Influence of Chlorophyll and Colored Dissolved Organic Matter (CDOM) on Lake Reflectance Spectra: Implications for Measuring Lake Properties by Remote Sensing

by

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Abstract

Light reflected from lake surfaces can convey much information about water quality, especially algal abundance, humic content, turbidity, and suspended solids. Light reflectance from lakes is complicated and detailed spectra are needed for analysis of controlling factors. We obtained detailed reflectance spectra from the water surfaces of 15 lakes in east-central Minnesota and found patterns related to chlorophyll *a* (chl *a*), turbidity and humic matter (colored dissolved organic matter, CDOM). Increasing chl *a* and turbidity generally resulted in higher reflectance across the visible and near-infrared spectrum. Increasing CDOM led to low reflectance, especially below ~500 nm. Spectra of lakes with high chl *a* were distinguishable from those of lakes low in chl *a*, and lakes with low or high CDOM had readily distinguishable spectra. Several optical characteristics of lake water can be estimated from reflectance intensities measured over narrow wavelength bands. The ratio of reflectance at 700 nm to that at 670 nm was the best predictor of chl *a* over a wide range of conditions, including high turbidity and CDOM. Several relationships involving reflectance at 412, 443, 488, and 551 nm, the wavelengths used to calculate oceanic chl *a* from MODIS satellite data, also yielded a high R^2. The ratio of reflectance at 670 nm to 571 nm provided the best estimates of humic color despite the low absorbance of CDOM at these wavelengths. Relationships involving reflectance for all 15 lakes in the range 400-500 nm, where CDOM absorbs light, had low r^2 values; none was high enough for reliable estimates of lake color. For 10 lakes with low to medium chl-*a* levels ($\leq$ 10 mg m^{-3}), regressions involving 412 and 443 nm yielded moderately good relationships. Airborne and satellite remote sensing thus might be used to identify lakes high in CDOM, and may provide reasonable estimates of humic color in lakes with low chl-*a* levels.

Key words: reflectance hyperspectra, CDOM, humic color, chlorophyll, remote sensing, Secchi disk, transparency

Introduction

Satellite-based remote sensing is being used increasingly for regional-scale assessments of optically related water quality characteristics in lakes. For example, Kloiber et al. (2000, 2002a) developed a procedure to measure lake water clarity, expressed as Secchi depth (SD), using Landsat TM imagery. The procedure has been applied statewide in Minnesota and Wisconsin (Kloiber et al. 2002b; Olmanson et al. 2002; Chipman et al. 2004; http://water.umn.edu; http://www.lakesat.org/). A common measure of water quality, SD is used (along with chlorophyll and phosphorus) to quantify lake trophic state. However, the broad spectral bands of Landsat TM (and other satellite sensors with sufficient spatial resolution for measurements on small lakes) are not optimally designed to measure optical characteristics of water. Consequently, although Landsat TM and related imagery can provide reliable estimates for SD, it is not necessarily a strong predictor of other optically related water quality indicators, such as chlorophyll and humic color, and it is uncertain whether the nature of the material controlling SD (i.e., chlorophyll, humic color, or suspended minerals) in a given water body can be inferred from such imagery.

Hyperspectral sensors provide detailed visible and near-IR spectra of light reflected by a water body. Such spectra can provide information about dissolved and suspended constituents in water that have optical properties, including turbidity, suspended solids, humic color (hereafter referred to as colored dissolved organic matter, CDOM), and algal pigments such as chlorophyll *a* (chl *a*). Many detailed reflectance spectra have been measured and published previously, but most such studies have focused on terrestrial surfaces, especially vegetation and geology. Vertucci and Likens (1989) published the most detailed study of light reflectance spectra from lake surfaces. They studied 44 lakes with varying CDOM and chlorophyll levels in the Adirondack region of northern New York and reported that the spectra could be grouped into five categories based on shape and wavelength of maximum reflectance. In this study, we measured the reflectance spectra of 15 Minnesota lakes with a range of spectral characteristics, including lakes with low and high concentrations of both CDOM and chl *a*, to (i) aid in interpreting spectral data on lakes from satellite imagery and (ii) assess the feasibility of using hyperspectral measurements to quantify these constituents in lakes.

Background

When light reaches a water body, a small amount is reflected from the surface, but most of it is transmitted into the water, where it is attenuated by suspended and dissolved substances, as well as by water molecules. Absorbance by water is small across the visible spectrum, but increases sharply above 700 nm (Smith et al. 1981). Three types of material are responsible for light scattering and/or absorbance and resulting optical properties of water, such as color and transparency: (i) phytoplankton (suspended algae) and suspended particles related to algal activity, (ii) non-algal suspended solids–clays and other soil-derived material that is mostly inorganic, and (iii) humic substances, i.e., colored dissolved natural organic matter (CDOM).

Phytoplankton-related spectral features are complicated and often the most important in lakes. In the blue spectral range, reflectance by algae is low because of high absorbance by algal pigments. Chlorophyll absorbance causes a reflectance minimum near 440 nm (Gitelson et al. 2000), and the ratio of reflectance at 440 and 550 nm was used by Gordon and Morel (1983) to estimate chlorophyll levels in oligotrophic waters. A reflectance minimum at 490 nm results from absorbance by carotenoids (Yacobi et al. 1995). Absorbance by CDOM and scattering by particles can affect reflectance in the blue range of the spectrum more than chlorophyll does; for this reason, Gitelson et al. (2000) concluded that reflectance in this region has low sensitivity to phytoplankton density in productive waters.

Algae are green because their pigments absorb blue and red light but have minimal absorbance in the green region. The resulting green reflectance peak is at ~550 nm. Peak size is affected by the amount of backscattering by cell walls; non-organic suspended matter also contributes to backscattering, and the peak shifts upward as carotenoid concentrations increase (Schalles et al. 1998). A reflectance minimum at 670 nm results from absorbance by chl *a*, but Gitelson et al. (2000) found that light scattering by cell walls offset this absorbance such that reflectance spectra were insensitive to algal density at 670 nm. A reflectance peak at ~700 nm results from lower chl-*a* absorbance and strong scattering by algal cell walls and other seston.

Oceanographers have developed a physically-based model to estimate chl-*a* levels in the oceans using reflectance values at 412, 443, 488, and 551 nm (e.g., Carder et al. 2003). The basis for selection of these wavelengths is as follows. Chlorophyll in phytoplankton has an absorbance peak at 443 nm and low absorbance at 412 nm. In contrast, CDOM absorbance increases with decreasing wavelength and is much greater at 412 nm than at 443 nm. Phaeopigments (partial degradation products of chlorophyll) also absorb more strongly at 412 nm. The model uses these two wavelengths to estimate relative amounts of chl *a* and other light-absorbing substances (CDOM and phaeopigments), and it uses reflectance values at 488 and 551 nm to estimate effects of particle backscattering. The physically-based model produces valid results only at low chl *a* (< ~2 mg/m^3); at higher concentrations an empirical polynomial relationship based on the ratio of reflectance at 488 and 551 nm is used. Because chl-*a* levels in most inland waters are higher than 2 mg/m^3 during the growth season, a physically-based model similar to that used for the oceans is unlikely to be useful to estimate chl-*a* levels in lakes.

Soil-derived mineral turbidity tends to be more important in rivers and reservoirs than in lakes; exceptions include lakes in agricultural watersheds where poor management practices lead to soil erosion and urban areas where erosion from building or road construction is not controlled. Such conditions did not exist in the region where we conducted our study, and the effect of mineral turbidity on lake reflectance spectra thus was not a focus of the study.

