

Spectrofluorescence of Sediment Humic Substances and Historical Changes of Lacustrine Organic Matter Provenance in Response to Atmospheric Nutrient Enrichment

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Humic substances were extracted from the sediments of two small alpine lakes in the Colorado Front Range and characterized by three-dimensional fluorescence spectroscopy. The fluorescence index (FI), defined as the ratio of fluorescence emitted at 450 nm to that emitted at 500 nm from an excitation wavelength of 370 nm, was computed and thereafter compared to additional sediment proxies of recent environmental change. Stratigraphic changes in both sediment C:N ratios and diatom assemblages parallel those of FI, together indicating pronounced increases in the contribution of autochthonous organic matter to lake sediments since the mid-20th century. This result is consistent with increased algal production attributable to nutrient enrichment, given that the region undergoes episodic nitrogen saturation in response to anthropogenic N emission. The validation of sediment FI measurements through comparisons with independent methods demonstrates the utility of this technique for characterizing shifts in the provenance of lake sediment organic matter arising from changing environmental conditions.

Introduction

Significant effort has been dedicated to identifying and quantifying the sources of organic matter preserved in lake sediments (1–3). Interest in this area is stimulated by the possibility of developing a primary sediment geochemical proxy for assessing changes between the proportions of lacustrine and terrestrial organic matters delivered to lakes, arising from either natural processes or anthropogenic perturbations. Previous studies have relied on techniques such as sediment C:N ratios to identify sources of organic matter (4) because protein-rich algae have low C:N between 4 and 10, whereas cellulose- and lignin-rich terrestrial organic

matter typically has a C:N greater than 20 (1, 5). Decreases in C:N values have been used to identify periods when lake sediments receive an enhanced proportion of autochthonous (algal) organic matter due to eutrophication (6). However, the use of sediment C:N ratios to infer changes in organic matter sources has been questioned due to the possibility of diagenetic alteration (7). For example, low sediment C:N ratios may result from microbial immobilization of N in the presence of increased C mineralization, as observed in soils (8). But such diagenetic overprinting may ultimately be less important in the majority of lake sediments, allowing bulk measurements to faithfully retain a signature of organic matter provenance (9).

Other approaches appear even more susceptible to diagenetic alteration. Although sediment $\delta^{13}\text{C}$ measurements may partially track organic matter source variability, post-depositional losses of isotopically enriched carbohydrate may complicate interpretations (1). Furthermore, lake algae and the majority of north-temperate land plants share the C3 photosynthetic pathway, resulting in an overlapping range of initial biomass $\delta^{13}\text{C}$ values. The analysis of geolipid fractions, including their characterization and C isotopic composition, is perhaps a more promising approach in this area. However, compound-specific analyses are typically labor- and sample-intensive, which ultimately limits the stratigraphic resolution that can be attained. Certain compounds are also highly vulnerable to diagenetic transformation. In oligotrophic lakes, this appears especially evident with respect to the *n*-fatty acids and *n*-alkanols, for which sediment distributions can be influenced by both selective microbial utilization as well as de novo synthesis (1, 10).

In contrast, humic substances (including humin, humic acids, and fulvic acids), appear to be diagenetically stable on time scales of hundreds to thousands of years once archived in sediments (11). Humics are operationally defined biomolecular classes that include a wide range of recalcitrant organic compounds, themselves resulting from the decomposition of aquatic and terrestrial organic matter. The ability to characterize these compounds spectroscopically has been recognized for over 20 years (12). More recently, methods have been developed to assess sources of the humic fraction in dissolved organic matter (DOM) from whole-water samples from lakes and streams using the spectrofluorescence signatures of dissolved humic substances (13–15). The apparent stability of sedimentary humic material, which has been established by a variety of approaches in a broad spectrum of ecosystems (11, 12, 16, 17), suggests that considerable potential exists for the adaptation of fluorescence techniques to fossil humic substances. However, the viability of spectrofluorescence as a new methodology to reconstruct historical changes of organic matter provenance remains untested. In this paper, humic substance fluorescence results are presented from the sediments of two small alpine lakes in the Colorado Rocky Mountains and are thereafter evaluated in relationship to independent indicators of changes in organic matter provenance, including C:N ratios and paleoecological inferences from diatom microfossils.

