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Recent ecological and biogeochemical changes in alpine lakes of Rocky Mountain National Park (Colorado, USA): a response to anthropogenic nitrogen deposition

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ABSTRACT

Dated sediment cores from five alpine lakes (>3200 m asl) in Rocky Mountain National Park (Colorado Front Range, USA) record near-synchronous stratigraphic changes that are believed to reflect ecological and biogeochemical responses to enhanced nitrogen deposition from anthropogenic sources. Changes in sediment proxies include progressive increases in the frequencies of mesotrophic planktonic diatom taxa and diatom concentrations, coupled with depletions of sediment $\delta^{15}N$ and C : N values. These trends are especially pronounced since approximately 1950. The most conspicuous diatoms to expand in recent decades are *Asterionella formosa* and *Fragilaria crotonensis*. Down-core species changes are corroborated by a year-long sediment trap experiment from one of the lakes, which reveals high frequencies of these two taxa during autumn and winter months, the interval of peak annual limnetic $[NO_3^-]$. Although all lakes record recent changes, the amplitude of stratigraphic shifts is greater in lakes east of the Continental Divide relative to those on the western slope, implying that most nitrogen enrichment originates from urban, industrial and agricultural sources east of the Rocky Mountains. Deviations from natural trajectories of lake ontogeny are illustrated by canonical correspondence analysis, which constrains the diatom record as a response to changes in nitrogen biogeochemistry. These results indicate that modest rates of anthropogenic nitrogen deposition are fully capable of inducing directional biological and biogeochemical shifts in relatively pristine ecosystems.

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INTRODUCTION

Rocky Mountain National Park (RMNP, Fig. 1) is a federally managed Class 1 conservation and recreation area that protects outstanding examples of mid-latitude alpine and subalpine environments. The numerous alpine lakes of RMNP are frequently perceived as pristine ecosystems. However, recent analyses from several sites in RMNP and elsewhere in the Colorado Rocky Mountains have revealed trends in surface water quality that reflect atmospheric additions of fixed inorganic nitrogen (NO_3, NO_4^+, NH_3) of anthropogenic origin (Caine, 1995; Williams *et al.*, 1996a; Baron *et al.*, 2000; Williams & Tonnessen, 2000). The sources of this nitrogen include automotive, industrial and agricultural activities in the expanding Front Range urban corridor, which is part of the South Platte River basin (population: 2 885 000), and includes the cities of Denver, Boulder and Fort Collins. Anthropogenic N may induce the transition from a natural state of nitrogen limitation to one of 'nitrogen saturation', with associated consequences to ecosystem function that include transient N enrichment, base cation leaching, acidification, and changes in both N and C storage patterns in soil and biomass (Aber *et al.*, 1989, 1998; Köchy & Wilson, 2001; Neff *et al.*, 2002).

Nitrogen limitation was probably common in Colorado alpine lakes prior to the intensification of N deposition (Morris & Lewis, 1988). Under pre-industrial levels of N availability, nutrient models do not predict the leakage of excess N from forest and tundra ecosystems in RMNP (Baron *et al.*, 1994), indicating widespread N limitation of surface waters. We predict these ecosystems to be highly sensitive towards even modest anthropogenic subsidies. Wetfall inorganic N for the

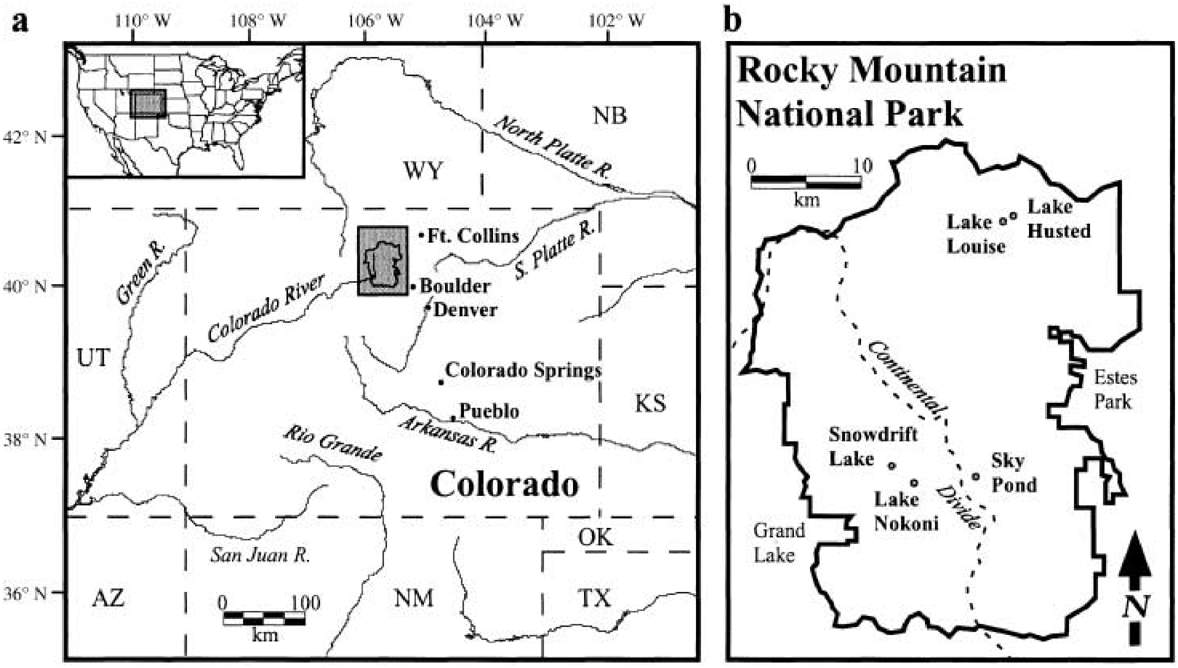

Fig. 1 Map of Colorado showing the location of Rocky Mountain National Park in relation to urban centres (a) and locations of the five study lakes within the park (b).

region is in the range of 2–4 kg N ha^{-1} yr^{-1}, with an estimated current rate of increase of ~0.3 kg N ha^{-1} yr^{-1} (Williams & Tonnessen, 2000). Dry deposition contributes another 0.9 kg N ha^{-1} yr^{-1} to high elevation areas in RMNP (Campbell *et al.*, 2000). Although these rates are considerably lower than in many industrialized regions, they are clearly well above natural background levels of the order of 0.1–1.0 kg N ha^{-1} yr^{-1}, the range observed in highly remote regions (Galloway *et al.*, 1982; Hedin *et al.*, 1995).

Transport of anthropogenic N to RMNP from the Front Range urban corridor requires easterly upslope winds generated by convective heating over the plains. Such easterly air-mass trajectories are secondary to Pacific flow in the region's climatology, which is comparatively less polluted (Langford & Fehsenfeld, 1992). Upslope contaminated air may be consistently overpowered by westerly flow above 3000 m asl (Sievering *et al.*, 1996). However, coal-fired power plants on the western slope of Colorado, notably at Hayden and Craig, emit NOx that may reach RMNP via prevailing westerly winds. Thus, point sources for N loading occur both east and west of the Continental Divide. Annually averaged $NO_3^- + NO_4^+$ concentrations in summer precipitation (1992–97) are higher on the eastern slope by a factor of two, whereas concentrations in winter deposition, associated with westerly storm tracks, are slightly higher west of the Continental Divide (Heuer *et al.*, 2000).

Contrasts in surface water chemistry also exist between watersheds on the east and west sides of the Divide, typically showing higher dissolved inorganic N (DIN) in lakes on the eastern slope (Baron *et al.*, 2000). Previous investigations of two RMNP lakes situated east of the Continental Divide have revealed pronounced shifts of diatom assemblages and nitrogen isotopic ratios in recent decades (Wolfe *et al.*, 2001), and attendant changes in sedimentary organic matter composition towards an increasingly aquatic provenance (Wolfe *et al.*, 2002). These ecological shifts have been interpreted to reflect a suite of responses to the increased availability of N derived from anthropogenic sources, including alteration of phytoplankton community structure and increased autochthonous production. These two sites, Sky Pond and Lake Louise, are reconsidered in the present paper in the context of a new regional synthesis that adds three new palaeolimnological records. The new data address whether alpine catchments on both slopes of the Continental Divide in RMNP have been impacted by atmospheric deposition. We hypothesize that if such a response exists, it may be subdued relative to what is observed in sites closer to the Denver – Fort Collins urban axis (Wolfe *et al.*, 2001), if indeed this corridor constitutes the dominant source of N deposition. Furthermore, by comparing neighbouring lakes with different catchment characteristics and fish stocking histories, we assess the consequences of both edaphic and trophic factors on the sediment record.

