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BIO-OPTICAL PROPERTIES OF THE ARABIAN SEA AS DETERMINED BY IN SITU AND **SEAWIFS DATA**

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TABLE OF CONTENTS

INTRODUCTION	1
RESULTS	2
REFERENCES	6
PUBLICATIONS GENERATED FROM NASA SUPPORT	7

APPENDIX A

Revised SeaWiFS Pre-Launch Algorithm for the Diffuse Attenuation Coefficient K(490), CTM 006-96.

INTRODUCTION

"Bio-optical Properties of the Arabian Sea as Determined by *In Situ* and SeaWiFS Data" was a four year grant starting in February 1993. The overall objective of this work was to characterize optical and fluorescence properties in the euphotic zone during two British Ocean Flux Study (BOFS) Arabian Sea cruises. This was later expanded in 1995 to include three U.S. JGOFS Arabian Sea Cruises. The region was to be divided into one or more "bio-optical provinces", within each of which a single set of regression models was to be developed to relate the vertical distribution of irradiance attenuation and normalized fluorescence (SF and NF) to remote sensing reflectance and diffuse attenuation coefficient [K(490)]. The working hypothesis was that over relatively large spatial and temporal scales, the vertical profiles of bio-optical properties were predictable.

The specific technical objectives were:

- 1. To characterize the vertical distribution of the inherent and apparent optical properties by measuring downwelling and upwelling irradiances, upwelling radiances, scalar irradiance of PAR, and beam transmissions at each station. From these data, spectral diffuse attenuation coefficients, irradiance reflectances, remote sensing reflectances, surface-leaving radiances and beam attenuation coefficients were determined.
- 2. To characterize the spectral absorption of total particulate, detrital, and dissolved organic material at each station from discrete water samples.
- 3. To describe the vertical distribution of photoadaptive properties in the water column by measuring profiles of stimulated (SF) and natural (NF) fluorescence and examining relationships between SF and NF as a function of diffuse optical depth, pigment biomass and primary productivity.
- 4. To establish locally derived, in-water algorithms relating remote sensing reflectance spectra to diffuse attenuation coefficients, phytoplankton pigment concentrations and primary productivity, through intercomparisons with *in situ* measurements, for application to SeaWiFS data.

During this funding period, we participated on 4 cruises in the Arabian Sea collecting bio-optical data. Summaries of the measurements made for each cruise are listed below:

BOFS Arabesque I Cruise (45 days) – 26 August - 5 October 1994

26 optical profiles of E_d(λ), E_u(λ) & L_u(λ) at SeaWiFS wavelengths
205 pigment samples for High Performance Liquid Chromatography (HPLC) and fluorometric analyses

208 particulate absorption samples

UOR tows between all stations measuring $E_d(\lambda)$, $L_u(\lambda)$, fluorescence, c(660), depth and temperature

US JGOFS Process Cruise 2 (28 days) - 14 March - 10 April 1995

14 optical profiles of $E_d(\lambda)$, $E_u(\lambda)$ & $L_u(\lambda)$ at SeaWiFS wavelengths, fluorescence, c(660)

24 bio-optical profiles of PAR and $L_u(680)$ or natural fluorescence 8 deployments of moored natural fluorometers on the productivity array 298 particulate absorption samples

US JGOFS Process Cruise 6 (28 days) – 29 October - 26 November 1995

- 39 optical profiles of $E_d(\lambda)$, $E_u(\lambda)$ & $L_u(\lambda)$ at SeaWiFS wavelengths, fluorescence, c(660)
- 351 particulate absorption samples
- UOR tows between all stations measuring $E_d(\lambda)$, $L_u(\lambda)$, fluorescence, c(660), depth and temperature

US JGOFS Process Cruise 7 (28 days) – 30 November - 27 December 1995

26 optical profiles of $E_d(\lambda)$, $E_u(\lambda)$ & $L_u(\lambda)$ at SeaWiFS wavelengths, fluorescence, c(660)

305 particulate absorption samples

In addition to these cruises, particulate absorption samples (107) were collected during Arabesque II (16 November – 19 December 1994) for processing at CHORS. All of this bio-optical data has been submitted to both NASA SeaWiFS and U.S. JGOFS data bases.