Methods

Study Sites. The primary study site is Lake Louise (40°30'28" N, 105°37'13" W; Figure 1), a small (2.7 ha; $Z_{\text{max}} = 8$ m), oligotrophic (total phosphorus [TP] <0.01 mg L⁻¹) alpine lake in Rocky Mountain National Park (RMNP). The lake is situated at treeline in an east-facing cirque at 3360 m above sea level, within a basin dominated by bedrock (Precambrian granite and gneiss) and talus. Lake waters are dilute (electrical

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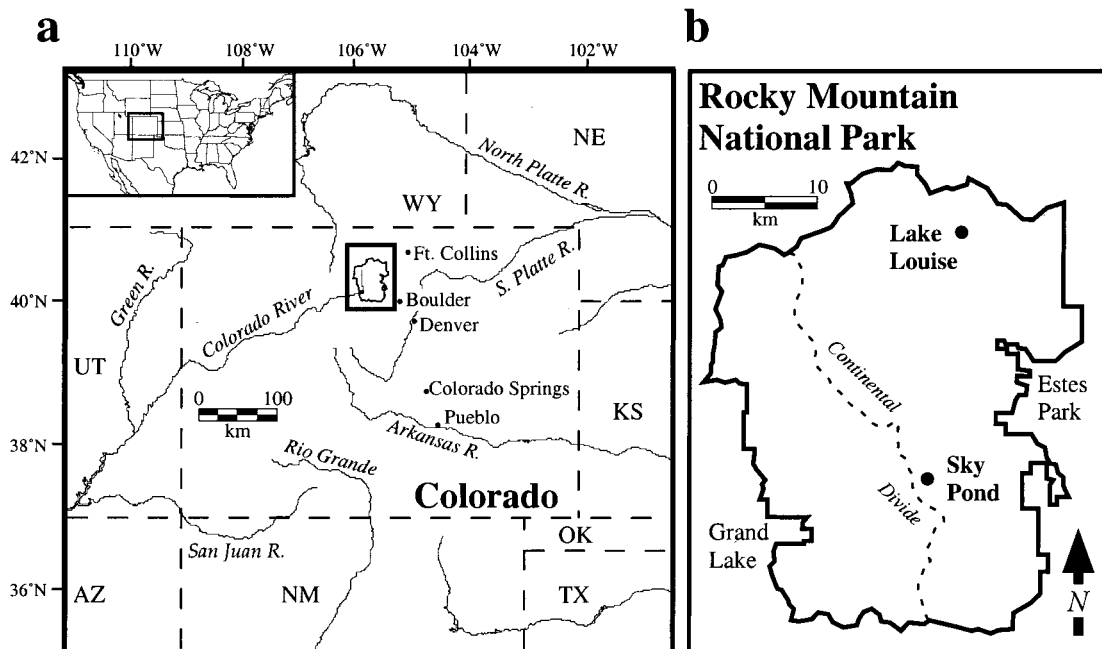


FIGURE 1. Location map of Rocky Mountain National Park (a), situating Lake Louise and Sky Pond to the east of the Continental Divide (b).

conductance $<20 \mu\text{S cm}^{-1}$) and slightly acidic ($\text{pH} \sim 6.5$). A second site, Sky Pond ($40^{\circ}16'42''\text{N}$, $105^{\circ}40'06''\text{W}$), is located 23 km to the south and was investigated primarily to assess the results obtained from Lake Louise in the context of regional environmental change. Sky Pond lies immediately east of the Continental Divide at 3322 m above sea level and is morphometrically (3.1 ha; $Z_{\text{max}} = 7$ m) and limnologically very similar to Lake Louise. In typical years, both lakes are ice-covered from November to June.

Despite being situated in Class 1 lands that are federally managed for the prevention of ecological impairment by air pollution, there is regional evidence for episodic nitrogen saturation resulting from atmospheric deposition of inorganic N of anthropogenic origin (18). Increased population and automotive use in the Denver–Ft. Collins urban axis and the widespread deployment of synthetic agricultural fertilizers east of the Rocky Mountains are responsible for nitrogen enrichment in precipitation from easterly upslope air mass trajectories. Westerly Pacific flow, the dominant source of winter precipitation in the alpine, scours nitrogen emissions from several coal-fired power plants on the western slope and is therefore also N-enriched (19). Although rates of wetfall N deposition in the region are typically $2\text{--}5 \text{ kg of N ha}^{-1} \text{ yr}^{-1}$, which is modest by comparison to many industrialized regions, these levels are still well above the natural background (20). Accordingly, Lake Louise and Sky Pond have relatively high average dissolved inorganic N ($\text{NO}_3^- + \text{NH}_4^+$) concentrations: 1.06 and 1.20 mg L^{-1} , respectively. These levels are elevated by comparison to alpine areas elsewhere in the conterminous United States. Stratigraphic records of diatom assemblage changes and nitrogen isotopic excursions from these two lakes strongly imply that present N deposition rates are sufficient to induce directional ecological and biogeochemical changes (21).

