

# Do spectrally inferred determinations of chlorophyll *a* reflect trends in lake trophic status?

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**Abstract** Visible reflectance spectroscopy (VRS) has been used to reconstruct lake sediment chlorophyll *a* concentrations. Despite good concordance between inferred and measured chlorophyll *a* values, questions remain as to whether this spectral technique is tracking past changes in aquatic primary production, or simply recording a diagenetic signal. In this study, we critically evaluate how well VRS chlorophyll *a* determinations track past trends in aquatic primary production using sediment cores from several lake systems with well-known trophic histories. Our study sites include Arctic, boreal and prairie lakes that encompass a gradient of trophic states. In general, our

spectrally inferred chlorophyll *a* values tracked past trends in lake trophic status consistent with historical measurements of production, or as inferred by independent proxies of primary production. We conclude that VRS chlorophyll *a* inferences indeed track histories of lake production trends and that this method is widely applicable as a rapid, inexpensive and non-destructive alternative to wet-chemical analyses of sediment chlorophyll *a* concentrations.

**Keywords** Visible reflectance spectroscopy · Chlorophyll *a* · Primary aquatic production · Trophic status

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## Introduction

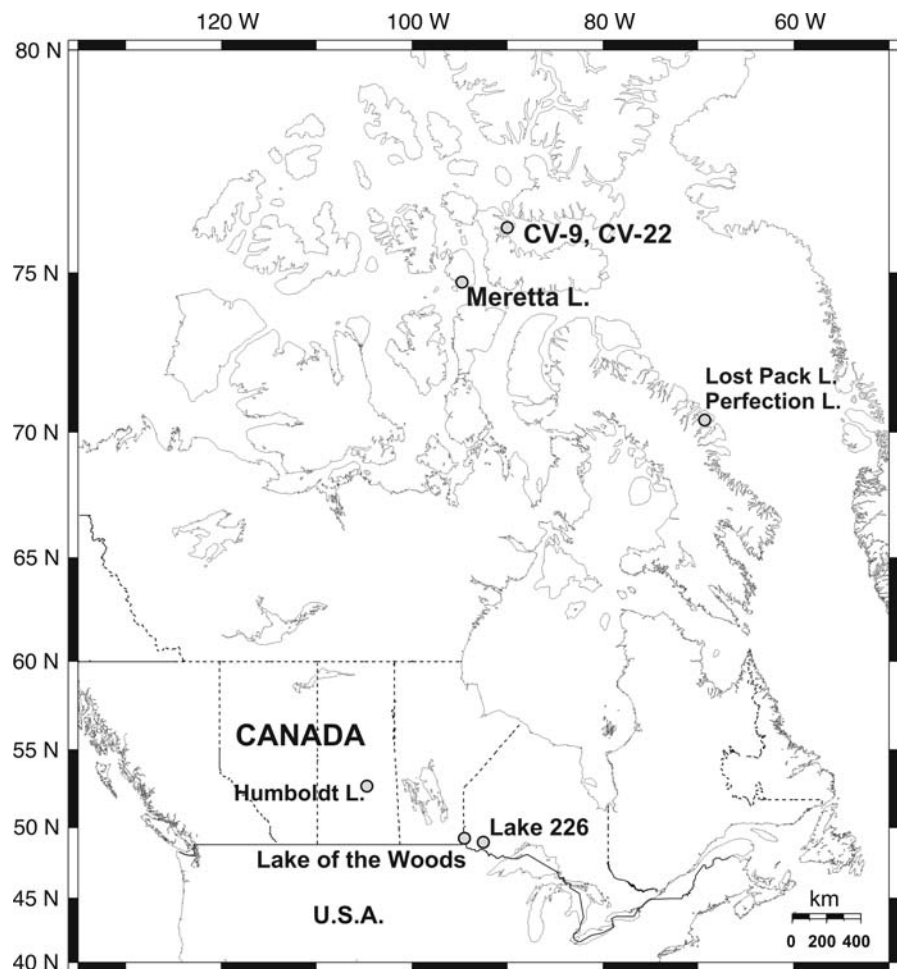
High resolution, multi-proxy paleoecological investigations are becoming more common (Birks and Birks 2006). This demands the analysis of a large number of samples and places a high premium on a finite amount of sediment core material, if destructive sample preparation techniques are used (Last and Smol 2001a, b; Smol et al. 2001a, b). As a result, the use of reflectance spectroscopy to reconstruct geochemical and other environmental variables is becoming increasingly attractive as it offers a rapid, inexpensive, and non-destructive alternative to conventional techniques (Korsman et al. 2001).

Recently, a new application of visible reflectance spectroscopy (VRS) has allowed for the reconstruction of sedimentary chlorophyll *a* concentrations (Wolfe et al. 2006; Michelutti et al. 2005). This technique has been used to reconstruct trophic histories in a range of lake types over the timescales of decades to millennia (e.g., Michelutti et al. 2005, 2007; Das et al. 2005). With few exceptions, the VRS chlorophyll *a* reconstructions obtained to date display exponential declines in concentration from the surface of the core. Although the recent production increases recorded in each study are entirely consistent with the timing of known triggers that could stimulate primary production such as recent climate warming (Michelutti et al. 2005), catchment development (Wolfe et al. 2006), and atmospheric nitrogen deposition (Das et al. 2005), the largely similar

stratigraphic profiles obtained thus far have left persistent questions regarding the effect of diagenetic processes on this VRS signal.

Here, we use VRS to infer chlorophyll *a* concentrations in highly resolved, radiometrically dated sediment cores from Arctic, boreal and prairie lake systems (Fig. 1) with well-known trophic histories, including sites where no modern eutrophication has been recorded. This allows for a proper assessment of how accurately VRS chlorophyll *a* determinations reflect lake trophic status versus diagenetic processes. Although we discuss each of our chlorophyll *a* profiles within the context of the main factors influencing aquatic production, we note that the focus of this paper is on assessing the validity of VRS chlorophyll *a* determinations rather than the environmental significance of the data.