RESULTS

<u>Objective 1</u> - The optical instruments used during these cruises were radiometrically calibrated before and after each deployment following calibration protocols listed in Mueller and Austin (1995). From this data, spectral diffuse attenuation coefficients, irradiance reflectances, remote sensing reflectances, surface-leaving radiances and beam attenuation coefficients were determined.

For the analysis of phytoplankton pigments for Arabesque I, the Wright *et al.* (1991) method was used with canthaxanthin as an internal standard. To quantitatively separate monovinyl chlorophyll *a* from divinyl chlorophyll *a*, the two wavelength peak absorption method of Latasa *et al.* (1996) was used. HPLC pigment samples were also collected by Dr. Ray Barlow, Plymouth Marine Laboratory, for analysis on the ship. A comparison between the two laboratories is shown in Figure 1 for 32 duplicate samples.

<u>Objective 2</u> - Particulate absorption samples were collected during these cruises on GF/F glass fiber filters. A refurbished Perkin-Elmer Lambda 3b spectrophotometer was purchased and used throughout the British and U.S. cruises. For two of the cruises in which we did not participate (Process Cruises 1 and 5), Dr. John Marra of Lamont-Doherty borrowed the spectrophotometer and measured particulate absorption.

The correction for the pathlength amplification factor, β , following SeaWiFS Optical Protocols (Mueller and Austin, 1995) and Mitchell 1990, was determined during two intercalibration exercises at Scripps and Bigelow Laboratory. The first intercalibration at Scripps used only two diatom cultures, where as the effort at Bigelow incorporated 9 cultures (2- diatoms, 1-dinoflagellate, 1-cyanobacteria, 2-cryptophytes, 2-prasinophytes, and 1prymnesiophyte). The β correction factor for the Lambda 3b is plotted in Figure 2 for both exercises.



Figure 1. Comparison between PML and CHORS laboratories for monovinyl plus dinvinyl chlorophyll a on 32 replicate HPLC samples collected during Arabesque I.

-3-



Figure 2. Relationship between $OD_s(\lambda)$ and $OD_r(\lambda)$ for the Perkin Elmer Lambda 3b. The "+" represents absorption data from the Bigelow Laboratory intercalibration exercise.

Dave Phinney of Bigelow participated on the Navy funded Arabian Sea cruises, making measurements of particulate absorption. By intercalibrating at Bigelow with Phinney's spectrophotometer, we now have an internally consistent particulate absorption data set for the Arabian Sea covering 17 months from August 1995 to December 1996.

To estimate the contribution of detritus to total particulate absorption, the hot methanol extraction technique of Kishino *et al.* (1985) was used. By subtracting the residue absorption from the total absorption, the spectra of living phytoplankton is obtained. This

-4-

assumes that the β correction factor for the total particulate filter is the same as the methanol washed one and that the contribution to absorption by non-photosynthetic detrital pigments is relatively small. In addition, the "Kishino Method" does not remove phycobiliproteins which are found in cyanobacteria and are water soluble. For many of the Arabian Sea samples, cyanobacteria were present in significant concentrations to seriously affect the estimate of detrital absorption component (See Fig. 3, Bidigare *et al.*, 1996). Our approached has been to fit the detrital absorption curve to an exponential function so as to correct for absorption peaks at 490 and 545 nm caused by phycobiliproteins. Due to the extended delay in processing HPLC pigments by Dr. Ralf Goericke of Scripps, specific absorption coefficients normalized to chlorophyll *a* have not been computed.

<u>Objective 3</u> - The working hypothesis, that over relatively large spatial and temporal scales, the vertical profiles of bio-optical properties are predictable, was initially tested using vertical profiles of irradiance at 490 nm. A robust relationship was found between the depth of the first attenuation length (37% light depth) and the 10%, 1% and 0.01% light depths over the entire Arabian Sea and Gulf of Oman for the two British cruises (See Fig. 5, Pinkerton *et al.*, 1997). For the U.S. JGOFS cruises, there were differences between this relationship, but they were predictable.

We will continue with our efforts towards predicting the vertical distribution of chlorophyll biomass using natural and stimulated fluorescence, once the HPLC pigment analyses have been completed. Because of the delays in the Arabian Sea HPLC pigment data, we have focused our efforts with colleagues at CICESE, Ensenada, Mexico, to apply the concept of 'bio-optical provinces' to the CalCOFI data. Empirical relationship were developed relating the depth and concentration of the chlorophyll *a* maximum to surface chlorophyll *a* (Millán-Nuñez *et al.*, 1996). The region was divided into six subregions and temporally into warm and cool seasons. Comparison of chlorophyll profiles obtained during the 1994 CalCOFI cruise (not used for constructing the models) with those estimated with our models showed good agreement (Millán-Nuñez *et al.*, 1997).