Sediment Samples and Chronology. Sediment cores were obtained in 1997 from the deepest part of each lakes with a modified Kajak–Brinkhurst gravity corer that captures the mud–water interface intact (22). Samples were extruded in the field in continuous 0.5-cm increments to avoid any possibility of sample disturbance. The cores were dated using sediment ^{210}Pb activity determined by α -spectroscopy, to which the constant rate of supply (CRS) model was applied

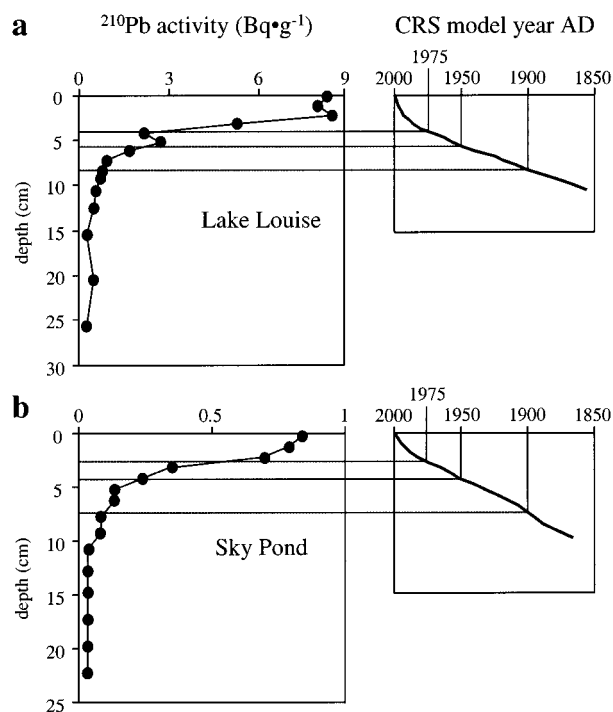


FIGURE 2. ^{210}Pb activities and CRS age–depth models from the Lake Louise (a) and Sky Pond (b) gravity cores.

(23). The ^{210}Pb dating results and corresponding age–depth curves are shown in Figure 2. Because the present study is based on the same cores analyzed in detail by Wolfe et al. (21), sample availability was partially limited, especially for the surface of Lake Louise (0–1.5 cm) and the 0.5–4.0-cm interval from Sky Pond. Core sample depths and CRS-estimated ages (in parentheses) are as follow: Lake Louise: 1.5–2.0 cm (1994), 2.0–2.5 cm (1991), 2.5–3.0 cm (1988), 3.5–4.0 cm (1976), 4.5–5.0 cm (1960), 5.5–6.0 cm (1945), 7.0–7.5 cm (1915), 8.5–9.0 cm (1886), 10.0–10.5 cm (1882), and 12.0–12.5 cm (pre-1840; unsupported ^{210}Pb inventory exhausted); Sky Pond: 0–0.5 cm (1996), 4.0–4.5 cm (1951),

6.0–6.5 cm (1923), 7.0–7.5 cm (1907), 8.0–8.5 cm (1888), 10.0–10.5 cm (1856), and 12.0–12.5 cm (pre-1840). In addition, four samples of sediment trap material were analyzed from Sky Pond. These samples enable the assessment of diagenetic processes through comparisons to the lake's surface sediments. The trap design includes a 2 m diameter focusing funnel and baffled collector (24). The sediment trap was deployed at a depth of 2.5 m in the lake's center between August 1995 and August 1996. Sedimenting material accumulated in a 3 cm diameter collecting tube and was extruded vertically upon retrieval. The lower (trap-1) and upper (trap-4) samples most likely reflect summer sedimentation, and the intervening samples reflect under-ice accumulation.

Sediment Humic Substance Extraction. Two wet chemical methods were initially employed to extract humic substances from the Lake Louise sediment samples, primarily for comparative purposes. Samples from Sky Pond were extracted using the first method only, once it was proven more effective. The first isolation technique, modified from Schnitzer (25), is more time-consuming and chemically aggressive and was used to target the complete fulvic acid fraction incorporated into sediment. Both humic and fulvic acids were extracted from freeze-dried samples of 1.0 g dry mass by continuous agitation in 0.5 N NaOH (pH 13.7) for 24 h. Sample to extractant ratio was 1:10 by volume. The headspace of the sample tubes was replaced with inert N₂ gas to prevent oxidation during extraction. The extracted mixture was separated by centrifugation and acidified to pH 1.0 to precipitate humic acids. This precipitate was collected after further centrifugation, and the fulvic acid supernatant was retained for spectrofluorescence analysis.