STUDY SITES

Rocky Mountain National Park is located in the Colorado Front Range, a north–south-trending massif that defines the western margin of the South Platte River basin (Fig. 1). The five investigated lakes are clear ($Z_{\text{Secchi}} > 5$ m), chemically dilute (conductivities < 10 μS cm^{-1}), slightly acidic (pH

Table 1 Locations, physical characteristics and surface water chemistry of the five study lakes. Chemical data are means of all available measurements and were determined by ion chromatography

Lake name	Lat. N	Long. W	Elevation (m asl)	Area (ha)	Depth (m)	$[NO_3^-]$ (μM)	$[NO_4^+]$ (μM)	[TP] (μM)
Nokoni	40°15′15″	105°43′50″	3292	7.6	38	1.26	1.28	0.03
Snowdrift	40°20′30″	105°44′11″	3389	3.2	14	1.73	0.83	0.04
Husted	40°30′56″	105°36′50″	3350	4.0	11	4.31	1.83	0.05
Louise	40°30′28″	105°37′13″	3360	2.7	8	16.55	1.72	0.09
Sky Pond	40°16′42″	105°40′06″	3322	3.1	7	19.35	2.66	0.09

range of 6.2–6.5), and characterized by prolonged ice cover, lasting from November to June. The lakes are all similar with regards to their altitude and overall watershed characteristics (Table 1), each being situated at the alpine treeline within glacial cirques of last glacial (Late Pinedale) age. Talus and bedrock (Precambrian granites and monzonites) are the dominant catchment substrate. Two of the lakes, Nokoni and Snowdrift, are situated west of the Continental Divide, respectively, 6 and 8 km west of a third site, Sky Pond (Fig. 1). The two additional sites, lakes Louise and Husted, are located 30 km to the north. Lake Nokoni is significantly larger and deeper than the other lakes. Lake Husted differs from the other four lakes in that it is surrounded to the north by an alpine wetland dominated by sedge, willow and dwarf birch. However, because of the proximity between lakes Louise and Husted (< 1 km), they experience identical deposition regimes. In lakes Nokoni and Snowdrift, measured NO_3^- concentrations are 2–3 times less than that of Lake Husted, and an order of magnitude lower than in Lake Louise and Sky Pond (Table 1).

Most precipitation at the study sites is snowfall (75% of approximately 1100 mm annually). Accordingly, peak annual fluxes of DIN in lakes and streams are associated with melting of the snowpack in May and June. At this time, solutes transit rapidly through catchments at the interface between the snowpack and talus or soil, remaining largely unavailable for uptake by terrestrial plants remaining in winter dormancy (Baron & Campbell, 1997). Surface-water DIN concentrations are also high during fall and winter, when terrestrial uptake of N is minimal. Despite a reduced light environment, diatoms and other algae capitalize on these intervals of enhanced N availability and bloom regularly under lake ice during both winter (Spaulding *et al.*, 1993) and spring snowmelt (McKnight *et al.*, 1990).

Because trophic interactions associated with non-native fish introductions may also affect nutrient cycling in alpine lakes (Leavitt *et al.*, 1994), the stocking history of each of the lakes is a relevant consideration, in part because the lakes were originally fishless owing to waterfalls near their outlets. Snowdrift Lake is the only site that has no recorded salmonid introductions (Rosenlund & Stevens, 1990). Lake Nokoni received 119 000 brook trout (*Salvelinus fontinalis*) fingerlings in eight stockings between 1925 and 1959. Sky Pond received 64 000 fish in six stockings between 1931 and 1939. Lake Husted was stocked three times (1934, 1938 and 1944) totalling 24 000 fish, but antimycin was applied in 1986 to restore a fishless state. Lake Louise was only stocked once, in 1938 (2000 fingerlings). Of the five study lakes, only two (Sky Pond and Lake Nokoni) now sustain reproducing brook trout populations.

METHODS

Sediment coring and chronology

The lakes were cored at their deepest points in 1997 (Sky Pond, lakes Louise and Husted) and 1998 (Nokoni and Snowdrift) with a modified Kajak–Brinkhurst device that preserves intact the mud–water interface (Glew, 1989). All cores were extruded in the field to eliminate disturbance, and sectioned in continuous 0.25-cm intervals for the uppermost 5 cm, and 0.50-cm increments thereafter (Glew, 1988). In the laboratory, samples were freeze-dried for permanent archiving. The chronology of sediments is based on α-spectrometric measurements of sediment ^{210}Pb activity (half-life = 22.3 years), to which the constant rate of supply (CRS) model is applied (Appleby & Oldfield, 1978).

Diatoms

For diatom analysis, 0.20 g of dry sediment was digested in hot 30% H_2O_2, centrifuged and rinsed with deionized water, then diluted to a volume of 10.0 mL. In order to estimate absolute diatom abundances, diluted slurries were spiked with a known concentration of *Eucalyptus* pollen (Wolfe, 1997). Aliquots (200 μL) of the final suspension were pipetted onto coverslips, allowed to dry at room temperature, then mounted permanently to slides with Naphrax®. Diatoms and external markers (*Eucalyptus* grains) were counted together in random slide transects including coverslip edges at 1000× under oil immersion. Between 300 and 500 diatom valves were identified and counted from each slide, using standard freshwater floras (Patrick & Reimer, 1966, 1975; Foged, 1981; Germain, 1981; Camburn & Charles, 2000; Krammer & Lange-Bertalot, 1986–1991). Diatom results are presented as relative frequencies of individual and collated taxa in relation to the total number of valves counted, as well as total valve concentrations per unit dry sediment mass, estimated by the recovery of introduced markers (Battarbee & Kneen, 1982). Multiple cores (10) from one of the sites (Sky Pond) indicate that between-core variability of diatom relative frequencies is less than ±5% for the dominant taxon, *Asterionella formosa*.

Sediment trap

A sediment trap was deployed in Sky Pond between August 1995 and August 1996 in order to assess the annual pattern of diatom sedimentation and seasonal community structure development. The trap design (Anderson, 1977) includes a large diameter (2.0 m) focusing funnel and a baffled sediment collector above the trap. Formalin was added to the accumulation tube to prevent microbial activity and invertebrate burrowing. The trap was installed over the deepest part of the lake's western basin (7 m) and suspended 2.5 m below the surface. During the year it was deployed, 7.5 cm of highly flocculent material accumulated, which was extruded in consecutive 0.5-cm increments upon retrieval. Diatom analyses were performed on each sample using the same protocols as those applied to the cores.

Sediment geochemistry

Down-core measurements of the nitrogen stable isotopic ratio ($^{15}N/^{14}N$) in sediment organic matter were undertaken to explore potential changes in lake N biogeochemistry and their relationship to changes in the source of N or patterns of N utilization. All results are reported using the $\delta^{15}N$ notation, where $\delta^{15}N$ (‰ relative to air) $= (R_{sample}/R_{standard} - 1) \times 1000$, where R is the measured $^{15}N/^{14}N$ atomic ratio. All $\delta^{15}N$ measurements were determined using a continuous flow isotope ratio mass spectrometer (CF-IRMS, Finnigan Delta Plus) coupled to a CNS elemental analyser (Carlo Erba 2500). Analytical reproducibility for $\delta^{15}N$ is ± 0.1‰. Sediment organic C and N concentrations were obtained from pyrolysis and transformed to C : N molar ratios to facilitate comparison with other studies (Meyers, 1994; Kaushal & Binford, 1999). Not all depths analysed isotopically have reliable associated C : N values. To explore the possibility that nitrogen source is the dominant control of sediment $\delta^{15}N$ (Talbot, 2001), a series of two-component isotope mixing calculations were performed (e.g. Phillips & Gregg, 2001), based upon the following equations: $\delta^{15}N_{lake} = (f_{nat} \cdot \delta^{15}N_{nat}) + (f_{anthro} \cdot \delta^{15}N_{anthro})$ and: $f_{nat} + f_{anthro} = 1$, so that $f_{anthro} = (\delta^{15}N_{lake} - \delta^{15}N_{nat})/(\delta^{15}N_{anthro} - \delta^{15}N_{nat})$, where the isotopic signature of the lake's accumulating organic matter ($\delta^{15}N_{lake}$) combines contributions from both natural ($\delta^{15}N_{nat}$) and anthropogenic ($\delta^{15}N_{anthro}$) pools, each represented by their respective fractions (f_{nat} and f_{anthro}) contributed to $\delta^{15}N_{lake}$. In order to simplify the exercise, $\delta^{15}N_{nat}$ was defined as the mean value of sediment $\delta^{15}N$ measurements prior to 1950 for each lake, and $\delta^{15}N_{lake}$ as the post 1950 mean. Values of $\delta^{15}N_{anthro}$ were set at 0, −5 and −15‰, reflecting the range of atmospheric $\delta^{15}N$ values measured at Boulder (Moore, 1977) and Loch Vale (Campbell *et al.*, 2002). Then, f_{anthro} was solved for each lake.

