Remote Measurement of Algal Chlorophyll in Surface Waters: The Case for the First Derivative of Reflectance Near 690 nm

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Abstract

Remote sensing is an important technology for measuring algal-chlorophyll concentrations in surface waters. Our paper provides hyperspectral signatures, in the visible and near-infrared, associated with two experiments conducted outdoors in large water tanks; one involving relatively low amounts of chlorophyll over a narrow range and a second involving relatively high amounts over a wide range. The principal finding was that the commonly used near-infrared/red ratio is best for estimating pigment amounts when the concentration of chlorophyll is relatively low, and the first derivative of reflectance around 690 nm is best when the concentration is relatively high.

Introduction

Algal chlorophyll is measurable and quantifiable in a laboratory by extracting the plant pigments from the cells and analyzing the pigment concentration in the extract (Nusch, 1980). However, because the amount of algal chlorophyll is indicative of the productivity and trophic status of surface waters, it is desirable to monitor pigment densities over expanses of geographic space and at numerous points in time, both within one "growing season" and from one year to the next. Therefore, remote sensing is viewed as an important technology for assessing chlorophyll concentration (e.g., Johnson, 1978).

Purpose of Study

The general goal for our research project was to investigate basic relationships between spectral reflectance and widely varying densities of algal chlorophyll, while the specific objective was to compare techniques for analyzing amounts of algal chlorophyll in surface waters. The work summarized in this paper differs from previous studies in two ways. First, while most researchers study only a narrow range of relatively low densities of algal chlorophyll in water, we chose to analyze spectra for two experiments, one comprising a narrow range of relatively low chlorophyll amounts and one based on a wide range including very high pigment densities. Second, while we tested established procedures for measuring amounts of algal chlorophyll in surface waters, we also introduced the use of the first derivative of reflectance.

A fundamental contention guiding our research is that empirical relationships between spectral radiance and algal chlorophyll in water can best be elucidated by collecting data at close range in manipulated tank mesocosms using a hyperspectral sensor. This approach allows one to eliminate entirely, or at least minimize, certain problems associated with data acquired at aircraft and satellite altitudes, not the least of which is the atmosphere.

Literature Review

Several investigators have analyzed the relationship between algal chlorophyll and remotely acquired measures of reflectance using hyperspectral instruments at close range. Gitelson (1992) pointed out that the magnitude and the position of the maximum reflectance in the near-infrared (near 705 nm) can be used in predicting chlorophyll concentration. Mittenzwey *et al.* (1992) found a high correlation (0.98) between chlorophyll and a near-infrared (NIR)/red reflectance ratio. Quibell (1992) examined the links between reflectance measured over different freshwater algal genera and chlorophyll concentrations and found that, for inland waters, the volume reflectance in the NIR was best for estimating algal-chlorophyll concentrations. Rundquist *et al.* (in press) found that there was a stronger relationship between chlorophyll concentration and NIR/red for data acquired over a black surrogate bottom in shallow water than for white, and that the NIR/red ratio was more robust for predicting algal-chlorophyll concentration than was a simple NIR-red difference. The reader is referred to other related works, including Gower *et al.* (1984), Carder and Steward (1985), Vos *et al.* (1986), Hoge and Swift (1987), Vertucci and Likens (1989), Gower and Borstad (1990), Dekker *et al.* (1991), Gitelson and Kondratyev (1991a), Gitelson and Kondratyev (1991b), Gower and Kondratyev (1991), and Quibell (1991).

Experimental Design

Study Site and Sky Conditions During Data Collection

Two chlorophyll-dilution experiments were conducted at the Mead Research and Development Center (96°25'51" W and 41°10'34" N), an agricultural research station of the University of Nebraska-Lincoln, on 8 June and 4 August 1993, both un-

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der clear skies (Table 1). All data collection occurred between 11:56 AM and 13:43 PM, and between 10:26 AM and 11:22 AM Central Daylight Saving Time, respectively. Because the measurements were relatively close to solar noon (approx. 1:30 PM), variability in solar elevation was minimized and solar illumination was maximized (Deering, 1989).