<u>Objective 4</u> - A SeaWiFS *in-water* pigment algorithm that exploits the full functionality of SeaWiFS, yet is compatible with past algorithms developed for CZCS, was developed (Aiken *et al.*, 1995). Using optical and pigment data that was acquired during three cruises in the Greenland, Iceland and Norwegian Seas (1986 & 87) and two US JGOFS EqPac cruises (1992), along with cruises from Dr. Aiken's group (PML), algorithms were developed relating chlorophyll *a* to total pigment, carotenoids, photosynthetic carotenoids and photoprotectant carotenoids. The best single-band water leaving radiance ratio for chlorophyll *a* was 490:555, where as, 443:555 and 490:555 was the best for multiband algorithms. Pigment and diffuse attenuation coefficient [K(490)] algorithms were also

-5-

developed for the Arabian Sea using bio-optical data from the two British cruises (Pinkerton *et al.*, 1997). There was no justification for defining more than one 'bio-optical' province for the Arabian Sea and Gulf of Oman regions for estimating surface pigment concentration or K(490) for these cruises.

Using optical profiles from the Arabian Sea, Gulf of California, North and South Atlantic, California Current System and the Sargasso Sea, a revised SeaWiFS pre-launch algorithm for the diffuse attenuation coefficient K(490) was calculated (Mueller and Trees, 1996). Comparing this new SeaWiFS K(490) algorithm with the Austin and Petzold (1981) CZCS algorithm, showed only small differences even though there is a change in wavelengths from 550 to 555 nm for the SeaWiFS sensor. Appendix A reviews these results.

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APPENDIX A



CHORS TECHNICAL MEMORANDUM 006-96

REVISED SEAWIFS PRE-LAUNCH ALGORITHM FOR THE DIFFUSE ATTENUATION COEFFICIENT K(490)

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James L. Mueller and Charles C. Trees

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TABLE OF CONTENTS

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INTRODUCTION	1
DATA AND METHODS	2
RESULTS	3
DISCUSSION	4
REFERENCES	5

FIGURES

FIG. 1	Scattergram comparing K(490) and the normalized ratio $L_{WN}(443/L_{WN}(555))$ 6
FIG. 2	Linear K(490) vs a logarithmic scaling $L_{WN}(443)/L_{WN}(555)$ display of the
	data and regression fit from Fig. 17

REVISED SEAWIFS PRE-LAUNCH ALGORITHM FOR THE DIFFUSE ATTENUATION COEFFICIENT K(490)

INTRODUCTION

The diffuse attenuation coefficient at 490 nm, K(490), was one of the standard ocean data products calculated from Nimbus-7 Coastal Zone Color Zone (CZCS) imagery. Austin and Petzold (1981) derived the Nimbus-7 CZCS algorithm relating K(490) [in m⁻¹] to the ratio of water-leaving radiances $L_w(443)/L_w(550)$, at wavelengths of 443 and 550 nm, as

$$K(490) = 0.022 + 0.088 \left[L_w(443) / L_w(550) \right]^{-1.491} m^{-1}.$$
 (1)

Root-mean-square (RMS) uncertainties in K(490) estimated from CZCS data are < 20% (1 σ) based on direct comparisons with *in situ* radiometric profiles (*e.g.* Mueller 1993).

The SeaWiFS Science Team has formally recommended that Eq. (1) (the Austin and Petzold 1981 algorithm) be adopted as the pre-launch K(490) algorithm for SeaWiFS data processing, substituting the SeaWiFS normalized water-leaving radiances $L_{wN}(443)$ and $L_{wN}(555)$ for $L_n(443)$ and $L_w(550)$. However, some members of the SeaWiFS Science Team questioned whether the shift from 550 to 555 nm might lead to significant systematic errors in SeaWiFS K(490) estimates if the coefficients in Eq. (1) are used. Mueller (1995) compared K(490) and normalized remote sensing reflectance ratios $L_{wN}(443)/L_{wN}(555)$ derived from a limited number (45) of radiometric profiles made during recent cruises using instruments configured with SeaWiFS wavelengths; profiles comprising this small sample were contributed by C. Trees of San Diego State University (SDSU) Center for Hydro-Optics and Remote Sensing (CHORS) (16 profiles from the Arabian Sea), G. Mitchell of University of California Santa Diego/Scripps Institution of Oceanography (UCSD/SIO (18 profiles from the California Current System), and D. Siegel of University of California Santa Barbara (UCSB) (11 profiles from the Sargasso Sea). The logarithmic regression analysis of these data resulted in the algorithm