Multivariate analysis

To compare objectively the trajectories of ecological change among the five study lakes, direct ordination using canonical correspondence analysis (CCA; ter Braak, 1986) was applied to a subset of the diatom and sediment geochemical results. CCA, which models unimodal species responses in relation to measured environmental variables, was performed on data sets comprising sediment $\delta^{15}N$ and C : N as environmental predictors, and the down-core frequencies of the 15 most abundant diatom taxa from the five lakes as the biological response. Not every diatom assemblage was used in the CCA, because not each core depth analysed for diatoms has corresponding $\delta^{15}N$ and C : N measurements. This resulted in the inclusion of 63 active samples in the CCA. Diatom relative frequencies from the sediment trap (15 samples) were included as passive samples, projected in the same ordination space as the core samples without influencing the results in any other way. Thus, the objective of the CCA is to evaluate the relationship between diatom assemblage variability and lake biogeochemistry as reflected by the sediment geochemical parameters. Additional CCA ordinations were also conducted with the inclusion of an additional environmental variable: the presence–absence of brook trout obtained from available stocking records. Monte Carlo permutation tests (199 iterations) were used to assess the statistical significance of the environmental variables as determinants of diatom assemblage composition. Ordinations were carried out using CANOCO v.4 (ter Braak, 1998).

RESULTS

Chronology

The entire unsupported ^{210}Pb inventory is contained within the upper 10 cm of each core (Fig. 2a), indicating consistently low average sediment accumulation rates (i.e. <1.0 mm yr^{-1}). Although isolated reversals exist in lakes Nokoni, Husted and Louise, ^{210}Pb activity otherwise decreases predictably with depth, allowing for the development of robust CRS chronologies. These reversals probably reflect slight degrees of bioturbation. Living chironomid larvae were occasionally observed during sediment extrusion, burrowed to depths up to 7.5 cm. This is also consistent with the homogenous visual appearance of all of the cores (olive-grey silty gyttja). The CRS results (Fig. 2b) indicate that 1900 AD falls between 7 and 9 cm in each lake, and the year 1950 lies between 4 and 7 cm. Sediment accumulation rates increased after about 1975 in each of the cores (Fig. 2b), reflecting the higher water content of uncompacted surficial sediments. The lakes have very similar sediment accumulation histories, despite considerable

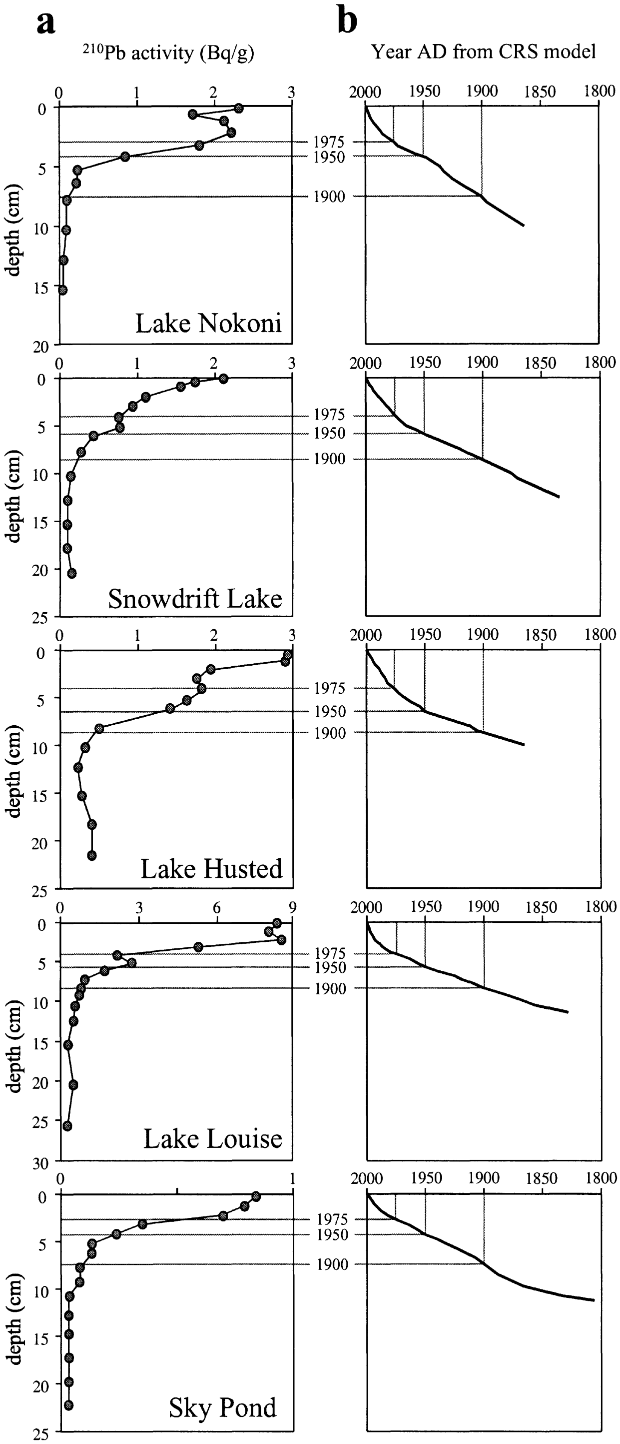

Fig. 2 Stratigraphic plots of sediment ^{210}Pb activities from the five study lakes (a), and age–depth models of sediment accumulation patterns based on CRS models (b).

variability in the levels of both supported and unsupported ^{210}Pb activities as a result of catchment geological differences, notably in Lake Louise. The ^{210}Pb results verify the stratigraphic integrity of each of the cores. All dates reported hereafter in association with individual sediment proxies are based on the CRS depth–age curves (Fig. 2b).

Diatom stratigraphy

Diatoms are well preserved in the sediments of all five lakes, where between 33 (Lake Nokoni) and 68 (Sky Pond) taxa were identified. At no depths in any of the cores was there evidence of diatom dissolution, such as pitting of valves or preferential preservation of heavily silicified components. The pre-industrial sediments of four of the five lakes (Snowdrift, Husted, Louise and Sky) are dominated by *Aulacoseira* spp. (*A. alpigena*, *A. distans*, *A. lirata* and *A. perglabra*), small colonial alkaliphilous *Fragilaria* spp. (*F. brevistriata*, *F. construens* var. *venter*, *F. pinnata* and *F. pseudoconstruens*), in addition to at least eight small *Achnanthes* species (Fig. 3). Lake Nokoni, the deepest and largest lake, is strongly dominated by *Cyclotella stelligera*, which is also common in the pre 1900 sediments of lakes Louise and Husted. These assemblages are typical of undisturbed oligotrophic alpine lakes (Lotter *et al.*, 1997; Koinig *et al.*, 1998).