The second technique is a weaker and less time-consuming procedure that results in the incomplete extraction of a more labile pool of mixed sedimentary humic substances (i.e., humic + fulvic acids). Slurries were prepared using a 1.0 mg:1.0 mL ratio of freeze-dried sediment and 1.0 N Na₄P₂O₇ (pH 7.0). These were agitated at 150 rpm for 24 h, after which the extracted humic substance solution was passed through a 0.1-mm filter. For both techniques, extracts were stored in the dark in amber vials at 4.0 °C. Prior to the spectrofluorescence measurements, the extracts were diluted with deionized water to yield dissolved organic carbon (DOC) concentrations of 1.0–3.0 mg of C L⁻¹ (26). The pH of diluted extracts was adjusted to 2.0 with concentrated HCl in order to minimize quenching of fluorescence due to metal complexation.

Fluorescence Spectroscopy. Fluorescence was measured using a Horiba FluoroMax-2 multiwavelength fluorescence spectrophotometer. Fluorescence intensity was measured from excitation wavelengths of 250–400 nm in 10-nm increments, over emission wavelengths of 400–550 nm in 2-nm increments. Intensity values were corrected for lamp spectral properties and Raman scattering according to McKnight et al. (15). The results are primarily reported as the ratio of fluorescence emitted at 450 nm to that emitted at 550 nm (I_{450}/I_{550}), for an excitation wavelength of 370 nm. This ratio, known as the fluorescence index (FI), has successfully been used to differentiate dissolved organic matter derived from terrestrial (lignous) and aquatic (algal and bacterial) precursors in water samples (13–15). The reproducibility of FI measurements is ± 0.05 .

Elemental Analysis and Diatoms. Organic C and N contents of lyophilized bulk sediment samples were determined by combustion in a Carlo Erba 1100 elemental analyzer. Thereafter, atomic C:N ratios were computed. Reproducibility of organic C and N contents is <1%.

Diatom slides were prepared for light microscopy following standard methods (27). A minimum of 500 diatom valves were counted from each level at 1000 \times under oil

immersion and thereafter converted to the relative frequencies of individual taxa. For the purpose of this investigation, we focus on the frequencies of two mesotrophic taxa, *Asterionella formosa* and *Fragilaria crotonensis*, which are indicative of recent nutrient enrichment and were either absent or only present in trace proportions in assemblages of pre-industrial age. More complete floristic details are presented elsewhere (21). In addition, total diatom valve concentrations were estimated from sediment samples by the addition of a known quantity of external microscopic marker grains and their recovery during microfossil enumeration (28). Given fairly uniform sedimentation rates (150–210 g m⁻² yr⁻¹), valve concentration trends are interpreted to reflect total diatom paleoproduction, which is supported by accompanying floristic shifts toward taxa with mesotrophic ecological affinities.

Results and Discussion

Spectrofluorescence of Sediment Humic Substances. The utility of fluorescence spectroscopy in the characterization of humic substances arises from the fact that all humic substances fluoresce. A large proportion of this fluorescence is caused by the presence of quinone functional groups within humic substances (29). These quinone groups are directly derived either from the degradation of quinone-containing biopolymers or from the polymerization or condensation of smaller biomolecules, such as substituted phenols. Because the fluorescence signature of quinones (and their multiple oxidation states) is affected by the substrates attached to them (such as aromatic, carboxyl, and/or methoxy groups), fluorescence spectroscopy can be used to explore the original sources of humic substances.

Several fluorophore characteristics are revealed by the three-dimensional emission–excitation matrixes (EEMs) of NaOH-extracted fulvic acids from lake sediments. Figure 3 illustrates spectra representative of Lake Louise's recent and pre-industrial sediments. Similar to fulvic acids from whole waters, sedimentary counterparts preserve both primary and secondary excitation–emission maxima. In the near-surface sediments, the primary emission peak is broad and centered at approximately 400 nm from an excitation wavelength of 320 nm. The secondary excitation–emission maximum is also broad, exhibiting a 90% maximum peak intensity between 415 and 445 nm from an excitation of 275 nm. In contrast, the primary peak in the older sample is more narrowly constrained, emitting at a slightly longer wavelength, with a 90% maximum peak intensity between 410 and 420 nm from an excitation of 320 nm. The secondary maximum emits 90% peak intensity between 430 and 450 nm, from an excitation centered on 260 nm. These between-sample differences are entirely consistent with the identification of two distinct dominant sources of fulvic acids (15). A displacement of both peaks toward slightly higher emission wavelengths is observed in dissolved fulvic acids having large proportions of terrestrial precursor material, such as lignin. If this trend holds true for sedimentary fulvic acid, then the lower core samples are more terrestrially influenced in relation to surface sediments, where a greater proportion of fulvic acid appears to be derived from aquatic (algal and microbial) sources.