**Fig. 1** Map of Canada showing the locations of our study sites

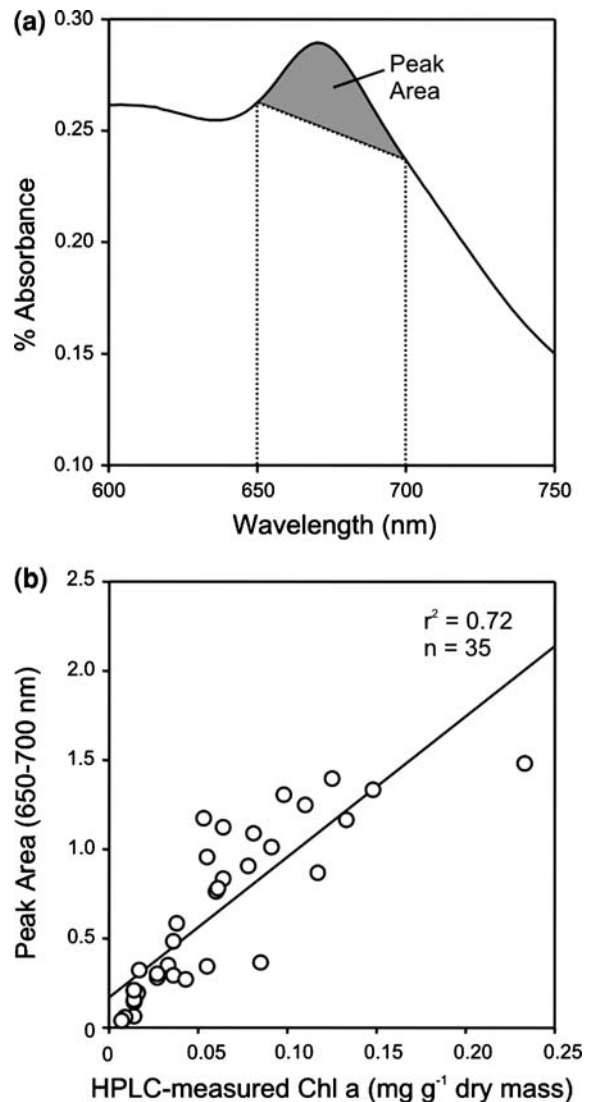


## Methods

Spectral measurements, sediment calibration, and model development

The details of the experimental calibration of lake sediment spectra to chlorophyll *a* concentrations are described in Das et al. (2005), with later refinements by Wolfe et al. (2006). In brief, sediment samples are first lyophilized and sieved (125  $\mu\text{m}$  mesh) in a pre-treatment process designed to remove the influence of particle size and water content on the spectral signal. Next, sediment reflectance spectra obtained using a spectroradiometer are considered in relation to calibration samples covering a range of sedimentary chlorophyll *a* concentrations, as measured by high performance liquid chromatography (HPLC). Wolfe et al. (2006) demonstrated that distinct reflectance troughs (or absorbance peaks) observed in the spectra near 675 nm have been shown to vary in magnitude with the concentration of the summed ‘family’ of HPLC-derived chlorophyll *a* and its derivatives, which include chlorophyll *a* + all chlorophyll *a* isomers (i.e., primary chlorophyll *a*), and pheophytin *a* and pheophorbide *a* (i.e., pheopigments from degraded chlorophyll *a*). Thus, prediction models can be developed using a linear regression between a simple reflectance metric and the summed concentration of total sedimentary chlorophyll *a* and its derivatives (Fig. 2). In this instance, the area under the absorbance peak between 650 and 700 nm is the reflectance metric. Hereafter, we refer to  $\text{VRS}_{650-700 \text{ nm}}$ -inferred sedimentary chlorophyll *a* and its derivatives, simply as inferred chlorophyll *a*.

The spectroradiometer used in the initial calibration studies of Michelutti et al. (2005) and Wolfe et al. (2006) was a FieldSpec<sup>®</sup> Pro spectroradiometer (Analytical Spectral Devices Inc., Boulder, Colorado). We obtained all reflectance spectra using a Model 6500 series Rapid Content Analyzer (FOSS NIRSystems Inc.), operating over the range of 400–2,500 nm. Sediments were analyzed directly through the base of glass vials, with each sample representing an average of 32 scans. This method produces a high-quality, low-noise spectrum. A ceramic reference paddle equipped in the Rapid Content Analyzer was used as a stable, consistent reflectance reference that was taken between every sample. The time required for each



**Fig. 2** **a** A typical lake sediment spectrum showing the distinct peak centered near 675 nm. **b** The relationship between the absorbance peak area between 650 and 700 nm and HPLC-measured chlorophyll *a* concentrations for the 35 calibration samples in this study. The calibration samples include five lakes from a broad range of trophic states (described in Das et al. 2005) and algal-inoculated sediment following the mass ratios of sediment to algae of 250:1, 500:1, and 1000:1 (described by Wolfe et al. 2006)

analysis, including the reference scan, was about 1 min.

In developing our calibration model, we followed the exact procedures and used the identical calibration sediments to those reported in the initial studies of Michelutti et al. (2005) and Wolfe et al. (2006).

Similar to the aforementioned calibration studies, our data showed a significant relationship between HPLC-measured chlorophyll *a* and the peak area between 650 and 700 nm ( $r^2 = 0.72$ ;  $P < 0.05$ ; Fig. 1). Using this linear relationship, we inferred sediment chlorophyll *a* concentrations with the equation:

$$\text{Chlorophyll } a + \text{ derivatives} = 0.0919 \times \text{peak area}_{650-700\text{nm}} + 0.0011 \quad (1)$$

Our spectral data also produced a significant relationship ( $r^2 = 0.78$ ;  $P < 0.05$ ) between the primary products of chlorophyll *a* degradation (i.e., pheophytin *a* and pheophorbide *a*) and the peak area from 650 to 700 nm, indicating that our model tracks both primary and degraded chlorophyll *a* in sediments. The standard error for the estimate is  $0.050 \text{ mg g}^{-1}$ . We estimate the lower limits of detection for this method to be approximately  $0.01 \text{ mg g}^{-1}$  (Michelutti et al. 2005). A comparison of the performance between the FieldSpec Pro<sup>®</sup> spectroradiometer used in earlier studies (Michelutti et al. 2005) and the Rapid Content Analyzer used in this study shows identical trends in sediment chlorophyll *a* profiles from Lost Pack Lake ( $r = 0.99$ ) and Perfection Lake 3 ( $r = 0.91$ ; Fig. 3). However, the absolute values are not always identical (Fig. 3). In the two cores from Baffin Island, the ratios of inferred

chlorophyll *a* between the two instruments varied in the range of 0–1.8.