The Water Container

The water tank used for the experiment was an 8543-litre vinyl pool, 366 cm in diameter and 91 cm in depth. The walls and bottom of the pool were lined with black plastic to eliminate extraneous internal reflectances (McCluney, 1976). The pool was located in an open field at the Mead site.

Instrumentation and Procedures for Measuring Surface Spectral Reflectance

A Spectron Engineering SE-590* spectroradiometer was used to collect radiance upwelling from the pool. This instrument acquires data in 256 discrete channels, among which 252 are used for recording radiance with four reserved for file-header information. The spectral range of the instrument is from 368.4 to 1113.7 nm. For this study, data from 402.1 to 896.4 nm (170 channels) were used because of significant noise in the water signal at wavelengths shorter than 400 nm and longer than 900 nm. The SE-590 "camera" was attached to a telescoping, truck-mounted boom, which was pointed south with the truck oriented east-west. The spectroradiometer was positioned over the center of the pool at a height of 135 cm. A nadir view angle was selected for use (Novo *et al.*, 1989). The 15° optic resulted in an instantaneous field of view of 35 cm by 35 cm on the water surface. A microcomputer initiated spectroradiometer scanning and stored the data.

A Kodak 18 percent gray card (25 cm by 20 cm), cross-referenced to a Barium-Sulfate ($BaSO_4$) panel (70 cm by 70 cm), was used in calibrating spectral data to solar downwelling radiation. The equivalent wavelength-specific radiance for the $BaSO_4$ reference panel ($S(\lambda)$) was computed using a regression model in the form of

$$S(\lambda)=a(\lambda)+b(\lambda)*G(\lambda) \quad (1)$$

where $G(\lambda)$ is the measured wavelength-specific radiance from the gray-card, and $a(\lambda)$ and $b(\lambda)$ are the regression coefficients.

Thus, bi-directional reflectance factors ($R(\lambda)$, in percent) were calculated using the following equation:

$$R(\lambda)=\frac{L(\lambda)}{S(\lambda)}Cal(\lambda)\times 100 \quad (2)$$

where $L(\lambda)$ is the wavelength-specific target radiance and $Cal(\lambda)$ is the calibration factor for the $BaSO_4$ panel. The latter allowed correction both for the non-Lambertian properties of the panel and the slight changes in solar-zenith angle. Two replicate scans were taken for each sample and the mean of the two was used in the analyses.

Algal-Chlorophyll Manipulation

The dilution sequences began with water containing 2190 µg/l of chlorophyll for Experiment #1 and 277 µg/l for Experiment #2. Both algal densities were induced by fertilization with a commercial garden product over a period of several weeks prior to the experiments. Algal-chlorophyll concentrations were determined in the laboratory by extracting chlorophyll-*a* and phaeophytin using standard chloroform-methanol extraction procedures (Wood, 1985). The values are not acid-corrected and represent total chlorophyll (chlorophyll-*a* and phaeophytin pigments; similar to Quibell, 1992).

Dilution sequences were designed to generate a wide range of total-chlorophyll concentration in Experiment #1 and a narrow range in Experiment #2. The amount of water to be removed from the pool and the amount of fresh well water to be replaced in order to achieve a specific chlorophyll concentration were determined. The dilution procedures included (1) removing the calculated amount of water by means of a pump, (2) replacing the subtracted amount with fresh well water, and (3) mixing well. Therefore, during the dilution sequences, algal-chlorophyll concentration was lowered stepwise.

For the first experiment, a total of ten dilutions with clear well water were carried out to generate a broad range of chlorophyll concentrations (measured at 2190 µg/l down to an estimated 340 µg/l). A total of nine dilutions were done in the second experiment to produce small gradients (between a measured 277 and an estimated 156 µg/l of chlorophyll). The pool was scanned with the spectroradiometer three times after each dilution, and the three derived datasets were averaged.

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TABLE 1. WEATHER CONDITIONS DURING DATA COLLECTION*

Date	Time	Air Temp. (F)	Rel Hum. (%)	Wind Sp. ($m\ s^{-1}$)	Wind Dir. (Degrees)	Solar ($W\ m^{-2}$)
6/8/93	1100	75.76	42.69	4.82	238.2	844.00
6/8/93	1200	76.80	41.06	5.89	230.60	914.00
6/8/93	1300	77.58	39.79	6.48	234.00	931.00
8/4/93	1100	72.18	68.58	1.52	310.00	758.00
8/4/93	1200	72.82	64.53	1.61	151.70	847.00

*We acknowledge the High Plains Climate Center at University of Nebraska-Lincoln for providing climate information.

