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San Jose State University

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OPTICAL AND BIOLOGICAL PROPERTIES
IN THE EQUATORIAL PACIFIC OCEAN

A Thesis
Presented to
The Faculty of Moss Landing Marine Laboratories
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
Michael Edward Feinholz
December 1996

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APPROVED FOR MOSS LANDING MARINE LABORATORIES

William Broenkow

Dr. William W. Broenkow

N. Welschmeyer

Dr. Nicholas A. Welschmeyer

Kenneth H. Coale

Dr. Kenneth H. Coale

APPROVED FOR THE UNIVERSITY

Serena H. Stanford

ABSTRACT

OPTICAL AND BIOLOGICAL PROPERTIES IN THE EQUATORIAL PACIFIC OCEAN

By Michael Edward Feinholz

Vertical profiles of optical, biological, physical, and chemical properties were measured in the equatorial Pacific Ocean at 140°W during the summer of 1990 to test a new, simple radiometer design. Vertical and meridional structure of *in situ* beam attenuation, stimulated and natural chlorophyll *a* fluorescence, and spectral reflectance were compared with phytoplankton pigment concentration and biomass abundance estimated from discrete water samples. Statistically significant correlations were found between optical and biological data compiled from all profiles. Beam attenuation and stimulated chlorophyll *a* fluorescence provided the most precise estimates of particulate organic carbon and phytoplankton pigment concentration, respectively. Less precise, though highly significant estimates of pigment concentration were achieved via natural fluorescence and reflectance measurements made by the new radiometers. Effects of the equatorial current system, particularly upwelling and the Equatorial Undercurrent, were apparent in all measured parameters, and were examined in relation to optical and biological structure.

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INTRODUCTION

Light can be used in many ways to study phytoplankton. Single-celled algae, the phytoplankton, are studied because they comprise the base of the oceanic web of life, and as such regulate the flux of carbon within the ocean / atmosphere system as well as provide food for higher trophic levels. Photons of solar energy are collected by plant "antenna" pigments, for example chlorophylls, and converted to chemical energy, in the presence of nutrients and water, through the process of photosynthesis. By absorbing specific wavelength bands of solar radiation, phytoplankton pigments alter the color of sunlight in the sea. Energy absorbed by pigments, but not converted to chemical energy is dissipated either as heat, or reradiated at longer wavelengths as fluorescence. Photons not absorbed by particles, or by water itself, are either transmitted along their original path through the water column or scattered in altered directions. Measurement of reflected/scattered, transmitted, or fluoresced light, either from a natural (i.e. solar) or artificial source, can be used to study phytoplankton dynamics. These measurements can be made in three settings: *in vitro*, with pigments extracted from phytoplankton cells; *in vivo*, with living or non-living cells in an artificial environment; or *in situ*, with live cells in the water column. Depending upon the method employed, optical quantities can provide information over wide spatial and temporal scales, with varying degrees of accuracy and precision, regarding the dynamics of particles suspended in the sea.

In an attempt to utilize the spectral quality of underwater light fields to quantitatively access the biological dynamics in seawater, four 3-channel radiometers were designed and built by Dr. W. Broenkow and M. Yarbrough during the North

Atlantic Bloom Experiment (Sambrotto *et al.*, 1993), and deployed during an MLML-led expedition in 1990 in the high nutrient-low chlorophyll (HNLC) waters of the equatorial Pacific (Chavez *et al.*, 1991; Martin *et al.*, 1991; Johnson *et al.*, 1994). Two spectral bands at blue and green wavelengths were measured using a simple instrument in an attempt to reproduce Clark's ground-truthing experimental results for the Coastal Zone Color Scanner (CZCS) (Hovis *et al.*, 1980; Clark *et al.*, 1980; Gordon *et al.*, 1983). The CZCS estimated ocean surface chlorophyll concentrations by ratioing two or more wavelength ranges of water-leaving radiance. Algorithms to correlate pigment concentration with the color of sunlight reflected out of the ocean were developed by Clark and associates using an 80-channel underwater radiometer deployed from a ship in different regions of coastal and open-ocean waters. The attenuation of light between two depths was calculated to determine the light level just below the surface which was then be "transferred" through the water-air interface. Contemporaneous shipboard measurements were made of hydrographic, chemical, biological, and optical parameters to develop an understanding of the relationship between dissolved and particulate matter and the spectral composition of underwater sunlight.

This paper describes experiments performed to investigate the relationships between physical, chemical, biological, and optical properties during the *FeLine-I* research cruise aboard the R/V Wecoma to the equatorial Pacific Ocean near 140°W in June and July 1990. The hypothesis tested was: a simple *in situ* radiometer is an effective tool in the mapping of open ocean phytoplankton pigments. This hypothesis is addressed by first presenting background information about the optical properties

investigated. Methods are then presented to describe: 1) which variables were measured; 2) what instruments were used and how they were calibrated; 3) where field measurements were made; and 4) how data were acquired, processed, and analyzed. Next, results of processed field data are presented, followed by a discussion of hydrographic characteristics and relationships between measured variables. Lastly, conclusions are drawn regarding the capabilities of present instrumentation.

BACKGROUND

Definitions are presented here of optical properties which will be discussed throughout this paper. Concepts fundamental to this research include: electromagnetic radiation and its spectral distribution; absorption, scattering, attenuation, and reflectance of electromagnetic radiation; and how phytoplankton pigments affect electromagnetic radiation underwater.

Electromagnetic radiation transports solar energy across space to the earth's surface. It is measured as the time rate of flow of energy, or power Φ ($J s^{-1}$), and is expressed using the System International (SI) derived units of watts (W). The wavelength distribution of solar radiation penetrating below the surface of the ocean is centered in the visible region of the electromagnetic spectrum between 400 and 700 nm (Figure 1).

Two photon-collection geometries are defined in ocean optics: radiance and irradiance. Spectral radiance, $L(\lambda)$ ($W m^{-2} sr^{-1} nm^{-1}$), is measured as the amount of radiant energy, ΔQ (J), during a time interval, Δt (s), impinging upon a surface area, ΔA (m^2), as collected through a solid angle, $\Delta \Omega$ (sr), over a range of wavelengths, $\Delta \lambda$ (nm) (Figure 2):

$$L(\lambda) = \frac{\Delta Q}{\Delta t \Delta A \Delta \Omega \Delta \lambda} (W m^{-2} sr^{-1} nm^{-1}) . \quad (1)$$

Irradiance, $E(\lambda)$ ($W m^{-2} nm^{-1}$) is measured as the flow of energy, per unit time, impinging on a given area, over a wavelength range:

$$E(\lambda) = \frac{\Delta Q}{\Delta t \Delta A \Delta \lambda} (W m^{-2} nm^{-1}) . \quad (2)$$

Additionally, the measurement of irradiance involves collecting radiance over all incremental solid angles ($d\omega$) in a hemisphere and weighting each partial radiance by the cosine of its angular direction perpendicular to the detection surface (θ) (Figure 2):

$$E = \int_0^{2\pi} L \cos\theta d\omega . \quad (3)$$

Figure 2 shows diagrams of sensors (collectors, detectors and meters) to measure radiance and irradiance. Detectors are typically oriented vertically - a sensor directed downwards collects upwelled radiance or irradiance, $L_u(\lambda)$ or $E_u(\lambda)$, and a sensor directed upwards collects downwelled photons, $L_d(\lambda)$ or $E_d(\lambda)$. For the remainder of this paper, the wavelength notation (λ) is sometimes omitted to simplify notation, since radiance and irradiance are hereafter defined as spectral quantities.

Electromagnetic radiation is attenuated as it passes through matter. The attenuation coefficient expresses the fractional loss of energy per unit distance, with SI units m^{-1} . Attenuation coefficients (c) are measured for a beam of light over a path length (l , m), and for diffuse radiance (K_L), or irradiance (K_E), over a depth range (z , m):

$$c = \frac{1}{dl} \times \frac{d\Phi}{\Phi} \quad (m^{-1}) , \quad (4)$$

$$K_L = \frac{1}{dz} \times \frac{dL}{L} \quad (m^{-1}) , \quad (5)$$

$$K_E = \frac{1}{dz} \times \frac{dE}{E} \quad (m^{-1}) . \quad (6)$$

The beam attenuation coefficient measures the sum affects of absorption, a , plus scattering, b :

$$c(\lambda) = a(\lambda) + b(\lambda) \quad (m^{-1}) . \quad (7)$$

In the ocean, the total beam attenuation coefficient is a summation of beam attenuation coefficients for seawater (c_w), particles (c_p), and dissolved matter (c_d):

$$c = c_w + c_p + c_d . \quad (8)$$

The magnitude of the total beam attenuation coefficient in the open ocean is dominated by particulate scattering (Kiefer, 1984). Phytoplankton and their degradation products, and sometimes bacteria, are the primary source of particles within the open-ocean euphotic zone (Morel and Prieur, 1977; Fuhrman *et al.*, 1989). Attenuation by dissolved organic matter and other solutes in the open sea is generally small (Hoejerslev, 1980). Absorption and scattering by pure seawater itself at any wavelength are constant (Smith and Baker, 1981), hence, the beam attenuation coefficient varies with the number, size, and type of phytoplankton cells in the open sea (Figure 3).

The Spectrum of Electromagnetic Radiation

Energy (eV)	Frequency (Hz)	Radiation	Wavelength (m)	Use
	Hz 10^0			
10^{-12}	KHz 10^3	Electric Current	10^6	Power
10^{-9}	MHz 10^6	Radio	10^3 km	AM
10^{-6}	GHz 10^9		10^0 m	FM TV
10^{-3}	THz 10^{12}	MicroWave	10^{-2} cm	Radar
			10^{-3} mm	Microwave
10^0	10^{15}	Infrared	10^{-6} um	Heat Sight
		Visible		
10^3	10^{18}	Ultraviolet	10^{-9} nm	Diagnosis & Therapy
		X Rays		
10^6	10^{21}	Gamma Rays	10^{-12} pm	Deep Therapy
10^9	10^{24}	Cosmic Rays	10^{-16} uÅ	

Wavelengths of Visible Electromagnetic Radiation (nm)

400	450	500	550	600	650	700
VIOLET 400-450	BLUE 450-500	GREEN 500-570	YELLOW 570-590	ORANGE 590-610	RED 610-700	

Figure 1. The wavelength spectrum of electromagnetic radiation between 10^8 and 10^{-16} m. Energy (eV), frequency (Hz), radiation designation, and popular use of wavelength ranges are listed. Visible wavelengths between 400 and 700 nm are highlighted with approximate spectral ranges of colors from violet to red.

$$\text{Radiance } L(\lambda) = \frac{\Delta Q}{\Delta t \Delta A \Delta \Omega \Delta \lambda} \quad (\text{W m}^{-2} \text{ sr}^{-1} \text{ nm}^{-1})$$

$$\text{Irradiance } E(\lambda) = \frac{\Delta Q}{\Delta t \Delta A \Delta \lambda} \quad (\text{W m}^{-2} \text{ nm}^{-1})$$

Figure 2. Schematic diagrams of sensor design for the measurement of spectral radiance (top), and spectral irradiance (bottom) (adapted from Mobley, 1994; his Figs. 1.5, 1.6). The radiance "telescope" is typically oriented with its accepting aperture directed downwards to collect upwelled photons, $L_u(\lambda)$, while irradiance typically measures downwelled energy, $E_d(\lambda)$.