$$\hat{K}(490)=0.022+0.0984 \ [L_{wN}(443)/L_{wN}(555)]^{-1.403} m^{-1},$$
 (2)

with a standard error of 0.018 m⁻¹. The coefficients of Eq. (1) (Austin and Petzold, 1981) fell well within the 90% confidence intervals of the coefficients of Eq. (2). Therefore, Mueller (1995) concluded that there was insufficient evidence to reject the hypothesis that the two algorithms are equivalent.

During the past year, a much larger number (242) of K(490), $L_{wN}(443)$ and $L_{wN}(555)$ data triplets has accrued using radiometric profile data from 3 additional cruises in the Arabian Sea (C. Trees of SDSU/CHORS), 1 cruise in the Gulf of California (E. Valdez, H. Maske, *et al.*, of Centro de Investigacion Científica y de Educacion Superior de Ensenada, B.C. (CICESE)/Mexico and J. Mueller of SDSU CHORS), and the British transit of the North and

South Atlantic Oceans in September/October 1995 (G. Moore of Plymouth Marine Laboratory (PML), United Kingdom). These cruises were carried out (at least in part) under the SeaWiFS Science Team investigations of the participants. The regression analysis of this larger sample yields algorithm coefficients with much narrower 95% confidence intervals than those associated with Eq.(2) (Mueller, 1995), and in contrast to that earlier result, the new algorithm is significantly different from Eq. (1) (Austin and Petzold, 1981).

DATA AND METHODS

Profiles of spectral downwelling irradiance $E_d(z,\lambda)$ and upwelling radiance $L_u(z,\lambda)$ at SeaWiFS wavelengths (within 2 nm) were obtained from cruises in the Arabian Sea (C. Trees, SDSU CHORS), the California Current System (G. Mitchell, UCSD SIO), the Sargasso Sea near Bermuda, the Joint Global Ocean Flux Study (JGOFS) Bermuda Atlantic Time Series (BATS) site (D. Siegel, UCSB), and the Central Gulf of California (J. Mueller SDSU/CHORS, E. Valdez and H. Maske, CICESE) and the N. and S. Atlantic Oceans, the British Atlantic Meridional Transit (AMT) of September/October 1995 (G. Moore, PML, Plymouth, U.K.). The Arabian Sea profiles were measured using a MER-1032 and a MER-2040 radiometer calibrated at CHORS. The California Current profiles were measured with a MER-2040 also calibrated at CHORS and Biospherical Instruments, Inc. The Sargasso Sea data were measured using a PRR-600 calibrated at CHORS. All four MER instruments were manufactured by Biospherical Instruments, Inc., (BSI) of San Diego, CA. The AMT 95 profiles were measured using a Satlantic OCI-200 system calibrated at PML.

Each calibrated set of profiles of $E_d(z,\lambda)$, $L_u(z,\lambda)$ and $E_s(\lambda)$ (as measured with each instrument's deck radiometer) was analyzed using the integral least-squares solution of Mueller (1991) to determine profiles of $K_d(z,\lambda)$ and $K_L(z,\lambda)$, the vertical attenuation coefficients for $E_d(z,\lambda)$ and $L_u(z,\lambda)$, respectively. The AMT 95 profiles, however, were analyzed by G. Moore at PML. From these profiles, we extracted irradiance above the sea surface $E_s(\lambda)$ and upwelling radiances just below the sea surface $L_u(0^-,\lambda)$ for wavelengths λ of 443 and 555 nm, together with remote sensing K(490) calculated by averaging K(z,490) over the first optical attenuation length, *i.e.*

$$K(490) = \frac{1}{z_{90}} \int_{0}^{z_{90}} K(z, 490) dz, \qquad (3)$$

where z_{90} is the depth where

$$\frac{\mathrm{E}(490,z)}{\mathrm{E}(490,0)} = \mathrm{e}^{-\int_{0}^{290} \mathrm{K}(z,490)\mathrm{d}z} = \mathrm{e}^{-1} \cong 0.37 \tag{4}$$