Results and Discussion

Spectral Characteristics of Algal Chlorophyll

Reflectance spectra for varying algal-chlorophyll levels in both experiments are summarized graphically as Figure 1. The spectral features signifying the presence of algal chlorophyll in the water column include (1) low reflectivity between 400 and 500 nm (noted as *A* in Figures 1a and 1b) due to absorption of blue light (maximized at 441 nm in our experiments); (2) maximum green reflectivity between 560 and 570 nm (at *B*); (3) a minor inflection at about 640 nm (*C*), presumably due either to backscattering from dissolved organic substances (Gitelson, 1992) or accessory pigments; (4) classic red absorption near 676 nm (*D*) for both experiments; (5) prominent NIR reflectivity at about 697 nm for Experiment #1 and 693 nm for Experiment #2 (*E*); and (6) a minor NIR reflectance feature, at about 810 nm, (*F*), probably caused by backscattering from organic matter (e.g., algal cells), combined with the general absorption of NIR in clear water. It seems important to note that the prominent feature at *E* has been explained variously as the fluorescence of phytoplankton pigments (Carder and Steward, 1985; Hoge and Swift, 1987), anomalous scattering caused by absorption minima at 675 to 680 nm (Morel and Prieur, 1977), and a minimum in the combined absorption curves of algae and water (Vos *et al.*, 1986; Giltelson and Kondratyev, 1991b).

In general, for both experiments, as chlorophyll amounts increased, reflectance increased at *B*, *C*, and *E* in a regular pattern. Minor exceptions occurred at chlorophyll concentrations between 340 and 740 µg/l (Figure 1a), which may have been caused by ripples on the water surface due to a slight breeze during the experiment (see Table 1). Also, as chlorophyll amounts increased in both experiments, reflectance at *A* and *D* tended to decrease, as expected; however, the pat-

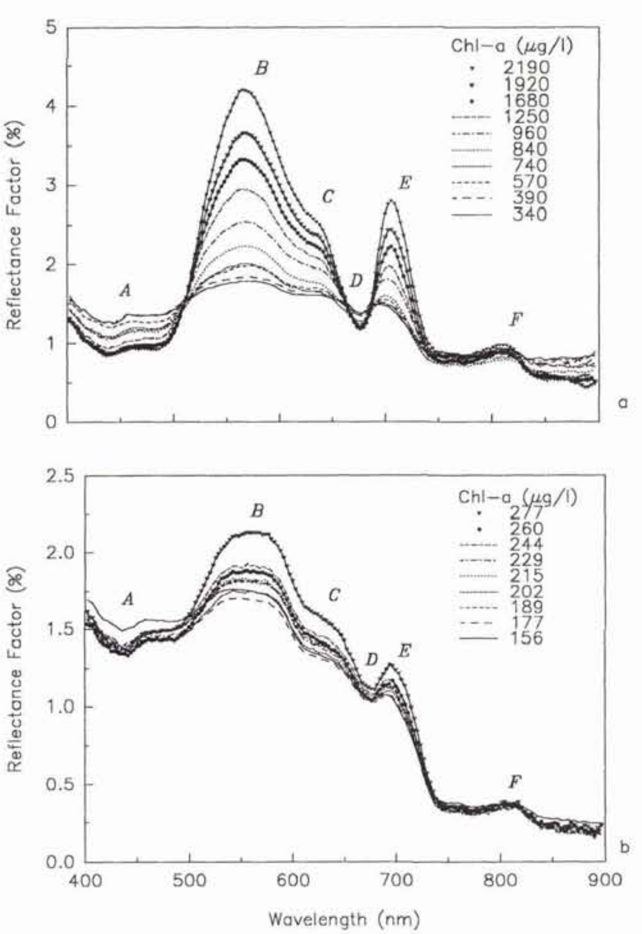

Figure 1. Surface reflectance with varying chlorophyll concentrations. (a) Experiment #1. (b) Experiment #2.