Figure 3. Spectral absorption, scattering, and attenuation coefficients for seawater and major phytoplankton pigments. Absorption and scattering coefficients for pure seawater (aw and bw, respectively) were measured by Smith and Baker (1981). Absorption coefficients for chlorophyll *a* (Chl *a*), photosynthetically active carotenoids (PSC), and photoprotectant carotenoids (PPC), were calculated for 1 mg/m³ concentrations from pigment-specific coefficients by Bidigare *et al.* (1990). Estimated total scattering coefficient (b est.), was calculated for 1 mg/m³ pigments from statistical results of Gordon and Morel (1983) and added to bw. Estimated total attenuation coefficient, (c est.), was calculated from the results of Voss (1992) for 1 mg/m³ pigments and summed with aw and bw.

All photosynthetic algae contain chlorophyll *a* which strongly absorb blue and red light, centered at 440 and 670 nm (*in situ*), and fluoresce red light, centered at 683 nm (with 25 nm half-bandwidth; Gordon, 1979). Chlorophyll *a* fluorescence can be stimulated *in situ* by an artificial light source or by sunlight (Kiefer *et al.*, 1989). All chlorophylls and their degraded phaeopigments fluoresce when dissolved in an organic solvent, i.e. *in vitro*. Algae often contain auxiliary photosynthetic and photoprotectant pigments which absorb blue and green light but do not fluoresce *in situ*, with the exception of phycoerythrin (Figure 4).

Reflectance describes the relative amount of light reflected by a surface - the ratio of reflected to incident light. Moreover, the spectral quality of reflectance quantitatively describes color (Morel, 1988). The ratio $L_u : E_d$ is referred to as remote-sensing reflectance, R_{rs} , an oceanographic approximation of irradiance reflectance, R :

$$R = \frac{E_u}{E_d} , \quad (9)$$

$$R_{rs} = \frac{L_u}{E_d} \text{ (sr}^{-1}\text{)} . \quad (10)$$

The color of ocean waters can be estimated via the ratio of remote-sensing reflectances at two wavelengths (λ_i, λ_j), termed the reflectance ratio, $r(i,j)$:

$$r(i,j) \equiv \frac{R_{rs}(\lambda_i)}{R_{rs}(\lambda_j)} . \quad (11)$$

The color of ocean water, and hence the reflectance ratio, is altered by dissolved and particulate matter (and by seawater itself) which spectrally absorb and scatter light.

By selecting wavelengths in the blue ($\lambda_i \approx 450$ nm) where chlorophyll a absorption is maximal, and in the green ($\lambda_j \approx 500$ nm) where chlorophyll a absorption is minimal, the reflectance ratio $r(i,j)$ is most sensitive to changes in phytoplankton pigment concentration (Clarke *et al.*, 1970; Gordon and Morel, 1983).

Simple radiometers were designed at Moss Landing Marine Laboratories to estimate water color as well as solar stimulated, or natural chlorophyll a fluorescence. Three of these instruments measure $E_d(\lambda)$ to quantify incident solar energy at a depth in the ocean, and $L_u(\lambda)$ to quantify the amount of energy reflected upwards from below that depth. Blue (450 nm), and green (500 nm) upwelled radiance and downwelled irradiance, were used to calculate the reflectance ratio:

$r(1,2) = R_{rs}(450) / R_{rs}(500)$, which was subsequently compared with phytoplankton pigment concentration. Emission of natural chlorophyll a fluorescence was estimated from far red (650+ nm) upwelled radiance relative to broad-band solar excitation irradiance (400 to 700 nm). Details of these, and other instruments used during this study are presented in the *Methods* section.

Figure 4. Excitation and emission spectra for chlorophyll *a* (Chl *a*) and phycoerythrin (Phyco) taken from Yentsch and Phinney (1981), and emission spectra for bacteriochlorophyll *a* (Bchl) from Broenkow *et al.* (1985). All spectra are shown normalized to peak response. The MLML fluorometer excitation and emission channels, F590, F680, and F740 were selected to measure fluorescence from Chl *a*, Phyco, and Bchl, respectively.

METHODS

Data for this study were collected during an oceanographic cruise, *FeLine-I*, in the central equatorial Pacific Ocean between 20 June and 10 July 1990 aboard the R/V Wecoma. Data were collected at five oceanographic stations along 140° west longitude between 3° south and 9° north latitude (Table 1, Figure 5). Station locations were selected by Drs. Johnson and Martin to sample high nutrient-low chlorophyll (HNLC) Pacific equatorial waters and conduct experiments to explain lower-than-expected primary productivity and phytoplankton biomass encountered there (Chavez *et al.*, 1991; Martin *et al.*, 1991).

Four classes of measurements (optical, biological, chemical, and physical) were obtained to investigate their inter-relationships within the euphotic zone of the equatorial Pacific Ocean. Optical measurements included vertical profiles through the water column of beam attenuation, stimulated and "natural" chlorophyll *a* fluorescence, and upwelled and downwelled spectral radiance and irradiance. Spectral radiance, irradiance, and natural fluorescence were also measured during 24 hour time-series experiments. Water samples were taken at discrete depths and analyzed for concentrations of photosynthetic pigments and particulate organic carbon, and for nutrients. Physical properties of seawater conductivity, temperature, and pressure were measured with an integrated CTD/rosette profiler. The profiler also measured dissolved oxygen concentration. Visual estimates of Secchi disc depths were made and water color was matched with Munsell color chips (Munsell Color Company, Baltimore, MD).

Table 1. *FeLine-I* station locations and deployment schedule.

Stn #	Date (GMT)	Time (GMT)	Position Latitude	Longitude	Deployment	Type
01	20 Jun 1990	22:47	17°55.9' N	154°29.6' W	CTD 3381	Deep
02	23 Jun 1990	01:03	14°35.9' N	148°45.9' W	CTD 4011	Deep
03	25 Jun 1990	16:00	09° N	140° W	GoFlo 3-2	POC
03	25 Jun 1990	23:18	09°04.5' N	139°57.3' W	CTD 3383	Radiom
04	27 Jun 1990	23:03	05°59.6' N	139°59.1' W	CTD 3384	Deep
04	28 Jun 1990	13:30	06° N	140° W	GoFlo 4-7	POC
04	28 Jun 1990	22:24	05°58.2' N	139°53.3' W	CTD 3386	Radiom
05	30 Jun 1990	22:35	00°04.5' N	139°59.9' W	CTD 3387	Shallow
05	01 Jul 1990	06:32	00°04.5' N	139°59.3' W	CTD 3388	Deep
05	02 Jul 1990	13:30	00° N	140° W	GoFlo 5-18	POC
05	02 Jul 1990	21:51	00°11.4' S	139°59.5' W	CTD 3389	Radiom
06	04 Jul 1990	10:34	03°00.5' N	139°59.5' W	CTD 4017	Shallow
06	04 Jul 1990	13:30	03° N	140° W	GoFlo 6-12	POC
06	04 Jul 1990	22:58	02°59.6' N	140°02.3' W	CTD 3390	Radiom
06	05 Jul 1990	07:15	02°58.1' N	140°03.9' W	CTD 3391	Deep
07	07 Jul 1990	11:01	02°59.9' S	140°00.9' W	CTD 3393	Deep
07	08 Jul 1990	14:00	03° S	140° W	GoFlo 7-8	POC
07	08 Jul 1990	17:12	02°58.9' S	140°00.5' W	CTD 4018	Radiom
07	08 Jul 1990	21:06	02°59.2' S	140°00.5' W	CTD 4019	Radiom
07	09 Jul 1990	00:21	02°59.1' S	140°01.1' W	CTD 4020	Radiom
07	10 Jul 1990	09:39	02°55.2' S	139°58.0' W	CTD 4023	Deep
07	10 Jul 1990	19:39	02°53.6' S	139°57.3' W	CTD 4025	Radiom

Schedule of time-series Radiometer Deployments

Stn #	Position Latitude	Longitude	Deployed (GMT)	Recovered (GMT)	Depths (dbar)
03	09°04.5' N	139°57.3' W	25 Jun 17:55	26 Jun 17:55	05, 15
04	05°58.2' N	139°53.3' W	28 Jun 15:30	29 Jun 15:30	10, 30
05	00°11.4' S	139°59.5' W	02 Jul 15:40	03 Jul 15:50	10, 20
06	02°59.6' N	140°02.3' W	04 Jul 16:05	05 Jul 16:10	10, 20
07	02°58.9' S	140°00.5' W	08 Jul 16:10	09 Jul 16:00	10, 20

Figure 5. Map of *FeLine-I* station locations.

Instrumentation

Instrumentation employed to collect data during this investigation included the Moss Landing Marine Laboratories (MLML) integrated CTD/rosette (Yarbrough *et al.*, 1989). The CTD measured seawater conductivity, temperature, pressure, and dissolved oxygen. The rosette carried six 3-liter sampling bottles. *In situ* data measured by the CTD were transmitted real-time to a shipboard computer for viewing during each cast. Submersible optical instruments were integrated with the CTD to measure light at different wavelengths within the visible region of the electromagnetic spectrum between 350 and 700 nm (Figure 1). These instruments were classified as either active or passive, depending upon whether they used an artificial light source or sunlight. Active instrumentation included a transmissometer and fluorometer, while radiometers were considered passive.

Integrated with the CTD was a modified Martek 1-meter folded-path transmissometer based on the Scripps Institute of Oceanography Visibility Laboratory design (Austin and Petzold, 1977). The transmissometer light source was a 1 Watt tungsten-filament lamp. Light was spectrally modified by Kodak Wratten #45 (490 nm peak transmittance), Schott BG-18, and Schott KG-1 (UV-blocking) filters (Table 2, Figure 6). Transmitted light was detected by United Detector Technologies UDT-555D silicon photodiode. Percent transmitted light at 490 nm was used to calculate *in situ* beam attenuation coefficient, referred to as c_{490} (m^{-1}).

The MLML three-channel fluorometer was also integrated with the CTD. Excitation energy was supplied by a xenon flash lamp passed through a Balzer 450/530 broad-band filter (336-572 nm) with 490 nm center wavelength (Table 2,

Figure 6). Fluorescent emission was detected by three Centronic Inc. OSD50-2AR silicon photodiodes paired with the following filters: Corion S10-590, center wavelength 590 nm; Corning 2-64, 667 nm high-pass; and Hoya RT-830, 733 nm high-pass. Electronics were modified from a Variosens II Fluorometer (Frunzel and Koch, 1980). Fluorescence excitation light exits a port on the end of the main electronics housing and three external heads containing fluorescence emission detectors, filters, and focusing optics are oriented perpendicular to, and surrounding the axis of the excitation beam. The three fluorometer channels were referred to as F590, F680, and F740. Wavelengths at 590, 667+, and 733+ nm were chosen to measure fluorescent emission from phycoerythrin, chlorophyll *a*, and bacteriochlorophyll, respectively (Broenkow *et al.*, 1985; Broenkow *et al.*, 1992; Figure 4).