When FI values are computed from the EEMs of the NaOH-extracted core samples from Lake Louise, relatively stable values (~ 1.5) are obtained in sediments deposited before 1950. Thereafter, a gradual increase toward a maximum FI of 1.75 is observed (Figure 4a). In the analysis of natural waters, high FI values are significantly correlated with both autochthonous organic matter provenance and low fulvic acid aromaticity (15). Waters deriving their DOC from dominantly terrestrial sources are characterized by lower FI values. Assuming that this same general pattern holds true

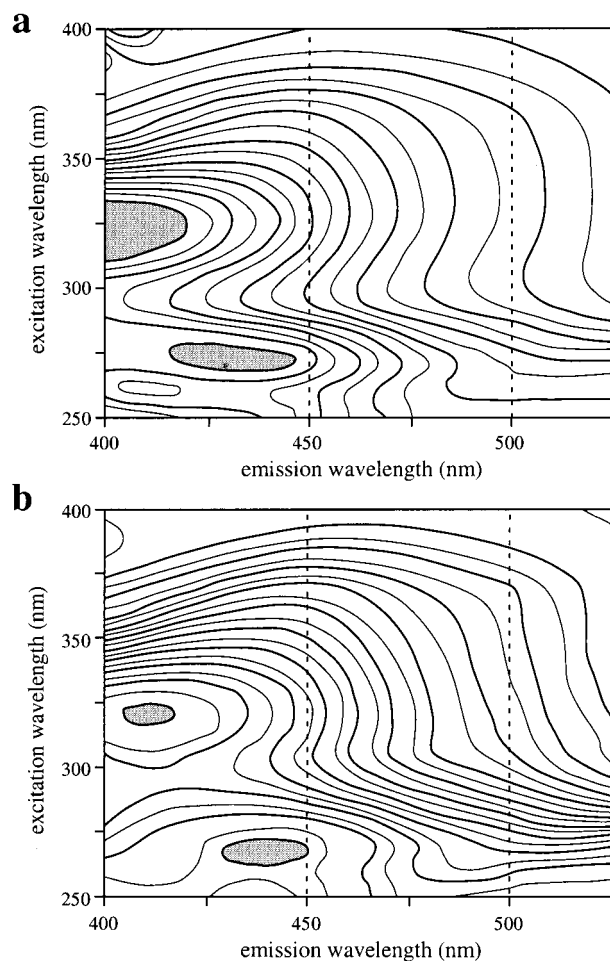


FIGURE 3. Emission–excitation matrices (EEMs) of NaOH-extracted fulvic acid from (a) the upper (1.5–2.0 cm; 1994) and (b) lower (12.5–13.0 cm; pre-1840) sediment samples from the Lake Louise core. Fluorescence emissions have been normalized to the maximum peak intensity of each sample. Shaded regions exceed 90% of peak intensities. The FI values from these samples are 1.68 and 1.51 for panels a and b, respectively.

for fulvic acids in sediment, the results from Lake Louise suggest a progressive increase in the supply of autochthonous organic matter in recent decades. This coincides with independent inferences of increased algal production in response to anthropogenic nitrogen deposition (21).

In comparison, the FI values of $\text{Na}_4\text{P}_2\text{O}_7$ -extracted fractions were less useful for assessing historical changes in the provenance of humic substances to the sediments of Lake Louise. Although the EEMs of the $\text{Na}_4\text{P}_2\text{O}_7$ extracts are broadly similar to those described above (Figure 3), the FIs of these samples do not show any directional stratigraphic trends down-core. FI values from the $\text{Na}_4\text{P}_2\text{O}_7$ extracts consistently center around 1.07, similar to values reported elsewhere for $\text{Na}_4\text{P}_2\text{O}_7$ -extracted autochthonous humic materials (29). Because the Lake Louise catchment is very sparsely vegetated with minimal soil development, a dominantly aquatic signal is not surprising. However, these results imply that the weaker and less selective $\text{Na}_4\text{P}_2\text{O}_7$ extraction method at pH 7.0, albeit easier, may underestimate the yield of tightly bound terrestrial humic substances, in particular those in the fulvic acid fraction. This, in turn, has a pronounced effect on the spectrofluorescence signatures of sediment extracts and on their utility to decipher changes in provenance. For sites such as Lake Louise, the more aggressive NaOH extraction appears necessary to capture both the full spectrum of humic substance sources and their progressive changes through

time. The $\text{Na}_4\text{P}_2\text{O}_7$ extraction, which targets a more labile pool of humic substances, failed to produce pronounced down-core stratigraphic trends, as observed in the NaOH-extracted fulvic acid pool.