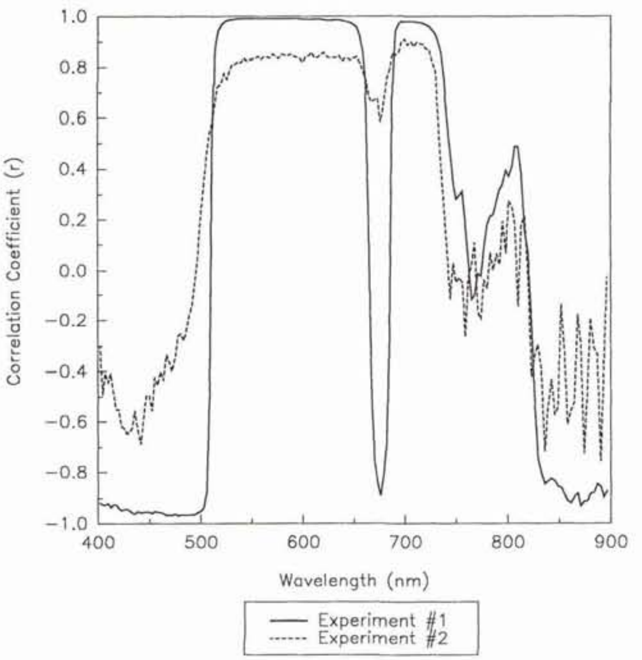

Figure 2. Correlation between surface reflectance and chlorophyll concentrations.

tern at D for Experiment #2 was not as regular as that for Experiment #1. The minor irregularities in the spectral pattern associated with Experiment #2 (Figure 1b) probably occurred because the overall chlorophyll levels were very low.

Correlating Reflectance and Chlorophyll Amounts

Correlation coefficients (r) were calculated to examine the strength of the relationship between chlorophyll amounts and corresponding spectral reflectance measured at each spectroradiometer channel between 400 and 900 nm (Figure 2). The highest r values for Experiment #1 (0.99) occurred at numerous wavelengths between 530 and 600 nm while the highest for Experiment #2 (0.91) was at 699.6 nm. Notice the difference in the overall strength of the correlations between Experiments #1 and #2.

Correlating the NIR/Red Ratio and Chlorophyll Amounts

Because NIR reflectivity tends to be directly related to chlorophyll density and red reflectivity tends to be inversely related, a simple ratio between NIR and red has been used by others in estimating chlorophyll concentration (e.g., Quibell, 1991; Mittenzwey *et al.*, 1992). In order to test this approach for measuring chlorophyll amounts, the NIR/red ratios from our data were plotted against chlorophyll concentrations (Figures 3a and 3b). In our case, the calculation was based on the ratio between the spectral band with maximum NIR

