Inferring sedimentary chlorophyll concentrations with reflectance spectroscopy: a novel approach to reconstructing historical changes in the trophic status of mountain lakes

Biplob Das, Rolf D. Vinebrooke, Arturo Sanchez-Azofeifa, Benoit Rivard, and Alexander P. Wolfe

Abstract: Reflectance spectroscopy has made it possible to rapidly and nondestructively assess the chlorophyll content of plants and natural waters. However, to date this approach has not been applied to chlorophyll and chlorophyll derivatives preserved in lake sediments. Here, we explore the relationships between visible-near-infrared spectral properties of lake sediments and measured pigment concentrations for lakes that have been exposed recently to anthropogenic nitrogen deposition. Down-core decreases in pigment concentrations and changes in reflectance properties effectively chronicle increases in whole-lake primary production since 1950. Specifically, reflectance spectra of sediments from four alpine lakes in Rocky Mountain National Park (Colorado Front Range, USA) preserve salient troughs near 675 nm that covary in magnitude with concentrations of chlorophyll $a$ and associated pheopigments. The area of the trough in reflectance between 600 and 760 nm best explains the sum of total chlorophyll $a$ and its derivatives ($r^2 = 0.82$, $n = 23$, $P < 0.01$). This result suggests that chlorophyll $a$ preserved in lake sediments can be remotely sensed using a simple index derived from reflectance spectroscopy, thus providing a new paleolimnological strategy for rapid exploratory assessments of changing lake trophic status.

Introduction

Among the most important applications of paleolimnology is the reconstruction of historical changes in lake trophic status, including those pertaining to cultural eutrophication (Hall and Smol 1999). To this end, robust methodologies have been developed using diatoms (Reavie et al. 1995; Bennion et al. 1996), sediment geochemistry (Engstrom et al. 1985; Schelske et al. 1986), and combined multiproxy approaches (Fritz et al. 1993; Anderson and Rippey 1994). Sedimentary pigments (chlorophylls, carotenoids, and their derivatives) are of considerable utility in this objective, in...
part because they enable the quantification of past production by algal groups that do not produce morphological fossils (Millie et al. 1993; Leavitt and Hodgson 2001). However, the analysis of sedimentary pigments is expensive and labor intensive, which ultimately limits the attainable spatial and temporal resolution of analyses. Because lake primary production is also linked to climate (Schindler et al. 1990; Hobbie et al. 1999; Flanagan et al. 2003), the development of techniques that facilitate the rapid assessment of lake trophic changes from the sediment record is increasingly of broad relevance.

Reflectance spectroscopy is a powerful tool for lake sediment analysis, in part because it is rapid, reagent-free, and nondestructive (Korsman et al. 1999, 2001). To date, applications include calibration of visible-near-infrared (VNIR; 400–2500 nm) spectra to air temperatures for paleoclimate reconstruction (Rosén et al. 2000) and use of the near-infrared band (NIR; 780–2500 nm) to infer organic and inorganic sediment constituents (Nilsson et al. 1996; Malley et al. 1999). In paleoceanography, green reflectance (550 nm) has been used as a quantitative measure of sediment color (Peterson et al. 2000). However, these studies have not explored explicitly the relationships between localized spectral features and sediment geochemical composition. On the other hand, the spectral properties of chlorophylls in natural waters have been examined more closely (Gitelson 1992; Rundquist et al. 1996; Schalles et al. 1998). These studies reveal consistent absorption by algal chlorophylls in the red bandwidth of the electromagnetic spectrum (600–700 nm), which broadly parallels the spectral behavior of chlorophylls in higher plants (Gitelson and Merzlyak 1997; Richardson et al. 2002) and bryophytes (Lovelock and Robinson 2002). Similarly, red absorption is fundamental in remote sensing of phytoplankton (Richardson 1996) and macroalgae (Guillaumont et al. 1997) in marine environments.

