

## Degradation of water quality in Lough Neagh, Northern Ireland, by diffuse nitrogen flux from a phosphorus-rich catchment

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### *Abstract*

Annually resolved fossil records of nitrogen (N) inputs (as sedimentary  $\delta^{15}\text{N}$ , N content), aquatic production ( $\delta^{13}\text{C}$ , C content), and algal abundance and gross community composition (pigments, nonsiliceous microfossils) from Lough Neagh, Northern Ireland (NI), were compared with annual records of climatic variability, atmospheric and urban nutrient loading, whole-catchment nutrient budgets, and limnological monitoring data to identify the unique effects of N on the eutrophication of a phosphorus (P)-rich lake during ca. 1933–1995. Cluster analysis revealed two major biostratigraphic zones. Zone I (ca. 1933–1955) was characterized by moderate lake production, as inferred from low concentrations of most fossil pigments and reduced  $\delta^{15}\text{N}$  signatures but elevated  $\delta^{13}\text{C}$  values and chlorophyte microfossil concentrations. In contrast, Zone II (ca. 1955–1995) exhibited greatly increased contents of  $^{15}\text{N}$ , N, C, and algal pigments, combined with strongly reduced  $\delta^{13}\text{C}$  ratios and chlorophyte fossil abundance, a pattern consistent with recent severe eutrophication. Overall, microfossils of diazotrophic cyanobacteria were most abundant during the transition period between zones (ca. 1955–1964). Regression analysis revealed that past N influx to the lake (as  $\delta^{15}\text{N}$ ;  $r^2 = 0.916$ ,  $p < 0.0001$ ), colonial cyanobacterial abundance (as myxoxanthophyll;  $r^2 = 0.837$ ,  $p < 0.0001$ ), and total algal standing crops (as  $\beta$ -carotene;  $r^2 = 0.388$ ,  $p < 0.0001$ ) were all strongly correlated to agricultural inputs of N to NI farmland, weakly correlated to P inputs to NI farmland ( $r^2_{\delta^{15}\text{N}} = 0.503$ ,  $p < 0.0001$ ;  $r^2_{\text{cyanobacteria}} = 0.296$ ,  $p < 0.0001$ ;  $r^2_{\text{total algae}} = 0.046$ ,  $p > 0.05$ ), and uncorrelated to most measures of climatic variability and atmospheric or urban nutrient inputs. Thus, degradation of water quality during the 20th century resulted from excessive loading of diffuse N to the lake from P-rich agricultural lands.

Lake eutrophication remains a significant environmental problem despite over 40 years of research to identify the factors that degrade water quality (Carpenter et al. 1998;

Schindler 2006). To date, eutrophication of many lakes has been linked most clearly to point sources of nutrients (e.g., municipal waste water, factory farms), and significant improvements of water quality have been achieved following diversion of effluent (Jeppesen et al. 2005). In contrast, lake eutrophication by nonpoint nutrient sources (e.g., agriculture, atmospheric deposition) has been more difficult to quantify and regulate, possibly because diffuse fluxes are often intermittent, linked to seasonal agricultural activity or to irregular climatic events (e.g., storms), or are derived from large-scale land-use practices (Carpenter et al. 1998). Unfortunately, recent analyses suggest that such diffuse nutrient inputs are now the main cause of aquatic pollution in many regions of Europe and North America (Smith 2003).

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### *Acknowledgments*

This project was funded by a European Social Fund (ESF) Grant to L.B., a Natural Sciences and Engineering Research Council (NSERC) Canada Discovery Grant to P.R.L., the Canada Research Chairs Program, Canada Foundation for Innovation, Saskatchewan Learning, and Queen's University of Belfast. We thank Nicole Knezacek and Mark Graham for laboratory assistance, Suzanne McGowan for assistance with numeric analyses, Suzanne Leroy for core collection, Crawford Jordan for atmospheric deposition data, and Robert H. Foy for agricultural nutrient budgets.

Water quality degradation can arise from diffuse nutrient sources for several reasons. First, inputs of phosphorus (P) and nitrogen (N) to agriculture in the form of chemical fertilizer and animal feed supplements often exceed outputs in agricultural product (e.g., Foy et al. 2002). Second, excessive densities of livestock can lead to manure production and application that exceeds the regional requirements of crops. Third, excess application of N in the form of chemical fertilizer or manure can lead to ammonia (NH<sub>3</sub>) volatilization and N deposition at remote locations (Schlesinger and Hartley 1992; Vitousek et al. 1997). In all cases, excess nutrient application can lead to soil surpluses of both N and P that are mobile and can leach into downstream aquatic ecosystems (Smith et al. 1995; Bennett et al. 1999). Globally, this process is particularly pronounced for P (Bennett et al. 2001) and, in principle, can lead to situations in which excess P runoff leads to N limitation of algal production in receiving water bodies.