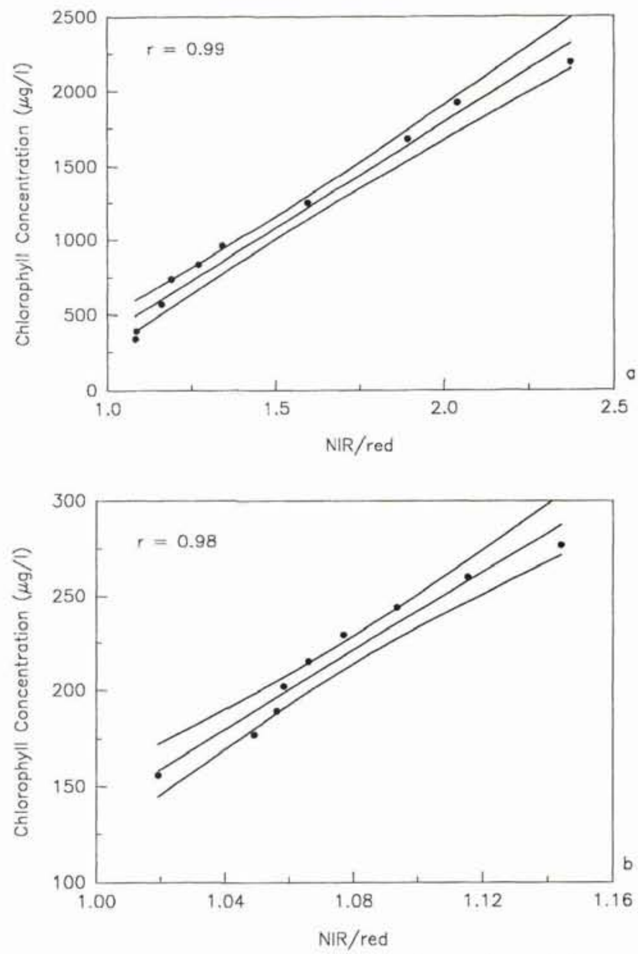

Figure 3. Correlation between the NIR/red ratio and the varying chlorophyll concentrations. (a) Experiment #1. (b) Experiment #2.

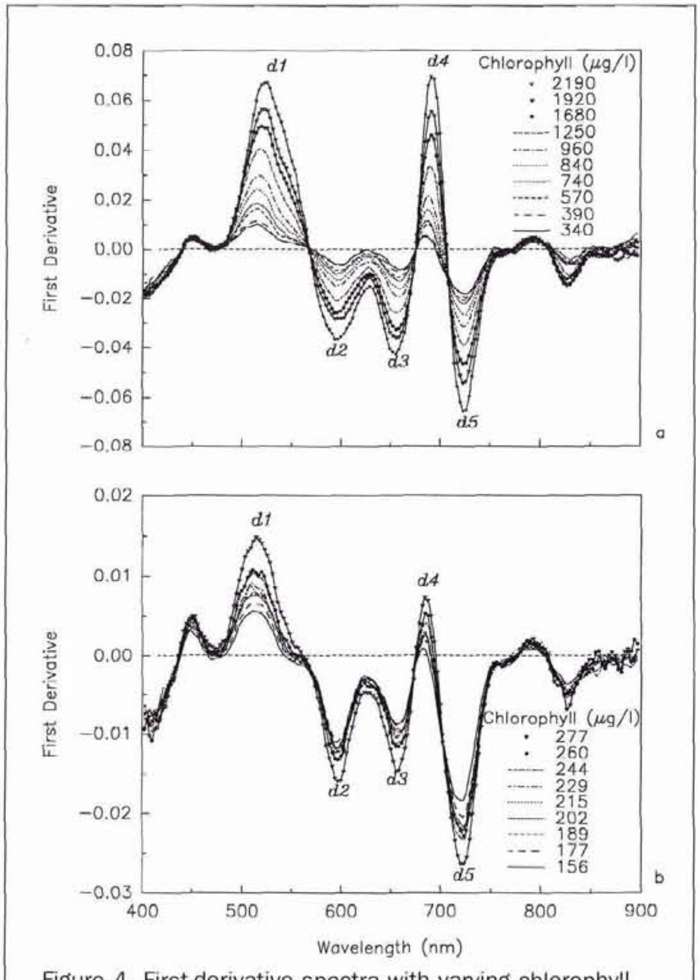

Figure 4. First-derivative spectra with varying chlorophyll concentrations. (a) Experiment #1. (b). Experiment #2.

reflectance and minimum red absorbance. As expected, strong linear correlations between the ratios and the chlorophyll were found for both datasets ($r = 0.99$ for Experiment #1 and 0.98 for Experiment #2)

Examining the First Derivative of Reflectance

Derivative spectra have been used both for measuring amounts of suspended sediment concentration and for removing the sediment signal from the composite reflectivity of surface waters (Chen *et al.*, 1992; Goodin *et al.*, 1993; Han and Rundquist, 1994). However, it appears that no researcher has exploited derivatives to explain amounts of algal chlorophyll in surface waters.

The first derivative of a spectral reflectivity can be defined as its rate of change with respect to wavelength (dy/dx). We applied the technique in hopes of elucidating further the chlorophyll and reflectivity relationship. First derivatives were computed by dividing the difference between successive reflectance values by the wavelength interval separating them, after applying a seven-point smoothing filter (Demetriades-Shah *et al.*, 1990).