The present study builds on these observations by assessing a new application of VNIR reflectance spectroscopy: the prediction and reconstruction of sedimentary chlorophyll concentrations in lake sediments. Specifically, we explore the use of simple reflectance indices to infer concentrations of sedimentary chlorophyll a and its derivatives for a set of mountain lakes, exploiting a priori knowledge of the absorption spectra of these pigments (Gitelson 1992; Rundquist et al. 1996; Schalles et al. 1998).

Materials and methods

Study sites and sediment cores

The primary materials used in this study are sediments from four lakes situated in Rocky Mountain National Park (RMNP), Colorado Front Range, USA (Fig. 1). Sediments from a fifth site, in the Mount Zirkel Wilderness Area approximately 80 km to the northwest, are used to validate observations from the other four lakes. The study sites are typical midcontinental alpine lakes characterized by clear ($Z_{secch} > 5$ m), chemically dilute (conductivities <10 $\mu$S·cm$^{-1}$), and slightly acidic (pH 6.2–6.5) waters. The lakes have short ice-free seasons (July–October). All five catchments occupy high elevation cirques (3200–3400 m above sea level) of last glacial (Pinedale) age and are situated at or slightly above the alpine tree line. The dominant catchment substrates are bedrock (Precambrian granites, gneisses, and quartz monzonites) and talus derived from these lithologies. Although the lakes are oligotrophic (total phosphorus, TP < 0.01 mg·L$^{-1}$), inorganic nitrogen concentrations ($NO_3^- + NH_4^+$) are well above natural background levels (Table 1).

Short (22–40 cm total length), undisturbed sediment cores were obtained from the deepest midpoint of each lake basin using a modified Kajak–Brinkhurst apparatus (Glew 1989) and extruded in consecutive 0.5- or 1.0-cm increments once
Spectral and pigment analyses were conducted on 23 core depths from the RMNP lakes (Lake Louise: eight samples; lakes Husted, Snowdrift, and Nokoni: five samples each). VNIR reflectance spectra were obtained from an additional 17 depths in the Pristine Lake core. These samples include both pre- and post-1950 sediments from each lake. Each core has been dated using excess $^{210}$Pb activities determined by $\alpha$ spectroscopy, to which the constant rate of supply model has been applied (Wolfe et al. 2003). Because our objective is to focus on stable inventories of sedimentary algal pigments, samples from the uppermost 1.5 cm of the cores were not analyzed. This represents the zone of most intense sediment redox cycling and hence of maximum potential chemical instability among pigments (Leavitt and Hodgson 2001).

The recent paleolimnology of this region has been examined in considerable detail (Baron et al. 2000; Wolfe et al. 2001, 2002), revealing a suite of recent ecological and biogeochemical changes that reflect initial ecosystem responses towards enhanced anthropogenic deposition of fixed nitrogen from industrial, agricultural, and automotive sources. These stratigraphic shifts, which include increased representations of mesotrophic diatom taxa (e.g., Asterionella formosa), declining sediment C:N and $\delta^{15}$N values, and greater autochthonous organic matter production, have accelerated markedly since approximately 1950 AD.

### Table 1. Site characteristics and water chemistry of the studied lakes.

<table>
<thead>
<tr>
<th>Lake name</th>
<th>Latitude (°N)</th>
<th>Longitude (°W)</th>
<th>Elevation (m a.s.l.)</th>
<th>Area (ha)</th>
<th>Depth ($Z_{\text{max}}$; m)</th>
<th>[NO$_3^-$] (mg·L$^{-1}$)</th>
<th>[NH$_4^+$] (mg·L$^{-1}$)</th>
<th>[TP] (mg·L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rocky Mountain National Park</strong></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Louise</td>
<td>40°30′28″</td>
<td>105°37′13″</td>
<td>3360</td>
<td>2.7</td>
<td>8</td>
<td>1.026</td>
<td>0.031</td>
<td>0.009</td>
</tr>
<tr>
<td>Husted</td>
<td>40°30′56″</td>
<td>105°36′50″</td>
<td>3350</td>
<td>4.0</td>
<td>11</td>
<td>0.267</td>
<td>0.033</td>
<td>0.005</td>
</tr>
<tr>
<td>Snowdrift</td>
<td>40°20′30″</td>
<td>105°44′11″</td>
<td>3390</td>
<td>3.2</td>
<td>14</td>
<td>0.107</td>
<td>0.015</td>
<td>0.004</td>
</tr>
<tr>
<td>Nokoni</td>
<td>40°15′15″</td>
<td>105°43′50″</td>
<td>3290</td>
<td>7.6</td>
<td>38</td>
<td>0.078</td>
<td>0.023</td>
<td>0.003</td>
</tr>
<tr>
<td><strong>Mount Zirkel Wilderness Area</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>40°41′27″</td>
<td>107°40′53″</td>
<td>3370</td>
<td>2.4</td>
<td>9</td>
<td>0.658</td>
<td>0.019</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Note: TP, total phosphorus; m a.s.l., metres above sea level.

