \lambda_m)$  for CDOM is assumed to be

Table 1. FA and HA sample information.

sample name	location	sample date	sample volume (liters)	extraction method	tot. mass extracted (mg)
HA1	Peru upwelling (El Nino)	-	-	XAD2	-
HA2	Gulf of Mexico, outside Loop Cur.	-	-	XAD2	-
HA4	Gulf of Mexico, mouth of Tampa Bay	12oct89	26	XAD2	0.156
HA5	Gulf of Mexico, oligotrophic	15oct89	57	XAD2	0.004
HA6	Gulf of Mexico, mid-West Florida Shelf	04mar90	55	XAD2	0.65
FA7	Gulf of Mexico, mid-West Florida Shelf	04mar90	32	C18	12.66
FA8 HA8	Gulf of Mexico, mouth of Tampa Bay	05mar90	20	C18	2.24 0.42
FA9	North Atlantic 60°N 20°W	24may91	55	C18	19.06
FA11 HA10	North Atlantic 60°N 20°W	20aug91	55	C18	6.99 ≈0

13. L. Prieur and S. Sathyendranath, "An optical classification of coastal and oceanic waters based on the specific spectral absorption curves of phytoplankton pigments, dissolved organic matter, and other particulate materials," *Limnol. Oceanogr.*, 26(4), 671-689, 1981.
14. T.L. Petzold, "Volume scattering functions for selected ocean waters, San Diego," *Scripps Inst. Oceanogr. Ref.*, 72-78, 1972.
15. J.E. Tyler, "Radiance distribution as a function of depth in an underwater environment," *Bull. Scripps Inst. Oceanogr.*, 7, 363-411, 1960.
16. W.W. Gregg and K.L. Carder, "A simple 1 nm resolution solar irradiance model for cloudless maritime atmospheres," *Limnol. Oceanogr.*, 35, 1657-1675, 1990.
17. H.R. Gordon and A.Y. Morel, Remote assessment of ocean color for interpretation of satellite visible imagery, 114 pp., Springer-Verlag, Berlin, 1983.
18. L.R. Poole, and W.E. Esaias, "Water Raman normalization of airborne laser fluorosensing measurements: a computer model study," *Appl. Opt.*, 21, 3756-3761.
19. K.L. Carder, S.K. Hawes, K.A. Baker, R.C. Smith, R.G. Steward and B.G. Mitchell, "Reflectance model for quantifying chlorophyll a in the presence of productivity degradation products," *J. Geophys. Res.*, 96(C11), 20,599-20,611, 1991.
20. A.J. Stewart and R.G. Wetzel, "Asymmetrical relationships between absorbance, fluorescence, and dissolved organic carbon," *Limnol. Oceanogr.*, 26(3), 590-597, 1981.
21. P.G. Coble, "Fluorescence of DOM: Implications for development of *in situ* instrumentation," in press in Autonomous Bio-Optical Observing Systems Symposium Proceedings, Monterey, CA April 6-10, 1992.