#### Rationale for site selection

The primary criterion for site selection was that each system had a well-known trophic history as documented by historical measurements of aquatic production, or as inferred by independent proxies of production. Our study sites encompass a gradient of trophic states from Arctic, boreal and prairie environments (Fig. 1), which allows for a good test on the wide scale applicability of VRS chlorophyll *a* determinations.

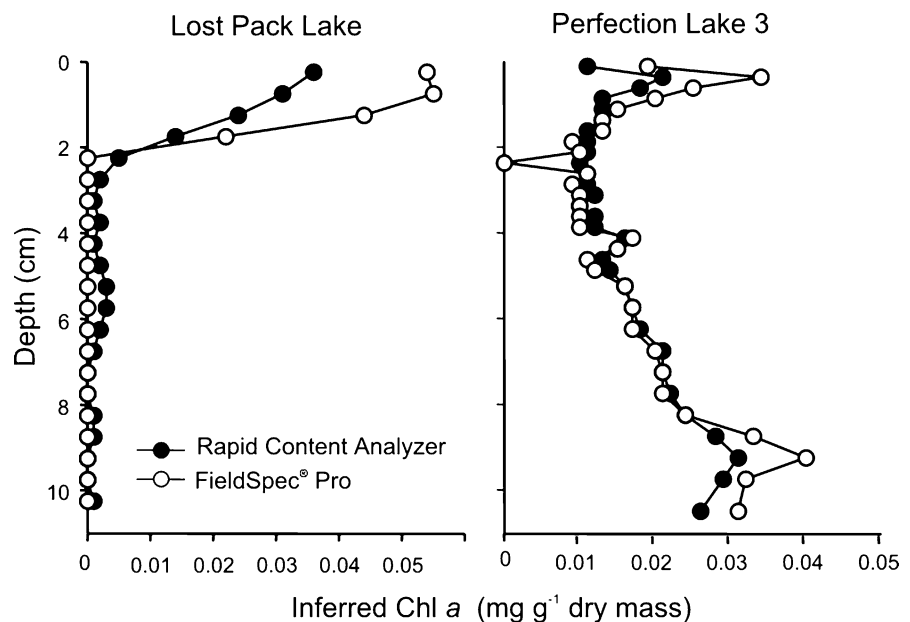
#### Results and discussion

Table 1 provides a brief summary of all the site locations including the rationale for their inclusion in this study. Detailed site descriptions for each location are given below.

##### Lake of the Woods, central Canada–USA border

Lake of the Woods (LOW) is an international waterbody spanning the provinces of Ontario and Manitoba in Canada, and the state of Minnesota in the USA

**Fig. 3** A comparison of VRS-inferred chlorophyll *a* concentrations between the FieldSpec<sup>®</sup> Pro spectroradiometer used in the original calibration studies of Wolfe et al. (2006) and Michelutti et al. (2005) and the Rapid Content Analyzer (FOSS NIRSystem Inc.) used in this study. The two study cores are from Baffin Island, Arctic Canada

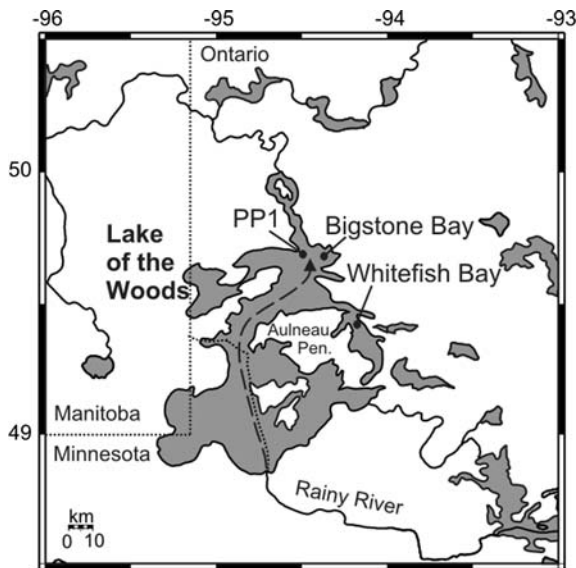


**Table 1** A listing of all study sites, their latitudes and longitudes, as well as brief descriptions of their trophic histories and the rationale for their inclusion in this study

Site	Location	Brief trophic history	Selection rationale
PPI (LOW)	49°69'N, 94°49'W	Meso-to-eutrophic basin; TP range 22–40 mg/l; recent algal blooms	The three sites from LOW allow for within-lake comparisons among basins with different trophic states
Bigstone Bay (LOW)	49°67'N, 94°35'W	Mesotrophic basin; TP range from 17 to 25 mg/l; recent algal blooms	
Whitefish Bay (LOW)	49°41'N, 94°17'W	Oligotrophic basin; TP range 7.5–10 mg/l; no recent algal blooms	
CV-9 (Cape Vera)	76°13'N, 89°14'W	Receives nutrient-rich seabird inputs; eutrophic; TP = 40 mg/l	The Cape Vera sites allow for comparison between two similar-sized ponds from the same region but with different trophic states
CV-22 (Cape Vera)	76°17'N, 89°17'W	No seabird inputs; oligotrophic; TP = 3 mg/l	
Meretta Lake	72°41.75'N, 94°59.58'W	Raw human sewage inputs from 1949 to 1998; currently oligotrophic; TP = 5 mg/l	Known eutrophication and subsequent recovery
Lake 226	49°07'N, 92°08'W	Artificially eutrophied (C, N, P additions) from 1973 to 1980; has returned to pre-impact conditions	Known eutrophication and subsequent recovery
Humboldt Lake	52°08.4'N, 105°06.3'W	Closed-basin prairie lake that has undergone many changes in water quality and abundance over last 5,000 years	Highly-resolved 5000-yr record