Radiometers were designed at MLML to measure upwelled radiance and downwelled irradiance at blue and green wavelengths, as well as upwelled radiance at red wavelengths. Incident radiation was filtered by 40 nm band-pass Corion S40-450 interference filters with 450 nm center wavelength, 40 nm band-pass Ealing 35-5040 interference filters centered at 500 nm, and Schott RG-645 colored glass filters with 650 nm high-pass response. Light was detected by United Detector Technologies UDT-UV100 ultra violet-enhanced silicon photodiodes (Table 2, Figure 7). Blue, green, and red upwelled radiance sensors were referred to as Lu450, Lu500, and Lu650, respectively. Blue and green downwelled irradiance channels were called Ed450 and Ed500, respectively.

Integrated with each radiometer was a submersible Li-Cor LI-193SA spherical (4π collector) quantum sensor which measured quantum scalar irradiance in the 400 to

700 nm waveband: EoPAR ($\mu\text{M}/\text{m}^2/\text{s}$). Radiometers also included a thermistor, and pressure transducer. All analog signals were digitized with 14 bit resolution and stored by a Li-Cor LI-1000 data logger (Figure 8). A Li-Cor LI-190SA cosine (180°) quantum sensor was mounted on the ship above the water to monitor quantum surface-incident downwelled irradiance: EsPAR ($\mu\text{M}/\text{m}^2/\text{s}$). Data from the EsPAR sensor was recorded by a separate Li-Cor data logger.

Table 2. Sources, detectors, and filters used in optical instruments during *FeLine-I*.

Instrument	Source	Filter	Detector	Filter	Wavelength
Transmissometer	1W Tungsten	Wratten #45 Schott BG-18 Schott KG-1	UDT-555D	(none)	490
Fluorometer	Xenon flash	Balzer 450/530	OSD50-2AR OSD50-2AR OSD50-2AR	Corion S10-590 Corning 2-64 Hoya RT-830	590 667+ 733+
Radiometer	Sun	(none)	UDT-UV100 UDT-UV100 UDT-UV100	Corion S40-450 Ealing 35-5040 Schott RG-645	450 500 650+

Figure 6. Percent transmission spectra of optical filters used with the Martek transmissometer (top), and MLML fluorometer (bottom). The transmissometer detects one filtered channel while the fluorometer filters both the excitation source and three emission channels.

Figure 7. Percent transmission spectra of optical filters used with the MLML radiometers for sampling radiance (top) and irradiance (middle) at blue, green, and red wavelengths. Spectral responsivity of silicon photodiodes used in the radiometers to detect the filtered energy (bottom).

Figure 8. Cross-sectional sketch of MLML radiometer components. Radiation sensors include downwelled irradiance at 450 and 500 nm, quantum PAR irradiance, and upwelled radiance at 450, 500 and 650+ nm. Water temperature and pressure are also sensed and all data are digitized and stored by an on-board Li-Cor data logger.

All instruments were calibrated in the laboratory before field use, and in some cases calibrated in the field during experiments. CTD temperature, pressure, and conductivity sensors were calibrated at MLML using triple-point-of-water and gallium cell temperature standards, a dead-weight pressure test stand, and International Association for the Physical Sciences of the Ocean (IAPSO) standard salinity water. Radiometer Lu and Ed sensors were calibrated at MLML using Gamma Scientific GS-RS13 and GS-RS10A radiance and irradiance sources. Immersion corrections for underwater sensors were calculated for radiance (Austin, 1976), and approximated for irradiance (Petzold and Austin, 1988). Li-Cor quantum PAR sensor calibrations and immersion factors were provided by the manufacturer. Secondary salinity calibrations were performed at sea from rosette-collected water samples using IAPSO standard water and an AGE Instruments MiniSal salinometer. The dissolved oxygen sensor was also calibrated from water samples using a modified Winkler titration method (Carpenter, 1965). Air calibrations representing 100% transmission were performed on the beam transmissometer before and after each cast.

Sampling Design

A vertical water column profile with the CTD/rosette was classified as a shallow, deep, or radiometric cast. Upon arriving at an oceanographic station a shallow CTD cast to approximately 250 m was performed to quickly determine the mixed layer depth and the vertical structure of chlorophyll *a* fluorescence. This was used to help determine sampling depths for GoFlo bottle casts. Deep CTD casts, typically to 2000 m, required approximately two hours to complete, and were made once per station.

Radiometric casts consisted of one or more radiometers attached to, and lowered with, the CTD. A radiometric cast was performed near local apparent noon, outside the ship's shadow, and under clear sky whenever possible. A radiometric cast was stopped at 5 to 10 meter depth increments for approximately 5 minutes at each stop. The radiometer's data logger sampled at 5 second intervals and was configured to integrate readings over a 1 minute period before recording data. Light levels were thus integrated over several 1 minute periods at each depth during a cast. This technique allowed the highly variable nature of the underwater light field to be averaged. Before each cast, data loggers were programmed to begin sampling at an approximate start-of-cast time, then sealed inside the water-tight housing and the radiometer was secured to the CTD frame. After each cast, the data logger was removed from the radiometer to stop data collection and download data to a computer for storage and subsequent processing.

Surface-incident PAR irradiance, EsPAR, was measured to account for changing sky conditions during underwater radiometry. The cosine collector was mounted high in the ship's superstructure to avoid shadows, and data were recorded via Li-Cor data logger with 5 minute integration. This "deck cell" ran during the entire cruise except for approximately 1 hour every 5th night when data were downloaded to a computer.

At 5 stations during *FeLine-I*, a free-floating buoy was deployed for 24 hours - released and recovered near dawn (Table 1). The array was designed and built for *in situ* phytoplankton bottle incubations and included two MLML radiometers suspended at approximately 10 and 20 m. EsPAR levels were measured at incubation

bottle depths for productivity purposes. The data logger integration time was increased to 5 minutes on these "time-series" radiometer deployments. While two radiometers were deployed from an array, a noon-time radiometric CTD cast was performed using a third radiometer to characterize vertical water column optical structure.

Water samples for nitrate, phytoplankton pigments, and particulate organic carbon analysis were collected with Teflon-coated thirty-liter General Oceanics GoFlo bottles deployed on Kevlar hydrowire. Water samples were collected by other cruise participants using trace-metal clean techniques (Bruland *et al.*, 1991).

Near local apparent noon, Secchi depth measurements were made with a 30 cm, all white Secchi disc. Depth estimates were made by lowering the disc until it faded from view and raising it until it was again in sight, carefully avoiding surface sun glint. Reported Secchi depth was the mean of the two readings. Ocean color as sensed by the human eye was estimated using Munsell Color Company color chips selected by R.W. Austin (Scripps Visibility Lab). Two or more observers compared the color of the Secchi disc suspended at half its disappearance depth with a hand-held set of Munsell color chips.

Processing and Analysis

CTD data were processed during and after the *FeLine-I* cruise. Raw data were converted to scientific units, and derived properties of salinity, density, dynamic height and relative geostrophic current speed were calculated using standard methods (Fofonoff and Millard, 1983). Derived salinity profiles were compared with calibration water samples collected with CTD/rosette samplers and analyzed with an

AGE Instruments MiniSal salinometer standardized with IAPSO standard water.

Polarographic oxygen electrode results were compared with rosette-sampled water titrated by modified Winkler methods (Carpenter, 1965). Deep temperature and salinity were compared for precision and accuracy with nearest station data from the Geochemical Ocean Sections Study (GEOSECS; Craig *et al.*, 1981).

Chlorophyll *a* and phaeopigment concentrations were determined fluorometrically (via Turner Designs model 10 fluorometer) from 90% acetone extracts of samples filtered onto Whatman GF/F glass-fiber filters. Inorganic nitrate was determined with an Alpkem RFA segmented analyzer (Strickland and Parsons, 1972). Particulate organic carbon (POC) was determined by combustion analysis (University of Maryland, 1992). Pigment and nutrient analyses were performed by S. Tanner, while POC analysis was performed by C. Hunter, both of MLML. Chlorophyll *a* and phaeopigment concentrations were summed and subsequently referred to as chlorophyll-like pigments, *Chl*, as suggested by Gordon and Clark (1980), because their effects upon spectral reflectance are indistinguishable using coarse-bandwidth radiometry.

Raw beam transmissometer data ($\%T_{\text{raw}}$) were corrected using the average in-air calibration performed before and after each CTD cast. The expected transmission in air, due to Fresnell losses at four air-glass interfaces is 85.5%. Corrected transmission ($\%T$) was calculated from average before-and-after air calibration for each cast $\%T_{\text{air}}$ via:

$$\%T = \%T_{raw} \times \frac{85.5}{\%T_{air}} . \quad (12)$$

Beam attenuation coefficient at 490 nm (c_{490}) was calculated from equation 4 and corrected percent transmission:

$$c_{490} = -\frac{1}{l} \times \ln\left(\frac{\%T_{raw}}{100}\right) \quad (m^{-1}) , \quad (13)$$

where path length, l , for the Martek transmissometer was 1 m.

In situ stimulated chlorophyll a fluorescence at 680 nm, measured by the MLML fluorometer (F680) was "rescaled" to approximate chlorophyll a concentrations by a regression-determined equation developed by Yuen (1990):

$$F680' \approx 10^{(0.0384 \times F680 - 2.59)} \quad (mg \ m^{-3}) . \quad (14)$$

Approximate surface chlorophyll concentration was calculated from Secchi disc depth, SD (m), as described by Nolten (1980):

$$Chl_{est} \approx \left(\frac{15}{SD}\right)^2 \quad (\sim mg \ m^{-3}) . \quad (15)$$

Pigment and nutrient measurements taken at different times and depths, from different bottle and CTD casts, were binned and smoothed. Generally, an n -point running linear fit was applied to data compiled from each station. Data from n consecutive depths, possibly with multiple points at a depth, were fit with a linear regression equation. The mean depth was then used to calculate a best-fit value. The parameter n was typically set equal to 2, with some adjustment made for the shallowest and deepest depths. The resulting profile was then cubic-spline interpolated

to integer depths.

Raw radiometric data were edited, converted, normalized, smoothed, and interpolated before calculating derived quantities. The "editing" process selected data acquired during each at-depth integration period, or conversely, discarded data acquired while the instrument was between depths. Edited data were converted from raw Analog-Digital Units (ADU) to engineering units via calibration polynomials. Converted EsPAR ($\mu\text{M}/\text{m}^2/\text{s}$) was interpolated to times of underwater measurements, then used to normalize underwater measurements for changes in the above-water light field. Normalization and smoothing procedures are described below.