Fig. 2. Comparison of reflectance spectra (%R from 400 to 700 nm) between (a) chlorophyll $a$ dilutions of lake water with living *Chlorella* spp. cells (Schalles et al. 1998) (numbers are chlorophyll $a$ concentrations ($\mu$g·L$^{-1}$)) and (b) the upper lake sediment samples from the present study. The region of chlorophyll absorption is clearly identifiable in both examples. In (c), representative spectra (%R from 450 to 900 nm) are illustrated for the most recent (1.75 cm, ~1990) and oldest (10.0 cm; pre-industrial) sediments from Lake Louise. The first derivative of these spectra is shown in (d). The key wavelengths used in defining spectral indices for chlorophyll prediction are indicated in panel (c).
der, Colorado, USA) over the 350- to 2500-nm range. The VNIR portion of the spectrum (350–1050 nm) was quantified using a 512-channel silicon photodiode array overlain with an order separation filter. Each channel, an individual detector itself, is geometrically positioned to receive light within a narrow (approximately 1.4 nm) bandwidth. Light...
was brought to the instrument using a Lowel Pro® (Brooklyn, New York, USA) lamp with an effective view of approximately 45°. Working distance to the sample surface was ~16.5 cm. Light energy was collected through bundled optical fibers with a conical view of ~15°. Reflectance was standardized to a white reference panel (spectalon) between each measurement. Percent reflectance ($R$) was computed as $(R_{\text{sample}}/R_{\text{reference}}) \times 100$ for the spectral region of greatest interest, 450–900 nm.

**Pigment analysis**

Sedimentary pigment concentrations were quantified us-
ing reverse-phase high-performance liquid chromatography (HPLC; Vinebrooke et al. 2002). Pigments were extracted by soaking freeze-dried sediments in acetone, methanol, and deionized water (80:15:5 by volume) for 24 h in darkness at 10 °C. Extracts were then filtered (0.2-μm pore size), dried under N₂, and stored in the dark at –20 °C until analysis. Dry extracts were reconstituted with an injection solution (70% acetone – 25% ion-pairing reagent – 5% methanol) containing Sudan II (3.2 mg·L⁻¹) as the internal reference. The ion-pairing reagent consisted of 0.75 g tetrabutyl ammonium acetate and 8.00 g ammonium acetate in 100 mL deionized water. Pigments were separated on an HP 1100 HPLC (Hewlett-Packard Ltd., Mississauga, Ontario, Canada) equipped with a Rainin 200 C18 column (10-cm length, 5-μm particle size). Pigments were detected with an in-line diode array detector (435-nm detection wavelength) and a fluorescence detector (435-nm excitation wavelength, 667-nm detection wavelength). Analytical separation included isocratic delivery (1.0 mL·min⁻¹) of mobile phase A (10% ion-pairing reagent in methanol) for 1 min, a linear succession to 100% solution B (27% acetone in methanol) for 7 min, and isocratic retention for 12.5 min. The column was re-equilibrated between samples by continuous isocratic delivery for 3 min, a linear return to 100% solution A over 3 min, and a final isocratic delivery for 4 min. Pigment concentrations were quantified using equations derived from dilution series of authentic standards from the US Environmental Protection Agency (National Exposure Research Laboratory, Cincinnati, Ohio) or commercially available standards (Sigma Chemical Co., St. Louis, Missouri, USA). All pigment concentrations are expressed as their mass per gram organic matter (mg·g⁻¹ OM), which was determined by mass loss on ignition at 550 °C for 2 hours (Heiri et al. 2001). Normalization of pigment concentrations to organic content eliminates any potential biasing from dilution by inorganic sediment constituents (Leavitt 1993; Vinebrooke et al. 2002).