CDOM consists of naturally occurring, water-soluble, biogenic, heterogeneous organic substances that are yellow to brown in color (e.g., Aiken et al. 1985). Autochthonous CDOM originates from algae and other organisms in lake; allochthonous CDOM originates outside the lake, especially from areas rich in organic matter, such as peat soils and bogs. CDOM absorbs visible light especially below ~ 500 nm, and its absorbance increases exponentially with decreasing wavelength. Nonetheless, Strömbeck and Pierson (2001) reported that absorbance of red light can be significant at high CDOM concentrations.

As implied above, two approaches have been used to relate reflectance to optically related constituents of water bodies. Most previous studies have relied on empirical regression relationships of the general type $C_{op} = a_1R_1 + a_2R_2 + \ldots$, where C_{op} is the value (e.g., concentration) of an optically related property (e.g., chl *a*), the R_i are reflectance intensities at specific wavelengths or ratios of reflectance at two wavelengths, and the a_i are regression-fitted coefficients. A few studies (e.g., Calder et al. 2003) have used a more fundamental (and complicated) approach based on inverse fitting of an equation relating reflectance to fundamental optical variables (Vertucci and Likens 1989): $R = Cbb_b/(a + bb_b)$, where R is irradiance reflectance from the water surface, C is a coefficient dependent on radiance distribution, b = total scattering coefficient (m^{-1}), b_b = backward scattering coefficient (m^{-1}), and a = total absorption coefficient (m^{-1}); R, a, b, and b_b all vary with wavelength. In turn, coefficients a, b, and b_b can be expressed as additive functions of scattering or absorption caused by pure water, CDOM, organic detritus, inorganic suspended matter, and phytoplankton (pigments).

Methods

Site selection and description

Reflectance spectra were obtained from 15 lakes in east-central Minnesota (Table 1) selected to represent a wide range of light absorbance and scattering resulting from several water quality characteristics. Background data on some lakes were available from a state agency database (www.dnr.state.mn.us/lakes) to guide the selection process, but most lakes were selected after an initial ground-based reconnaissance. At the extremes, Lake Francis and Typo Lake were selected for high algal density; Hanging Horn and Net Lakes were chosen for high humic color (CDOM); and Square Lake was chosen for its clear water (low CDOM and low algal abundance). Grace Lake was selected to represent lakes with both high algal density and high CDOM. The other lakes were selected for having intermediate (but varying) levels of algae and CDOM.

Lakes Calhoun, Harriet, and Nokomis and Cedar Lake are located in an urban setting. Square Lake is in a rural area dominated by deciduous forest. Cross and Typo Lakes and Lake Francis are in mixed agricultural and forested watersheds. The latter two are very shallow (maximum depth, ~ 2 m). The remaining lakes are in forested areas dominated by conifers and numerous bog wetlands and have a wide range of areas and depths.

Reflectance measurements

Reflectance measurements were made in August 2001 with a Spectron Engineering SE-590 spectrometer. Measurements were taken near midday (10 a.m. to 2 p.m.) from a small boat in the middle of the lakes, except for Cedar Lake and Lakes Harriet and Nokomis, where measurements were taken from a dock. Water depth at the ends of the docks was sufficiently large and water clarity sufficiently small that these measurements were not biased by light reflectance from bottom sediments. The radiometer was fitted with a 15^{o} field-of-view lens and a 1.8 m aluminum rod to hold the spectrometer over the water and away from the boat or dock. A bubble level was used to ensure that the spectrometer was perpendicular to the water surface. Data were collected on a laptop computer connected to the spectrometer using software from CALMIT Laboratories, University of Nebraska, Lincoln. The software assigned wavelength values to each instrument channel based on calibrations performed at CALMIT Laboratories in June 2000. The instrument recorded the average of eight scans over the range 365-1125 nm as a single scan. At least six such scans were recorded on each lake, each preceded by a scan of a Spectralon® calibration panel, which provides a nearly 100% reflectance surface in the range 400-1000 nm.

Some clouds were present on several measurement dates, and scans were made only when clouds were not obstructing the sun. Incoming irradiance can vary when clouds are present because light reflected from clouds changes as they drift across the sky. Errors from changing cloud reflectance were minimized by taking measurements in a 10-minute period and alternating scans between the calibration panel and lake. Data were imported to a spreadsheet and plotted. Scans suspected of error from changing cloud cover or poor sensor positioning were compared with other scans for a lake. Scans with a noticeable difference were discarded. After erroneous scans were removed, average spectra were computed for lake and calibration panel radiance. Reflectance was computed by dividing average lake radiance by average calibration radiance.

Lake water characteristics

Lake transparency was measured by Secchi disk. Surface water samples were collected in 1 L Nalgene® bottles concurrently with reflectance measurements, stored on ice in a cooler, and returned to the laboratory for analysis of chl *a*, total suspended solids (TSS), turbidity, and color of filtered water. Chl *a* was analyzed (Eaton et al. 1995) on samples filtered through Whatman 0.7 µm GF/F glass fiber filters. Filters were frozen in a sealed bag until analysis. Chl *a* was extracted by macerating filters in a tissue grinder in 90:10 acetone: saturated magnesium carbonate solution. Macerated samples were steeped for 16-18 h at 4°C in the dark before centrifugation. Absorbance at 664 and 750 nm was measured on an aliquot of centrifuged extract and after acidification with 0.1 mL of 0.1 N HCl, absorbance was measured at 665 and 750 nm. Absorbance at 750 nm before and after acidification was subtracted from the values at 664 and 665 nm to correct for residual turbidity.

TSS was determined by filtering a volume of water through 0.7 µm glass fiber filters (Whatman GF/F) that had been pre-dried at 105°C and weighed. Filters containing TSS were dried at 105°C and re-weighed. Turbidity was measured on unfiltered samples with a Hach 52600 turbidimeter. Absorbance at 440 nm was measured on 0.7 µm-filtered water with a 4-cm quartz cell on a spectrophotometer and converted to an absorption coefficient (*a*) by the formula derived from Beer's Law: a_{440} (m^{-1}) = $2.303A_{440}/\ell$, where A_{440} is measured absorbance and ℓ is cell path length (m). From a_{440} we computed (humic) color, C_{440}, in chloroplatinate units (CPU) using the relationship (Cuthbert and del Giorgio 1992): C_{440} (CPU) = $18.22a_{440} - 0.209$.

Statistical analyses

Statistical relationships were explored between measures of reflectance and optically related lake water characteristics using Systat 8.0 and 11.0. Data from Lake Francis and Typo Lake often had large effects (leverage) on regression relationships because of their much higher reflectance values and high values for several water quality characteristics compared with other lakes. These lakes are extreme cases–only a very small percentage of Minnesota lakes have chl-*a* levels as high as these lakes. To avoid problems caused by these outliers, most analyses were repeated with these lakes excluded from the data set. All regressions reported in this paper were statistically significant at $p < 0.05$.

Results

Lake water characteristics

The 15 lakes for which reflectance spectra were measured had a wide diversity of water quality characteristics, especially optically active substances (Table 2) such as algae and CDOM (quantified by chl *a* and C_{440}, respectively). Chl *a* ranged from 1.8 to 397 mg/m^3, and C_{440} ranged from 6 to 217 CPU. At the lowest C_{440} values the water had no noticeable color, but lakes with C_{440} > ~80 CPU were visibly brown. SD ranged from 20 cm to 6.1 m. Square Lake had high transparency and low concentrations of optically active substances. Lake Francis and Typo Lake were very turbid with high chl *a*. Net and Hanging Horn Lakes had low chl *a* but high C_{440}, and Grace Lake had high chl *a* and C_{440}.