Pronounced stratigraphic changes are evident in the twentieth-century sediments of Lake Louise and Sky Pond, recorded by increased representations of two mesotrophic planktonic taxa, *Asterionella formosa* and *Fragilaria crotonensis.* Prior to 1950, these taxa were present in both lakes, albeit in trace abundances. This suggests that their expansions have been environmentally stimulated, and do not reflect recent colonization events as invading species. Ecologically and chronologically similar stratigraphic changes are detected in the sediments of lakes Nokoni and Husted, but their expression is considerably more subtle (Fig. 3). In addition to *A. formosa* and *F. crotonensis* (in Lake Husted only), *Synedra radians* is a third taxon restricted to the youngest sediments in these two lakes. However, these three diatoms collectively account for no more than 10% of assemblages in lakes Nokoni and Husted, in contrast to Sky Pond and Lake Louise, where they represent >40% of recent diatom assemblages (Fig. 3). When expressed as absolute total diatom abundances in sediment (valves per g dry mass), only Snowdrift Lake fails to preserve an increase in the last century (Fig. 4a). Therefore, the four lakes that record increased frequencies of mesotrophic taxa all have attendant increases of diatom concentrations, presenting strong evidence that these shifts collectively reflect increased diatom production in recent decades. This does not imply that Snowdrift Lake has not undergone some degree of recent limnological change. As seen in the stratigraphy (Fig. 3), relative frequencies of *Aulacoseira* spp. have declined sharply in this lake, much as they have in lakes Husted and Louise, and in Sky Pond.

Although the diatom response is quite variable among the studied lakes, which is not surprising given limnological and floristic differences, there are nonetheless temporally and ecologically coherent trends that can be identified in both the

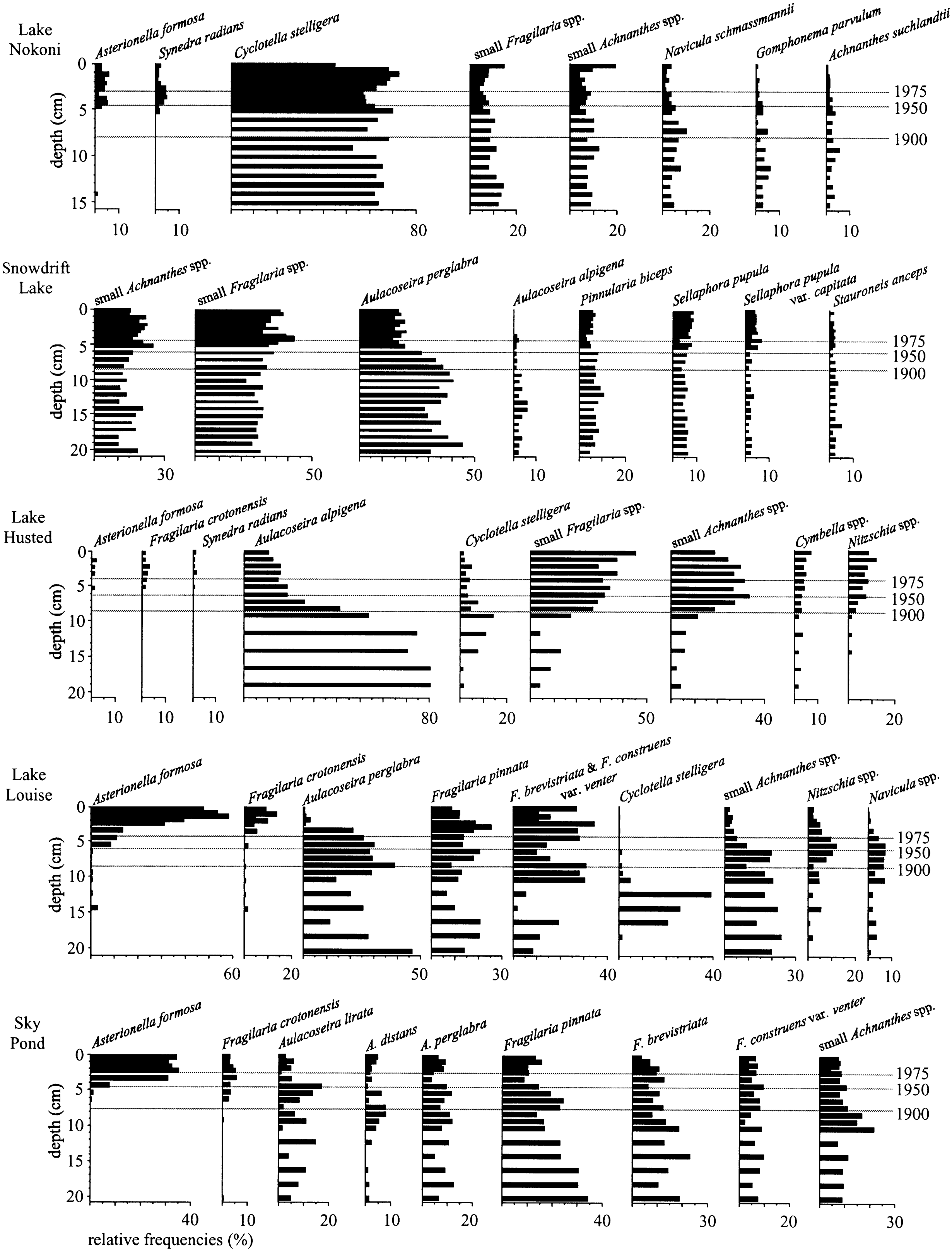

Fig. 3 Relative frequencies of dominant diatom taxa in cores from the five study lakes. Collective taxonomic categories are as follows: small *Achnanthes* spp. *A. conspicua*, *A. didyma*, *A. helvetica*, *A. laterostrata*, *A. levanderi*, *A. marginulata*, *A. minutissima* and *A. oestrupii*; small *Fragilaria* spp. *F. brevistriata*, *F. construens* var. *venter*, *F. pinnata* and *F. pseudoconstruens*. CRS ^{210}Pb ages are indicated to the right.

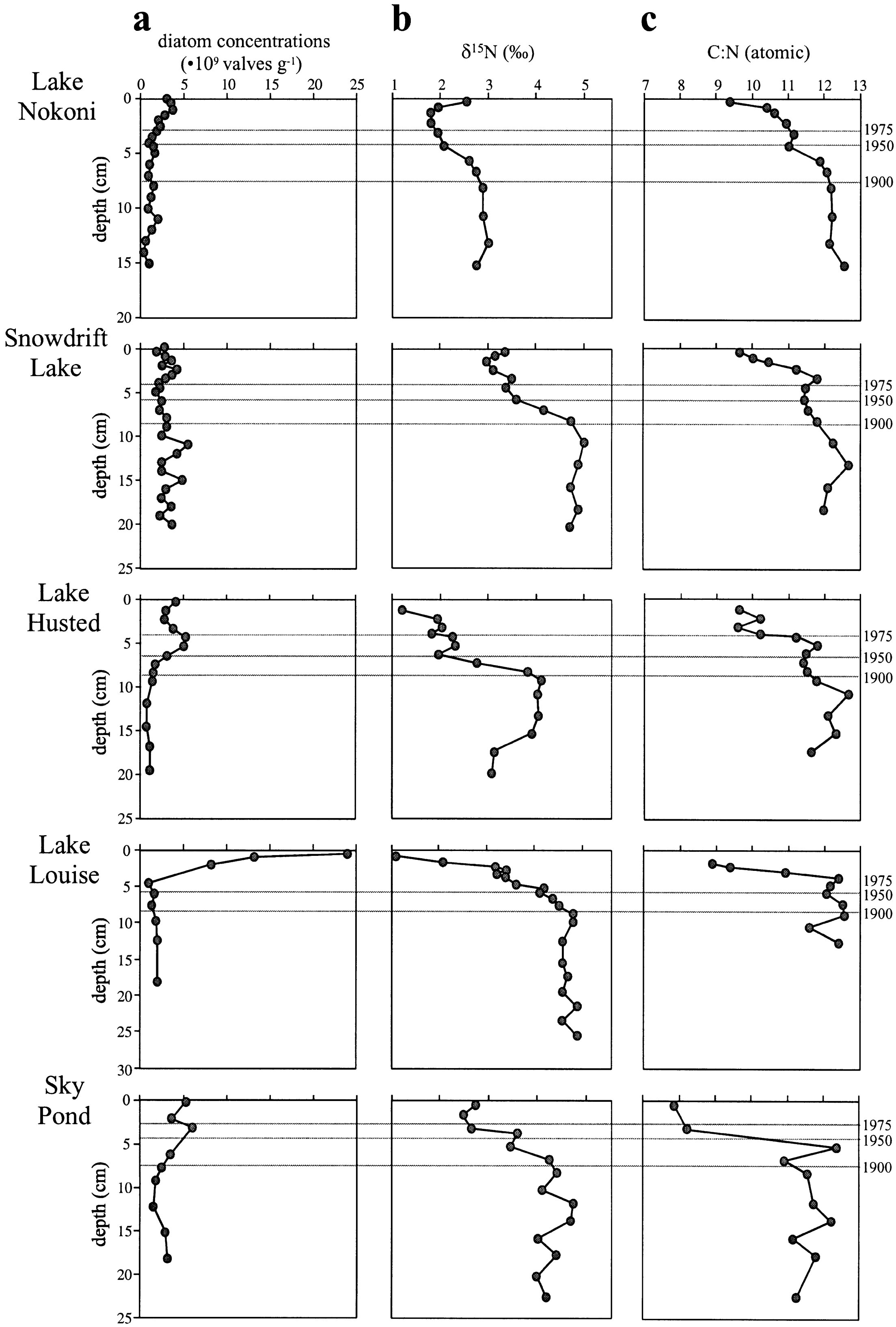

Fig. 4 Diatom valve concentrations (a), nitrogen stable isotopic composition ($\delta^{15}N$ as ‰ relative to air; b), and C : N molar ratios (c) from the sediment cores of the five study lakes.