(Fig. 4). It is underlain by Precambrian Shield in its northern region and by the glacial bed of Lake Agassiz in its southern extent. The lake is large (3,850 km<sup>2</sup>), of variable depth ( $Z_{\text{mean}} = 7.9$  m) and contains several basins with over 14,000 islands and hundreds of inlets and bays (Heiman and Smith 1991). Although its hydrology is complex, the primary source of tributary inflow is from the Rainy River to the south, with the Winnipeg River to the north forming its main outlet (Fig. 4). The Rainy River accounts for over 70% of the inflow to LOW and is likely its most important source of nutrients. This is evidenced by a north–south gradient in water quality that generally follows the flow of the Rainy River through the main channel (dotted arrow in Fig. 4), with higher nutrient levels and lower water transparencies in the south (Pla et al. 2005). The lowest TP concentrations are typically recorded in the embayments in the northwest and eastern portions of the lake that are hydrologically isolated from the main flow through of the Rainy River ([http://www.ene.gov.on.ca/envision/water/lake\\_partner/index.htm](http://www.ene.gov.on.ca/envision/water/lake_partner/index.htm)).

Lake of the Woods provides an excellent opportunity to assess the ability of VRS chlorophyll *a* determinations to differentiate among three distinct basins that differ in trophic status due to varying degrees of connectivity to the nutrient-rich flow from the Rainy River. The sediment cores used in this study are part of a larger investigation on the spatial and temporal variability of water quality within LOW (<http://biology.queensu.ca/low/index.html>), and thus have been carefully selected to represent basins of both high and low nutrient concentrations (Fig. 4). The coring sites at PP1 (49°69'N, 94°49'W) and Bigstone Bay (49°67'N, 94°35'W) represent locations of high nutrient concentrations due to their location in the central-north portion of the lake, which is within the main direction of flow from the Rainy River. For example, TP concentrations at Bigstone Bay can reach as high as 40  $\mu\text{g l}^{-1}$ , but typically average  $\sim 22 \pm 8 \mu\text{g l}^{-1}$  during May through October. Likewise, TP concentrations at the coring site PP1 range from  $\sim 17$  to 25  $\mu\text{g l}^{-1}$  ([http://www.ene.gov.on.ca/envision/water/lake\\_partner/index.htm](http://www.ene.gov.on.ca/envision/water/lake_partner/index.htm)). The most nutrient-poor site is

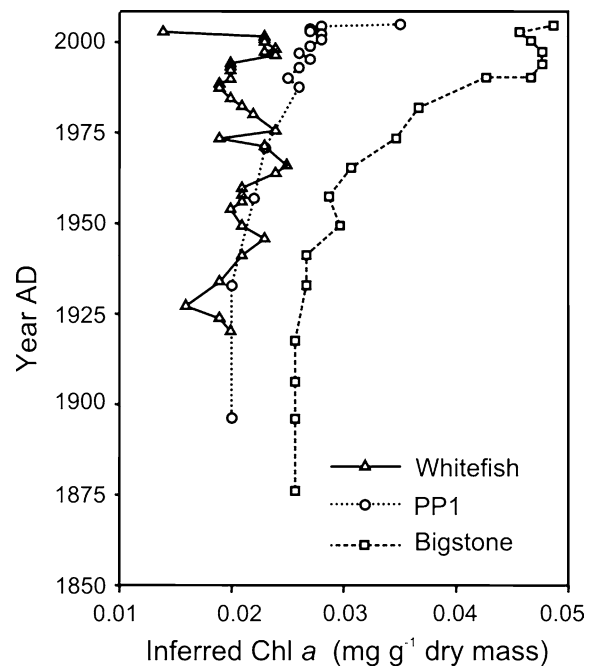


**Fig. 4** Map showing the coring locations of PP1, Bigstone Bay, and Whitefish Bay in Lake of the Woods. The dashed arrow indicates the main direction of nutrient flow from the Rainy River through the lake

Whitefish Bay (49°41'N, 94°17'W), which is hydrologically isolated from the Rainy River flow due to a narrow isthmus that connects the Aulneau Peninsula with the mainland (Fig. 4). Whitefish Bay records the lowest nutrient concentrations (TP  $\approx 7.5\text{--}10.0 \mu\text{g l}^{-1}$ ) and highest water transparencies in LOW. In recent years there is anecdotal evidence that there has been an increase in the frequency and intensity of algal blooms at the northern end of LOW (Pla et al. 2005). There is no evidence for recent or historical algal blooms in Whitefish Bay, and all available limnological data indicate that this section of LOW has not experienced any recent increases in production.

The VRS-inferred chlorophyll *a* profiles for the three sediment cores from LOW (Fig. 5) show the highest concentrations in Bigstone Bay and PP1, the most nutrient-rich sites, followed by Whitefish Bay, the basin that is largely isolated from the Rainy River inflow. The profiles from Bigstone Bay, and to a lesser extent PP1, show increases beginning in the mid-1950s, with the greatest changes occurring post  $\sim 1985$ . The profile from Whitefish Bay fluctuated several times within a small range, but showed no detectable trend over time.

The increased inferred chlorophyll *a* concentrations recorded at LOW were significantly correlated



**Fig. 5** VRS-inferred chlorophyll *a* profiles for PP1, Bigstone Bay and Whitefish Bay in Lake of the Woods

to local mean annual temperature data ( $P < 0.001$ ) extending back to the early 1900s for both PP1 ( $r = 0.88$ ) and Bigstone Bay ( $r = 0.66$ ). This suggests that recent warming superimposed on an already nutrient-rich system may have synergistically triggered an increase in the frequency and/or intensity of algal blooms in these basins. Similar trends with increases in chlorophyll *a* have not been recorded in Whitefish Bay, as the naturally low nutrient levels do not predispose this section of LOW to large algal blooms. In general, algal blooms are rare in waters with TP concentrations less than  $\sim 20 \mu\text{g l}^{-1}$  (MOE 1994). The absence of elevated chlorophyll *a* levels in the recent sediments from Whitefish Bay, a section of LOW that is relatively low in nutrients, demonstrates that the recent VRS-inferred chlorophyll *a* increases recorded at PP1 and Bigstone Bay are not merely reflecting diagenetic processes, but are, in fact, tracking changes in aquatic production.