Reflectance measurements

Reflectance spectra varied greatly for the 15 lakes (Figure 1A). Several lakes had reflectance values below 1% across the entire visible and near-IR range; a few lakes had reflectance well above 2% over much of the visible and near-IR range with peaks > 10% at 720 nm. The rest of the lakes had spectra between these extremes.

The six lakes with low reflectance values (generally < 1%, Figure 1B) had low chl *a* but varying C_{440}. Square Lake was the clearest, most transparent lake and had the lowest C_{440} (6 CPU) and chl *a* (2 mg/m^3) of the 15 lakes. Its spectrum differed from the other five low-reflectance lakes by having higher reflectance across the 400-600 nm region and a peak in reflectance at 550 nm. Razor and Rock-P had similar but smaller peaks near 570 nm. The other three lakes had similar flat spectra. Although shapes of the spectra varied little among these five lakes, the magnitude of reflectance and their optically related water quality characteristics varied (Table 2); e.g., C_{440} varied from 34 to 217 CPU. In the 400-600 nm range, the five lakes separated into two groups. Two lakes with the lowest C_{440} (Razor and Rock-P) had an average reflectance of ~0.5%; three lakes with C_{440} > 100 CPU had an average reflectance of ~0.4%. In addition, reflectance at 412 nm generally decreased with increasing C_{440}.

Seven lakes had peak reflectance values of 1.5 to 3.7%, categorized here as moderate (Figure 1C). These lakes are more difficult to characterize because of the competing effects of several optically active constituents. Spectra of these lakes varied considerably in shape, and they had a wide range of optically related water characteristics: SDT, 0.75-2.6 m; chl *a*, 3.2-90 mg/m^3; and C_{440}, 8.2-179 CPU. Lake Nokomis had the highest reflectance in the visible range–attributable to high algal biomass (chl *a* = 90 mg/m^3, highest in this group). In contrast, Cross and Grace Lakes (chl *a* = 55 and 46 mg/m^3, respectively) had slightly smaller peaks at 720 nm and much smaller peaks around 560 nm. Higher CDOM in these lakes apparently decreased reflectance at and below 560 nm. Lakes Calhoun, Harriet and Cedar had similar spectra (Figure 1C) and relatively low chl *a* and C_{440}. Although chl *a* in Rock-A Lake was similar to that in Lake Calhoun and Cedar Lake, its spectrum lacked a peak at 560 nm, and it had higher reflectance above 600 nm. These trends can be attributed to its higher color compared with the other two lakes.

Lake Francis and Typo Lake (Figure 1D) had high reflectance across the spectrum, with minima and maxima at approximately the same wavelengths. SD was 0.20 m for both lakes, and

C_{440} levels in the lakes were nearly identical (~ 100 CPU). Both lakes had very high chl-*a* levels (> 200 mg m^3). Their high reflectance can be attributed to high algal and detritus levels.

Relationships between reflectance and water quality characteristics

Values of r^2 for simple regressions of five optically related water-quality characteristics versus reflectance values were plotted as continuous lines across the spectrum, but results actually were calculated at 2-3 nm intervals corresponding to the wavelength ranges of the radiometer's data channels. When all 15 lakes were included (plot not shown), all variables except C_{440} had high r^2 values across the spectrum because of high leverage exerted by the high reflectance values and extreme water quality values of Lake Francis and Typo Lake. Without these lakes, plots for all five characteristics changed dramatically (Figure 2). Highest r^2 for ln(SD), turbidity, chl *a*, and TSS were in the 600-800 nm range. Turbidity and chl *a* had r^2 peaks around 0.9 near 710 nm and much lower values in the range 410-530 nm. In contrast, the highest r^2 for ln(SD) was only ~0.52 (also at 710 nm), and r^2 were < 0.1 below 550 nm. Much better relationships (R^2 typically > 0.8) are found (e.g., Kloiber et al. 2002ab) using reflectance ratios and multiple regression analysis. The highest r^2 for C_{440} were in the range 400-550 nm, but maxima were < 0.4 (peak at 477 nm).

Chl *a*. A variety of regression relationships were investigated to predict chl *a* from reflectance data (Table 3). A simple regression using the primary MODIS wavelength for chl *a* (443 nm) was moderately strong, but a regression using the wavelength for CDOM correction (412 nm) surprisingly was slightly stronger (Table 3A). A two-variable model using both wavelengths yielded an r^2 of 0.85, but two lakes were outliers. Simple regressions using ratios of the MODIS wavelengths for chl *a* yielded moderately strong relationships, but neither was strong enough for predictive purposes. A linear relationship using the ratio proposed by Gitelson et al. (2000) (R_{700}/R_{670}) yielded $r^2 = 0.84$ (Table 3B), and inclusion of R_{412} as a second variable to correct for CDOM improved the fit to $R^2 = 0.88$. The best relationship found for the MODIS wavelengths involved the ratio R_{488}/R_{551} in the MODIS empirical equation for chl *a*; fitting this polynomial equation to the data for our lakes yielded an R^2 of 0.97 (Table 3A).

Nonlinear relationships of the form chl $a = a_0R^{a1}$, where R is reflectance at a given wavelength, and a_0 and a_1 are constants, were calculated for eight wavelengths that Arenz et al. (1996) described as common features of aquatic reflectance spectra: 440, 670, and 810 nm (reflectance minima); 520, 550, 571, 700 and 716 nm (reflectance peaks). When all lakes were included, all eight wavelengths yielded high r^2 (Table 3B) because of high leverage exerted by Lake Francis and Typo Lake. When these lakes were removed, the best relationships ($r^2 > 0.9$) were found at 670, 700, and 716 nm.

Nonlinear relationships involving wavelength ratios also were investigated using the form, chl $a = a_0R_R^{a1}$, where R_R is the reflectance ratio. The ratios R_{440}/R_{520}, R_{716}/R_{571}, and R_{806}/R_{670} yielded high r^2 values when all lakes were included, but values were much lower without Lake Francis and Typo Lake (Table 3C). The ratio R_{571}/R_{520} inexplicably had the opposite trend. The ratios R_{700}/R_{670} and R_{716}/R_{670} yielded high r^2 whether these lakes were present or not. The former ratio was the best predictor of all those we evaluated ($r^2 \geq 0.98$, Table 3C). A plot of chl *a* versus R_{700}/R_{670} for all lakes shows an exponential relationship (Figure 3). When data for Lake Francis and Typo Lake were removed, a linear relationship fit the data ($r^2 = 0.93$), but a slight curvilinear relationship still is apparent in the plot; a nonlinear fit of the data for chl *a* < 100 mg/m^3 increased r^2 to 0.98. Gitelson et al. (2000) reported a linear relationship between chl *a* and the ratio R_{700}/R_{670} for lakes with chl *a* < 200 mg/m^3, but at higher chl-*a* concentrations they also found that the relationship was exponential.

Color. When all lakes were included, r^2 for the regression of C_{440} versus reflectance at 412 nm (MODIS wavelength used to correct chl-*a* estimates for CDOM) was only 0.04 (Table 4A). Inspection of the spectra in Figure 1 suggests that increasing reflectance caused by high chl *a* overwhelms the absorbance (hence low reflectance) due to CDOM. A regression involving R_{412} for the six low reflectance lakes (Figure 1B) yielded a higher r^2 (0.59), and a similar regression for the ten lakes with chl $a \leq 10$ mg/m^3 yielded $r^2 = 0.41$. Multiple regressions that included R_{412} and the ratio R_{700}/R_{670} (a good predictor of chl *a*) or chl *a* itself—to correct for the influence of chl *a* on reflectance at 412 nm—yielded R^2 ~0.7 for the six low reflectance lakes and ~0.6-0.7 for the ten low chl-*a* lakes (Table 4A). The highest r^2 values for simple regressions of C_{440} with various reflectance ratios involving MODIS wavelengths were ~0.6 for the low reflectance and low chl-*a* lakes. The best fit ($R^2 = 0.73$) for this group of lakes was a multiple regression involving the two ratios R_{412}/R_{443} and R_{700}/R_{670}. For all 15 lakes, the best regression included R_{412} and the reflectance ratio R_{700}/R_{670}, but r^2 was only 0.45.