The FI results of NaOH-extracted fulvic acid from the Sky Pond core also reveal marked stratigraphic changes, with a sharp inflection toward higher values between 6 and 7 cm (Figure 4b). However, these results differ from those obtained from Lake Louise in two fundamental ways. First, although the amplitude of FI increases in both lakes is similar (about 0.2), the absolute FI values obtained from Sky Pond are considerably lower (1.2–1.5) as compared to the data from Lake Louise (1.5–1.7). Second, the trend toward higher FI values is more abrupt in Sky Pond, and it occurs somewhat earlier than in Lake Louise: between 1910 and 1920 according to the ^{210}Pb age model. Furthermore, the surface sample (0–0.5 cm) reveals a slight decrease from the FI value measured at 4.0–4.5 cm (Figure 4b). Unfortunately, insufficient archived material remained for additional analyses in the 0.5–4.0-cm interval. However, the highest FI values measured from Sky Pond are from the four sediment trap samples, which range from 1.46 to 1.56 (Table 1). Although the direction and amplitude of stratigraphic changes in FI are comparable between the two lakes, it appears that subtle differences exist in the properties of each lake's sedimentary humic material. One possibility is that DOM in Sky Pond is more strongly influenced by terrestrial contributions, in sediments of both pre- and post-industrial age. Until this possibility can be tested more explicitly, it therefore seems prudent at this stage to view the FI results as semiquantitative, in keeping with results from surface waters (15). However, in the cases of both aquatic and sediment samples, shifts in FI values greater than 0.1 appear indicative of changing sources of fulvic acid. In this sense, the Sky Pond results nonetheless confirm that FI represents a useful screening tool for ascertaining source changes in lacustrine organic matter.

Comparison with Other Paleolimnological Proxies. The observed increase in FI values of NaOH-extracted fulvic acids is synchronous with increases in the organic carbon and nitrogen contents of the sediments of Lake Louise (Figure 4a). However, the rate of increase in sediment N is greater than that of C, so that the C:N ratio decreases dramatically in the three uppermost samples. This result suggests that the overall increase in organic matter relates to a greater aquatic contribution derived from enhanced aquatic production, further supporting the results from fulvic acid spectrofluorescence. At Sky Pond, changes in FI are not associated with synchronous shifts in organic C and N concentrations, and these are markedly lower than in the sediments of Lake Louise (Figure 4b). This may relate to between-site differences in FI values. However, C:N decreases sharply in the upper two samples from the Sky Pond core, a trend that, as in Lake Louise, occurs somewhat after the initial increase of sediment FI.

The diatom records from both lakes corroborate the inferences from fulvic acid spectrofluorescence and C:N ratios. Total diatom concentrations progressively increase from $<3.0 \times 10^9$ valves g^{-1} in sediments pre-dating 1950 to a maximum of 23×10^9 valves g^{-1} in the most recent sample analyzed from Lake Louise and 6×10^9 valves g^{-1} in Sky Pond (Figure 4). The nearly 4-fold greater maximum diatom concentration attained in Lake Louise is consistent with this site's higher maximum FI values. In both lakes, diatom concentration trends are primarily due to marked increases in the representations of the two mesotrophic taxa, *A. formosa* and *F. crotonensis*. These diatoms are not characteristic of the pre-industrial floras of pristine, oligotrophic alpine lakes (21). Their expansions suggest a moderate degree of nutrient enrichment to the aquatic system, which, in the absence of local catchment-scale disturbances, is attributed to anthro-