### Spectral indices and regression

From the sediment reflectance spectra obtained for the 23 samples that were also analyzed for pigments, seven indices were calculated to summarize the large volume of spectral information. The selection of wavelengths used in defining the following indices is based on comparative observations of the general patterns of R observed in both time frames (e.g., Fig. 2). The first two indices are the amplitudes (maximum–minimum) of R shifts between 645 and 675 nm and between 675 and 750 nm. The third and fourth indices are ratios of reflectance between the same wavelengths: \( R_{660/R_{675}} \) and \( R_{675/R_{750}} \). The fifth and sixth indices are based on the first derivative of \( R (R' ) \): both the value of \( R' \) at 675 nm and amplitude of \( R' \) between 660 and 690 nm were calculated. The final index is the dimensionless area between a straight line joining \( R \) values at 600 and 760 nm and the underlying curve; this trough in \( R \) is recognized in all spectra.

Univariate linear regression analyses were performed using each of the spectral indices as an explanatory variable of the following representative fractions of HPLC-derived pigment concentrations: chlorophyll \( a \) + all chlorophyll \( a \) isomers (i.e., primary chlorophyll \( a \), pheophytin \( a \) + pheophorbide \( a \) (pheopigments from chlorophyll \( a \) degradation), and the sum of these two fractions (primary and degraded chlorophyll \( a \)). All regressions were performed with SPSS v. 10.0 (Norusis 2000). The distributional properties of the data could not be evaluated owing to the lack of replication of the independent variable. However, log-transformation of the data prior to regression analysis generated regression or correlation coefficients that were highly similar to those presented here using the raw data. Therefore, we were confident in the robustness of our statistical analyses regarding the assumptions of normality and homogeneity of variance.

### Results and discussion

#### Spectral characteristics of RMNP lake sediments

The most prominent feature of VNIR reflectance spectra obtained from RMNP lake sediments is a trough centered on 675 nm that is attributed to the presence of chlorophylls. This trough is seen in both natural waters inoculated with *Chlorella* spp. (Schalles et al. 1998) and RMNP lake sediments (Figs. 2a, 2b). We confirmed that the reflectance trough in the lake sediments was solely attributable to chlorophyll by organic extraction of the pigment and its derivatives (Vinebrooke et al. 2002) and subsequent VNIR analysis of the dried sediment residue, which no longer retained a reflectance trough at 675 nm. Therefore, differences between the spectral signatures of chlorophyll-amended water (Fig. 2a) and lake sediments (Fig. 2b) arise from the markedly different reflectance properties of the media (aqueous versus par-

### Table 2. Correlation coefficients for linear regressions between various spectral indices and sediment pigment concentrations.