Only weak relationships were found between reflectance at one wavelength and color using the nonlinear form $C_{440} = a_0 R_i^{a1}$ for the eight wavelengths of Arenz et al. (1996). The best wavelength was 440 nm, but r^2 was only 0.20 (all lakes) and 0.36 (Francis and Typo removed). Results for the four wavelengths above 600 nm had r^2 values ≤ 0.02. Linear regressions of C_{440} for all 15 lakes versus reflectance ratios calculated with $R_{440}$and R_{716} as denominator values and R values for the entire spectrum as numerator values (Figure 4) also were not strong. With R_{440} as the denominator, the best fits occurred with wavelengths < 500 nm in the numerator, but r^2 was only ~0.3-0.4. With R_{716} as the denominator, the highest r^2 was 0.48. In contrast, plots with R_{520} and R_{571} as denominator terms had strong correlations with numerator values around 600-700 nm. The highest r^2 (0.86) involved the ratio R_{691}/R_{571}. These results suggest that reasonable predictive relationships for color exist, but the best relationships were found at wavelengths where light absorbance by CDOM is low. Good correlations between color and reflectance ratios at these wavelengths were unexpected. Better correlations were expected in the region where CDOM absorbs more strongly (400-500 nm), but the best relationships for those wavelengths explained < 50% of the variance in C_{440}.

Nonlinear relationships with C_{440} and reflectance ratios (Table 4B) yielded results in general agreement with the linear regressions. The best ratio (R_{670}/R_{571}) yielded $r^2 = 0.74$ (all lakes) and 0.88 (Lake Francis and Typo Lake removed). When all lakes were included, four lakes had large errors (Figure 5). Predicted C_{440} values of Lake Francis and Typo Lake (~45 CPU) are less than half the measured values (~100 CPU). Lake Harriet also had higher predicted than measured C_{440}. Removal of Lake Francis and Typo Lake from the analysis improved the prediction for Lake Harriet but increased the error for Cross Lake.

Kallio et al. (2001) predicted absorbance at 400 nm (their measure of color) in Finnish lakes with the radiance ratio: $(R_{567\text{-}574} - R_{603\text{-}610})/R_{603\text{-}610}$. They found good linear relationships (r^2 = 0.72-0.89) when the data were divided seasonally, but only when they excluded the most colored lake (a_{400} = 13-14 m^{-1}). Use of similar wavelengths ($(R_{571} - R_{608})/R_{608}$) to estimate color in the 15 Minnesota lakes yielded $r^2 = 0.56$ (linear regression); an exponential fit yielded r^2 = 0.71.

Discussion

Comparison of the spectra for the 15 lakes shows clear trends associated with optically active constituents in the water. As algae become more abundant, reflectance increases dramatically over portions of the spectrum where algal cells and pigments reflect light strongly. Low reflectance occurs where algal pigments absorb light. The visible range of the spectra for Lake Francis and Typo Lake resemble spectra reported by others for waters with high chl *a*. Spectra of fish ponds in Israel (chl a = 134-155 mg/m^3) had similar shapes but lower reflectance (Gitelson et al. 2000) although some differences were noted in the 700-850 nm region. For example, the 700 nm peaks were much higher than the 570 nm peaks for Lake Francis and Typo Lake, but the Israeli ponds had slightly lower peaks at 700 nm than at 570 nm. Lake Francis and Typo Lake had a peak at 800 nm, but the Israeli ponds lacked this peak. A laboratory algae culture also showed a small peak at 800 nm (Gitelson et al. 1999). Arenz et al. (1996) attributed this peak to inorganic suspended sediments.

None of our spectra for Minnesota lakes is similar to the type 1 spectra described by Vertucci and Likens (1989) for Adirondack lakes. Type 1 spectra have high reflectance in the blue region, with a maximum at 405 nm (the lowest wavelength measured). Lakes with these spectra had very clear water (similar to blue ocean water), and molecular scattering by water molecules was thought to dominate the reflectance spectrum. Type 2 waters (Vertucci and Likens 1989) also had high reflectance in the blue region, but maximum reflectance occurred between 500 and 580 nm; these lakes also were considered clear-water lakes. The spectrum for Square Lake (the clearest of the Minnesota lakes) is similar to Adirondack type 2 spectra. The rest of the low-reflectance Minnesota lakes (Figure 1B) had spectra similar to the type 4 Adirondack lakes. These Minnesota lakes were characterized by low to moderate chl *a* and moderate to high CDOM, such that reflectance was low across the visible spectrum. Type 4 Adirondack lakes had relative high DOC and chl *a*, but the latter levels were low in comparison to most of our lakes.

Minnesota lakes with moderate reflectance levels (Figure 1C) had spectra similar to Vertucci and Likens' type 3 (green) spectra, but three lakes (Nokomis, Cross, Grace) differed from any of the Adirondack types in also having a well-defined reflectance peak around 640-650 nm and an even larger peak around 700-710 nm. None of the spectra reported for the Adirondack lakes had either of these peaks, and such spectra may be considered "type 6.". Finally, our high reflectance lakes (Francis and Typo, Figure 1D), which had much higher chl-*a* levels than any of the Adirondack lakes, had spectra similar to those for Nokomis, Cross and Grace (type 6).

CDOM absorbs light and decreases reflectance in the visible portion of the spectrum, especially in the blue region. This is best demonstrated by comparing the spectra of three humic-rich lakes (Hanging Horn, Net, Stevens) with the spectrum of the lake with lowest C_{440} (Square). All four lakes had low chl *a*, but the three humic-rich lakes had considerably lower reflectance from 400 to 600 nm (Figure 1B). The spectra of our lakes with high C_{440} resemble spectra of humic lakes from studies by Arenz et al. (1996) and Kallio et al. (2001), who reported that humic lakes with low levels of other optically active constituents had very low reflectance and no distinguishable peaks and troughs across the spectrum.

Reflectance measured over a single, narrow wavelength band is useful for estimating some water quality characteristics but not for others. Characteristics that show the best potential (Figure 2) are chl *a* and turbidity, followed by TSS and SD. C_{440} shows the least potential. It is not surprising that first four characteristics show peak r^2 values at roughly the same wavelengths; these characteristics all are highly interrelated when algae is the predominant optical constituent in water. Nonlinear and multi-variable relationships improved the estimation of chl *a*, and high R^2 values were found using several wavelengths (Table 3A). Several researchers have shown the feasibility of using airborne hyperspectral measurements to monitor chl *a* in lakes (Pulliainen et al. 2001; Koponen et al. 2001; George and Malthus 2001).