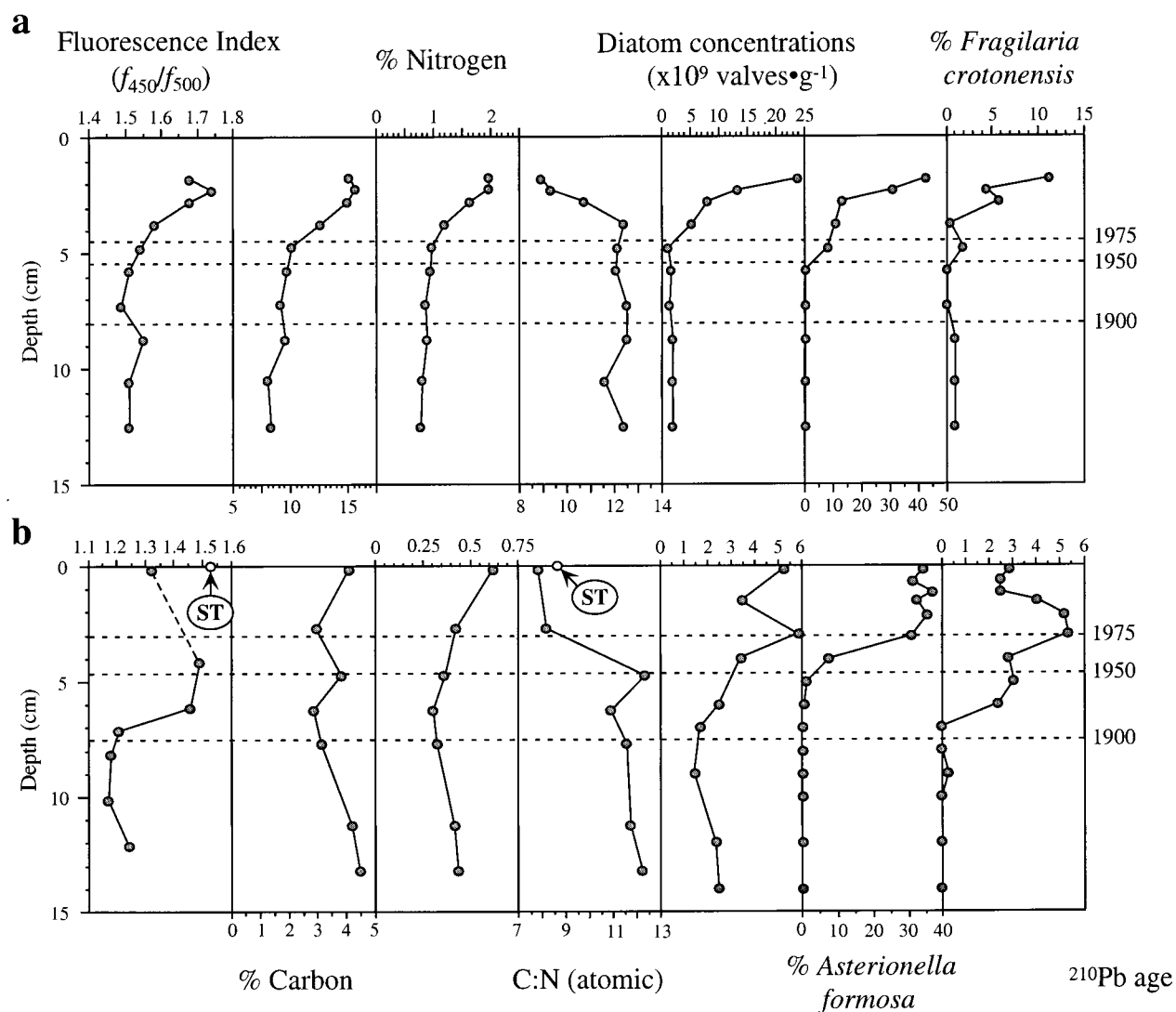


FIGURE 4. Stratigraphies of sediment fulvic acid FI index (NaOH extracts), organic C and N contents, atomic C:N ratios, total diatom concentrations, and relative frequencies of *Asterionella formosa* and *Fragilaria crotonensis* in the gravity cores from Lake Louise (a) and Sky Pond (b). The dashed time lines are based on the CRS ^{210}Pb chronologies of each core. The mean FI and C:N values from four sediment trap samples collected between August 1995 and August 1996 are indicated by ST and open circles in panel b.

TABLE 1. Comparison between the Sky Pond Sediment Trap Samples and Surface Sediment (0–0.5 cm) for FI and Other Proxies Relating to the Source of Lacustrine Organic Matter Source

sample	FI (f_{450}/f_{500})	%C	%N	C:N (atomic)	% <i>Asterionella formosa</i>
trap-4 (spring–summer 1996)	1.46	9.3	1.3	8.5	32
trap-3 (winter)	1.55	10.7	1.4	8.9	26
trap-2 (winter)	1.56	10.8	1.4	9.1	36
trap-1 (summer–fall 1995)	1.53	19.2	2.8	7.9	50
mean trap value	1.53	12.5	1.7	8.6	36
standard deviation (as %)	0.05 (3.3)	4.5 (36.0)	0.7 (41.2)	0.5 (5.8)	10 (28)
core top (0–0.5 cm)	1.32	4.2	0.6	7.9	34
core top:trap mean	0.86	0.34	0.36	0.91	0.96

pogenic nitrogen loading. In support of this interpretation, it is noted that the growth of *A. formosa* has been stimulated by N additions to in situ cultures from a nearby lake in RMNP (30). As previously mentioned, the FI increase at Sky Pond occurs decades earlier than at Lake Louise, according to the ^{210}Pb chronologies, but this inflection is synchronous to with the initial rises in diatom concentrations and in the representation of *F. crotonensis* (Figure 4b). This confers a high degree of sensitivity to sediment FI measurements in relation to changing limnological conditions.