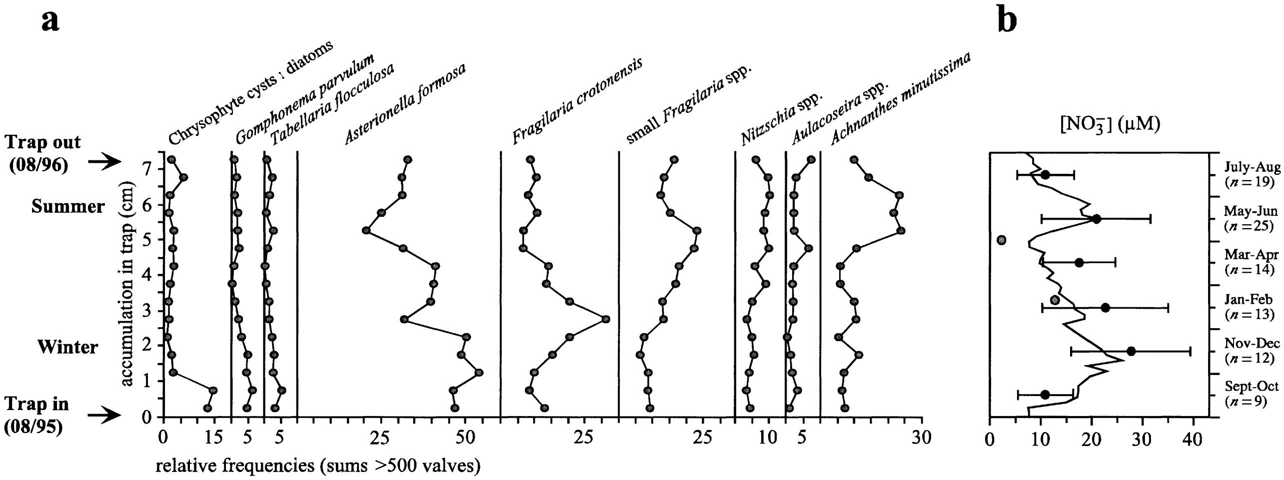

Fig. 5 Frequencies of the most abundant diatom taxa from the Sky Pond sediment trap deployed between August 1995 and August 1996 (a). The diatom data are shown in relation to available surface water NO_3^- concentrations from the catchment (b), collected within the Loch Vale Watershed ecological research and monitoring programme. Black dots and bars are mean ± 1 SD of bimonthly Sky Pond epilimnetic [NO_3^-] between June 1982 and May 1995. The solid line is the Loch Vale time-series for the year the trap was deployed, whereas the grey dots are measurements from Sky Pond for the same period.

relative frequency and absolute abundance data. Importantly, the modern diatom assemblages in each of the five lakes are measurably different from their pre-industrial counterparts.

Annual cycle of diatom sedimentation

The pattern of diatom sedimentation from August 1995 to August 1996 is preserved in the samples from the Sky Pond sediment trap (Fig. 5). Even relatively subtle features, such as the autumn bloom of Chrysophyceae that results in high stomatocyst representations in the lower trap samples, can be clearly identified. The basal 4.5 cm of the trap reflect sedimentation during autumn and winter months. These sediments are strongly dominated by *Asterionella formosa* and *Fragilaria crotonensis*. Although *A. formosa* still constitutes 20–35% of assemblages in the upper 3 cm of the trapped material, inferred to represent spring and summer deposition, small colonial *Fragilaria* spp. are much better represented, as are *Achnanthes* spp. and other attached forms (e.g. *Nitzschia* spp., *Cymbella* spp., *Navicula schmassmannii*). This is consistent with high summer periphytic production, coupled with facilitated detachment and transport during the open-water season. When compared with 13 years of average limnetic [NO_3^-] data (Fig. 5b), and assuming that the annual cycle of diatom sedimentation in 1995/96 is representative of a typical year, it appears that maximum frequencies of *F. crotonensis* and *A. formosa* coincide with elevated limnetic NO_3^- concentrations. However, in comparing the sediment trap diatom assemblages to those in cores, it must be noted that the former consistently underestimates the representation of benthic taxa, which are only introduced to the trap by detachment, resuspension and transport from periphyton. Core assemblages, by contrast, contain a proportion of *in situ* benthic (epipelic) diatoms.

Isotope geochemistry and C : N ratios

Prior to 1900, sediment $\delta^{15}N$ values were relatively stable between 3 and 5‰ in all of the cores (Fig. 4b). Subsequently, each site records a decline in $\delta^{15}N$ of at least 1‰ by mid-century. The trend towards lighter isotopic values accelerated after 1950 in the east slope lakes, with further depletions ranging from 1 to 3‰. The magnitude of post 1950 $\delta^{15}N$ depletion is considerably smaller in the two western slope lakes. Additionally, there are minor rebounds (0.2–0.7‰) in near-surface $\delta^{15}N$ values from Sky Pond and lakes Nokoni and Snowdrift, which possibly reflect a diagenetic effect associated with sediment denitrification. Sediment C : N molar ratios also decline in all five lakes, again with the greatest magnitude of change in the east slope lakes (Fig. 4c). Pre-industrial C : N ratios are about 12 in the sediments of all five sites. Values begin to decline around 1950, and subsequently drop below 10 in each lake, and below 9 in Lake Louise and Sky Pond. Whereas the $\delta^{15}N$ values from Lake Husted are similar to those of the other east slope lakes, the trend in C : N from this site is more comparable with those registered in the two western slope lakes. In all cases, the declines of sediment C : N are driven by increased N concentrations in near-surface sediments, to a maximum of 1.9% N in Lake Louise. This suggests that remineralization of organic N is a negligible factor in the interpretation of the sediment biogeochemical record.

Canonical correspondence analysis

The first two axes of CCA ordination constraining the 15 most dominant diatoms to corresponding sediment C : N and $\delta^{15}N$ values (63 samples) collectively explain 25.9% of the variance