Availability of P has been widely regarded as the principal determinant of lake production, particularly algal growth (e.g., Schindler 1977). However, evidence is accumulating that N can limit lake production, as either the primary or the colimiting nutrient with P (Elser et al. 1990; James et al. 2003; Leavitt et al. 2006). Unfortunately, because N and P fluxes from point sources often covary and because soil surpluses of N have increased as much or more than those of P (Isermann 1991), there is little consensus on whether excess N inputs can cause eutrophication of lakes, even though environmental degradation of estuaries by N is well established (Smith 2003, 2006).

In this paper, annually resolved fossil records of N inputs (as  $\delta^{15}\text{N}$ , N content), aquatic production ( $\delta^{13}\text{C}$ , C content), and algal abundance and gross community composition (pigments, nonsiliceous algal microfossils) from Lough Neagh, Northern Ireland (NI), were analyzed to trace the development of nutrient enrichment during ca. 1933–1995. Further, fossil records were compared statistically with annual records of climatic variability, atmospheric and urban nutrient loading, whole-catchment nutrient budgets, and limnological monitoring data to identify the correlates of water quality change during the 20th century. Together, these analyses suggest that N rather than P has been the main element regulating cyanobacterial development, total algal production, and the recent eutrophication of P-rich Lough Neagh.

## Methods and materials

**Site description**—Lough Neagh is a shallow, polymictic, hypertrophic lake situated at ~12.5 m above sea level (a.s.l.) in NI (54°35'N, 6°24'W; Fig. 1). The Lough is the largest freshwater lake in the British Isles, with a mean and maximum depth of 8.9 m and 34.0 m, respectively, a surface area of 383 km<sup>2</sup>, and a total volume of  $3.45 \times 10^9$  m<sup>3</sup>. The low relative depth of the lake ( $z_r = 0.15\%$ ; sensu Wetzel 2001), combined with the high mean wind speed ( $>4.5$  m s<sup>-1</sup>) experienced in NI (Betts 1997), ensures that the water column is mixed completely (Wood and Smith 1993) and that oxygen saturation rarely declines below

60%, despite high dissolved organic carbon (DOC) inputs from catchment peat deposits (Jewson 1977) and low light penetration (mean secchi depth ~1.1 m;  $K_d = 0.925$  m<sup>-1</sup>; Gibson et al. 2000). As a result of elevated precipitation (~200 d yr<sup>-1</sup> with  $>0.2$  mm rain) from low intensity events ( $<4$  mm h<sup>-1</sup>) (Betts 1997), mean hydraulic residence time is only ~1.2 yr (Foy et al. 2003).

The catchment of Lough Neagh is 4453.4 km<sup>2</sup>, accounts for 30% of NI land area, and is composed mainly of agricultural lowland (68.6% grassland, 4.4% arable land) with rough grazing (12.7%) and forestry (2.7%) in the upland regions ( $>200$  m a.s.l.). The remaining area (11.7%) is comprised of towns and industry that include 64% of the 390,000 inhabitants of the catchment. Six major rivers drain into the Lough, while the sole outflow, Lower River Bann, discharges north into the Atlantic Ocean (Fig. 1). Soils with impeded drainage predominate throughout NI, with gleyed soils and peat accounting for 54% and 16% of the land area, respectively (Cruickshank 1997). Consequently, river flow responds rapidly to rainfall, especially during winter (October–March), when soils are at or near field capacity and runoff is threefold greater than during other seasons (Wilcock 1997). Not surprisingly, diffuse agricultural runoff presently accounts for ~50% of the annual P influx ( $617 \times 10^3$  kg P) and  $>75\%$  of the annual N loading ( $8,226 \times 10^3$  kg N) to the lake (Foy 2002).

Nutrient enrichment of Lough Neagh began ~1700 with forest clearance and agricultural expansion and increased after 1900 with urbanization and intensification of farming (Carter 1977; Battarbee 1978). Periodic monitoring during the 20th century revealed a shift from mesotrophic conditions ca. 1900 (West and West 1902; Dakin and Latache 1913) to an advanced state of eutrophy by the mid-1960s (Wood and Gibson 1973), with elevated concentrations of TP (~100  $\mu\text{g TP L}^{-1}$ ), dissolved nitrate (NO<sub>3</sub>; ~300  $\mu\text{g NO}_3 \text{ L}^{-1}$ ), and chlorophyll *a* (Chl *a*; ~40  $\mu\text{g Chl } a \text{ L}^{-1}$ ). By the late 1960s, algal species richness had declined substantially relative to samples taken during the early 20th century and was dominated by cyanobacteria, including diazotrophic species (Gibson 1993). Since 1970, there have been substantial increases in TP (45%), NO<sub>3</sub> (70%), and Chl *a* (100%); further reductions in algal species diversity; and a shift from diazotrophic to non-N<sub>2</sub>-fixing cyanobacteria (*Planktothrix agardhii*) (Gibson et al. 2000).