<table>
<thead>
<tr>
<th>Spectral index</th>
<th>Chlorophyll ( a + ) isomers</th>
<th>Pheophorbide ( a + ) pheophytin ( a )</th>
<th>Chlorophyll ( a + ) derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflectance trough area 600–760 nm</td>
<td>0.84**</td>
<td>0.94**</td>
<td>0.92**</td>
</tr>
<tr>
<td>Amplitude of reflectance 675–750 nm</td>
<td>0.74*</td>
<td>0.88**</td>
<td>0.83**</td>
</tr>
<tr>
<td>Amplitude of first derivative 660–690 nm</td>
<td>0.66*</td>
<td>0.86**</td>
<td>0.82**</td>
</tr>
<tr>
<td>Ratio of reflectance 645/675 nm</td>
<td>0.63*</td>
<td>0.67*</td>
<td>0.68*</td>
</tr>
<tr>
<td>Ratio of reflectance 675/750 nm</td>
<td>–0.57*</td>
<td>–0.71*</td>
<td>–0.68*</td>
</tr>
<tr>
<td>First derivative value at 675 nm</td>
<td>–0.39</td>
<td>–0.58</td>
<td>–0.56</td>
</tr>
<tr>
<td>Amplitude of reflectance 645–675 nm</td>
<td>0.27</td>
<td>0.44</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Note: *, \( P < 0.05 \); **, \( P < 0.01 \).
ticular) in which chlorophyll is diluted rather than the spectral behavior of chlorophyll itself. Further differences between algal and sedimentary spectral reflectance signatures occur around 550 nm (Figs. 2a, 2b) and are likely attributable to accessory nonchlorophyll pigments contained in the algal cells. HPLC analyses revealed relatively low carotenoid concentrations in RMNP lake sediments, suggesting partial degradation of these compounds. Furthermore, the development of this trough does not appear related in any way to background values of $R$, which progressively increase between 450 and 900 nm. Between-lake differences in the values of $R$ (Fig. 2b) likely reflect subtle variations in the reflective properties of sediment mineral components.

Comparison of recent and old sediments from Lake Louise (Figs. 2c, 2d) and the other lakes (Fig. 3) showed that chemical changes associated with algal death, sedimentation, and decomposition did not induce substantial shifts in the wavelength of minimum red reflectance. Indeed, pre- and post-1950 sediments from the four mountain lakes exhibited reflectance spectra that are very similar, except for the 675-nm trough, which is more pronounced following 1950 (Fig. 3). Although the preservation of chlorophyll reflectance features in sediment has been recognized for some time (Schalles et al. 2000), these have not previously been calibrated to quantitative sedimentary pigment concentrations.

**Fossil pigment stratigraphy**

The organic content of sediments from the four RMNP lakes varies between 10% and 35%, and, with the exception of Lake Husted, increases towards the mud–water interface. Chlorophyll $a$ and associated pheopigments are consistently preserved in all samples analyzed. For this reason, and given that our primary interest lies in whole-lake algal production, only chlorophyll $a$ and its degradation products are considered further. With few exceptions, the stratigraphic trend in concentrations of these pigments is an increase towards the surface of each of the analyzed cores (Fig. 4). Concentrations of total sediment chlorophyll $a$ and derivatives range

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from < 0.1 mg·g⁻¹ OM in pre-1950 sediments to a maximum of 0.9 mg·g⁻¹ OM at the surface in Snowdrift Lake. These values are typical for oligotrophic lake sediments, as is the relatively large degree of between-lake variability in sediment pigment concentrations (Vinebrooke et al. 2002). Clearly, neither the production nor the preservation of algal pigments is uniform across the sediment surface, and this mandates a critical assessment of the possibility that consistent between-lake stratigraphic trends (Fig. 4) are merely preservational artifacts.

An appropriate approach to assessing diagenesis is by comparing chlorophyll a concentrations to those of its principal degradation product, pheophytin a (Vinebrooke et al. 2002). Our data do not reveal high pheophytin a concentrations in samples of low chlorophyll a concentration, the expected pattern if diagenetic processes were modulating the down-core distribution of pigments. Indeed, the chlorophyll a/pheophytin a ratio does not show any consistent stratigraphic trends among the four lakes (Fig. 4). Pheophorbide a concentrations, which have widely been interpreted as proxies for algal grazing by invertebrates (e.g., Leavitt et al. 1994), are several fold lower than those of pheophytin a in RMNP lake sediments. However, both pheopigments have very similar down-core stratigraphies (Fig. 4). This does not support the regulation of pheophorbide a as a unique by-product of grazed algal standing crop, even more so since the four lakes have markedly different fish stocking histories (Wolfe et al. 2003), which constitutes the dominant regulator of invertebrate herbivory. The production of pheophorbide a in the absence of grazing has been recognized in marine ecosystems (Head et al. 1994) and can therefore be suspected for lakes. Thus, the stratigraphic profiles of both pheopigments can be simply attributed to greater sources of reactive chlorophyll a in the most recently deposited sediments, in turn due to increased algal standing crop. Although pigment degradation is clearly occurring in the sediments of the RMNP lakes (incompleteness of carotenoid record, abundance of pheopigments), this does not appear to obscure the primary environmental signal suggested by the pigment stratigraphy: progressive increases in algal production and sedimentation over recent decades.