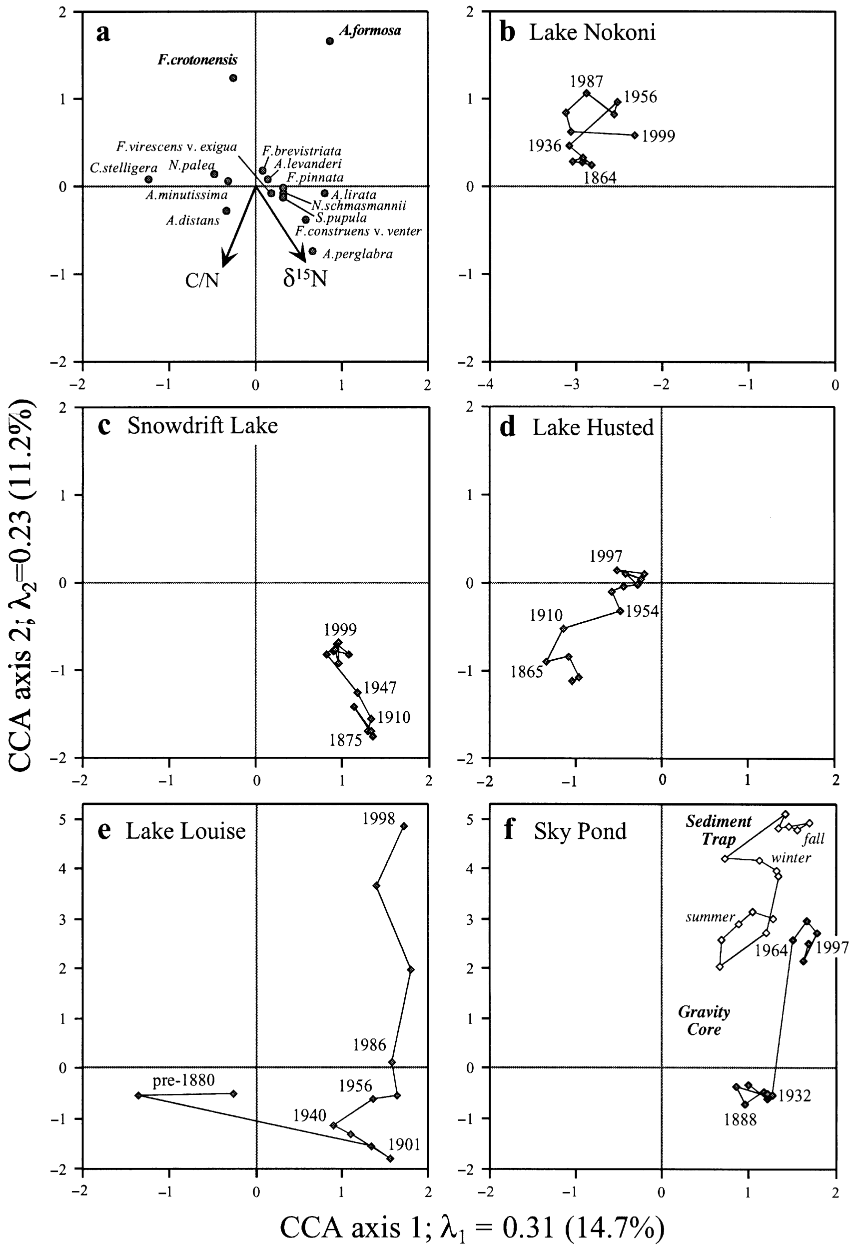

Fig. 6 Results of the CCA ordination: (a) biplot of the 15 dominant diatom species (grey circles) constrained to sediment $\delta^{15}N$ and C : N ratios (arrows) on the first two axes, and (b–f) sample scores from the five lakes connected to depict their trajectories of change in relation to the diatom and biogeochemical proxies. Samples from the Sky Pond sediment trap, which were entered passively into the CCA, are included next to this lake's trajectory in (f). Arrows indicate the direction of temporal change.

within the diatom assemblage data ($\lambda_1 = 0.31$, 14.7%; $\lambda_2 = 0.23$, 11.2%). The species–environment correlation is 0.73 for CCA axis 1 and 0.83 for axis 2, confirming strong relationships between the diatom assemblages and nitrogen biogeochemical proxies. Unrestricted Monte Carlo permutation tests show both of these axes to be statistically significant ($P < 0.01$). These CCA results are displayed as a biplot of the environmental gradients and taxon scores, as well as time-trajectories of the five lakes in the ordination space defined by sample scores on the first two axes. The indicator taxa *Fragilaria crotonensis* and *Asterionella formosa* have exceptionally high scores on axis 2, reflecting their close association with decreasing values of sediment C : N and $\delta^{15}N$ (Fig. 6a). The results also provide graphical representations of how each lake has changed over time with respect to sediment biogeochemistry and diatom assemblage composition. The length of each lake's trajectory (Fig. 6b–f) illustrates the relative magnitude of change that this lake has undergone. Lake Louise and Sky Pond have therefore changed more than the other lakes. Lake Husted is more similar to the western slope lakes, with a relatively short trajectory of change. However, all of the lakes have evolved in the direction of lighter $\delta^{15}N$, lower C : N ratios, greater representations of mesotrophic diatoms and decreased frequencies of the genus *Aulacoseira*. The Sky Pond sediment trap samples, entered passively in the CCA, all produce high axis 2 scores, owing to strong representations of *A. formosa* and *F. crotonensis* (Fig. 6f), and the underrepresentation of benthic taxa. Samples related to autumn and winter deposition have especially high scores along this axis, supporting a relationship to high NO_3^- during these seasons (Fig. 5b). It is further noted that the length of the annual trajectory of trap diatom assemblages is almost as long as that of the entire Sky Pond core. This illustrates how effectively the core record smoothes the effects of seasonal variability, thus reflecting average conditions that retain high proportions of signal-to-noise.

DISCUSSION

In prefacing the discussion of our preferred interpretation of these data, we first consider two alternative hypotheses. This approach is necessary given the possibility that multiple environmental stressors acting synchronously, and potentially synergistically, are responsible for the changes we have documented. Our objective is to isolate the most important of these stressors.

Alternative hypothesis 1: the role of fish introductions

The first hypothesis for our observations is that non-native fish introductions have induced cascading trophic interactions (CTI) through zooplankton predation and attendant increases in algal standing crop under conditions of reduced grazing. For example, sediment pigment records from lakes in the Canadian Rocky Mountains suggest increased algal production following fish stocking (Leavitt *et al.*, 1994). Of the five lakes considered in the present study, only Snowdrift has remained fishless, the other four having been stocked intermittently and to variable extents with brook trout. Although Snowdrift Lake does not record the recent increases in *A. formosa* and *F. crotonensis* observed in the other lakes, there is nonetheless a coeval shift in diatom assemblages as oligotrophic *Aulacoseira* spp. decline sharply (Fig. 3). Furthermore, the $\delta^{15}N$ and C : N trends in this lake are synchronous and of similar amplitude to the lakes having received fish introductions. We also note that the introduction of a new predator is predicted to introduce ^{15}N-enriched N to the stocked lakes as a result of increased trophic complexity (Talbot, 2001), which is inconsistent with the trends of isotopic depletion manifested in both stocked and fishless lakes. As an explicit test of the effects of fish stocking on diatom assemblages, we conducted three additional ordinations constraining the first axis of CCA to the following variables taken individually: presence–absence of fish from stocking records, $\delta^{15}N$ and C : N. In these analyses, sediment C : N and $\delta^{15}N$ accounted for 13.5% and 13.4% of the variance explained by axis 1, corresponding to species–environment correlations of 0.83 and 0.75, respectively. In comparison, the presence of fish accounted for 9.2% of axis 1 variance, and a species–environment correlation of 0.65. These results imply that, whereas it is naïve to suggest that fish have had no impact on nutrient cycling in the RMNP lakes in which they have become established, this role is secondary to changes in N biogeochemistry that we associate with atmospheric deposition. Moreover, CTI appear to be best expressed in naturally productive ecosystems (Pace *et al.*, 1999), suggesting that oligotrophic alpine lakes may exhibit weakened responses to trophic reorganizations resulting from introduced fish. For example, in Sky Pond and Lake Louise, where stocked fish have, respectively, succeeded and failed, *A. formosa* has synchronously progressed from an infrequent component of the diatom flora to become the dominant taxon in the phytoplankton of both lakes.

Alternative hypothesis 2: climate change

Biogeochemical changes involving atmospheric deposition are intimately connected with climate because bulk precipitation regulates the quantity of pollution deposited in wetfall, even if ambient concentrations remain constant. High altitude areas of the Colorado Front Range (>3000 m asl) have experienced increased annual precipitation since 1950 (Williams *et al.*, 1996a). The alpine temperature record is less coherent both spatially and temporally, and lacks clear evidence for recent warming, despite the presence of a warming trend at lower elevations (Pepin, 2000). A likely possibility is that increased evaporation on the plains results from both warming and hydrological modifications that retard the routing of mountain runoff through the South Platte drainage, such as urban and agricultural irrigation. The result, enhanced cloudiness in adjacent mountains, reconciles the lack of an alpine warming trend in the Front Range to precipitation increases. However, climate change alone appears insufficient to explain the stratigraphic changes reported here. Analysis of the ~14 000-year record from Sky Pond, which covers the lake's entire history, reveals only trace frequencies of the diatoms *A. formosa* and *F. crotonensis* in pre-industrial sediments, and no sediment $\delta^{15}N$ values lighter than the post 1950 interval (Wolfe *et al.*, 2001). Hence, lakes such as Sky Pond and Lake Louise, where the most striking recent stratigraphic changes are observed, appear to have entered new limnological states that lack any adequate past analogues. This signifies that naturally mediated limnological variability has been exceeded under the current climatic and depositional regime.