**Field and laboratory methods**—A 330-cm-long sediment core was collected from the deep-water region (28-m) of the Lough in July 1995 using a Kullenberg corer (Fig. 1). The core was halved lengthwise, cleaned by removing the outermost 5 mm of sediment, and sectioned in 1-cm intervals every 5 cm. All samples were refrigerated ( $-2 \pm 2^\circ\text{C}$ ) in darkness until analysis for fossils. Because of the protracted period (6 yr) between core extraction and analysis, a second core was taken from a shallow-water region (9 m) during September 2001 using a Mackereth corer. Multivariate analysis of stable isotope content (C, N), elementary composition (%C, %N, C:N), and sedimentary pigment and nonsiliceous algal microfossil concentrations demonstrated that the timing and extent of

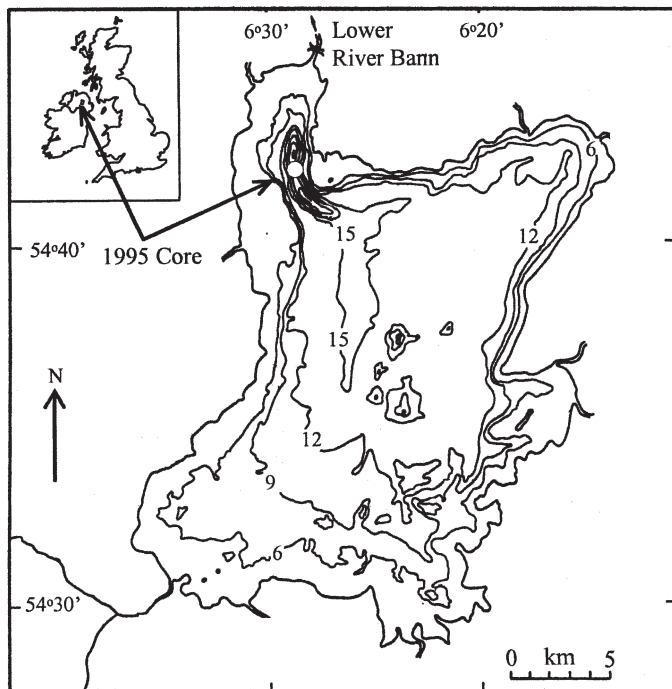


Fig. 1. Map of lake morphometry and core location (open circle) within Lough Neagh, Northern Ireland. Lake location presented in inset.

ecosystem changes were virtually identical in the two cores (Bunting 2004). Therefore, all subsequent analyses were conducted on the deep-water core because potential fossil degradation produced no notable bias in patterns of ecosystem change and because algal microfossil records were more highly resolved in the 1995 core.

Sediment chronology was established from lyophilized (48 h, 0.01 Pa) sediment samples analyzed for  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ , and  $^{241}\text{Am}$  content at 23 intervals evenly distributed over the length of the core using gamma spectrometry as described in Gallagher et al. (2001). Sediment age and mass accumulation rates ( $\text{g cm}^{-2} \text{yr}^{-1}$ ) were calculated using both constant rate of supply (CRS) and constant initial concentration calculations within the computer program of Binford (1990). All dates were presented as Common Era (CE).

Stable isotope content and elemental composition of sediments were determined from lyophilized sediment samples ( $\sim 2$  mg dry mass) using a Thermoquest model NCS 2500 elemental analyzer interfaced with a Thermoquest (F-MAT) DeltaPlus XL spectrometer equipped with continuous flow (ConFlo II) unit, as described in Savage et al. (2004). Stable nitrogen ( $\delta^{15}\text{N}$ ) and carbon ( $\delta^{13}\text{C}$ ) isotope compositions were expressed in the conventional  $\delta$ -notation, defined as per mil (‰) deviation versus atmospheric  $\text{N}_2$  and organic C standards previously calibrated against authentic Vienna Pee Bee Belemnite. Replicate samples varied less than 0.28‰ and 0.10‰ for  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  determinations, respectively.