Ratios of reflectance at two wavelengths appear to provide the best estimates of chl *a*. The best chl-*a* relationship reported by Vertucci and Likens (1989) was a log-log regression involving the reflectance ratio R_{525}/R_{554} ($r^2 = 0.77$). Our results (Figure 3) confirm the findings of Gitelson et al. (2000) of a strong relationship between chl *a* and the reflectance ratio R_{700}/R_{670} that is exponential at high concentrations. Other wavelength ratios (Table 3D) demonstrate how a model could work well for one group of lakes and poorly for another. For example, a nonlinear fit using the ratio R_{571}/R_{520} worked well for lakes with chl *a* < 100 mg/m^3 ($r^2 = 0.97$), but the ratio performed poorly when Lake Francis and Typo Lake were included. In contrast, the ratio R_{716}/R_{571} produced an r^2 of 0.95 for all lakes but performed poorly when those lakes were removed. The ratio R_{700}/R_{670} performed well regardless of the presence or absence of these lakes, as did the ratio R_{488}/R_{551} in a polynomial expression of the form of the MODIS empirical equation for chl *a*. In addition, there does not appear to be any large error in chl *a* estimation for highly colored lakes using these ratios. Absorbance by CDOM is weak and should have little effect on measured reflectance, especially at the higher wavelengths.

Humic color differs from the other lake water characteristics we measured in that it is not well correlated with algal abundance in lakes. Although light-absorbing CDOM may originate from algae in lakes (e.g., George and Malthus 2001), high color usually reflects allochthonous sources such as wetlands. Many of our lakes had high concentrations of allochthonous CDOM (i.e., algal abundance was low but color was high). The lakes with the highest color (e.g., Net and Grace) had large wetlands populated by tamaracks and other conifers along their shorelines.

The strongest correlations between C_{440} and reflectance in a narrow spectral band occurred in the 400-600 nm range, where correlations between other water characteristics and reflectance were weakest; r^2 for C_{440} reached ~0.36 at 490 nm when Lake Francis and Typo Lake were excluded but was < 0.1 across the spectrum when they were included. The only region where r^2 for C_{440} exceeded r^2 for the other characteristics was ~490 nm (Figure 2). Nonlinear relationships using reflectance at a single wavelength did not improve estimates of C_{440} substantially. Reflectance in a single narrow band thus does not appear useful to estimate lake color.

Ratios of reflectance at two wavelengths as predictors of C_{440} yielded surprising results. We expected that useful relationships would use wavelengths < 500 nm, where CDOM has the strongest absorbance. Instead, the best ratio was R_{670}/R_{571} ($r^2 = 0.88$ without Lake Francis and Typo Lake). CDOM absorbance at these wavelengths is low, and its influence on reflectance should be negligible in this region compared to that of algae and detritus. Other researchers also reported good performance for equations predicting DOC or CDOM using wavelengths > 570 nm (Vertucci and Likens 1989; Arenz et al. 1996; Witte et al. 1982; Kallio et al. 2001). We are unable to explain why the ratio R_{670}/R_{571} performed so well, and other researchers also were troubled by these results; e.g., "Retrieval of aquatic humus was problematic, since the best equation employed wavelengths where humus is optically inactive" (Kallio et al. 2001).

Lakes with high C_{440} tend to have the most error in remotely measured radiance because of the low amount of light reflected by such lakes. Kutser et al. (2001) described the interpretation of remotely sensed data from humic lakes as "practically impossible." Atmospheric effects (reflectance from aerosols) may contribute more to the signal received by airborne or satellite sensors than light reflected from humic lakes, and correction of reflectance spectra to remove this atmospheric interference is difficult. Flink et al. (2001) compared ground- and flight-level spectra taken simultaneously over a lake in Sweden. Upwelling radiance was 3-6-fold higher at flight level over the visible spectrum, especially in the blue region. Attempts at atmospheric correction resulted in near zero and negative reflectance values in a few portions of the spectrum. Nonetheless, Brezonik et al. (2005) found R^2 values as high as 0.77 for regressions of C_{440} for 15 Minnesota lakes versus brightness data for Landsat bands TM1 and TM4.

In summary, reflectance spectra are related to important optically-related constituents in lake water, and quantitative relationships exist between reflectance values at various wavelengths (or reflectance ratios at two wavelengths) and concentrations of CDOM and chl *a* in lakes. Over a broad range of chl a, the best relationships involve nonlinear functions of reflectance ratios. Because chl *a* increases reflectance in the wavelength region where CDOM decreases reflectance, quantitative estimation of CDOM is difficult at moderate to high chl *a* levels. Additional studies on a larger number of lakes with wide range of these constituents would be useful to confirm and strengthen the relationships found in this study.

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Table 1. Locations and surface areas of lakes in study.

Lake	County	Size (ha)	Location
Calhoun	Hennepin	170	Minneapolis
Cedar	Hennepin	69	Minneapolis
Cross	Pine	410	Pine City
Francis	Isanti	122	NW of Isanti
Grace	Pine	22	SW of Markville
Hanging Horn	Carlton	166	S of Barnum
Harriet	Hennepin	143	Minneapolis
Net	Pine	55	NE of Duquette
Nokomis	Hennepin	83	Minneapolis
Razor	Pine	40	SW of Markville
Rock**	Aitkin	128	NW of McGregor
Rock**	Pine	33	SW of Markville
Square	Washington	85	S of Marine on St. Croix
Stevens	Pine	6	SW of Markville
Typo	Isanti	119	W of Stacy

*Distinguished in the text as Rock-A (Aitkin County) and Rock-P (Pine County).

Table 2. Summary of optically related water quality characteristics of sampled lakes.

Lake	Secchi depth (m)	chl *a* mg m^{-3}	Turbidity NTU	TSS mg L^{-1}	a_{440} m^{-1}	Color CPU
Calhoun	2.6	8.1	2.1	1.6	0.58	10
Cedar	1.9	7.6	3.6	4.4	0.86	15.5
Cross	1.2	55.4	11.2	2.3	4.55	82.6
Francis	0.20	397	169	82.9	5.58	102
Grace	0.75	45.5	10.4	8.0	9.85	179
Hanging Horn	2.6	5.6	1.0	1.0	6.22	113
Harriet	2.1	3.2	2.4	4.0	0.46	8
Net	1.3	10.6	3.3	2.7	11.9	217
Nokomis	0.85	90.1	17.3	11.1	0.81	14.5
Razor	2.6	2.6	1.4	1.6	1.90	34.4
Rock-A	1.7	7.7	4.2	4.5	4.89	89
Rock-P	1.7	2.5	2.0	3.0	3.86	70
Square	6.1	1.8	0.7	1.0	0.35	6
Stevens	1.6	4.6	1.7	2.0	6.62	120
Typo	0.20	266	137	81.4	5.47	99

Table 3. Statistical relationships between chl *a* and measured reflectance (R).

A. Regressions with MODIS wavelengths

Simple linear*

Variable	R_{412}	R_{443}	R_{443}/R_{488}	R_{488}/R_{551}	R_{700}/R_{670}
r^2	0.707	0.655	0.430	0.505	0.843

Multiple linear*

Variables	R_{412}, R_{443}	R_{412}, R_{700}/R_{670}	R_{411}/R_{444}, $R_{444}R_{551}$
R^2	0.799	0.875	0.522

Nonlinear

log(Chl a) = 0.671 + 0.558(log)R_{443}/R_{551})) + 2.308(log)$R_{443}/R_{551})^2$) + 0.542(log)$R_{443}/R_{551})^3$)

$R^2 = 0.957$

log(Chl a) = 0.711 + 1.62(log)R_{488}/R_{551})) + 7.686(log)$R_{488}/R_{551})^2$) + 4.09(log)$R_{488}/R_{551})^3$) **