Palaeolimnological evidence for nitrogen enrichment: diatoms

Although *Asterionella formosa* and *Fragilaria crotonensis* are presently common diatoms in four of the five lakes considered here, and dominate the phytoplankton of Lake Louise and Sky Pond, these diatoms are not typically associated with oligotrophic high-elevation lakes. In a variety of boreal, prairie and pre-alpine lakes, they are among the first diatoms to expand following catchment settlement and agriculturalization, as seen in many examples from both North America (Bradbury, 1975; Hall *et al.*, 1999) and Europe (Anderson *et al.*, 1995; Lotter, 1998). Strong relationships between these taxa and DIN concentrations have been observed in several studies aiming to calibrate surface sediment assemblages to modern limnological conditions (Christie & Smol, 1993; Siver, 1999; Reavie & Smol, 2001). Growth rates of natural populations of *A. formosa* from The Loch, 3 km downstream of Sky Pond (3050 m asl), have been stimulated by *in situ* enclosure amendments with both $Ca(NO_3)_2$ and HNO_3, suggesting a pH-independent response of this taxon towards DIN availability (McKnight *et al.*, 1990). In laboratory cultures using strains of *F. crotonensis* from Yellowstone National Park lakes, strong growth responses to increased N have also been documented (Interlandi & Kilham, 1998). These findings are supported by the whole-lake N and P manipulation results of Yang *et al.* (1996), in which the abundances of *A. formosa* and *F. crotonensis* were correlated with increased N, but not P. *Synedra radians*, which accompanies the increased representations of the latter taxa in two lakes (Nokoni and Husted), has also been stimulated by whole-lake N additions (Zeeb *et al.*, 1994). Collectively, these data support the interpretation that the diatom assemblage changes observed in Sky Pond and lakes Husted, Louise and Nokoni (Fig. 3) reflect increasing N availability in recent decades. This conclusion is fully supported by the sediment trap results from Sky Pond (Fig. 5), as well as by the ability of CCA to explain statistically significant proportions of variance in down-core diatom assemblages with sediment parameters relating to changing N dynamics.

Isotopic evidence of nitrogen biogeochemical changes

A variety of recent studies have applied nitrogen stable isotopes to the identification of anthropogenic influences on N dynamics in aquatic ecosystems. The majority of these efforts document enriched $\delta^{15}N$ values that can be attributed to increased contributions from agricultural runoff (Teranes & Bernasconi, 2000; Hebert & Wassenaar, 2001), urban wastewaters (McClelland *et al.*, 1997; Lake *et al.*, 2001), and enhanced rates of sediment denitrification (Hodell & Schelske, 1998). The results from RMNP reveal progressive declines of lake sediment $\delta^{15}N$ in the order of 1–3‰ in recent decades, indicating that an entirely different suite of mechanisms is responsible. The most comparable results, in terms of chronology, amplitude and direction of change in sediment $\delta^{15}N$, are the records from Big Moose and Dart's lakes in the Adirondack Mountains (New York), where sediment $\delta^{15}N$ has declined progressively by 2‰ during the twentieth century (Fry, 1989; Owen *et al.*, 1999). Precipitation in this region has been strongly influenced by industrial NOx emissions (Driscoll & Newton, 1985). We explore two explanations for the isotopic trends observed in RMNP lake sediments.

The first of these involves the isotopic composition of source N to the lakes, and the possibility that low sediment $\delta^{15}N$ values reflect atmospheric contributions of isotopically depleted N. Anthropogenic N from sources other than human and animal waste is frequently depleted in ^{15}N relative to natural sources (Talbot, 2001). The $\delta^{15}N$ of fossil fuel NOx is highly variable (−7 to +12‰), whereas NH_3 from coal combustion ranges from −10 to 0‰ (Heaton, 1986, 1990). Nitrate and ammonium fertilizers typically have $\delta^{15}N$ of −3 to +3‰, but ammonia volatilized from confined animal feeding operations is substantially more depleted, ranging from −15 to −9‰ (Macko & Ostrom, 1994). Enhanced contributions from unspecified admixtures of these sources are therefore viable candidates for reconciling the progressive depletion of lake sediment $\delta^{15}N$ values. The second possibility involves the relaxation of N-limitation owing to atmospheric N loading. By reducing algal competition for available N, physiological fractionation against ^{15}N during DIN uptake can be sustained (Goericke *et al.*, 1994), resulting in isotopically depleted sedimenting organic matter. However, Rayleigh fractionation dictates that isotopic discrimination decreases as the DIN pool is utilized, until little or no fractionation occurs as N limitation is approached. Increased N availability associated with atmospheric deposition should create conditions under which strong algal physiological fractionation can be sustained throughout the growing season, a situation entirely consistent with the export of excess DIN from watersheds regionally (Williams *et al.*, 1996a; Campbell *et al.*, 2000). Thus, although primary production in the study lakes appears to have increased (trends in diatom assemblages and concentrations), competition for available N may nonetheless have become alleviated. Decreasing sediment C : N ratios indicate that greater proportions of sedimenting organic matter are aquatic in origin (Meyers, 1994; Kaushal & Binford, 1999), adding support to inferences of recent increases in algal production. For example, freshwater algal cells (including *A. formosa*) have a range of C : N values from 6 to 8 (Meyers & Ishiwatari, 1993). Increased algal contributions to recently deposited organic matter are thus consistent with the observed sediment C : N decreases (Fig. 4c).

Of course, the two explanations presented above are not mutually exclusive, because sustained physiological fractionation by algae will occur under any situation of increased N availability, irrespective of its original source or initial isotopic composition. However, fractionation effects associated with algal DIN assimilation are much more readily observed in culture than in nature, with the exception of ocean bloom conditions (Goericke *et al.*, 1994). As a consequence, many current freshwater studies favour the interpretation of algal and sediment $\delta^{15}N$ as, foremost, a signature of source N isotopic composition (Harrington *et al.*, 1998; Brenner *et al.*, 1999; Finney *et al.*, 2000; Teranes & Bernasconi, 2000). Following these examples, our mixing model calculations (Fig. 7) illustrate that lakes on the east slope of the Continental Divide require greater proportions of isotopically depleted (anthropogenic) N to produce the observed sediment

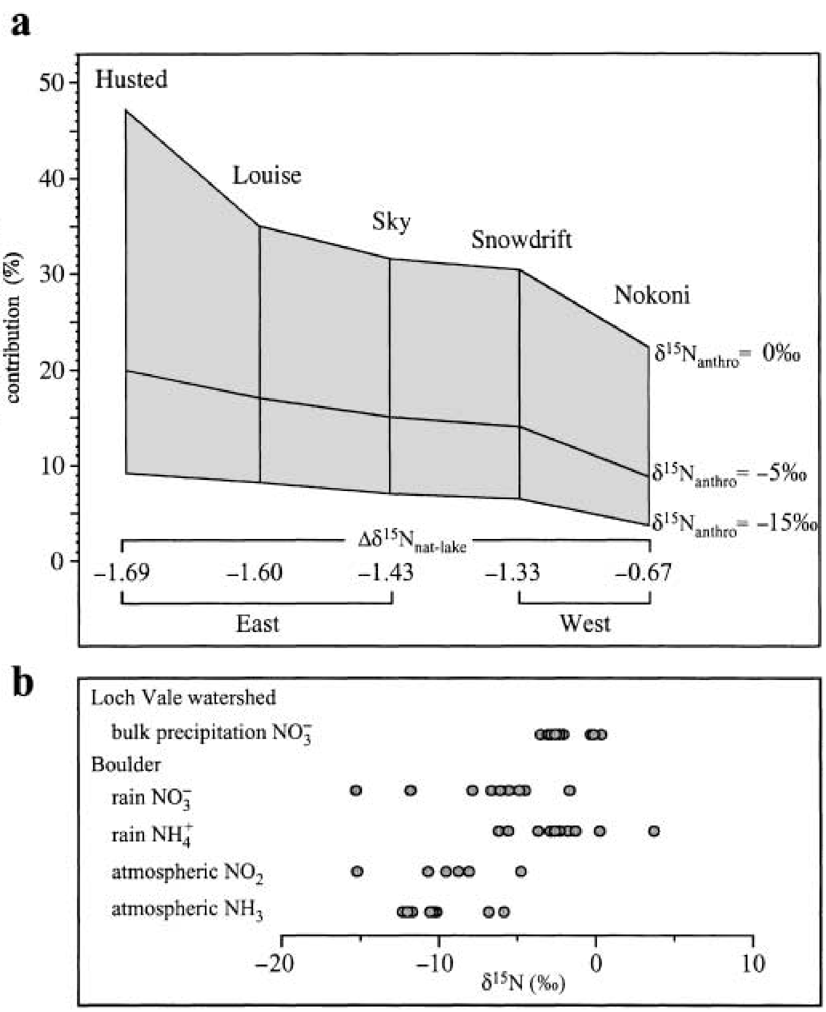

Fig. 7 Envelopes estimating the fraction of isotopically depleted nitrogen of anthropogenic origin required to produce the sediment isotopic excursions observed in each lake's sediments, given assigned $\delta^{15}N_{anthro}$ values of 0‰, −5‰ and −15‰ (a). Values of precipitation and atmospheric $\delta^{15}N$ from Loch Vale and Boulder (b), reproduced from the original sources (Moore, 1977; Campbell *et al.*, 2002).