Regression between spectral indices and sedimentary pigments

For the 23-sample population, seven reflectance indices were regressed against three categories of sedimentary pigments: chlorophyll a and its isomers; pheopigments from chlorophyll a degradation (pheophytin a + pheophorbide a); and the sum of the first two classes (hereafter chlorophyll a + derivatives). Of the indices, only two failed to produce significant correlations (the first derivative value at 675 nm and the amplitude of reflectance change between 645 and 675 nm). All other spectral indices were significantly (P < 0.05) correlated to all three categories of sedimentary pigment concentrations expressed per unit organic matter (Table 2). These correlations do not differ appreciably when sedimentary pigment concentrations are expressed per unit dry mass of sediment. The three most highly correlated indices are as follows: reflectance trough area between 600 and 760 nm, the amplitude of R between 675 and 750 nm, and the amplitude of R′ between 660 and 690 nm. The regressions obtained from these three indices and the three pigment categories are illustrated in Fig. 5.

Interestingly, spectral indices are more closely correlated to the sum of pheopigments than to their precursor, chlorophyll a. However, the correlation coefficients are similar for both pigment classes (Table 2), suggesting that both chlorophyll and its degradation products have similar reflectance properties. This implies that diagenesis of sediment organic matter is unlikely to significantly alter the portions of reflectance spectra that relate most strongly to algal production (i.e., 600–760 nm).

Development of predictive models

The strength of the above relationships allows the development of simple inference models based on the three most statistically robust spectral predictors of sedimentary pigments. These models are directed towards the reconstruction
of the most inclusive pigment category, chlorophyll a + derivatives, which is believed to best reflect total algal abundance and hence be of greatest potential utility for reconstructing lake trophic evolution. Linear regressions developed between spectral indices and pigment categories were applied to the 23 reflectance spectra and measured versus inferred values of chlorophyll a + derivatives were graphed (Fig. 6). The total integrated area of the reflectance trough from 600 to 760 nm was the best predictor of all three classes of sedimentary chlorophyll concentrations considered (Table 2). This index was particularly successful in producing a cluster of points closely surrounding the 1:1 line at concentrations <0.3 mg·g⁻¹ OM and a reduced scatter and trend in corresponding residuals (Fig. 6). Although more work is clearly needed for sediments with higher chlorophyll a concentrations, our analyses show that simple spectral indices are potentially sensitive to changes of sediment chlorophyll a + derivatives in the order of ±0.15 mg·g⁻¹ OM.

Another way of depicting this data is to plot stratigraphically both measured and inferred values alongside each other (Fig. 7). This enables the largest mismatches to be readily identified, for example the model’s overestimation at the top of the Lake Louise core and underestimations in the two most recent samples from Snowdrift Lake. However, with the exception of these points, the reflectance trough index faithfully reproduces measured sediment pigment concentrations with remarkable degrees of accuracy and precision. This implies that overall trends in sedimentary chlorophyll concentrations may be reconstructed in the absence of HPLC measurements. However, the inferred values shown here (Fig. 7) do not constitute reconstructions in the strict sense, because they represent the same samples used in the inference model’s development (Fig. 6). To avoid this element of circularity, we now apply the model to a fifth lake outside the calibration set and for which there exist several independent lines of evidence for increased production.

**Application to lake trophic reconstruction**

Pristine Lake receives significant amounts of nitrogen deposition originating from coal-fired power plants in the lower Yampa River valley, notably at Hayden and Craig (Turk and Campbell 1987). These emissions are transported to the Mount Zirkel Wilderness Area by prevailing westerly winds. Inorganic N deposition rates in the region thus exceed 4 kg N·ha⁻¹·year⁻¹ (Williams and Tonnessen 2000). This is directly comparable with RMNP lakes east of the Continental Divide, which are affected by N emissions from the Front Range urban corridor (Baron et al. 2000).