Effects of above-water light field fluctuations on underwater measurements need to be accounted for before underwater light attenuation can be attributed to properties of the water and its constituents. A cloud passing overhead and changing solar altitude, for example, could change underwater light intensity independent of in-water properties. Ideally, a spectro-radiometer floating just below the surface would be used to account for above-water and sea surface effects. Lacking such an instrument, changes in surface-incident downwelled PAR irradiance (EsPAR) were used to account for changing lighting conditions. An underwater radiometric measurement, L or E , taken at time t , was normalized to a reference time t_0 , by:

$$L(t)' = L(t) \frac{E_s\text{PAR}(t_0)}{E_s\text{PAR}(t)} . \quad (16)$$

The reference time used was the time of the surface-most underwater measurement.

Measurements of underwater light levels were smoothed to reduce environmental "noise" caused by surface wave focusing and depth changes induced by

ship pitch and roll. The smoothing method used was adapted from suggestions by Smith and Baker (1984, 1986). The approximately exponential decrease of light intensity in the sea with increasing depth (z) is described by the diffuse attenuation coefficient for either radiance, $\tilde{K}_L$, or irradiance, K_E (Equations 5, 6) as:

$$E(z) = E(0) e^{-K_E z} . \quad (17)$$

A linear least squares fit was applied to natural-logarithm-transformed radiance or irradiance values from n consecutive depths to obtain offset, A , and slope, K_E from:

$$\ln E = A - K_E z . \quad (18)$$

Smith and Baker (1984, 1986) suggested fitting data within intervals ± 2.5 meters from integer depths, but, since the depth resolution of these data were 5 to 10 meters, 2 to 5 consecutive depths were binned. "Smoothed" radiance or irradiance at the mean depth, z' of each interval was retrieved from regression coefficients using equations 18 and:

$$E(z') = e^A \times e^{K_E z'} . \quad (19)$$

Data were then cubic-spline interpolated to integer depths.

Derived radiometric parameters were calculated from processed data. Percent light level within the water column was derived from EoPAR at depth relative to its level just below the surface ($z = 0$ m). EoPAR at depth 0 m was extrapolated from the first few depth readings and the surface-most diffuse attenuation coefficient of EoPAR via equation 17. The lower extent of the euphotic zone was estimated as the depth where EoPAR reached one percent of its level just below the surface (see Kirk, 1994). Reflectance ratio, $r(1,2)$, within the euphotic zone was derived as an

index of ocean color from Lu and Ed at 450 and 500 nm using equations 10 and 11.

Passive, solar stimulated, chlorophyll *a* fluorescence was estimated by the natural fluorescence factor, F_n (sr^{-1}). Far-red upwelled radiance, $Lu650$ ($\mu\text{W}/\text{cm}^2/\text{sr}$) was converted to quanta ($\mu\text{M}/\text{m}^2/\text{s}/\text{sr}$) and divided by scalar quantum PAR irradiance, $E_o\text{PAR}$ ($\mu\text{M}/\text{m}^2/\text{s}$):

$$Lu650' = Lu650 \times \frac{1}{hc} \int \lambda \cdot d\lambda \times \frac{1}{N_A} \times \frac{1}{10^{11}} \left(\frac{\mu\text{M}}{\text{m}^2 \text{ s sr}} \right), \quad (20)$$

$$F_n = \frac{Lu650'}{E_o\text{PAR}} \quad (\text{sr}^{-1}). \quad (21)$$

Where wavelength λ for chlorophyll *a* fluorescence is centered at 683 nm (approximated by a Gaussian function with a width at half maximum of 25 nm; Gordon, 1979), Planck's constant $h = 6.626\text{E-}34$ ($\text{J} \cdot \text{s}$), the speed of light $c = 2.998\text{E}8$ (m/s), and Avogadro's number $N_A = 6.022\text{E}17$ ($\text{quanta}/\mu\text{M}$).

Data were processed and analyzed using MATLAB for Windows (Version 4.2c.1, The MathWorks, Inc., Natick, MA) on an IBM-compatible personal computer, and MLDBASE (MLML, Moss Landing, CA) on a Digital Equipment Corp. VAX 4000. Vertical profiles at 5 latitudes along the meridional transect were gridded (with the Kriging method) and contoured using Surfer (Version 6.01, Golden Software, Inc., Golden, CO).

RESULTS

Results of processed *FeLine-I* data are presented as contoured meridional cross-sections of physical, chemical, biological, and optical properties between 3°S and 9°N latitude along 140°W longitude in Figures 9, 12-15. The exceptions are reflectance ratio and natural fluorescence factor from time-series deployments, which are plotted as a function of time for each station in Figures 16, 17. Two depth ranges were contoured: 1) between the surface and 400 m for current speed, temperature, salinity, oxygen, and nitrate (Figures 9, 12); and 2) between the surface and 150 m for pigment, particulate organic carbon, and optical data (Figures 13-15). Results of curve-fit smoothing for nitrate, extracted pigments, radiance, irradiance, reflectance ratio, and natural fluorescence factor are presented as vertical profile plots for each station in the appendix (Figures 28 to 36). Also presented in the appendix are plots of temperature, pressure, radiance, and irradiance time-series radiometer data, and surface-incident PAR irradiance during the entire cruise (Figures 37 to 42). It is important to note here that upwelled sensors were sensitive to radiance above $10^{-2} \mu\text{W}/\text{cm}^2/\text{sr}$, EoPAR to $10^{-2} \mu\text{M}/\text{m}^2/\text{s}$, and downwelled irradiance to $10^{-1} \mu\text{W}/\text{cm}^2$.

CTD profiles of temperature and salinity along 140°W showed structure similar to the mean described by Wyrski and Kilonsky (1984) for transects at 150°W. The cross-equatorial temperature section displayed a well defined thermocline between about 27 and 14°C centered around 100 m deep and less than 100 m thick (Figure 9). Thermocline depth displayed a "ridge and trough" structure - shallowest at the equator and 9°N, and deepest at 3°S and 6°N. The thermocline thickness was 100 m between 3°N and 9°N, and 250 m at the equator, where the 27°C isotherm rose to 18 m and

the 12°C isotherm descended to near 300 m. The salinity distribution (Figure 9) showed lowest salinity water, 33.87 psu, at the surface near 6°N, associated with excess precipitation over evaporation in the Intertropical Convergence Zone (ITCZ). A tongue of high salinity water was associated with the thermocline between the south edge of the transect and about 6°N. Deep structure was very homogeneous, and displayed a tight temperature-salinity (TS) relationship below 400 m (Figure 10).

Water mass groupings outlined in Figure 10 were taken from Wyrski (1967). Warm, low salinity Equatorial Surface Water mass type was observed at all stations in the northern hemisphere. The 9°N and 6°N stations may have showed mixing of Equatorial Subsurface Water and California Current Surface Water at about 100 m. The straight line of TS pairs between 15°C, 35.15 psu and 8°C, 34.6 psu corresponded to Pacific Equatorial Subsurface Water. An Intermediate Water salinity minimum was reached at approximately 800 m with 5.3°C and 34.54 psu, below this depth the TS relation continues towards the 3°C, 34.6 psu bottom water.

Dynamic height and geostrophic flow (Figure 9) were calculated relative to 1000 dbar as suggested by Wyrski and Kilonsky (1984). Figure 11 shows the location of mean currents at 150°W over a 17 month period during the Hawaii-to-Tahiti Shuttle Experiment. Currents evident in Figure 9 include: 1) the eastward flowing Equatorial Undercurrent, EUC, centered 100 m deep at the equator in excess of 50 cm/s; 2) the westward flowing South Equatorial Current, SEC, greater than 20 cm/s above and to the North of the EUC; 3) a hint of the eastward flowing North Subsurface Counter Current, NSCC, less than 10 cm/s between 200 and 400 m at 3 to 6°N; and 4) the southern flank of the eastward flowing north Equatorial Counter Current, NECC,

Figure 9. Meridional distributions for dynamic height (ΔD) relative to 1000 dbar in dynamic cm, zonal geostrophic current speed (u) in cm/s, temperature (T) in °C and salinity (S) in psu between latitude 3°S and 9°N along longitude 140°W in the Pacific Ocean from the sea surface to 400 dbar during June and July 1990.

Figure 10. Temperature-salinity diagram for *FeLine-I* from CTD profiles between the sea surface and 2000 dbar. Water mass groupings, adapted from Wyrki (1967; his Fig. 4), show the range of the main surface and subsurface water types.

Figure 11. Mean zonal currents along 150°W between Hawaii and Tahiti in the upper 400 m from work by Wyrki and Kilonsky (1984, adapted from their Fig. 4). Westward flows are shaded dark and include the South Equatorial Current (SEC), Equatorial Intermediate Current (EIC), and North Equatorial Current (NEC). Lightly shaded eastward flowing currents are the Southern Subsurface Countercurrent (SSCC), Equatorial Undercurrent (EUC), Northern Subsurface Countercurrent (NSCC), and North Equatorial Countercurrent (NECC). Blank areas have zonal speeds less than 2 cm/s and include the South Equatorial Countercurrent (SECC). The longitude range covered during the *FeLine-I* transect is indicated above the diagram.

exceeding 20 cm/s near the surface between 6 and 9°N. The westward flowing Equatorial Intermediate Current, EIC, seen below the EUC at 150°W in Figure 11, was not observed during the *FeLine-I* transect.

The oxygen concentrations were higher, and nutrient concentrations lower, in the surface waters than in deeper waters, with high concentration gradients associated with the thermocline (Figure 12). Both the oxycline and nutricline, centered above or at 100 m, were deflected upwards at the equator and 9°N, and deflected downwards south of the equator and at 6°N. Similar to the thermocline, the nutricline diverged around the EUC at the equator. Nutrient concentrations in the upper 100 m were greater at the equator, than to the North or South. The minimum oxygen (greater than 40 μM) and maximum nutrient (greater than 30 μM) concentrations found in the transect were located below the strong gradients of isopleths at 9°N.

Extracted pigment and particulate organic carbon concentrations, sampled only in the upper 150 and 250 m respectively, also showed large vertical, and meridional variation. The cross-equatorial section displayed subsurface pigment maxima typical of the tropical ocean (Figure 13). Maximum extracted pigment concentrations (*Chl* = chlorophyll *a* + phaeopigment) along the transect were observed above the EUC at the equator at 50 m (0.65 mg/m^3) and at 70 m at 9°N (0.67 mg/m^3). Subsurface pigment maxima at 3°S, 3°N and 6°N were found at depths of 93, 78, and 69 m, with concentrations of 0.44, 0.54, and 0.47 mg/m^3 , respectively. Subsurface POC maxima were observed between 60 m at 3°S and 15 m at 6°N, but with greatest concentration, 4.36 μM , at the equator (Figure 14). POC showed no local concentration increase at 9°N as did *Chl*. Although pigments at the subsurface

chlorophyll maximum averaged three times greater concentration than near the surface, POC concentration only increased on average 13 percent between the surface and the deep POC maximum.