Normalized water leaving radiances $L_{wN}(\lambda)$ for λ equals approximately 443 and 555 nm are calculated as

$$L_{WN}(\lambda) = L_{u}(0^{-}, \lambda)t_{f}(\lambda)\frac{\overline{F}_{o}(\lambda)}{E_{s}(\lambda)}$$
(5)

where $L_u(\lambda)$ and $E_s(\lambda)$ are taken from the analyzed profiles, $t_f(\lambda)$ is upward Fresnel transmittance through the air sea interface for radiance, and is mean extraterrestrial solar spectral flux. Within < 1%, $t_f(443)/t_f(555)$ equals approximately 1.0, so that from Eq. (5) the ratio of normalized water leaving radiances at 443 and 555 nm may be expressed as

$$\frac{L_{WN}(443)}{L_{WN}(555)} \approx \frac{L_u(0^-, 443) \ \overline{F_o}(443) \ E_s(555)}{L_u(0^-, 555) \ \overline{F_o}(555) \ E_s(443)},$$
(6)

From Neckel and Labs (1984), $\overline{F}_0(443) = 198.5$ and overbar $\overline{F}_0(555) = 190.0 \ \mu \ W \ cm^2 \ nm^1$.

The logarithmic regression model relating K(490) to the ratio $L_{wN}(443)/L_{wN}(555)$ may be expressed as

$$\ln [K(490) - 0.022] = \ln A + B \ln \left\{ \frac{L_{WN}(443)}{L_{WN}(555)} \right\},$$
(7)

where we would have from Eq. (1) A = 0.088 and B = -1.491, or from Eq. (2) A = 0.0984 and B = -1.403. The attenuation coefficient for pure water, $K_w(490) = 0.022 \text{ m}^1$, is the minimum possible value for K(490). The present sample of 242 profiles measurements were used to determine best-fit coefficients for Eq. (7) using simple linear regression.

RESULTS

Data from the sample described above were combined, using Eqs. (6) and (7), to assemble a regression sample of size N = 42. The linear least-squares fit to this data is

$$\ln \left[\hat{K}(490) - 0.022 \right] = -2.30261 - 1.29966 \ln \left\{ \frac{L_{WN}(443)}{L_{WN}(555)} \right\}$$
(8)

with $R^2 = 0.90$ and residual standard deviation 0.293 (in log space). The scatter of these data are illustrated in Fig. 1, together with the best fit regression line defined by Eq. (8). Also shown in Fig. 1, as a dashed line, is Eq. (1) (Austin and Petzold 1981).

-3-

Equation (8) may be transformed to the form of Eq. (1) as

$$\left[\hat{K}(490) = 0.022 + 0.1000 \left\{ \frac{L_{WN}(443)}{L_{WN}(555)} \right\}^{-1.29966} m^{-1}.$$
(9)

The measured data pairs are compared to Eq. (9) in Fig. 2 $[L_{WN}(443)/L_{WN}(555))$ on a logarithmic scale compared to linear K(490)].

The linear residual standard deviation of carrot K(490) (standard error of the estimate) associated with Eq. (9) is

$$S_{Kx} = \left\{ \frac{\sum \left[\overline{K}(490) - K(490) \right]^2}{N - 2} \right\}^{1/2} = 0.017 \text{ m}^{-1}$$
(10)

and the fit is unbiased. When Eq. (1) is applied to this data set, the linear residual standard deviation (in this case the *standard error of prediction*) $S_{Kx} = 0.018 \text{ m}^{-1}$ and the mean linear bias of the Austin and Petzold (1981) estimates of $\hat{K}(490)$ is 0.007 m⁻¹.

The (upper, lower) 95% confidence limits of the intercept in Eq. (8) are (-2.27452, -2.36003), and the 95% confidence limits of the slope are (-1.24596, -1.35335). Both the intercept (-2.4303) and slope (-1.491) of the natural log-transform of Eq. (1) fall outside these limits. On this basis, there is sufficient evidence at the 95% confidence level to reject the hypothesis that Eq. (1) is equivalent to Eq. (9).