$R^2 = 0.966$

*Lake Francis was an outlier in all cases

**Same form as MODIS empirical equation for chl *a* (Carder et al. 2003)

B. Nonlinear regressions of form Chl $a = a_0 * R^{a1}$

Wavelength (nm)	All lakes a_0	a_1	r^2	Without Francis and Typo a_0	a_1	r^2
440	19.92	4.23	0.86	25.05	1.23	0.15
520	6.18	2.65	0.96	0.43	5.91	0.53
550	7.51	1.94	0.92	4.54	2.35	0.70
571	11.88	1.69	0.85	4.02	2.45	0.73
670	32.08	1.67	0.83	0.12	14.14	0.91
700	21.28	1.26	0.91	3.93	3.06	0.97
716	25.37	1.06	0.92	0.95	4.66	0.94
806	41.95	0.95	0.93	42.11	1.85	0.69

C. Nonlinear relationships with reflectance ratios of form Chl $a = a_0 * R_R^{a1}$

Wavelength (nm)	All lakes a_0	a_1	r^2	Without Francis and Typo a_0	a_1	r^2
440/520	2.00	-5.92	0.98	0.41	-8.25	0.78
571/520	14.28	5.46	0.36	0.23	14.40	0.97
700/670	5.91	4.96	> 0.99	8.28	4.33	0.98
716/571	23.46	5.45	0.95	34.76	1.48	0.24
716/670	18.25	2.74	0.99	14.88	3.60	0.96
806/670	59.00	2.04	0.97	91.71	2.93	0.37

Table 4. Statistical relationships between color (C_{440}) and measured reflectance (R).

A. Regressions involving MODIS wavelengths

Independent variable(s)	**All lakes (n = 15) r^2 or R^2**	**Low reflectance lakes, Figure 2b (n = 6) r^2 or R^2**	**Lakes with chl *a* ≤ 10 mg m^{-3} (n = 10) r^2 or R^2**
R_{412}	0.04	0.59	0.41
R_{443}	0.05	0.56	0.43
R_{412}/R_{443}	0.30	0.53	0.60
R_{443}/R_{488}	0.17	0.60	0.64
R_{488}/R_{551}	0.03	0.32	0.44
R_{412}, R_{443}	0.17	0.62	0.50
R_{412} and R_{488}/R_{551}	0.04	0.61	0.49
R_{412} and R_{700}/R_{670}	0.45	0.70	0.71
R_{412} and chl *a*	0.36	0.72	0.57
R_{412}/R_{443} and R_{443}/R_{551}	0.31	0.57	0.61
R_{412}/R_{443} and R_{700}/R_{670}	0.38	0.65	0.73

B. Nonlinear relationships with reflectance ratios of form $C_{440} = a_0 * R_R^{a1}$

Wavelength (nm)	**All lakes a_0**	**a_1**	**r^2**	**Without Francis and Typo a_0**	**a_1**	**r^2**
670/520	106.5	1.958	0.72	103.0	2.078	0.75
670/550	146.2	2.084	0.72	145.0	2.883	0.87
670/571	165.9	2.293	0.74	174.9	3.372	0.88
700/550	96.8	1.512	0.66	105.0	1.609	0.71
700/571	100.9	1.505	0.62	114.8	1.866	0.73

*Only relationships with $r^2 > 0.70$ are shown.

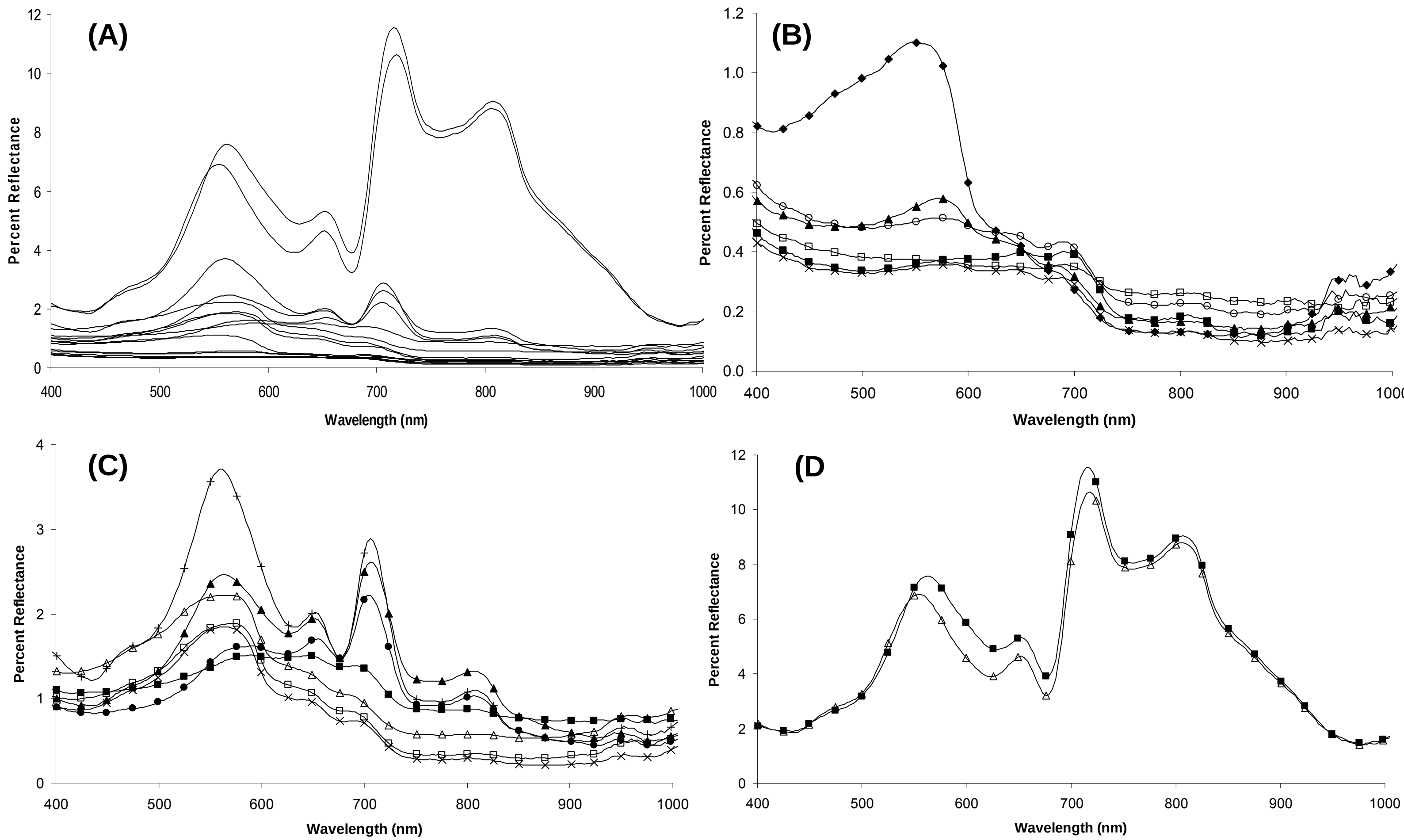

Figure 1. (A) Reflectance spectra for 15 lakes in east-central Minnesota; (B) spectra for the six low-reflectance lakes: Square, ♦; Razor, ▲; Rock, ○; Stevens, □ ; Net, ■; Hanging Horn, x; (C) spectra for the seven moderate reflectance lakes: Nokomis, +; Cross ▲; Harriet, Δ; Cedar, □; Calhoun, x; Grace, ●; Rock, ■; (D) spectra for the two high reflectance lakes: Francis, Δ; Typo, ■.