Sediments from Pristine Lake record a large increase in total diatom concentrations since 1950, associated with increased abundances of the mesotrophic planktonic taxa *Asterionella formosa* and *Fragilaria tenera* (*Synedra* sensu lato) (Fig. 8a). Sedimentary chlorophyll a + derivatives were inferred by NIRS for 17 intervals in the Pristine Lake core using the model derived from reflectance trough area (600–760 nm). This reconstruction yields estimates ranging from <0.05 mg·g⁻¹ OM before 1950 to values up to 0.4 mg·g⁻¹ OM in the last decade (Fig. 8b). Reflectance-inferred increases in chlorophyll concentrations were correlated significantly with other proxies of lake enrichment, including relative frequencies of *Asterionella formosa* \( r = 0.75, P < \)
0.01) and Fragilaria tenera ($r = 0.82, P < 0.01$), as well as organic carbon content ($r = 0.88, P < 0.01$). These changes (Fig. 8a) are directly comparable to those documented from five RMNP lakes, including those considered previously here (Wolfe et al. 2003). Moreover, the inferred sedimentary chlorophyll stratigraphy matches the chronology of regional energy development and population growth exceptionally well.

It is interesting to note that the parallel behavior of diatom and inferred sedimentary chlorophyll concentrations observed before 1975 appears to collapse in subsequent decades. This may suggest the progressive replacement of diatoms by nonsiliceous algal groups as resource ratios continue to shift. Irrespective of these finer points of interpretation, which remain to be confirmed, the data unequivocally support the contention that VNIR spectral data may produce realistic reconstructions of trends in sedimentary chlorophyll concentration, which is a more integrative measure of whole-lake production relative to proxies such as diatom concentrations (Vinebrooke et al. 2002). In the case of Pristine Lake, the remotely sensed data corroborate diatom-based inferences of recent nutrient enrichment, together providing a powerful case that this lake has markedly deviated from its natural, pre-industrial, trophic state.

In summary, the results of this investigation confirm that reflectance spectroscopy is a powerful tool in paleolimnology (Korsman et al. 2001). Specific regions of sediment reflectance, notably in the red portion of the spectrum, demonstrably relate to sedimentary concentrations of chlorophyll $a$ and its degradation products. Simple models can be developed to infer sediment photosynthate concentrations and thereafter be applied to the reconstruction of changing lake trophic regimes. This method does not supplant wet chemical methods, which remain necessary for the quantification of trace pigments such as carotenoids. Rather, VNIR methods enable rapid and nondestructive, semiquantitative assessments of bulk sediment chlorophyll concentrations. For many paleolimnological applications, including studies of eutrophication (Hall and Smol 1999) and animal-derived nutrient fluxes (Finney et al. 2000), this information may nonetheless be critical.

Measured pigment concentrations associated with total primary production (i.e., chlorophyll $a$ and its derivatives) have increased over recent decades in all four investigated RMNP lakes, in agreement with additional proxies such as diatoms, nitrogen stable isotopes, and organic matter provenance (Wolfe et al. 2002, 2003). The results from Pristine Lake in the Mount Zirkel Wilderness Area confirm that recent nutrient enrichment is widespread in the Colorado Rocky Mountains. Similar observations have now also been documented from the Beartooth–Absaroka Wilderness of Montana and Wyoming (Saros et al. 2003), as well as from Sequoia and Yosemite National Parks in the Sierra Nevada (Sickman et al. 2003). All of these regions are congressionally designated Class I wildernesses under the Clean Air Act, which in principle specifically mandates protection from human-induced ecological changes. Nonetheless, recent observations collectively constitute a mounting body of evidence indicating that midcontinental alpine lakes are changing directionally in response to increased nutrients transported atmospherically from a variety of anthropogenic sources.

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