DISCUSSION

Figures 1 and 2 emphasize scatter at different levels of K(490). In the log-log display of Fig. 1, the largest deviations from the regression fit occur at low values of K(490), within < 0.01 m⁻¹ of pure water. When the K(490) data are displayed on a linear axis (Fig. 2), it is immediately apparent that these deviations at low K(490), which appear to be very large in Fig. 1, are actually very small discrepancies. In fact, the linear K(490) scale (Fig. 2) shows clearly that the largest contributors to the linear standard error of the estimate, S_{Kx} [Eq. (10)], are at the high values [K(490) approximately >0.1].

The above analysis has addressed the question of whether the Austin-Petzold (1981) K(490) algorithm (Eq. 1), which was based on the ratio $[L_w(443)/L_w(550)]$, will produce accurate K(490) estimates when it is used with $L_{wN}(443)/L_{wN}(555)$ ratios. The log-transformed coefficients of Eq. (1) fall outside the 95% confidence intervals of the coefficients of Eq. (8), the log-linear least-squares fit to the present sample of 242 {K(490), $L_{wN}(443)/L_{wN}(555)$ }

-4-

pairs. Therefore, there is sufficient evidence at the 95% confidence level to reject the hypothesis that Eq. (1) is equivalent to Eq. (9). The difference between the two sets of predictions, while small, is nevertheless statistically significant at the 95% confidence level. Therefore, changing this algorithm's coefficients will improve the statistical uncertainty associated with SeaWiFS K(490) at-launch products. This change should be simple to implement, and we recommend that it be done.

In closing, it should be noted that the normalized water-leaving radiances used here have not been corrected for instrument self shading, or f/Q variability with solar zenith angle (A. Morel, personal comm., 1996). Furthermore the $E_d(490,z)$ profiles from which K(490) values were determined were not corrected for Raman scattering, These corrections, which we assume to be small, are deferred for possible use in a post-launch refinement of this SeaWiFS algorithm.

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Figure 1. Scattergram comparing K(490) and the normalized ratio $L_{WN}(443)/L_{WN}(555)$ from the Arabian Sea (Trees, SDSU), California Current System (Mitchell, UCSD), Sargasso Sea (Siegel, UCSB), Gulf of California (Mueller and Maske, SDSU and CICESE) and North and South Atlantic (Moore, PML). The solid line is the least-squares fit to the data, and the dashed line illustrates the CZCS K(490) algorithm of Austin and Petzold (1981).

-6-



Figure 2. Linear K(490) vs a logarithmic scaling $L_{wN}(443)/L_{wN}(555)$ display of the data and regression fit (solid curve) from Figure 1.

-7-

LIST OF ACRONYMS

- AMT Atlantic Meridional Transit
- BATS Bermuda Atlantic Time Series
- CHORS Center for Hydro-Optics and Remote Sensing
- CICESE Centro de Investigacion Científica y de Educacion Superior de Ensenada, B.C.
- CZCS The Nimbus-7 Coastal Zone Color Scanner
- JGOFS Joint Global Ocean Flux Study
- MER Marine Environmental Radiometer
- PML Plymouth Marine Laboratory
- RMS Root-Mean-Square
- SeaWiFS Sea-viewing Wide-image Field Spectrometer
- SDSU San Diego State University
- SIO Scripps Institution of Oceanography
- UCSD University of California, San Diego
- UCSB University of California, Santa Barbara

LIST OF SYMBOLS

 $E_d(z,\lambda)$ Downwelling irradiance (underwater)

- $E_s(\lambda)$ Downwelling irradiance incident at the sea surface (above water) Mean extraterrestrial solar flux (in units of irradiance)
- K(490) Remote Sensing diffuse attenuation coefficient, in m¹. The average of $K_d(z,490)$ over the first attenuation length. Regression model estimate of K(490) in m¹
- $K_d(z,\lambda)$ Vertical attenuation coefficient for $E_d(z,\lambda)$, in m¹
- $K_{L}(z,\lambda)$ Vertical attenuation coefficient for $L_{u}(z,\lambda)$, in m¹
- $L_u(z,\lambda)$ Upwelling spectral radiance at depth z
- $L_{wN}(\lambda)$ Normalized water-leaving radiance at the top of the sea surface (z = 0⁺) N Sample size
- S_{Kx} Linear residual standard deviation of modeled from water leaving radiance ratios
- $t_f(\lambda)$ Upward Fresnel transmittance through the air-sea interface for radiance
- z Depth, in m, below the air sea interface
- z₉₀ Depth, in m, equal to the first attenuation length
- λ Wavelength, in nm