Rescaled *in situ* chlorophyll *a* fluorescence and 490 nm beam attenuation showed structure similar to *Chl* and POC in the upper 150 m. All stations displayed subsurface fluorescence and attenuation maxima - the deepest occurred at 3°S, but highest concentrations were observed above the EUC at the equator (Figures 13, 14). At the equator, F680' reached 0.47 ~mg/m³ at 53 m, and c490 attained 0.227 m⁻¹ at 31 m. A second, though weaker, local maximum occurred at 9°N for F680' at 0.41 ~mg/m³ at 63 m, and for c490 at 0.220 m⁻¹ at 17 m. Rescaled fluorescence increased by a factor of 4 (on average) between the surface and deep maximum while beam attenuation increased on average only 13 percent. Not presented here are *in situ* stimulated fluorescence measurements at 590 nm (phycoerythrin) and 740 nm (bacteriochlorophyll), because no detectable signal was found within the euphotic zone.

Radiometric results include percent PAR irradiance, reflectance ratio, and natural fluorescence between the surface and 150 m (Figure 15). The 1% light level, traditionally taken as the bottom depth of the euphotic zone (see Kirk, 1994), was shallowest at the equator, 73 m, and 9°N, 76 m, and deepest at 3°S, 98 m, and 3°N, 91 m. A subsurface reflectance ratio minima was shallowest and most intense at the equator, 0.61 at 43 m, or at the 6% PAR depth, and deepest at 3°S, 0.64 at 96 m or 1% PAR, but least intense at 6°N, 0.71 at 61 m or 2% PAR. Natural fluorescence factor (Fn) showed distinct subsurface maxima only at the equator, 2.59E-5 at 44 m or 5% PAR, and at 3°N, 1.91E-5 at 55 m or 8% PAR.

Figure 12. Meridional sections in the upper 400 dbar of dissolved oxygen (O_2) and nitrate (NO_3) in μM . Notice the strong oxycline and nutricline near 100 dbar which spread around the Equatorial Undercurrent at the equator.

Figure 13. Distribution of *in situ* rescaled stimulated chlorophyll *a* fluorescence ($F680'$) in approximate pigment concentration, $\sim \text{mg/m}^3$, and extracted chlorophyll *a* plus phaeopigments (Chl) in mg/m^3 . Phytoplankton pigment samples were collected from CTD rosette and GoFlo samplers at depths above 120 m.

Figure 14. Distribution of beam attenuation coefficient at 490 nm (c_{490}) in m^{-1} , and particulate organic carbon (POC) in μM . Contoured data are shown for the upper 150 dbar of the water column, where highly variable structure was observed. Water samples for particulate organic carbon were obtained from GoFlo samplers in the upper 250 m (POC structure between 150 and 250 m was very homogenous).

Figure 15. Distribution of percent EoPAR (%PAR) relative to extrapolated levels just below the surface, remote-sensing reflectance ratio ($r(1,2)$) from 450 and 500 nm, and solar-stimulated "natural" chlorophyll a fluorescence (F_n) between the sea surface and 150 dbar.

Reflectance ratio and natural fluorescence results from 24 hour time-series deployments showed: 1) low variability from deployment near dawn until dusk; 2) undefined levels during the dark of night; and 3) the return of levels with the next dawn just before recovery (Figures 16, 17). The reflectance ratio ($r(i,j)$) was lower at the deeper of the two deployment depths, and lower at the equator than at other stations for a given depth. This was consistent with increased pigment concentration at depth and at the equator. Reflectance ratio domed slightly through the day at 3°S, the equator, and 3°N. Conversely, natural chlorophyll a fluorescence was greater at the deeper of the two deployment depths, and relatively greater at the equator. The natural fluorescence factor (F_n) showed a distinct decrease throughout the morning and a rise in the afternoon at the 3°S, equator, and 3°N stations. It is noted that sunny, clear sky days were encountered between 3°S and 3°N, while measurements at 6°N were made under heavy overcast skies, and at 9°N under variable cloudiness.

Figure 16. Remote-sensing reflectance ratios ($r(1,2)$) from radiometers deployed for 24 hours (dawn till dawn) at 2 depths (10 and 20, or 5 and 15 m) from free-drifting buoys. Each panel displays data from a single station between 3°S and 9°N. Local apparent noon (LAN) is shown by the dotted line near 21:00 GMT. Reflectance ratios were undefined during the night, greater at the deeper of the two depths, and domed slightly during the day at 3°S, the equator, and 3°N.

Figure 17. Natural chlorophyll *a* fluorescence (Fn) from 24 hour radiometer deployments at two depths at stations between 3°S and 9°N latitude. Local apparent noon (LAN) is shown by the dotted line near 21:00 GMT. Note: larger signal at shallower depth for all stations; signal decrease from morning to noon, and increase after noon at 3°S, equator, and 3°N. Skies had variable clouds at the 9°N station and were overcast at 6°N, while skies were cloudy at stations to the South (see Figure 42).

Secchi disc depths ranged between 19 to 35 m, and surface chlorophyll *a* concentration estimated from Secchi depth (Equation 15) varied between 0.18 and 0.62 mg/m³ (Table 3). The shallowest Secchi depth and largest chlorophyll concentration were found at 9°N, while the deepest depth and smallest chlorophyll concentration were at 3°N. Munsell color matches were blue everywhere except at the equator, where they were blue-green.

Table 3. Secchi disc depth, Munsell color and approximate surface chlorophyll concentration encountered during *FeLine-I*.

Stn #	Date (GMT)	Position Latitude	Longitude	Secchi (m)	Munsell Color	Chl _{est} (~mg m ⁻³)
01	20 Jun 1990	17°59.9' N	154°29.6' W	25	10B 7/8	0.36
02	23 Jun 1990	14°35.9' N	148°45.9' W	28	10B 7/8	0.29
03	25 Jun 1990	09°04.5' N	139°57.3' W	19	10B 7/8	0.62
04	27 Jun 1990	05°59.6' N	139°59.1' W	27	10B 7/8	0.31
04	28 Jun 1990	05°58.2' N	139°53.3' W	20	10B 7/8	0.56
05	30 Jun 1990	00°04.5' N	139°59.9' W	25	10BG 7/6	0.36
05	02 Jul 1990	00°11.4' S	139°59.5' W	28	10BG 7/6	0.29
06	04 Jul 1990	02°59.6' N	140°02.3' W	21	10B 7/8	0.51
07	08 Jul 1990	02°58.9' S	140°00.5' W	35	10B 7/8	0.18
07	10 Jul 1990	02°53.6' S	139°57.3' W	28	10B 7/8	0.29

DISCUSSION

Spatial and temporal structure of optical properties in the equatorial Pacific were found to be linked to biological activity in the upper water column, which, in turn, was partly determined by availability of nutrients distributed by ocean currents. Wind and solar heating drive ocean currents. Currents distribute nutrients and elements essential for oceanic plant life. Phytoplankton affect optical properties of attenuation, reflectance, and fluorescence. Results from *FeLine-I* experiments are discussed here in relation to this chain of events, which involve variable water circulation, nutrient distribution, primary production, and modification of optical properties.

As described by Sverdrup *et al.* (1942), the westward flowing South Equatorial Current (SEC) and North Equatorial Current (NEC) are located in the region of the southeast and northeast trade winds (Figure 18 upper panel). The SEC is about 2000 km wide, located between 5°S and 5°N and flows relatively fast at 40 cm/s. The NEC is narrower and slower than the SEC, approximately 1500 km wide, North of 10°N, 10 cm/s. The eastward flowing Equatorial Counter Current (ECC) is found between the SEC and NEC in a zone of weak and variable winds called the Intertropical Convergence Zone (ITCZ), or the doldrums. The ECC is relatively narrow and slow, 400 km wide flowing at 10 cm/s. These three currents are confined to the surface layer above about 100 m. Below the surface at the equator is the fast and compact, eastward flowing Equatorial Undercurrent, EUC: 300 km wide, 200 m thick, up to 150 cm/s; its core centered at about 100 m depth (Cromwell *et al.*, 1954; Knauss, 1963).

Figure 18. Map of surface water circulation in the equatorial Pacific between 20°S and 20°N (top) and cross-section of currents and winds between 10°S and 15°N showing sea surface tilt (greatly exaggerated) and thermocline ridge-trough structure (bottom, adapted from Knauss, 1978, his Figure 7.4). In the bottom panel, direction of flow is denoted as westward (W) or eastward (E), and heavy arrows show upwelling and downwelling centers driven by divergent and convergent Ekman flow.

Vertical water column hydrography in the tropical Pacific is modified by the trade winds and the equatorial currents. Typical structure is characterized by a warm well-mixed surface layer, separated from colder deeper water by a sharp thermocline. This highly stable layer generally inhibits mixing between high oxygen, low nutrient water above, and low oxygen, high nutrients below. The depth of the thermocline, however, is not constant from south to north of the equator (Figure 18 lower panel, adapted from Knauss, 1978; his Figure 7.4). A shoaled thermocline, or "ridge," located at the equator and 10°N is associated with upwelling caused by divergent Ekman flow, while a "trough" near 5°N is due to convergent Ekman flow and downwelling (Wyrski and Kilonsky, 1984; Fiedler *et al.*, 1991). Strong vertical motion was mostly confined to depths within and above the thermocline (Wyrski, 1981).

The position of the EUC within the thermocline allows vertical water mixing across this boundary at the equator (Knauss, 1963). Temperature, oxygen, and nitrate sections during *FeLine-I* showed the breakdown of the thermocline at the equator, with high nutrient concentrations mixed upward to near 50 m, and increased oxygen mixed down to near 300 m (Figures 9, 12). The EUC also affects another chemical property: Coale *et al.* (1996) measured elevated dissolved iron concentration associated with the core of the EUC during *FeLine-I*, *FeLine-II*, and two of the JGOFS EqPac cruises. They propose that this source of essential metal, advected possibly from the New Guinea Platform, dramatically influences primary producers at the equator.

Physical mixing processes associated with the equatorial currents affected the location and concentration of biological properties. Evidence of increased biomass centered at about 50 m below the surface at the equator was seen as distinct "bullseye"

features in contours of extracted pigment and particulate organic carbon (Figures 13, 14). An enhanced phytoplankton community at the equator is supported by upwelled nutrients (Cullen *et al.*, 1992), and by dissolved iron mixed out of the EUC core by shear stresses at the boundary of the EUC and SEC (Coale *et al.*, 1996). A second local pigment maximum, at 9°N, centered 15 m deeper and with 3% greater concentration than the equatorial crop, was situated near the top of the intense and shoaled nutricline, perhaps influenced by upwelling at the ECC / NEC boundary. The lack of an associated POC maximum at 9°N suggests physiological adaptation of phytoplankton (discussed below) rather than increased biomass, and supports the notion that the EUC's influence at the equator extends beyond nutrient enhancement.