#### Cape Vera, Devon Island, Arctic Canada

Cape Vera (76°15'N, 89°15'W) on Devon Island in the Canadian High Arctic is the site of a major breeding ground for a large seabird colony of

northern fulmars (*Fulmarus glacialis*). The fulmars form dense nesting sites on steep cliffs that rise above a small coastal foreland containing several freshwater ponds. Each breeding season (May through September) the ponds receive large amounts of nutrient-rich seabird inputs including guano, regurgitated stomach contents and carcasses. As a result, the ponds are relatively productive systems with elevated nutrient levels (Keatley et al. 2009; Blais et al. 2005).

Water chemistry variables and stable isotope ratios of nitrogen ( $\delta^{15}\text{N}$ ) in sediments were used to determine the influence of fertilization by the fulmar colony on the ponds at Cape Vera (Keatley et al. 2009). Fulmar tissue (and guano) is enriched in  $\delta^{15}\text{N}$  relative to N from terrestrial and freshwater sources because fulmars feed high on the marine foodweb and  $\delta^{15}\text{N}$  becomes enriched by  $\sim 3\text{--}5\text{‰}$  per trophic level (Hobson et al. 2002). Surface sediment  $\delta^{15}\text{N}$  values in Cape Vera ponds range from 7 to 20‰ (Blais et al. 2005), which are considerably greater than those commonly measured in Arctic lake sediments that are not influenced by marine nutrients, which range from 1 to 5‰ (Wolfe et al. 2006; Douglas et al. 2004). In addition to nutrient enrichment, Blais et al. (2005) showed that fulmar activity has elevated concentrations of persistent organic pollutants in the pond sediment at Cape Vera by 10–70 times background values because of the combined effects of biomagnification and biotransport. Thus, sediments in ponds that are impacted by seabirds have unique geochemical signatures relative to ponds not influenced by seabirds.

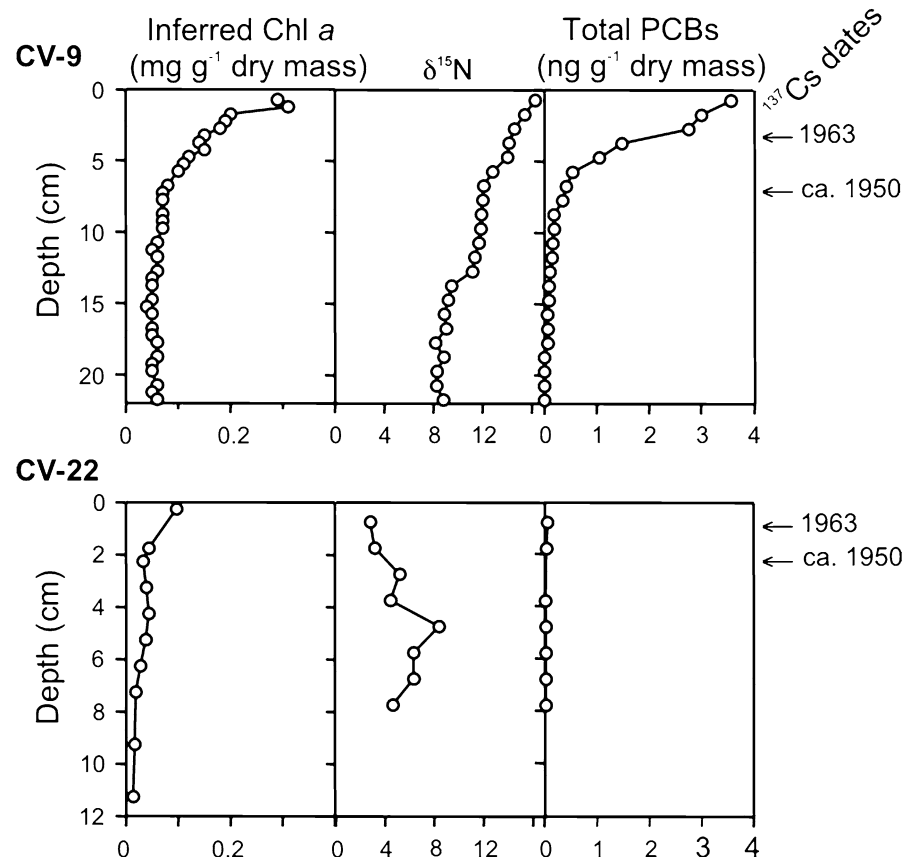
In the Cape Vera case study, we contrast VRS-derived chlorophyll *a* profiles from two similar-sized ponds, but with markedly different histories of seabird exposure. Pond CV-9 is located immediately adjacent to the nesting cliffs at Cape Vera and is characterized by high nutrient levels (total phosphorus<sub>(filt)</sub>  $\sim 40 \mu\text{g l}^{-1}$ ) and a moss-rich catchment (Fig. 6). Pond CV-22, located at Cape Hawes roughly 10 km north of CV-9, is presently completely outside the area influenced by seabirds and is characterized by oligotrophic waters (total phosphorus<sub>(filt)</sub>  $\sim 3 \mu\text{g l}^{-1}$ ) and a sparsely vegetated catchment (Fig. 6). We also assess how well our VRS chlorophyll *a* determinations match with other proxies of seabird abundance, notably  $\delta^{15}\text{N}$  and polychlorinated biphenyls (PCBs). Details of sediment core dating are given in Michelutti et al. (2008a).



**Fig. 6** Photographs of CV-9 and CV-22 at Cape Vera, Devon Island, High Arctic Canada. The close proximity of CV-9 to the nesting cliffs ensures that it receives abundant seabird-derived nutrients, as reflected by the extensive moss growth in its catchment. CV-22 is located roughly 10 km from the nearest seabird colony and thus receives negligible ornithogenic inputs. Photographs were taken in 2005 and are courtesy of Bronwyn Keatley

We recorded much higher chlorophyll *a* levels in the sediment core from the seabird-affected pond (CV-9) compared to the control pond (CV-22; Fig. 7). The inferred chlorophyll *a* profiles from both ponds show increases in the near-surface sediments (post  $\sim 1950$ ), which may be related partly to extended growing seasons associated with warmer temperatures (Smol and Douglas 2007). Nonetheless, the increase in inferred chlorophyll *a* recorded in the seabird-affected site (CV-9) was several fold greater than that recorded at the seabird-free site (CV-22), suggesting that nutrient input from the fulmars allows for enhanced primary production (Michelutti et al. 2008b).