Fossil pigments and derivatives were extracted from lyophilized sediment samples, filtered (0.2- $\mu\text{m}$  pore), and

dried under  $\text{N}_2$  gas as described by Leavitt and Hodgson (2001). Carotenoids, chlorophylls (Chls), and derivatives were isolated and quantified using a Hewlett-Packard (HP) model 1100 high-performance liquid chromatograph equipped with a Rainin model 200 Microsorb C-18 column (5- $\mu\text{m}$  particle size), an HP model 1100 fluorescence detector, and an HP model 1100 photodiode array spectrophotometer. Pigments were identified on the basis of their spectrophotometric characteristics and chromatographic mobility in comparison with authentic standards and extracts of known pigment composition. Past algal abundance and gross community composition were inferred from concentrations of chemically stable, taxonomically diagnostic carotenoids, including those characteristic of cryptophytes (alloxanthin), mainly diatoms (diatoxanthin), Oscillatoriaceae (oscillaxanthin), colonial cyanobacteria (myxoxanthophyll), Nostocales (canthaxanthin), total cyanobacteria (echinenone), total algae ( $\beta$ -carotene), as well as broadly distributed Chl *a* and *b* and their derivatives (Leavitt and Hodgson 2001). Isomeric carotenoids from chlorophytes (lutein) and cyanobacteria (zeaxanthin) were inseparable and were presented together as lutein-zeaxanthin ("potentially bloom-forming algae"), while other pigments were used to assess independent contributions from green algae (Chl *b*, pheophytin *b*) and cyanobacteria (echinenone, canthaxanthin, myxoxanthophyll). Similarly, complex glycosidic carotenoids from *Aphanizomenon* spp. (aphanizophyll), *Anabaena* spp. (4-keto-myxoxanthophyll), and the other colonial cyanobacteria ("oscillaxanthin-like") were incompletely resolved and were reported together as "aphanizophyll" (Leavitt and Findlay 1994). Consequently, aphanizophyll includes pigments from potentially  $\text{N}_2$ -fixing cyanobacteria as well as those from nondiazotrophic taxa. All pigment concentrations were expressed as nmol pigment  $\text{g}^{-1}$  organic matter, following estimation of organic matter content by mass loss on ignition at 500°C for 24 h.

Chlorophyte and cyanobacterial microfossils were isolated from fresh sediments and prepared for microscopy following the protocol of Cronberg (1986). Whole fresh sediment samples ( $1.0 \pm 0.5$  mL) were added to a graduated cylinder containing a 10% (by mass) solution of potassium hydroxide (KOH), and displacement volumes were estimated. A known volume of a calibrated suspension of *Lycopodium clavatum* spores was added to each sample to act as an internal standard for algal enumeration. This sediment-KOH solution was boiled 10 min and settled 24 h to deflocculate sediments and remove humic acids. Each sample was washed with distilled water. Slides were prepared for enumeration by decanting supernatant and resuspending an equal volume of processed fossil material in glycerol containing a 50% Fuchsin-B solution (1% by mass in ethanol) on glass microscope slides. Coverslips were mounted, and slides were permanently sealed by applying two coats of translucent nail polish to each edge of coverslip. For each sample,  $\geq 200$  nonsiliceous algal microfossils were identified and enumerated using light microscopy at 600 $\times$  magnification to determine species composition and concentration (microfossils  $\text{mL}^{-1}$  fresh sediment). Taxonomic identities of fossils were based on

both modern and fossil reference materials and texts, as detailed in Bunting (2004).

*Numeric analyses*—Statistical analyses were conducted on elemental composition (%N, %C, C:N by mass), stable isotope signatures ( $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$ ), sedimentary pigments ( $\text{nmol g}^{-1}$  organic matter), and nonsiliceous algal microfossil assemblages (microfossils  $\text{mL}^{-1}$  wet sediment). Numeric analyses were restricted to the 10 genera of chlorophytes and cyanobacteria with  $\geq 5\%$  microfossil abundance in at least one sample and the 15 most abundant fossil pigments.

Local assemblage zones were identified using stratigraphically constrained cluster analysis, performed on untransformed and standardized (mean = 0, SD = 1) geochemical, pigment, and microfossil time series using CONISS<sup>®</sup> v. 2.0 (Grimm 1987). Although algal microfossil data were not available for all depths, missing microfossil concentrations were not estimated because CONISS distinguishes between absent and missing data. Local assemblage zones were estimated using the Euclidian distance dissimilarity coefficient.