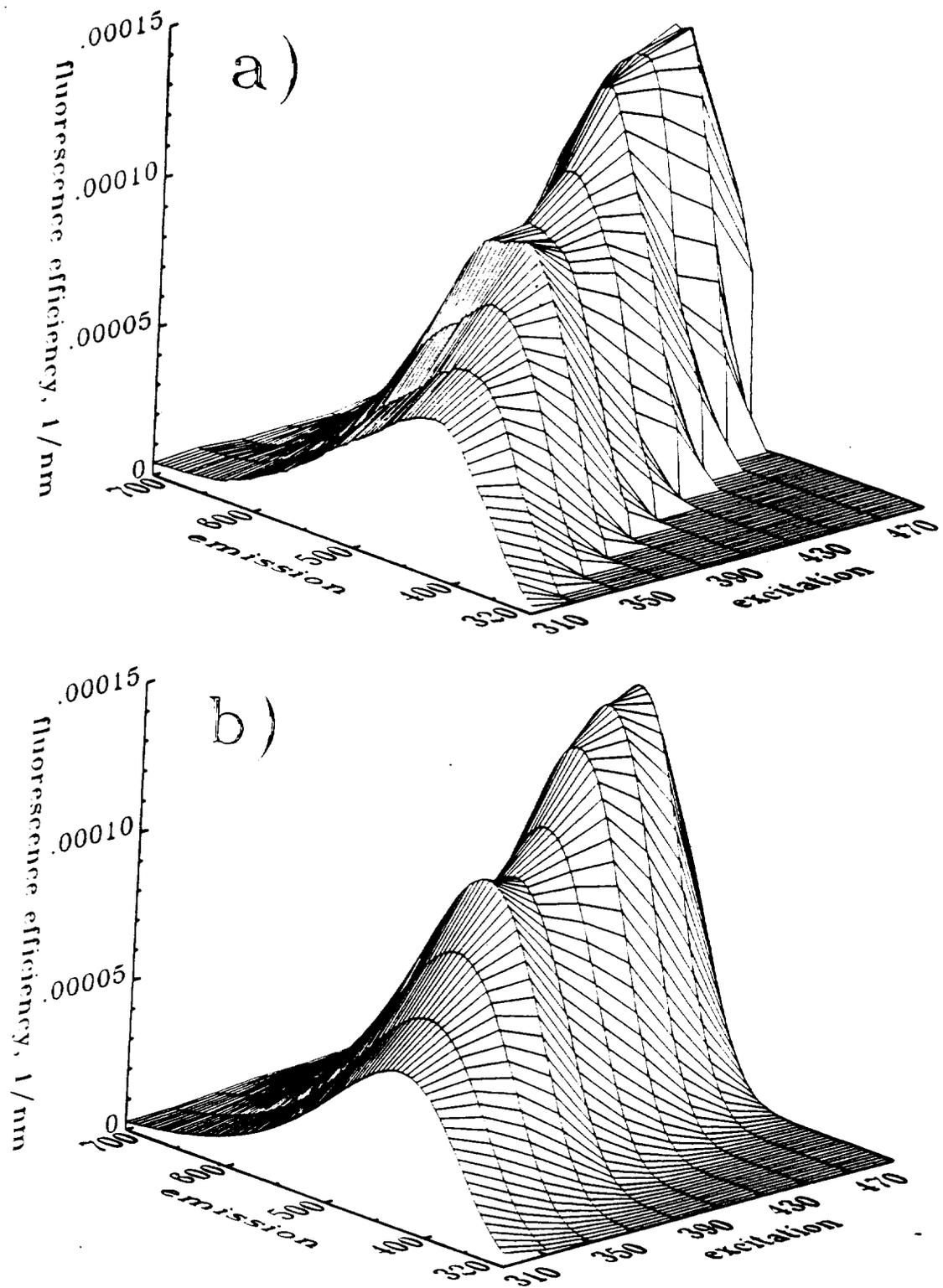


Fig. 1. a) Measured and b) modeled  $\eta(\lambda_x, \lambda_m)$  surfaces for FA7.

Table 2. Parameters for  $\eta(\lambda_x, \lambda_m)$  model.

	FA7	FA8	FA9	FA11	HA1	HA2
$A_0(\lambda_x) \times 10^5$						
$\lambda_x = 310$	5.18	4.48	5.21	5.09	2.49	2.78
330	6.34	5.67	6.57	6.27	2.68	3.13
350	8.00	7.23	7.93	7.93	2.95	3.73
370	9.89	9.26	9.93	9.76	3.34	4.42
390	9.39	9.06	0.93	8.72	2.77	4.03
410	10.48	9.22	9.47	7.93	2.26	3.91
430	12.59	10.14	10.21	8.15	2.63	4.41
450	13.48	9.90	10.08	7.75	2.72	4.52
470	13.61	9.70	10.11	7.70	2.65	4.75
490	9.27	7.90	8.34	5.98	2.20	4.29
$A_1$	0.470	0.389	0.466	0.471	0.304	0.379
$B_1 \times 10^4$	8.077	10.073	8.340	8.204	12.169	10.043
$A_2$	0.407	0.386	0.386	0.386	0.591	0.362
$B_2 \times 10^4$	-4.57	-4.20	-4.13	-4.20	-9.39	-3.17
$r^2$	0.987	0.989	0.975	0.991	0.712	0.985
	HA4	HA5	HA6	HA8	HA10	
$A_0(\lambda_x) \times 10^5$						
$\lambda_x = 310$	4.83	4.49	5.77	3.61	3.40	
330	5.11	5.71	6.86	4.01	4.02	
350	5.94	5.49	7.27	0.46	3.71	
370	7.20	5.52	8.37	5.48	4.28	
390	6.53	4.31	7.08	5.06	4.49	
410	6.41	-	7.80	5.05	5.07	
430	7.66	-	8.90	5.66	-	
450	7.55	-	9.30	5.70	-	
470	7.88	-	8.41	5.32	-	
490	6.81	-	6.68	4.42	-	
$A_1$	0.346	0.481	0.447	0.356	0.710	
$B_1 \times 10^4$	10.891	8.314	8.594	10.694	2.161	
$A_2$	0.411	0.311	0.417	0.406	0.490	
$B_2 \times 10^4$	-4.60	-1.80	-4.64	-4.42	-6.65	
$r^2$	0.985	0.985	0.985	0.986	0.987	