**Fig. 7** VRS-inferred chlorophyll *a* profiles for CV-9 and CV-22 from Cape Vera. Also shown are other sedimentary indicators of seabird activity, namely  $\delta^{15}\text{N}$  and  $\Sigma\text{PCB}$  concentrations



Given that  $\delta^{15}\text{N}$  appears to be a reliable tracer of seabird activity (Blais et al. 2005), and thus any associated nutrient inputs, sedimentary chlorophyll *a* concentrations should vary closely with  $\delta^{15}\text{N}$  values in the seabird-affected site. In fact, our chlorophyll *a* reconstructions from CV-9 are significantly correlated with sedimentary  $\delta^{15}\text{N}$  ( $r = 0.98$ ,  $P < 0.05$ ), and also show a good correspondence with PCB concentrations (Fig. 7). As expected, in CV-22, sedimentary chlorophyll *a* shows no relationship to either  $\delta^{15}\text{N}$  or PCB concentrations (Fig. 7). Thus, the VRS chlorophyll *a* determinations in CV-9 and CV-22 are entirely consistent with the different histories of seabird exposure and with independent geochemical markers of seabird activity such as  $\delta^{15}\text{N}$  and PCBs (Michelutti et al. 2008b).

Meretta Lake, Cornwallis Island, Nunavut, Canada

Meretta Lake (72°41.75'N, 94°59.58'W), located on Cornwallis Island in the Canadian High Arctic, is an

ideal site to assess the ability of VRS sedimentary chlorophyll *a* determinations to track the onset and recovery from cultural eutrophication. From 1949 to 1998, Meretta Lake was used for facultative treatment and disposal of human sewage from the Canadian Department of Transport Base. The raw sewage was released through discharge pipes and would slowly traverse downhill over a ~2 km stretch of water-courses until ultimately ending up in the lake. During peak sewage discharge in the late 1960s to early 1970s the lake was highly eutrophic, recording TP concentrations of ~70  $\mu\text{g l}^{-1}$  (Rigler 1972). With the complete cessation of sewage inputs by 1998, water quality in Meretta Lake started to improve and TP concentrations are presently <5  $\mu\text{g l}^{-1}$  (J. P. Smol and M. S. V. Douglas, unpublished data). Diatom-based paleolimnological studies have also tracked the eutrophication (Douglas and Smol 2000) and recovery (Michelutti et al. 2002) from sewage inputs.

In the Meretta Lake case study, we present VRS chlorophyll *a* determinations from a sediment core recovered in Meretta Lake in 2006. We also show



total organic carbon (TOC) and total organic nitrogen (TON) as additional proxies of aquatic production. The chlorophyll *a* profile from Meretta Lake is relatively stable up until about 6-cm depth when it shows a sharp rise towards the surface (Fig. 7). Although this core is not dated, we know from prior work on  $^{210}\text{Pb}$ -dated cores from Meretta Lake that this depth corresponds roughly to the onset of sewage inputs (Douglas and Smol 2000). TOC and TON show concomitant rises consistent with sewage additions (Fig. 8).

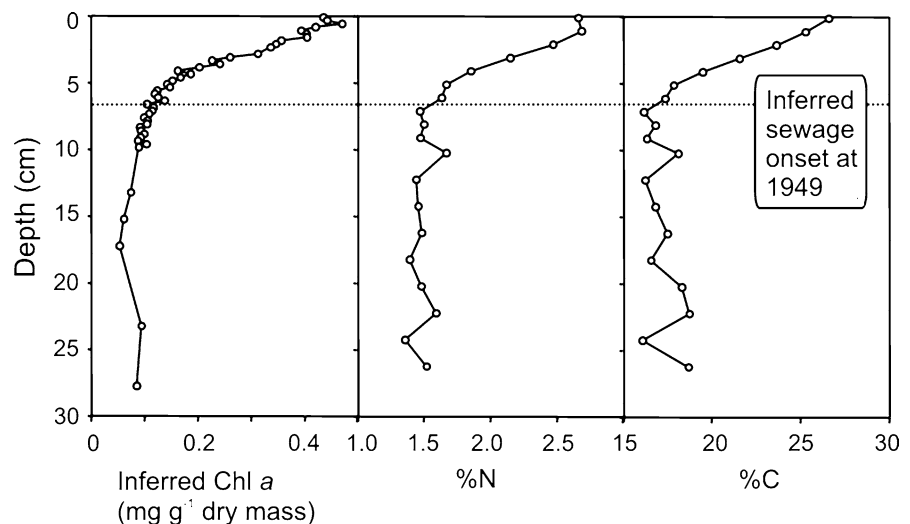
The VRS chlorophyll *a* inferences unquestionably track the eutrophication event at Meretta Lake. Although we record a slight decrease in concentration in the uppermost sediments, the inferred chlorophyll *a* profile does not show a return to pre-impact conditions that we would predict based on the current water chemistry data. For example, TP concentrations in Meretta Lake since the early 1990s have been consistently less than  $10 \mu\text{g l}^{-1}$  (Douglas and Smol 2000) and in recent years are commonly less than  $5 \mu\text{g l}^{-1}$  (J. P. Smol and M. S. V. Douglas, unpublished data). Despite low nutrient levels, there may be several reasons why sedimentary chlorophyll *a* concentrations remain high in Meretta Lake. One possibility is that nutrients from the abandoned sewage trail transported during rainfall or snowmelt events fertilize the lake and result in short-lived spikes in primary production. Alternatively, the low sedimentation rates in Meretta Lake ( $<0.09 \text{ cm year}^{-1}$ ; Douglas and Smol 2000) may obscure any signs of