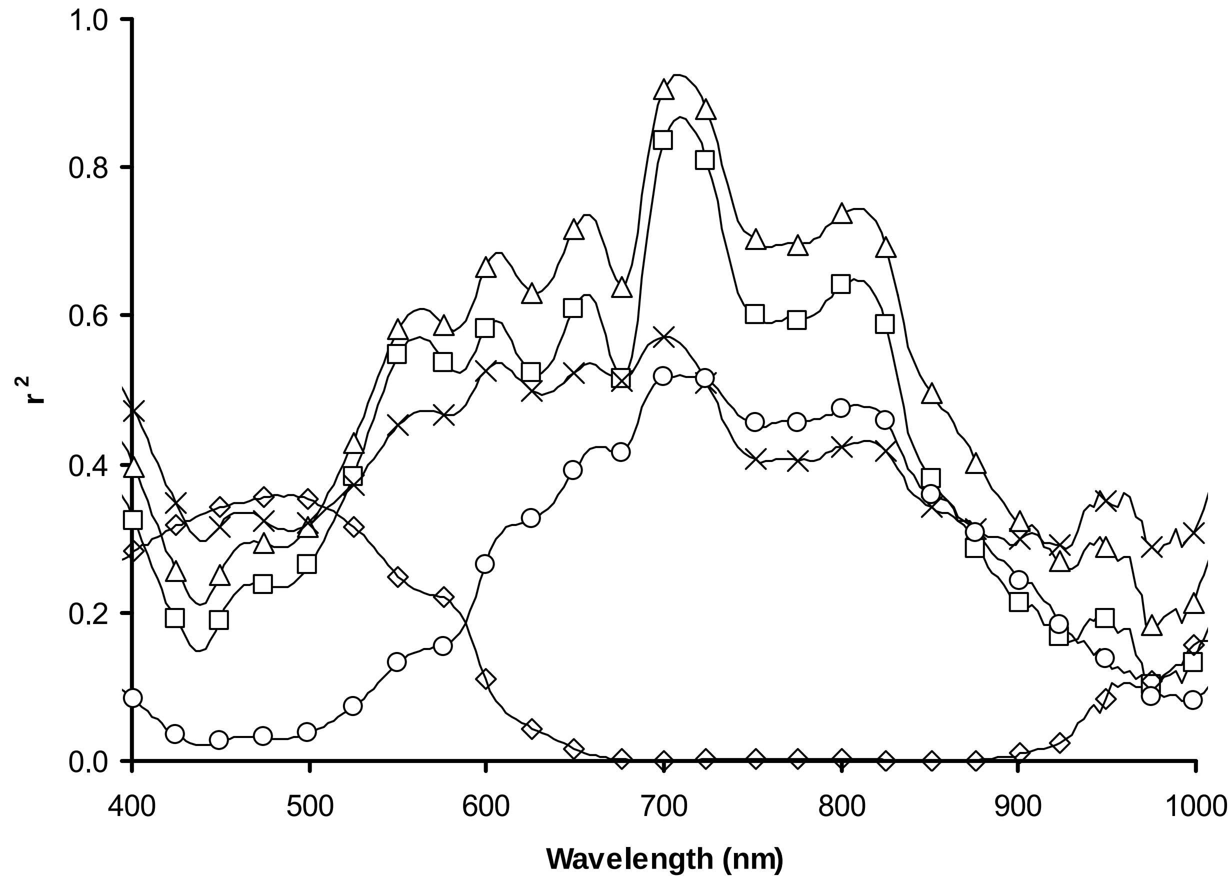

Figure 2. Values of r^2 for simple regression fits of water quality characteristics versus reflectance as a function of wavelength: chl a = □; turbidity = Δ; TSS = x; C_{440} = ◇; ln(SDT = ○; n = 13 (Francis and Typo removed). Note: symbols added to distinguish spectra; they represent only selected data points.

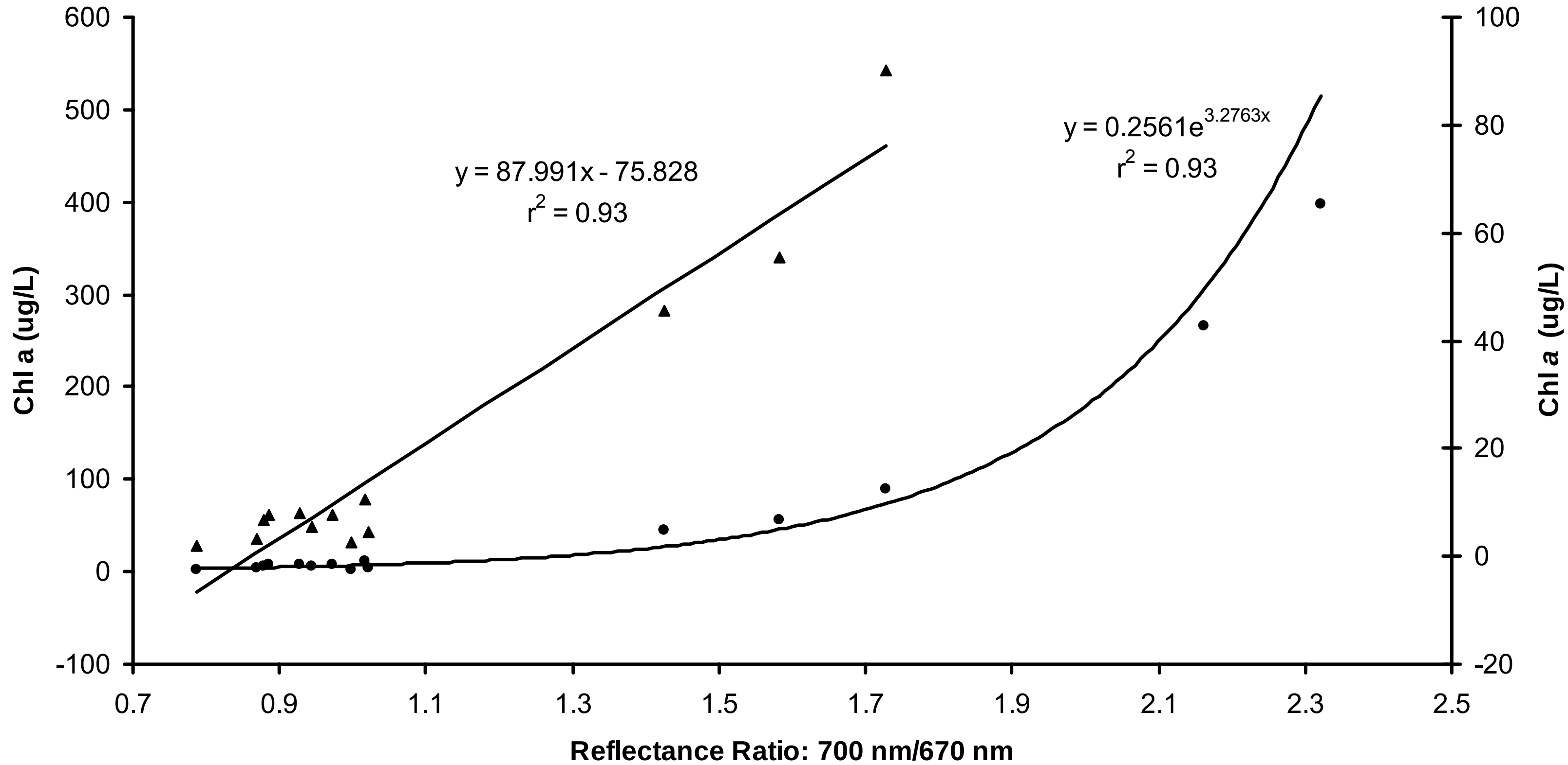

Figure 3. Chlorophyll *a* versus the ratio of reflectance at 700 nm to that at 670 nm. Left ordinate scale applies to exponential-like curve for all lakes; right ordinate applies to the nearly linear relationship for lakes with chl *a* < 100 μg L^{-1}.