One step removed from the physics of mixing, variability of underwater optical properties were found related to biological variability. *In situ* chlorophyll *a* fluorescence, beam attenuation, reflectance ratio, and natural fluorescence displayed bullseye contours near 50 m at the equator (Figures 13, 14, 15). Since fluorescence and reflectance were expected to correlate with pigments, and beam attenuation with particulates, data were pooled and four regression analyses performed. Statistically significant correlations were found between: F680 and *Chl*; c490 and POC; r(1,2) and *Chl*; and Fn and *Chl* (Table 4; Figures 19, 20). F680 was transformed to account for the MLML fluorometer's electronic logarithmic amplifier. Logarithmical transformation of reflectance and natural fluorescence slightly increased statistical confidence, similar to results of Gordon *et al.* (1983) and Chamberlin *et al.* (1990). Different regression sample sizes were due to: 1) only *Chl* from CTD rosette samples were used where contemporaneous F680 data were taken; 2) all POC samples taken

above 250 m were paired by depth with c490 data from the nearest (in time) CTD cast; 3) $r(1,2)$ and F_n , from Ed and Lu signals above the instrument dark current, were paired by depth with smoothed, interpolated *Chl* (see appendix for plots of smoothed *Chl*, $r(1,2)$, F_n).

Table 4. Results of regression analysis between *FeLine-I* optical and biological parameters. Regression parameters presented are: standard error of estimate (SE), coefficient of determination (r^2), sample size (N), Fisher's variance ratio (F), and probability (P).

Regression Equation	SE	r^2	N	F	P
<i>Chl</i> = $10^{(0.0248 \times F680 - 1.71)}$	0.1 mg/m ³	0.67	27	51	« 0.0005
POC = $24.6 \times c490 - 1.05$	0.5 µM	0.81	55	225	« 0.0005
<i>Chl</i> = $0.14 \times r(1,2)^{-2.71}$	0.1 mg/m ³	0.60	87	125	« 0.0005
<i>Chl</i> = $1.071.5 \times F_n^{0.728}$	0.1 mg/m ³	0.61	79	122	« 0.0005

Figure 19. a) Chlorophyll-like pigment concentration (Chl) versus raw chlorophyll *a* fluorescence (F680). b) Particulate organic carbon (POC) versus beam attenuation coefficient at 490 nm (c_{490}). Individual data points are displayed with least-squares regression line and regression equation, standard error (SE), coefficient of determination (r^2), and sample size (N).

Figure 20. Log₁₀ linearized chlorophyll-like pigment concentration (Chl) in mg/m³, versus a) remote-sensing reflectance ratio (r(1,2)), and b) natural chlorophyll *a* fluorescence (Fn) with linear regression line and its equation, standard error of the estimate (SE), coefficient of determination (r^2), and sample size (N).

The statistical relationship between F680 and *Chl* during *FeLine-I* (Table 4) compares well with previous experiments using the MLML three-channel fluorometer in the North Pacific (Equation 14; Yuen, 1990). The slope and offset from *FeLine-I* were 10% lower than before, probably because phaeopigment concentration was summed with chlorophyll *a* concentration during *FeLine-I*.

Beam attenuation coefficient (*c*) is commonly used to estimate the concentration of suspended particulate matter (SPM) in seawater, but the relationship between *c* and SPM may vary by more than an order of magnitude throughout the world's oceans (Baker and Lavelle, 1984). During the North Atlantic Bloom Experiment (NABE), Gardner *et al.* (1993) measured a ratio POC (μg/l) : *c_p* (660 nm) of 378 (*c_p* = *c* - *c_w*, assuming constant and negligible *c_d*; Equation 8). To compare this result with *FeLine-I* required converting POC (μM) to μg/l, subtracting *c_w* from *c*₄₉₀ (*c_w* (490 nm) = 0.0227 (m⁻¹); Smith and Baker, 1981), and (approximately) converting *c* between 490 and 660 nm (*c*-*c_w*(670) = 0.850 × *c*-*c_w*(490) - 0.032; Voss, 1992). This yielded a POC (μg/l) : *c_p*(670) ratio equal to 347 during *FeLine-I*, which was within 10% of NABE results (Figure 21a). In the equatorial Pacific, Gardner *et al.* (1995) found SPM (μg/l) : *c_p* (660 nm) equal to 642 during a non-El Niño time series, which also compares well with a converted *FeLine-I* SPM (ug/l) : *c_p* (670 nm) ratio of 694 (assuming POC/SPM = 0.5; Gardner *et al.*, 1993).

Since we had intended to reproduce Clark's CZCS experiments relating ocean color to pigment concentration, it was instructive to compare our results with his. Clark compared pigment concentrations (<*C*>) between 0.029 and 5.4 mg/m³ with ratios of water-leaving radiance *L_w*(λ) (calculated from upwelled radiance and the

diffuse attenuation coefficient for radiance, and transmitted through the air-sea interface) at two wavelengths, 443 and 550 nm: $R(1,3) = L_w(443)/L_w(550)$ (Gordon *et al.*, 1983). Regression equations obtained by Clark and during *FeLine-I* were not very well comparable (Figure 21b). First, pigments ranged between 0.13 and 0.64 mg/m³ during *FeLine-I* radiometric casts. Spectral resolution of Clark's radiometer was 4 nm while that of the MLML radiometer was 40 nm, and center wavelengths were different: 443 and 550 nm versus 450 and 500 nm. While Clark compared the color of light leaving the ocean to surface pigment concentrations, *FeLine-I* experiments compared *in situ* color and pigments. Lastly, Clark's radiance ratio is not equivalent to the reflectance ratio used here. Reflectance was employed during *FeLine-I* to account for the large spectral variability of downwelled irradiance with increasing depth. Water-leaving radiance, however, is the product of more spectrally constant surface-incident irradiance (under clear skies and within a short time interval), and downwelled irradiance was not remotely-sensed by the CZCS and hence not included in Clark's regression.

The design of our "natural fluorometer" was patterned after an instrument described by Kiefer *et al.* (1989). During work in the South Pacific gyre they found chlorophyll *a* concentration (less than 1 mg/m³) to be 2100 times their natural fluorescence coefficient (Ψ_f), defined as $4\pi 27 Lu(683) \times [k(PAR) + a(683)] / E_o(PAR)$. Their quantum $Lu(683)$ (1-nm-wide bandwidth) is multiplied by 27 to account for total fluorescence emitted in the far red, and is comparable to our broad-band quantum $F650'$ (Equation 20). The factor 4π converts between emitted radiance (sr⁻¹) and total fluoresced light, while $[k(PAR) + a(683)]$ accounts for attenuation of fluorescence with

depth and is approximately equal to 0.52 m^{-1} at chlorophyll concentrations less than 2 mg/m^3 (Kiefer *et al.* (1989). *FeLine-I* natural fluorescence factor (F_n) was converted ($\Psi_f \approx 4\pi \times 0.52 \times F_n$) and statistically compared with *Chl*, which yielded a slope of 2770, or about 30% greater than Kiefer's 2100 (Figure 21c). Furthermore, from Kiefer *et al.* (1989), the reciprocal of the slope is the product of the quantum yield of fluorescence (0.035 ± 0.005) and the *Chl a*-specific absorption coefficient (about $0.012 \text{ m}^2/\text{mg}$), or 0.00036 to 0.00048 (m^2/mg), which brackets $1/2770 = 0.000361$.

Figure 21. Comparison of *FeLine-I* regression equations with other experiments. a) Particulate beam attenuation coefficient ($c-c_w$ m^{-1}) at 660 nm (Gardner *et al.*, 1993), and at 670 nm (converted from *FeLine-I* c_{490} , see text) versus POC ($\mu\text{g/l}$). b) Water-leaving radiance ratio between 443 and 550 nm ($R(1,3)$; Gordon *et al.*, 1983) and *FeLine-I* reflectance ratio ($r(1,2)$) versus chlorophyll pigment concentration ($\langle C \rangle$ or Chl). c) Natural fluorescence coefficient (F_f) from Kiefer *et al.* (1989) and converted from *FeLine-I* fluorescence factor (F_n) versus chlorophyll concentration (Chl). See text for discussion of factors contributing to differences between equations.

Although statistical analysis revealed significant relationships between optical and biological parameters, additional information can be gained by studying within-profile variability (Cullen, 1982). This variability suggested possible changes in community structure and physiological status of the phytoplankton crop. Since direct measurements were not made during *FeLine-I* of parameters such as phytoplankton species composition, living versus detrital particle makeup, particulate shape and size, auxiliary pigment composition, or pigment-specific spectral absorption and scattering coefficients, the following discussion relies upon results of other research to postulate explanations for optical and biological variability observed during *FeLine-I*.

The ratio of particulate organic carbon to chlorophyll-like pigments, POC : *Chl* was examined as a proxy for the ratio of phytoplankton carbon to chlorophyll (C:Chl), and revealed characteristics of the primary producer population. The POC : *Chl* ratio was examined as a function of percent EoPAR to allow comparison of relative shapes independent of absolute light levels. Average POC : *Chl* from *FeLine-I* decreased from approximately 200 near the surface to about 50 at the 1% PAR depth (Figure 22a). Particles near the surface contained about three times more carbon than chlorophyll than those near the bottom of the photic zone. The observed shape and range of carbon : chlorophyll during *FeLine-I* was similar to reports from Welschmeyer and Lorenzen (1984) and Furuya (1990).

Diminished carbon : chlorophyll ratio (C:Chl) with depth may have represented phytoplankton photoadaptation to lower light levels, involving increased intracellular pigment concentration (Mitchell and Kiefer, 1988; Stramski and Morel, 1990). Increased C:Chl below the minimum may have been caused by an increase of non-

photoautotrophic or detrital particles, perhaps sinking out of the euphotic zone, or by a decrease of chlorophyll per cell, perhaps replaced by photosynthetic accessory pigments better able to absorb the modified spectral composition of light at depth. Another explanation for a changing ratio postulates changing taxonomic composition of the phytoplankton community within the water column (Cullen, 1982; Furuya, 1990). Coale (1991) found decreased C:Chl, by about a factor of 3, and larger size phytoplankton, principally diatoms, when iron was added to incubation samples from HNLC subarctic Pacific waters. Similarly, Greene *et al.* (1991) found three times increased C:Chl for temperate diatoms grown in iron limited culture.

After subtracting from c_{490} the attenuation coefficient of pure seawater, $c_{w490} = 0.0227 \text{ (m}^{-1}\text{)}$ (Smith and Baker, 1981), and dividing by phytoplankton pigment concentration, the pigment-specific beam attenuation coefficient, c_{490}^* , has been used to describe mechanics of light absorption by suspended particulates within the water column:

$$c_{490}^* = \frac{c_{490} - c_{w490}}{\text{Chl } a + \text{phaeo}} \text{ (m}^2 \text{ mg}^{-1}\text{)}. \quad (22)$$

Similar to POC : Chl structure, average c_{490}^* decreased nearly three fold from $0.7 \text{ (m}^2\text{/mg)}$ at the surface to 0.25 near the bottom of the photic zone, and increased below this minimum with increased optical depth (Figure 22b). Stramski and Morel (1990) found decreased c_{490}^* (1.11 to $0.17 \text{ (m}^2\text{/mg)}$) for picoplankton grown in culture with decreased growth irradiance, and attributed this to an increased "package effect." Bricaud *et al.* (1988) also concluded that packaging caused variation in c_{490}^* (0.65 to $0.05 \text{ m}^2\text{/mg}$) among 9 species of living phytoplankton cells in suspension.