Results from the derivative calculations are summarized in Figure 4. The derivatives with respect to the green peak, shown at *d1* (about 520 nm) and *d2* (about 600 nm), represent the rates of change for the "positive and negative sides" of the green maximum, respectively. Similarly, the derivatives at *d3* (about 660 nm) and *d4* (about 685 nm) characterize the slopes associated with the red-absorption minimum, and the derivatives at *d4* (about 685 nm) and *d5* (about 725 nm) can be linked to the NIR reflectance maximum. Notice that for both experiments, as chlorophyll concentration increased, the most noticeable changes in the plotted derivatives occurred at these five specific spectral locations (Figures 4a and 4b).

Correlating First Derivatives and Chlorophyll Amounts

To quantify the association between the first derivative of reflectance and chlorophyll concentration, correlation coefficients (r) were calculated and examined for each of the 170 channels of spectroradiometer data between 400 and 900 nm (Figure 5). The highest r value (to four decimal places) for Experiment #1 (0.9948) occurred at 690.7 nm, while the highest for Experiment #2 (0.98) occurred at 483.3 nm, although many wavelengths for Experiment #1 had comparably high correlations.

Comparing Models for Predicting Chlorophyll Amounts Using Reflectance, the NIR/Red Ratio, and the First Derivative of Reflectance Near 690 nm

To evaluate methods for estimating chlorophyll concentrations in surface water, three regression analyses were run for each of the two experiments. We compared the predictability of chlorophyll content using reflectance, the NIR/red ratio, and the first derivative of reflectance. Figure 6 shows the comparison involving the model linking chlorophyll concentration and reflectivity at 699.6 nm, the model linking chlorophyll concentration and NIR/red ratios, and the model linking chlorophyll and the first derivatives at 690.7 nm. The logic for using reflectance at 699.6 nm and the derivative at 690.7 nm were (1) the highest correlation ($r = 0.91$) between reflectance and chlorophyll for Experiment #2 was found at 699.6 nm while the highest correlation between the derivatives and chlorophyll for Experiment #1 occurred at 690.7 nm; and (2) these two wavelengths reside between the red-absorption minimum and the NIR reflectance maximum, so should theoretically be useful in quantifying chlorophyll concentration. Results from the comparison indicated that for both ex-

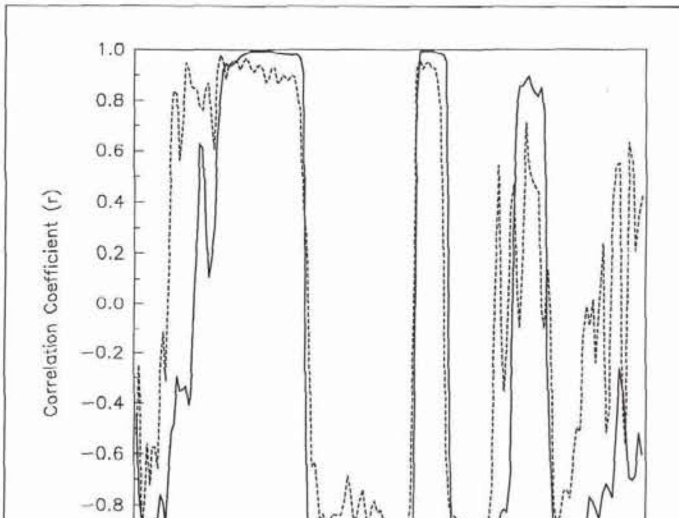

Figure 5. Correlation between first derivatives and chlorophyll concentrations.