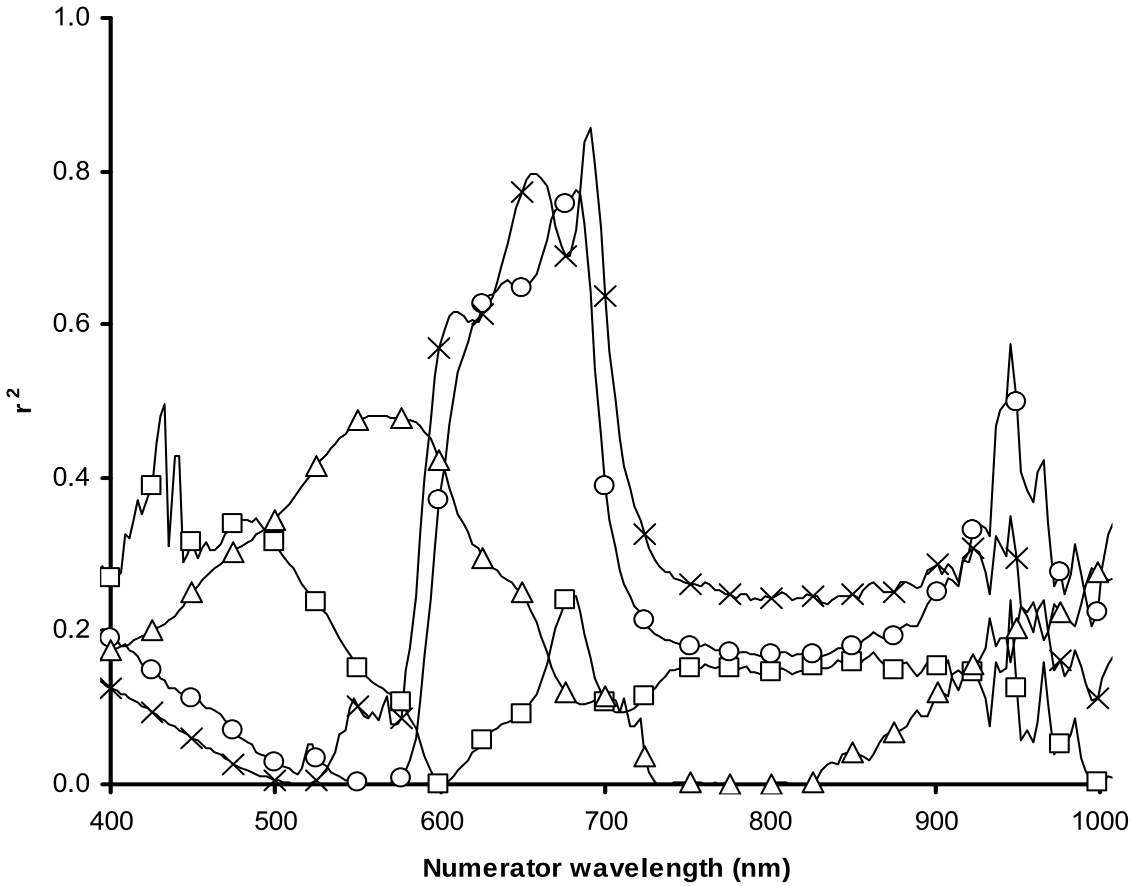

Figure 4. Values of r^2 for correlations of C_{440} versus reflectance ratios, where x-axis is the numerator wavelength and curves represent the following denominator wavelengths: 440 nm = □; 520 nm = ○; 571 nm = X; 716 nm = Δ. Note: the symbols are used to distinguish the curves; they represent only selected data points.

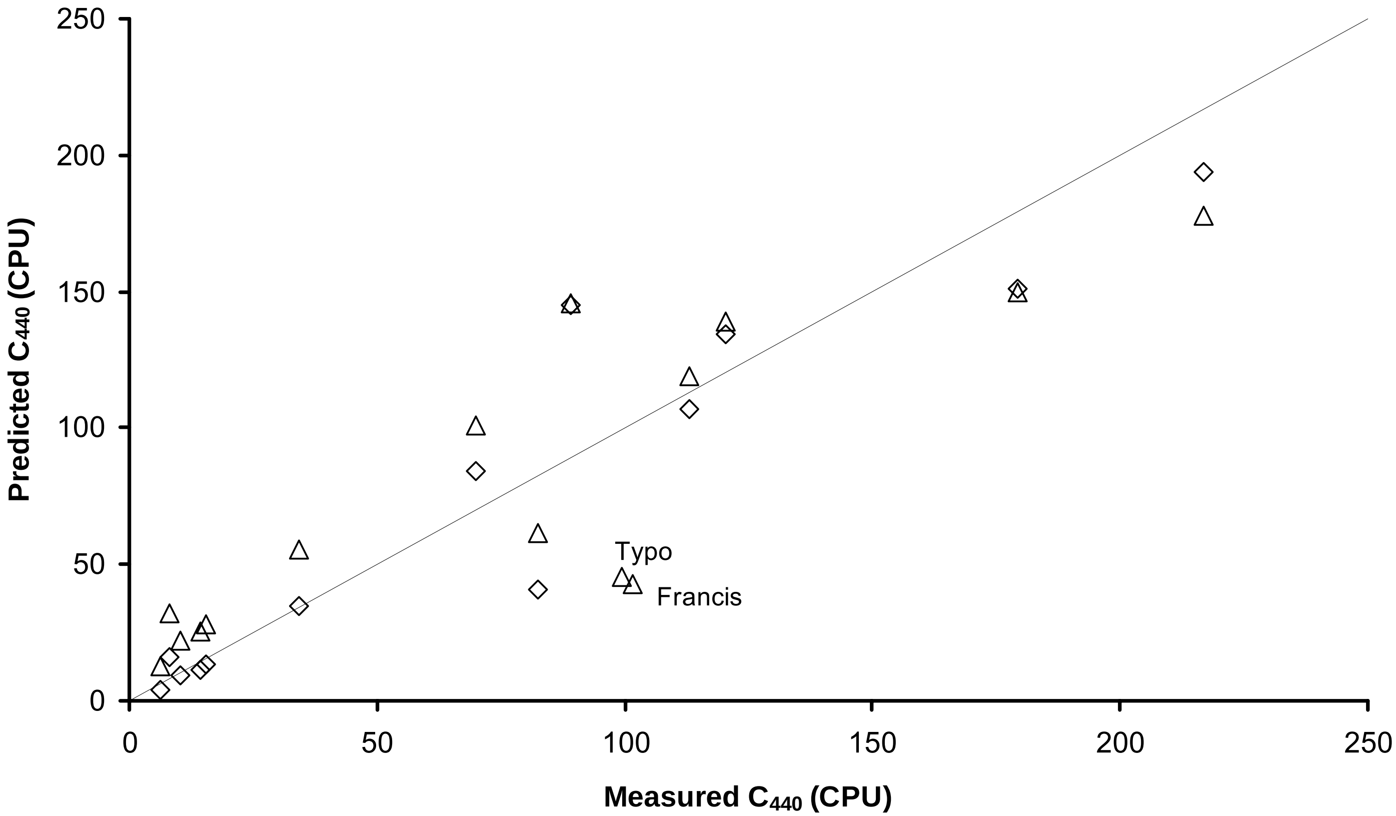

Figure 5. Predicted color (C_{440}) from the ratio of reflectance at 670 nm to that at 571 nm versus measured C_{440}: Δ = results for regression based on all 15 lakes; ◇ = results for regression based on 13 lakes (without Lake Francis and Typo Lake). Solid line = 1:1 relationship.