The package effect reduces light harvesting efficiency of intact cells, compared to dissolved cellular material, and is proportional to the product of cell size and intracellular pigment concentration (Kirk, 1975; Platt and Jassby, 1976; Welschmeyer and Lorenzen, 1981). In other words, taxonomic or photoadaptive changes, resulting in larger algae and/or higher internal pigmentation could reduce pigment-specific attenuation. Additionally, varying proportions of detritus relative to living cells, or accessory pigmentation relative to chlorophyll a , would also affect attenuation per chlorophyll. Phytoplankton above the c490* minimum may have contained non-photosynthetic (photoprotectant) carotenoids, and below the minimum, photosynthetic accessory pigments (Bricaud *et al.*, 1995).

Figure 22. Logarithmic scaled percent scalar PAR irradiance (EoPAR) profiles of a) particulate organic carbon to chlorophyll-like pigment ratio (POC : Chl) and b) pigment-specific 490 nm beam attenuation coefficient (c490*). Solid lines are the mean for all 5 *FeLine-I* stations and dotted lines are ± 1 standard deviation (Stdev). Structure suggests physiological adaptation and/or community adjustments of phytoplankton.

Although the quantum yield of fluorescence for chlorophyll *a* extracted in an organic solvent (i.e. *in vitro*) is a constant 25%, fluorescence *in situ* (or *in vivo*) is not linearly proportional to chlorophyll *a* concentration. Kiefer (1973) described variable fluorescence per unit chlorophyll *a* for different light and nutrient conditions, while Falkowski and Kiefer (1985) described fluorescence variability as a function of: 1) optical absorption cross-section; 2) self shading; and 3) fluorescence reabsorption. Variability of *in situ* pigment-specific stimulated chlorophyll *a* fluorescence, $F680^* = F680/Chl$, averaged from all *FeLine-I* stations, was examined as a measure of physiological stress in phytoplankton (Figure 23a).

Diminished fluorescence yield at high light levels, due to fluorescence photoinhibition or quenching, has been observed typically at PAR greater than $600 \mu M/m^2/s$ (see Cullen and Lewis, 1995). During *FeLine-I*, $F680^*$ was maximal at $400 \mu M/m^2/s$ EoPAR, and decreased with increased EoPAR (Figure 23a). Beneath this maximum, $F680^*$ decreased by about a factor of 2 while PAR diminished by two orders of magnitude, presumably due to a combination of lower light absorption efficiency by pigments, and/or lower fluorescence yield. Decreased light harvesting ability might have been caused by increased package effect, causing increased self shading. Decreased fluorescence yield could result from: 1) increased nutrient and/or iron availability (Greene et al., 1992, 1994; Kolber *et al.*, 1994); 2) increased fluorescence reabsorption by shade adapted cells; or 3) increased optical cross-section from larger algal species. Increased $F680^*$ at low PAR levels may have resulted from dark adapted algae utilizing auxiliary pigments for photosynthesis: leaving non-functioning chlorophyll molecules to dissipate absorbed photons as fluorescence.

Passive *in situ* solar-induced fluorescence of chlorophyll α is not only a function of pigment absorption and fluorescence yield, but also a function of the quantity and quality of excitation energy, and backscattering properties of the aquatic medium (Cullen and Lewis, 1995). The backscattering coefficient $b_b(\lambda)$ (m^{-1}) accounts for the redirection of downwelled photons into the field of view of a sensor measuring upwelled radiance. Although the source of red light at depths below about 20 m should be entirely fluorescent (Kiefer *et al.*, 1989), corrections for backscattered sunlight could be made using downwelled irradiance and reflectance measurements made at wavelengths covering the chlorophyll fluorescence emission band (Chamberlin *et al.*, 1990). Without such a correction, Lu650, and hence F_n used here may have been overestimated at shallow depths. Conversely, underestimated F_n in surface waters may have occurred by using EoPAR - a measure of available energy - to estimate fluorescence excitation energy, because PAR includes energy at wavelengths outside the fluorescence emission band. Examination of average natural fluorescence per pigment concentration, F_n^* (Figure 23b) revealed a profile shape similar to that of F_{680}^* , and suggested photoinhibition at EoPAR greater than $150 \mu\text{M}/\text{m}^2/\text{s}$. Natural fluorescence inhibition may be exaggerated if F_n were underestimated in the upper water column. Photoinhibition was also evident in time-series data under bright sunny skies at 3°S , the equator, and 3°N , but less so under overcast skies at 6°N , or under cloudy skies at 9°N (Figures 17, 42). These observations suggest that a simple natural fluorometer can yield information comparable to that gained from traditional stimulated fluorescence measurements.

Figure 23. Logarithmic scaled scalar PAR irradiance (EoPAR) in $\mu\text{M}/\text{m}^2/\text{s}$ versus a) pigment-specific stimulated chlorophyll *a* fluorescence (F680*) in $\text{mV m}^3/\text{mg}$, and b) pigment-specific natural chlorophyll *a* fluorescence (Fn*) in $\text{m}^3/\text{mg}/\text{sr}$. Solid lines are the average of all data and dotted lines are ± 1 standard deviation (Stdev). Variability suggests photoinhibition of fluorescence at high light levels and changing absorption and fluorescence efficiencies below.

Examination of reflectance ratio versus extracted pigments revealed a distinct "V" shape, with one "leg" of the "V" found between the surface and the deep chlorophyll maximum (DCM), and the other leg below the DCM (Figure 24). A nonlinear relationship between $r(i,j)$ and Chl can be partially due to wide-band sampling of spectral light. Downwelled irradiance in the open ocean is spectrally attenuated by seawater and particulate phytoplankton (assuming negligible dissolved matter attenuation), resulting in increasingly monochromatic light with increased depth (Yentsch, 1960). If a broad band of wavelengths were sampled, with a center wavelength offset from the light field's peak transmitted wavelength, the dominant wavelength of light would shift within the band as a function of depth and pigment concentration. Integrating light over a wide range of wavelengths does not accurately reflect changes of the center wavelength in a spectrally non-uniform light field.

Effects of wide-band spectral measurement were investigated using models developed by Morel (1988) and Gregg and Carder (1990). Gregg and Carder's model approximated spectral downwelled solar irradiance just below the sea surface, $Ed(\lambda,0^-)$, from average extraterrestrial solar irradiance (Neckel and Labs, 1984), variable atmospheric attenuation (Rayleigh scattering, ozone, oxygen, and water vapor absorption, and marine aerosol scattering and absorption), variable sea-surface reflectance, and variable time and location. For our purposes, $Ed(\lambda,0^-)$ was modeled at local apparent noon on 1 July 1990 at the equator, 140°W (Figure 25d). Morel's model estimated spectral coefficients for diffuse attenuation of downwelled irradiance, $Ke(\lambda,Chl)$, and irradiance reflectance, $R(\lambda,Chl)$ as a function of chlorophyll concentration, given coefficients for pure seawater of backscattering, $bw(\lambda)$, and

diffuse attenuation, $K_w(\lambda)$ (Smith and Baker, 1981). In conjunction with $E_d(\lambda, 0^-)$, $K_e(\lambda, Chl)$ and $R(\lambda, Chl)$ were modeled here using different pigment concentrations to investigate the response of reflectance ratio to varied filter bandwidth.

A theoretical water column containing the mean *FeLine-I* equatorial pigment profile was used to model spectral downwelled irradiance and upwelled radiance as a function of depth and pigment concentration (Figure 25). $E_d(\lambda, z)$ was calculated from modeled $E_d(\lambda, 0^-)$ and $K_e(\lambda, Chl)$ via equation 17, at depth (z). $L_u(\lambda, z)$ was calculated from $E_d(\lambda, z)$, $R(\lambda, Chl)$, equation 9 and $Q = E_u/L_u$ (set equal to π , which is approximately valid for a completely diffuse radiance distribution;

Gordon *et al.*, 1988). Spectral L_u and E_d were then sampled using different bandwidth filters centered at 450 and 500 nm. A 40 nm wide-band relative filter response (MLML radiometer, Figure 7), a 10 nm narrow-band (MER 1032, Channel No. 03; Petzold and Austin, 1988; their Figure 33), and a single wavelength ($\Delta\lambda = 1$ nm, response = 1) were multiplied by L_u and E_d and integrated over wavelength (Figure 26). The reflectance ratio $r(450, 500)$ was then calculated from modeled wide, narrow, and single-wavelength L_u and E_d using equations 10 and 11.

Relationships between modeled *Chl* and $r(450, 500)$ indicate a non-Log-linear correlation when underwater light fields are measured over wide bandwidths, relative to $r(450, 500)$ derived from single wavelengths (Figure 26). This effect was due to the dominant wavelength of underwater light shifting within the wide sampling band as water and phytoplankton selectively attenuate blue and red wavelengths, and reflect green. Rather than ratioing reflectances at two selected wavelengths, a wide-band $r(i, j)$ instrument essentially ratios a different pair of measurements at each increasing depth

below the surface. SeaWiFS validation protocols established a goal of deriving chlorophyll *a* concentration within 35% uncertainty, and suggested spectral bandwidths of 10 nm $\pm$ 2 nm full-width at half-maximum (FWHM) (Mueller and Austin, 1995). Results from this model suggest that filter bandwidth less than 30 nm is required to approximate *Chl* concentration within 35% (Table 5). High-resolution spectral measurements can increase the precision with which pigments are estimated, but a price must be paid: reduced energy throughput, and hence lower measurable signal, require detectors with greater sensitivity and reduced dark current. Such detectors are more expensive and require more power to operate than the photodiodes used during *FeLine-I*.

Table 5. Percent error in Chlorophyll-like pigment concentration estimated from reflectance ratio $r(450,500)$ for filter bandwidths between 1 and 40 nm. Pigment concentrations between 0.05 and 5 mg/m³ (Case 1 pigment range encountered by Gordon *et al.*, 1983) were used to approximate $Lu(\lambda)$ and $Ed(\lambda)$ from models by Gregg and Carder (1990), and Morel (1988).

Filter bandwidth (FWHM nm):	1	10	20	30	40
Percent error in Chlorophyll <i>a</i> :	0	10	20	40	60

Figure 24. Variability of chlorophyll-like pigment (Chl) and reflectance ratio ($r(1,2)$) data compiled for regression analysis (see figure 20) shown for each *FeLine-I* station. Surface-most and deepest data are denoted (sfc, deep) as are data associated with the deep chlorophyll maximum (DCM). Deviation from linear correlation resulting in the "V" shape can be partially explained by comparing modeled wide and narrow bandwidth light sampling strategies.

Figure 25. a) Mean equatorial pigment profile (Chl) used to calculate b) spectral diffuse attenuation coefficient for irradiance (K_e) and c) spectral irradiance reflectance (R) from a model by Morel (1988). d) Spectral downwelled irradiance (E_d) just below the sea surface ($z = 0$ m) was modeled from Gregg and Carder (1990) to calculate $E_d(\lambda)$ and e) spectral upwelled radiance (L_u) from $K_e(\lambda)$ and $R(\lambda)$ at circled depths in the pigment profile. (Note: dynamic ranges of irradiance and radiance do not necessarily match those of MLML radiometers.)