Assessment of Diagenetic Influences on Sediment Proxies. The comparison of these same proxies between the Sky Pond sediment trap and surface sediment samples allows the potential for diagenetic overprinting to be assessed. These results are summarized in Table 1. Surface sediments preserve between 86 and 96% of the signatures of sedimenting material for FI, C:N ratios, and the relative frequencies of the dominant diatom, *A. formosa*. On the other hand, concentrations of organic C and N are significantly lower in surface sediments than in the sediment trap material, indicating either sub-

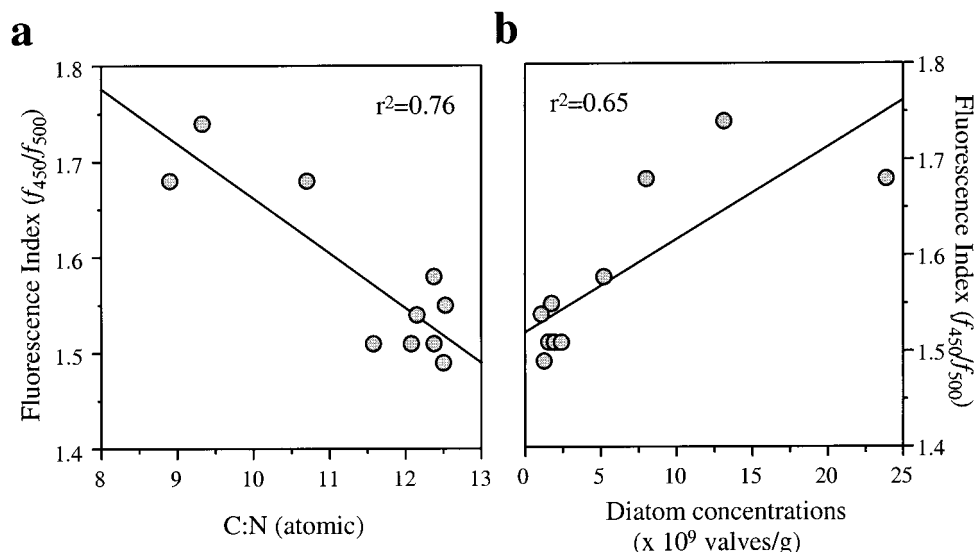


FIGURE 5. Relationships of sediment fulvic acid FI vs (a) C:N ratios and (b) total diatom valve concentrations in the Lake Louise core. Both linear correlations are significant at $p < 0.05$.

stantial mineralization during sedimentation, dilution by detrital inorganic material delivered to sediments by underflow, or a combination of these processes. Despite these differences in elemental concentrations, C:N ratios behave conservatively, with only slightly lower core-top values than those measured from the sediment trap samples. This validates the resilience of sediment C:N as a faithful tracer of organic matter source (5). From the sediment trap analyses, it appears that diagenetic processes exert relatively minor influences on sediment FI and C:N signatures, with the important implication that recorded stratigraphic changes reflect real environmental changes and not merely artifacts of post-depositional geochemical transformations. This conclusion is augmented by the diatom results presented in Table 1, which show the nearly complete integration of sediment trap floral assemblages into the surface sediments.

Implications for Recent Environmental Change. The FI of sediment fulvic acids from Lake Louise is significantly correlated ($p < 0.05$) with both C:N and total diatom concentrations (Figure 5). Similar correlations are not possible with the more limited and unequally sampled data from Sky Pond, although the overall pattern of stratigraphic evolution from this site mimics that expressed at Lake Louise. These results indicate that all three proxies are useful for sediment-based reconstructions of historical changes in autochthonous organic matter production. Fluorescence spectroscopy is especially valuable in cases where specific additional questions are being posed, such as inferences regarding aromaticity, optical properties, and/or sorption properties of sediments. Diatoms have the advantage of revealing part of the ecological legacy of environmental change as well as remaining largely unaffected by diagenetic alteration in the sediments of circumneutral oligotrophic lakes, inasmuch as the dissolution of biogenic silica is negligible. However, both techniques are more time-consuming relative to the measurement of sediment C:N ratios. Yet despite the considerable differences in organic C and N concentrations in the sediments of the two lakes considered here, the C:N ratio remained a robust indicator of changing organic matter provenance. Ultimately, all three proxies appear more time- and cost-effective and less vulnerable to diagenetic effects than alternative methodologies for tracing organic matter sources from lake sediments, such as compound-specific geolipid analyses.

The conclusion drawn from the detailed investigation of sediment properties in Lake Louise and Sky Pond is that

aquatic production has increased in recent decades, resulting in greater autochthonous organic matter supply to the sediments of both lakes. Because these shifts appear regionally coherent and causally linked to enhanced nitrogen availability from atmospheric deposition (20, 21), the possibility arises that rates of inorganic N deposition approaching the critical load of $4.0 \text{ kg of N ha}^{-1} \text{ yr}^{-1}$ proposed by Williams and Tonnessen (31) are fully capable of impacting lake biology and biogeochemistry. Current levels of N deposition are sufficient to alter both the quantity and the quality of organic matter in alpine lakes of the Colorado Rocky Mountains, in addition to inducing pronounced changes in the composition of algal floras. This highlights the sensitivity of these protected and seemingly pristine ecosystems to enrichment from anthropogenic N deposition.

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