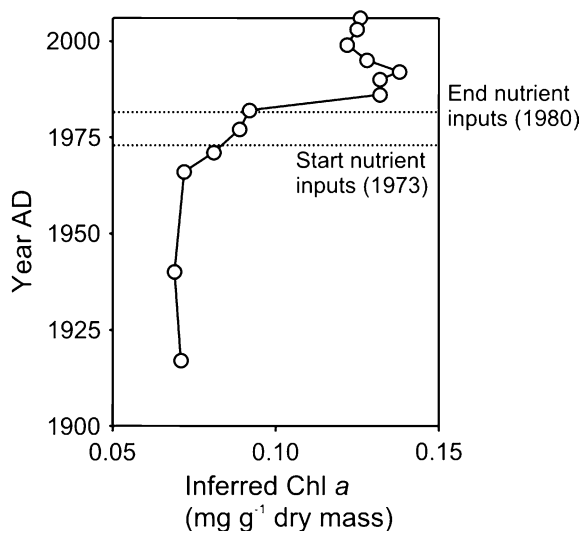
recent recovery to pre-impact production levels. In the next example, we circumvent the problem of obscured signals due to low sedimentation rates by inferring chlorophyll *a* concentrations in a temperate lake that was artificially eutrophied in the 1970s, and then allowed to recover.

#### Lake 226 (Experimental Lakes Area), Ontario, Canada

Lake 226 ( $49^{\circ}07'\text{N}$ ,  $92^{\circ}08'\text{W}$ ) is located in the Experimental Lakes Area (ELA) of northwestern Ontario. The lake was the site of a large-scale fertilization experiment undertaken in the 1970s, and is of historical significance with respect to elucidating the importance of phosphorus in relation to carbon and nitrogen in causing lake eutrophication (Schindler 1974). A natural narrowing near the center of Lake 226 allowed it to be partitioned into two sections. The north basin was fertilized with phosphorus, nitrogen and carbon, whereas the south basin only received nitrogen and carbon. The north basin that was enriched in phosphorus quickly eutrophied, recording algal biomass two orders of magnitude greater than the south basin that received only nitrogen and carbon amendments. After phosphorus amendments were discontinued in 1980, the major differences between the two basins were negligible after the first year, with complete chemical recovery in the north basin occurring after 7 years (Findlay and Kasian 1987).

**Fig. 8** Profiles of VRS-inferred chlorophyll *a*, %N, and %C for the Meretta Lake sediment core





**Fig. 9** The VRS-inferred chlorophyll *a* profile for Lake 226 in the Experimental Lakes Area, northwestern Ontario, Canada

We have inferred chlorophyll *a* concentrations from a sediment core raised from the north basin of Lake 226. The core was recovered in 2006 and sectioned at 0.25 cm intervals. The <sup>210</sup>Pb radiochronology (Fig. 9) indicates that ~6 cm of sediment have accumulated since the final phosphate additions in 1980. Thus, in this example, any subsequent recovery signal should not be blurred by low sedimentation rates.

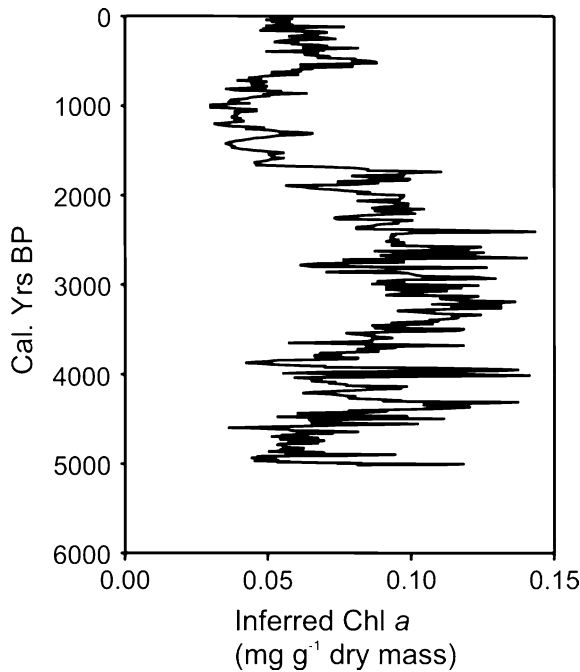
Our inferred chlorophyll *a* profile shows a clear rise nearly coincident with the onset of nutrient additions in 1973 (Fig. 9). After the cessation of phosphate amendments in 1980, inferred chlorophyll *a* concentrations level off, then decline slightly, but do not return to pre-fertilization levels. This is consistent with measurements of annual primary production during and after fertilization (Shearer et al. 1987). There are two factors that may have contributed to the incomplete recovery of Lake 226 (D. W. Schindler, Personnel communication). First, much of the catchment was burned during the late 1970s, potentially increasing the delivery of catchment nutrients to the lake. Second, after the fertilization experiment, lake levels were substantially drawn down as part of a subsequent experiment, with the net result of increasing lake-water residence times and hence internal nutrient cycling, particularly with respect to phosphorus. The impact of these processes is recorded in the sediment chlorophyll *a*

inferences from Lake 226 (Fig. 9). Furthermore, sedimentary chrysophyte assemblages from this same core have revealed that not all taxa have returned fully to pre-manipulation abundances (Clarke 2007). Thus, the biological recovery to experimental eutrophication, and the subsequent history of manipulations to Lake 226, present a recent lake history that is not as straightforward as the water chemistry data imply. As in the case of Meretta Lake, VRS inferred chlorophyll *a* determinations from Lake 226 track closely the onset of eutrophication, but do not indicate complete recovery to pre-disturbance conditions, despite water chemistry measurements that indicate full recovery.

#### Humboldt Lake, Saskatchewan, Canada

Humboldt Lake (52°08.4'N, 105°06.3'W), located in the mixed-grass prairie of central Saskatchewan, Canada, is a closed-basin lake that has been shown to be highly sensitive to Holocene climatic variability. Diatom-based salinity reconstructions at this lake record millennial-scale variations between wet and arid climatic conditions over the last 5,000 years (Michels et al. 2007). Due to the major changes in water quality and abundance between wet and dry periods, we hypothesized that Humboldt Lake may also show fluctuations in aquatic primary production over long-term timescales.