Figure 26. Spectral downwelled irradiance (E_d) and upwelled radiance (L_u) from figure 25 sampled via 40 nm-wide MLML radiometer filter functions (Figure 6) centered at 450 nm (a,c) and 500 nm (b,d). e) Pigment concentration versus remote-sensing reflectance ratio ($r(450,500)$) calculated from integrated MLML wide-band filters, MER narrow-band filters, and single-wavelength samples, centered at 450 and 500 nm. The changing spectral quality of underwater light seen in the upper panels results in the "V" shape of filtered reflectance ratios. (Note: dynamic ranges of irradiance and radiance do not necessarily match those of MLML radiometers.)

CONCLUSIONS

These results suggest a coupling of processes in the equatorial Pacific: physical mixing supplied nutrients essential to phytoplankton, whose distribution and abundance modified optical properties in the upper water column. Statistical correlation between optical and biological properties were significant ($P \ll 0.0005$) and were evident from visual inspection of contoured cross-sections. As suggested by Cullen (1982), interpretation of "systematic variation within profiles" of optical and biological data pooled for regression analysis revealed possible physiological adaptation of algae and community adjustments. Modeled spectral light fields helped explain uncertainty within pigment concentrations estimated from radiometric measurements, and revealed potential improvements to the present system.

Relationships between physical, chemical, biological, and optical parameters within the photic zone during *FeLine-I* are summarized in table 6 and Figure 27. The top of the thermocline, approximated by the depth of the 27°C isotherm showed a ridge-trough structure indicative of vertical water motion. Thermocline ridges at the equator and at 9°N were taken as evidence of upwelling and surface divergence, while a trough at 6°N suggested surface convergence and downward flow. Upper limits of the oxycline and nutricline, approximated by the 200 and 7 μM isolines, respectively, also displayed the ridge-trough structure. The depths of the extracted pigment maximum, stimulated and natural chlorophyll *a* fluorescence maxima, and reflectance ratio minimum were in general, well correlated and were found near or above the bottom of the photic zone, estimated by the 1% PAR light level.

Depths of particulate carbon and beam attenuation maxima were also correlated but differ from pigment depths because of depth separation of living algae and detritus, and also physiological conditioning of the algal crop.

Table 6. Significant depths (m) of physical, chemical, biological, and optical properties encountered during *FeLine-I*.

Parameter	Latitude:	3S	EQ	3N	6N	9N
27°C Isotherm		70	18	68	83	60
200 µM Oxygen		94	61	74	85	81
7 µM Nitrate		102	52	81	99	77
POC maximum		62	40	30	15	23
<i>Chl</i> maximum		93	52	78	69	69
c490 maximum		40	31	35	12	17
F680 maximum		87	53	54	60	63
Fn maximum		na	44	55	53	60
r(1,2) minimum		96	43	83	61	65
1% EoPAR		98	73	91	84	76

Figure 27. Summary of cross-equatorial water column properties encountered during *FeLine-I*. The thermocline ridge at the equator, and trough at 6°N are evident in the depth of the 27°C isotherm (dotted line). Depth of highest phytoplankton pigment concentration (Deep Chlorophyll Max, dash-dot line) was associated with the depth of minimum remote-sensing reflectance ratio ($r(1,2)$ Minimum, solid line). Depth of the euphotic zone, approximated by the 1% PAR light level (1% EoPAR, dashed line) shoaled at the equator and 9°N where local phytoplankton pigment maxima attenuated light more quickly in the upper water column.

Interpretation of vertical water column variability of pigment-specific optical properties revealed potential sources of error when estimating primary producer "biomass" from a single property. Particulate carbon concentration did not directly co-vary with extracted pigment concentration throughout the water column. Similarly beam attenuation and chlorophyll fluorescence per unit pigment were not constant as a function of depth or light level. Photoinhibition of stimulated and natural chlorophyll *a* fluorescence was evident at the highest irradiance levels. Between the surface and the 1% light level, variability suggested increased phytoplankton size and/or increased intracellular pigment concentration, possibly due to changing taxonomy or photoadapted state. Increased nutrient and/or iron supply with increased depth possibly affected taxonomic size and hence pigment packaging, light absorption efficiency, and fluorescence yield. Below the 1% light level, variability suggested increased photosynthetic accessory pigments and/or increased detritus, bacteria, or microzooplankton.

Analysis of data gathered during *FeLine-I* revealed both strengths and weaknesses of the present MLML radiometer configuration. The fact that reflectance ratio and natural fluorescence factor covaried with pigment concentration confirms that a relatively simple instrument can be an effective tool. Further investigations in more eutrophic waters are recommended to test this system with pigment concentrations greater than 0.7 mg/m³. The usefulness of natural fluorescence measurements near the sea surface might be increased by implementing a means to correct for backscattered light and more accurately estimate fluorescence excitation energy. Investigation of modeled spectral underwater light fields suggest that narrower bandwidth filters are

desirable: this would require an upgrade of detector sensitivity to cope with decreased photon throughput. In addition, deployment configuration might be updated to reduce measuring light perturbed by ship, CTD, and instrument shadows.

The success of the CZCS, and present plans for remote-sensing ocean color instruments, including the Sea-viewing Wide Field-of-view Sensor, SeaWiFS, and Moderate Resolution Imaging Spectrometer, MODIS (Hooker *et al.*, 1992), highlight the need for understanding variability of optical properties within the oceans. The US Joint Global Ocean Flux Study (JGOFS) program has placed remote assessment of ocean surface pigments prominently in their efforts to understand ocean/atmosphere carbon fluxes and interrelationships with global climate change (Dickey and Siegel, 1993). Ground-truthing of water-leaving radiance and associated water constituents from both traditional ship-based deployments and time-series moorings are required to interpret remotely sensed radiance, and to calibrate global pigment maps. The current MLML radiometer configuration has shown utility for investigation of biology of living particles, or alternately, for describing how biology affects apparent optical properties within the upper water column: within small budget and package-size requirements, deployable from small vessels or moorings.

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APPENDIX

Plots of smoothed data and time-series data.

Graphs in this appendix document results of vertical-profile data smoothing, time-series radiometer data, and surface-incident irradiance levels. Smoothing was performed on processed profiles of nitrate, chlorophyll-like pigments, upwelled radiance at 450 and 500 nm, scalar quantum irradiance, downwelled irradiance at 450 and 500 nm, reflectance ratio, and natural fluorescence. These graphs present processed data points as "pluses" (+) and smoothed profiles as solid lines, with 5 panels per page: one panel for each station between 3°S and 9°N latitude (Figures 28 through 36). Processed radiometer data from time-series deployments are displayed as a function of time (hrs GMT) (Figures 37 through 41). These Figures contain 8 panels per page: 1 panel for each of the following sensors: pressure, temperature, Lu450, Lu500, Lu650, EoPAR, Ed450, Ed500. Lastly, surface-incident quantum PAR irradiance (EsPAR) for 25 June to 10 July 1990 are presented in Figure 42.

Figure 28. Results of depth profile data smoothing (solid line) via best-fit line to individual nitrate (NO₃) measured at each *FeLine-I* station between 3°S and 9°N.

Figure 29. Results of depth profile data smoothing (solid line) via best-fit line to individual pigment (Chl) measured at each *FeLine-I* station 3°S between 9°N.

Figure 30. Results of depth profile data smoothing (solid line) via best-fit line to individual 450 nm upwelled radiance (Lu450) measured at each *FeLine-I* station between 3°S and 9°N.

Figure 31. Results of depth profile data smoothing (solid line) via best-fit line to individual 500 nm upwelled radiance (Lu500) measured at each *FeLine-I* station between 3°S and 9°N.

Figure 32. Results of depth profile data smoothing (solid line) via best-fit line to individual quantum scalar PAR irradiance (EoPAR) measured at each *FeLine-I* station between 3°S and 9°N.

Figure 33. Results of depth profile data smoothing (solid line) via best-fit line to individual 450 nm downwelled irradiance (Ed450) measured at each *FeLine-I* station between 3°S and 9°N.

Figure 34. Results of depth profile data smoothing (solid line) via best-fit line to individual 500 nm downwelled irradiance (Ed500) measured at each *FeLine-I* station between 3°S and 9°N.

Figure 35. Results of depth profile data smoothing (solid line) via best-fit line to individual remote-sensing reflectance ratios ($r(1,2)$) measured at each *FeLine-I* station between 3°S and 9°N.

Figure 36. Results of depth profile data smoothing (solid line) via best-fit line to individual natural chlorophyll *a* fluorescence (*Fn*) measured at each *FeLine-I* station between 3°S and 9°N.

Figure 37. Results of 24 hour radiometer deployments at 3°S showing data from each sensor versus time (hours GMT) for radiometers deployed at 2 depths (10 and 20 dbar). Sensors include: water pressure (Pres); water temperature (Temp); upwelled radiance at 450, 500, and 650+ nm (Lu450, Lu500, Lu650); quantum scalar PAR irradiance (EoPAR); and downwelled irradiance at 450 and 500 nm (Ed450, Ed500).

Figure 38. Results of 24 hour radiometer deployments at the equator showing data from each sensor versus time (hours GMT) for radiometers deployed at 2 depths (10 and 20 dbar). Sensors include: water pressure (Pres); water temperature (Temp); upwelled radiance at 450, 500, and 650+ nm (Lu450, Lu500, Lu650); quantum PAR irradiance (EoPAR); and downwelled irradiance at 450 and 500 nm (Ed450, Ed500).

Figure 39. Results of 24 hour radiometer deployments at 3°N showing data from each sensor versus time (hours GMT) for radiometers deployed at 2 depths (10 and 20 dbar). Sensors include: water pressure (Pres); water temperature (Temp); upwelled radiance at 450, 500, and 650+ nm (Lu450, Lu500, Lu650); quantum PAR irradiance (EoPAR); and downwelled irradiance at 450 and 500 nm (Ed450, Ed500).

Figure 40. Results of 24 hour radiometer deployments at 6°N showing data from each sensor versus time (hours GMT) for radiometers deployed at 2 depths (10 and 20 dbar). Sensors include: water pressure (Pres); water temperature (Temp); upwelled radiance at 450, 500, and 650+ nm (Lu450, Lu500, Lu650); quantum PAR irradiance (EoPAR); and downwelled irradiance at 450 and 500 nm (Ed450, Ed500).

Figure 41. Results of 24 hour radiometer deployments at 9°N showing data from each sensor versus time (hours GMT) for radiometers deployed at 2 depths (10 and 20 dbar). Sensors include: water pressure (Pres); water temperature (Temp); upwelled radiance at 450, 500, and 650+ nm (Lu450, Lu500, Lu650); quantum PAR irradiance (EoPAR); and downwelled irradiance at 450 and 500 nm (Ed450, Ed500).

Figure 42. Surface-incident PAR irradiance (EsPAR) versus time (day of month) from 20 June to 12 July 1990. Heavy bars show duration of time-series radiometer deployments and the "X" marks the time of radiometric CTD casts at each *FeLine-I* station between 3°S and 9°N (see Table 1 for schedule of instrument deployments). EsPAR data were missing for 10 and 11 July 1990.