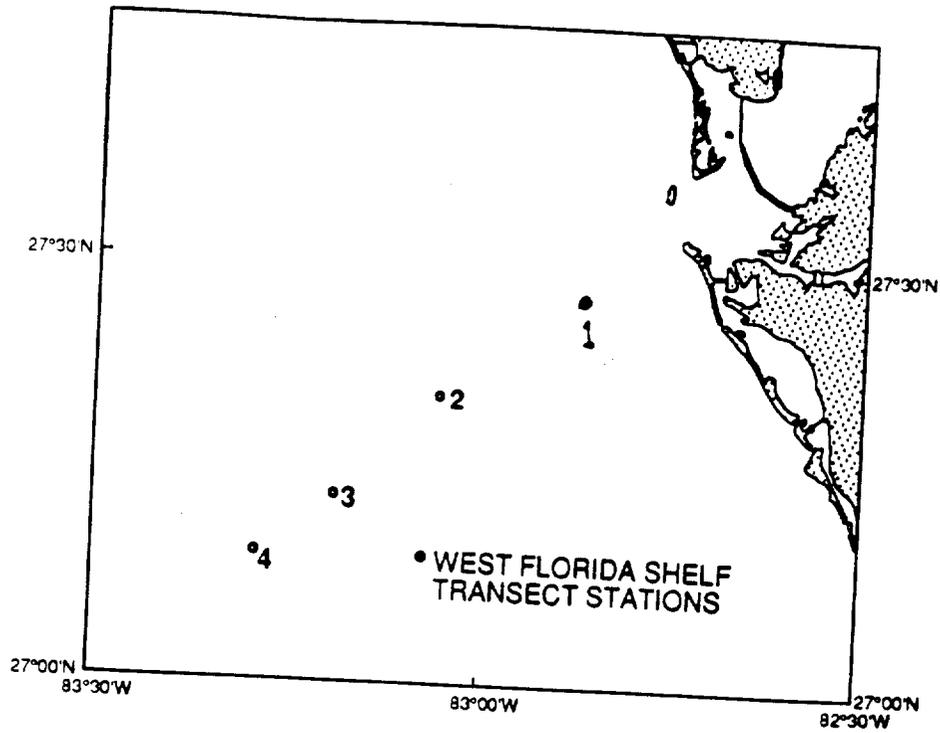


Fig. 3. Station locations.

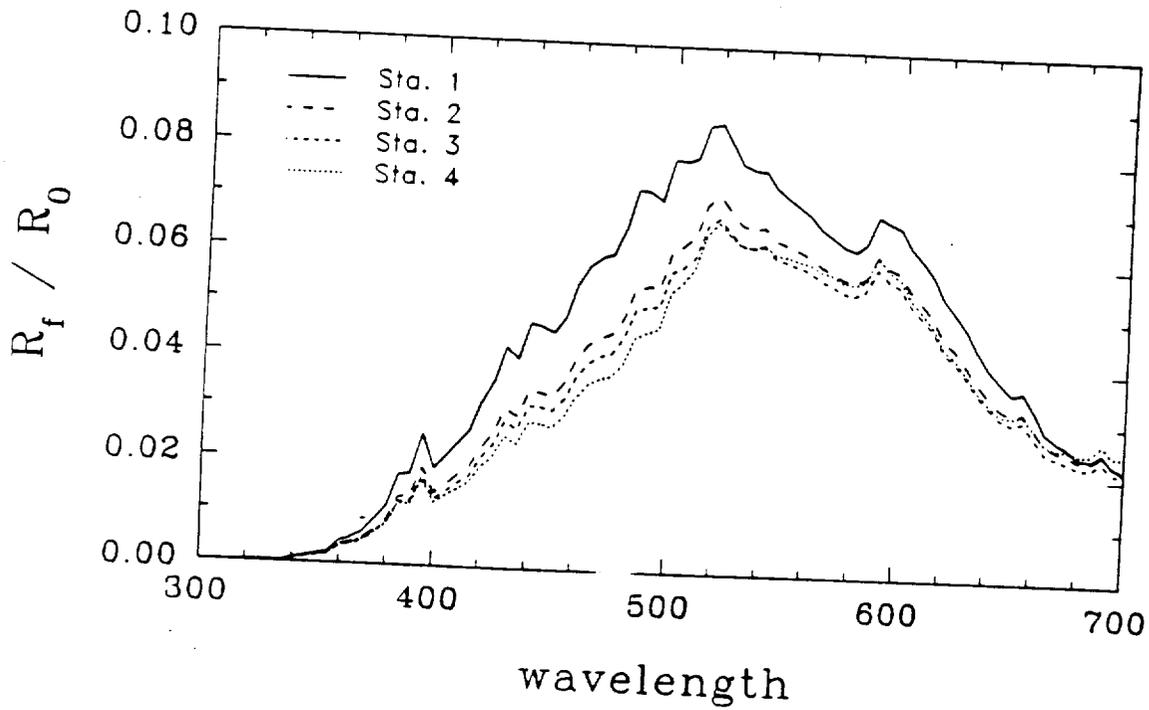


Fig. 4.  $R_f(\lambda)/R_0(\lambda)$  for all 4 West Florida Shelf stations.