The inferred chlorophyll *a* profile from Humboldt Lake displays variable concentrations over time with highest values between ~4,000 and 2,000 cal year BP, and the lowest values between ~1,500 and 500 cal year BP (Fig. 10). There is a positive significant correlation ( $r = 0.48$ ,  $P < 0.05$ ) between our inferred chlorophyll *a* data and diatom-inferred salinity (Michels et al. 2007), suggesting that primary production at this site is generally greater during the low-water drought periods, although further investigation of this relationship is needed. Perhaps most importantly, the Humboldt Lake inferred chlorophyll *a* reconstruction does not show an exponential decline from the surface, and in fact some of the lowest concentrations are recorded in the uppermost sediments. The many reversals in the inferred chlorophyll *a* profile provide evidence that VRS determinations are not overprinted by a signal of diagenetic chlorophyll *a* loss over time at this site.



**Fig. 10** The VRS-inferred chlorophyll *a* profile ( $n = 396$  sediment intervals) for Humboldt Lake, Saskatchewan, Canada over the past 5,000 years

Comparisons among sites

We chose lakes with well-known trophic histories to critically evaluate how well VRS inferred chlorophyll *a* determinations tracked overall trends in aquatic production at each site. However, another important test of this method is to compare the absolute values of inferred chlorophyll *a* concentrations among our study sites. Because our algorithm is based on a reflectance metric that was directly calibrated to HPLC-measured chlorophyll *a* (Fig. 1), the inferred values should also reflect differences in primary production among sites.

In Table 2, we rank our sites according to their mean sedimentary chlorophyll *a* concentrations. The site ranking in Table 2 is generally what we would have predicted based on the trophic states of these systems. For example, Meretta Lake, Lake 226 and CV-9 recorded the highest mean values (Table 2). All of these sites experienced marked eutrophication as a result of raw sewage effluent (Meretta Lake), seabird inputs (CV-9), and phosphate additions (Lake 226). The next highest mean inferred chlorophyll *a* values were recorded in cores from temperate lake systems

**Table 2** The mean, maximum and minimum VRS-inferred chlorophyll *a* values ( $\text{mg g}^{-1}$ ) for all sediment cores analyzed in this study

Study site	Mean	Max	Min
Eutrophied sites			
Meretta Lake	0.19	0.47	0.05
Lake 226	0.102	0.14	0.07
CV-9 (Cape Vera)	0.09	0.29	0.05
Temperate lakes and Arctic ponds			
Humboldt Lake	0.075	0.14	0.03
Bigstone Bay (LOW)	0.032	0.048	0.03
CV-22 (Cape Vera)	0.030	0.097	0.01
PP1 (LOW)	0.024	0.035	0.02
Whitefish Bay (LOW)	0.021	0.025	0.01
Large Arctic lakes			
Perfection Lake 3	0.016	0.031	0.01
Lost Pack Lake	0.006	0.036	0

Sites are listed in order of their mean chlorophyll *a* concentrations

including Humboldt Lake and LOW. Also within this group is the Arctic pond, CV-22. The small size of Arctic ponds allows them to warm more rapidly compared to larger and deeper lakes (Smol and Douglas 2007), and thus these ponds are reasonably productive, despite a short growing season. Not surprisingly, the lowest mean chlorophyll *a* values were inferred in the two large Arctic lakes from Baffin Island, Perfection Lake 3 and Lost Pack Lake (Fig. 3; Table 2). Generally similar patterns are found when sites are ranked according to their maximum chlorophyll *a* values (Table 2).

We note that direct comparisons of inferred chlorophyll *a* concentrations among sites, especially lakes located in disparate biogeographic locations, should be made with caution as variable sedimentation rates can affect concentration data. For example, although LOW is located in a temperate region and receives nutrient-rich runoff, sediment cores from this lake (Fig. 5) record inferred chlorophyll *a* concentrations similar to the oligotrophic Arctic lake cores from Baffin Island (Fig. 3). Generally, we would predict that primary production, as inferred by chlorophyll *a*, would be greater in a temperate lake than in a nutrient-poor Arctic lake with a short growing season. However, when mean chlorophyll *a* fluxes are calculated for the past ~100 years, the Whitefish Bay core from LOW records a mean flux of

3.9 mg m<sup>-2</sup> year<sup>-1</sup>, which is nearly four times greater than the value of 1.1 mg m<sup>-2</sup> year<sup>-1</sup> recorded at Lost Pack Lake on Baffin Island. Clearly, high sedimentation rates at LOW have diluted the sedimentary chlorophyll *a* concentrations, and thus flux data are more useful for inter-lake comparisons. Unfortunately, due to a lack of strong dating control on many of our sediment cores (Michelutti et al. 2008a), we cannot calculate chlorophyll *a* fluxes for all sites. Nonetheless, our chlorophyll *a* inferences, even when viewed solely as concentration data, appear to reflect overall differences in primary production among our study sites.

## Conclusions

The reconstruction of sedimentary chlorophyll *a* concentrations using the VRS method described here is a straightforward process that does not require complex multivariate modeling to interpret the spectral data. The relative ease of this non-destructive method, coupled with the ubiquity of chlorophyll *a* in most lake sediments, encourages us to continue to apply this approach across a broad range of lake types and environments. Indeed, our data show that VRS chlorophyll *a* determinations track overall trends in trophic histories in lakes from Arctic, boreal, and prairie ecosystems. The chlorophyll *a* profiles obtained from various lake systems with well-known trophic histories, including the complacent profiles from sites with no modern eutrophication (i.e., Whitefish Bay and CV-22), confirm that VRS profiles are tracking changes in aquatic primary production and not simply reflecting diagenetic trends. In lake systems that have been intentionally eutrophied (e.g., Lake 226, Meretta Lake), the VRS method tracks the onset of production increases, but does not suggest complete recovery as indicated by water chemistry measurements. The greatest utility of this approach likely lies in its ability to reconstruct overall trends in production within a particular lake system, ideally in concert with additional chemical and biological analyses. These data wholly support earlier contentions (Wolfe et al. 2006) about the widescale applicability of VRS chlorophyll *a* determinations as a rapid, cost effective, and non-destructive method for reconstructing trends in whole-lake production.

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