isotopic excursions. Even with the least depleted value of $\delta^{15}N_{anthro}$ used in the model (0‰), f_{anthro} values range from 25% (Nokoni) to 47% (Husted). These estimates seem entirely reasonable, considering that at Niwot Ridge, an east slope monitoring site 25 km south of RMNP, ~50% of DIN loading to surface waters is apportioned directly to precipitation (Williams *et al.*, 1996b). Furthermore, summer precipitation and atmospheric samples from both Loch Vale (Campbell *et al.*, 2002) and Boulder (Moore, 1977) only rarely exceed 0‰ (Fig. 7b), implying that this is a conservative value for $\delta^{15}N_{anthro}$. Although the value of −15‰ for $\delta^{15}N_{anthro}$ in the mixing model must be viewed as the lower end-member, a major unknown remains the degree of kinetic fractionation associated with the oxidation of atmospheric NH_3 and NH_4^+ during atmospheric transport (Freyer *et al.*, 1996).

Finally, we briefly evaluate several additional processes capable of modifying sediment $\delta^{15}N$, including early diagenesis. Enhanced N fixation is unlikely to be a factor in shaping the trends of declining sediment $\delta^{15}N$, because increased N availability is predicted to curtail, not augment, fixation rates. Furthermore, no carotenoids diagnostic of N-fixers are present in the surface sediments of these lakes (R. D. Vinebrooke & A. P. Wolfe, unpublished results). Synthesis of *de novo* bacterial biomass may also contribute isotopically depleted N to lake sediments, but this process appears restricted to anoxic conditions (Lehmann *et al.*, 2002). Owing to cold water temperatures and complete mixing early in the ice-free season, alpine lakes in RMNP do not experience summer hypolimnetic anoxia. Contemporary denitrification is also unlikely to be a dominant process in the context of the present study. This is because denitrification strongly favours ^{14}N, leading to progressive enrichment of $\delta^{15}N$ in the remaining substratum, which is opposite to the trend observed. Near-surface inflections in lakes Nokoni and Snowdrift, as well as Sky Pond, possibly reflect some degree of denitrification, but these are a minor feature of the overall isotopic signal. It has further been demonstrated (Lehmann *et al.*, 2002) that early diagenetic processes typically reach completion in days to months under both oxic and anoxic conditions. Because the $\delta^{15}N$ trends we report here are expressed on a timescale of several decades, it seems most likely that they are tracking isotopic variations in the overlying water column, as concluded elsewhere (Brenner *et al.*, 1999; Teranes & Bernasconi, 2000). Thus, we propose that the sediment isotopic trends predominantly reflect ever increasing additions of isotopically depleted N transported atmospherically, with the potential for additional fractionation effects associated with algal DIN uptake under conditions of alleviated N limitation. Most importantly, the conclusion that the sediment isotopic excursions reflect marked deviations from the natural N cycle of each lake is supported irrespectively of the exact degrees to which either of these processes influence down-core sediment $\delta^{15}N$ signatures.

Directional trends and edaphic considerations

Several independent lines of evidence demonstrate greater N deposition east of the Continental Divide relative to the western slope, including trends in precipitation (Heuer *et al.*, 2000), surface water (Baron *et al.*, 2000), and soil and foliar (Rueth & Baron, 2002) chemistry. In a general sense, the five lakes investigated here support the notion of an east–west gradient, with regards to both summer NO_3^- concentrations (Table 1), as well as the magnitude of down-core changes in diatom communities. By contrast, the two neighbouring lakes, Louise and Husted, have markedly different summer NO_3^- concentrations (Table 1) as well as diatom stratigraphic changes (Fig. 3). However, their N-isotopic stratigraphies are very similar (Fig. 5). Differences in the mixing model results between these two lakes (Fig. 7) are related to lighter pre-industrial $\delta^{15}N$ values in Lake Husted. Whereas Lake Louise is surrounded by talus and bedrock, Lake Husted is surrounded by wetland, which probably operates actively in both catchment-scale N retention and assimilation. Wetlands demonstrably export less DIN relative to talus in this region (Campbell *et al.*, 2000). Because both lakes are exposed to the same depositional regime, this underscores how edaphic characteristics have the potential to regulate the response of lacustrine ecosystems with respect to N deposition. Surface waters that percolate through talus and blockfields, the most important landcover type above treeline (>80% by area), typically have the highest measured DIN concentrations, owing to the combination of precipitation inputs to fluxes from transient pools of microbially cycled N (Campbell *et al.*, 2000). At the same time, weathering processes in these steep unvegetated environments lead to base cation enrichment in talus waters (Clow & Sueker, 2000). Considering that all streams and rivulets entering alpine lakes at or above treeline are directly influenced by talus, these processes have potentially important limnological consequences. For example, the diatom taxonomic shifts provide absolutely no evidence for lake acidification, which may attest to the influence of catchment sources of base cation neutralization. Nonetheless, with the persistence of N deposition, chronic surface water acidification should be viewed as an ominous threat, given that episodic declines of pH and acid-neutralizing capacity are well documented in east slope headwaters of the Front Range (Williams *et al.*, 1996b).

CONCLUSIONS

Our results substantiate the idea that alpine ecosystems of the Colorado Front Range are presently impacted by anthropogenic nitrogen deposition, adding to the growing number of susceptible aquatic systems (Jassby *et al.*, 1994; Jaworski *et al.*, 1997; Valigura *et al.*, 2000; Saros *et al.*, 2003). The greatest changes occur on the eastern slope of the Continental Divide, demonstrating that upslope winds are sufficient to transport N species (and other pollutants) from the Denver – Fort Collins urban corridor to altitudes well above 3000 m asl. However, watershed characteristics can mitigate ecological and biogeochemical responses to N deposition, notably through the presence of terrestrial N sinks such as wetlands. Lakes on the western slope of the Continental Divide also record changes consistent with enhanced N deposition, but the signal is muted in comparison with east slope lakes. Because the western slope receives less precipitation from upslope sources, coal-fired power plants west of RMNP probably represent the dominant source of N deposition to this region.

Because algae are among the first organisms to react to altered nutrient dynamics, the changes reported here can be viewed as harbingers of more serious ecological impacts predicted for surface waters of the Colorado Front Range, namely acidification (Kling & Grant, 1984). By pairing biological proxies and sediment geochemistry, palaeolimnology can effectively diagnose the sensitivity of ecosystems to anthropogenic N deposition, as long as natural lakes lacking direct inputs of catchment N (manure, wastewater) are present, and the influence of trophic interactions can be assessed independently. This methodology is applicable at broad geographical scales, which is important given the global scope of the problem (Vitousek *et al.*, 1997; Matson *et al.*, 2002). In the case of RMNP, the consequences of N deposition challenge the National Park Service in terms of devising and implementing management strategies aimed to protect, as much as possible, ecological integrity. As population and energy demands surrounding the Front Range continue to grow, ever increasing amounts of nitrogenous pollution are being generated. Wetfall DIN is regionally increasing by ~0.3 kg N ha^{-1} yr^{-1} (Williams & Tonnessen, 2000), implying that the ecological impacts detected here will probably become aggravated in the future, particularly in talus-dominated catchments east of the Continental Divide.

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