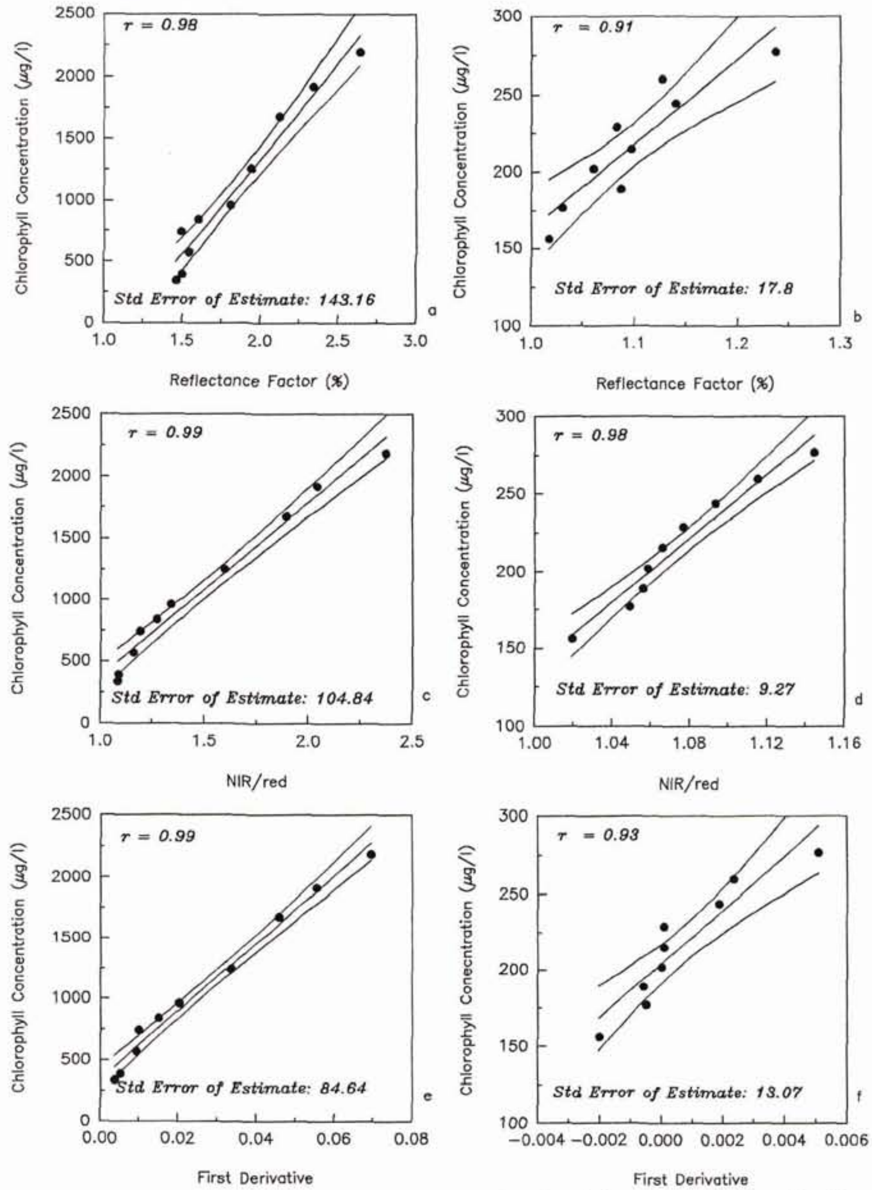

Figure 6. Comparison of linear regression models involving chlorophyll and reflectance at 699.6 nm, the NIR/red ratio, and the first derivative at 690.7 nm. (a) Reflectance, Experiment #1. (b) Reflectance, Experiment #2. (c) NIR/red, Experiment #1. (d) NIR/red, Experiment #2. (e) First derivative, Experiment #1. (f) First derivative, Experiment #2.

periments NIR/red (Figures 6c and 6d) and the first derivatives (Figures 6e and 6f) had stronger associations with chlorophyll concentrations than simple reflectance (Figures 6a and 6b). For Experiment #1, the derivative model was ranked the best ($r = 0.99$ and standard error of estimate = 84.64 μg/l) (Figure 6e) whereas the NIR/red model was the best for Experiment #2 ($r = 0.98$ and standard error of estimate = 9.27 μg/l) (Figure 6d).

Summary and Conclusions

The research summarized in this paper demonstrates that our experimental procedure, using hyperspectral remote sensing at close range and dilution sequences in a relatively large tank is both practical and useful. Controlled experimentation with algal chlorophyll in "clear water" should lead to a better understanding of chlorophyll concentration in natural water bodies, where the other constituents co-exist with phytoplanktonic algae.

Useful findings from the research included that the NIR/red ratio and the first derivative of reflectance near 690 nm were both proven effective in estimating chlorophyll concentrations. The most important result is that the ratio is well suited for low-chlorophyll concentrations with a narrow range and the derivative is better for high-chlorophyll concentrations with a wide range.

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