The strength of the relationships between fossil and historical time series (see below) were examined using Pearson correlation coefficients and least squares linear regression analyses performed with SYSTAT<sup>®</sup> v. 10.0 (SPSS Software Inc). However, for such direct comparisons, fossil records had to be harmonized with historical time series by rounding estimates of sediment age to the nearest calendar year. In cases where individual years included more than one fossil observation, a simple arithmetic mean of the observations was used. Such alterations were required for  $< 5\%$  of years, and there were no years that lacked a corresponding fossil record. Following harmonization, complete fossil records were available for the period 1933–1995, inclusive. Predictive relationships between fossil and concomitant environmental time series were prescreened using scatter-plot analysis; only potentially significant ( $p < 0.1$ ) relationships were selected for further analyses because of the large number of comparisons and the fact that some time series would be expected to be correlated solely by chance.

Regression analyses were conducted with both raw time series and those in which temporal autocorrelation had been removed using  $\log_{10}$  and first-difference transformations (Verleyen et al. 2004). However, only analyses of raw time series are presented herein because comparison of these analyses revealed that most correlation arose from long-term trends in time series rather than from short-term (interannual) variability and because the objective of this study was to identify correlates of these long-term changes. Potential effects of lags in factor interactions (e.g., delayed nutrient runoff; Foy and Lennox 2006) were addressed by performing cross-correlation analysis of candidate time series using SYSTAT v. 10.0. These time-series approaches were selected over canonical analyses (e.g., Hall et al. 1999) because nutrient flux time series were likely colinear (Foy et al. 2002), because weaker predictors would be eliminated by variance inflation analysis (Hall et al. 1999), and

because our aim was to directly contrast N and P as potential controls of lake eutrophication.

Continuous annual records of climatic variability, atmospheric inputs of inorganic N and P, urban nutrient loading, nutrient subsidies to NI farmland, and limnological characteristics were used to evaluate potential causes of water quality degradation (Fig. 2). Monthly meteorological records were obtained from the United Kingdom Meteorological Office weather station at Armagh, NI (<http://www.metoffice.gov.uk> and <http://climate.arm.ac.uk/archives.html>) to calculate annual estimates of mean maximum and minimum temperatures, total precipitation (January–December), days with snow at 09:00 h, and days with sunshine (Fig. 2 a–e). Monthly and winter (December–March) indices of the North Atlantic Oscillation (NAO) were obtained from the U.S. National Center for Environmental Prediction (<http://tao.atmos.washington.edu/data/sets/nao/>; Fig. 2f), while records of sunspot activity were obtained from the U.S. National Aeronautics and Space Administration (<http://science.msfc.nasa.gov/ssl/pad/solar/sunspots.htm>; Fig. 2g). In addition, estimates of mean annual inputs of inorganic N and P ( $\text{g m}^{-2} \text{yr}^{-1}$ ) in precipitation were obtained for the Lough Neagh catchment (C. Jordan, Department of Agriculture and Rural Development, Northern Ireland [DARDNI], unpubl. data; Fig. 2h).

Annual mass balances of N and P used by agriculture in NI (1933–1995; Fig. 2i–k) were obtained from Foy et al. (2002). These calculations balanced estimates of nutrient inputs to agricultural lands (inorganic fertilizer, imported animal feedstuffs) with outputs (agricultural products, nutrient runoff to aquatic ecosystems) to derive an annual nutrient balance for each element. For this study, it was assumed that areal estimates of nutrient fluxes within the Lough Neagh catchment (30% of NI land area) were the same as those within NI and that nutrient runoff has been a constant fraction of added supplements during the past 70 years, even though it was recognized that the quantity of nutrient runoff will depend also on timing and mode of fertilizer application, precipitation characteristics, and vegetative cover (Carpenter et al. 1998). Consistent with these assumptions, land-use composition in the catchment has been representative of the total area of NI during the past 70 years, although livestock densities have been moderately greater than national averages (Foy et al. 2002). Similarly, nutrient losses to the inflow rivers ( $110 \text{ kg P km}^{-2} \text{yr}^{-1}$ ;  $2,330 \text{ kg N km}^{-2} \text{yr}^{-1}$ ) were equivalent to an average of 4.7% and 12.6% of P and N supplements, respectively, for the period 1991–2000 (Foy et al. 2002), although annual  $\text{NO}_3$  losses can vary by fourfold for a given N input (Watson et al. 2000), and P influx to lakes is highly dependent on the quantity of runoff (Foy and Lennox 2006).

Historical information concerning human population growth in NI during the 20th century was obtained from the decadal census of NI (Census Office for Northern Ireland unpubl. data). Annual population estimates were calculated by linear interpolation between census years. Annual total P and N inputs ( $\text{kg yr}^{-1}$ ; 1971–1995) from the wastewater treatment works (WWTWs) in the catchment

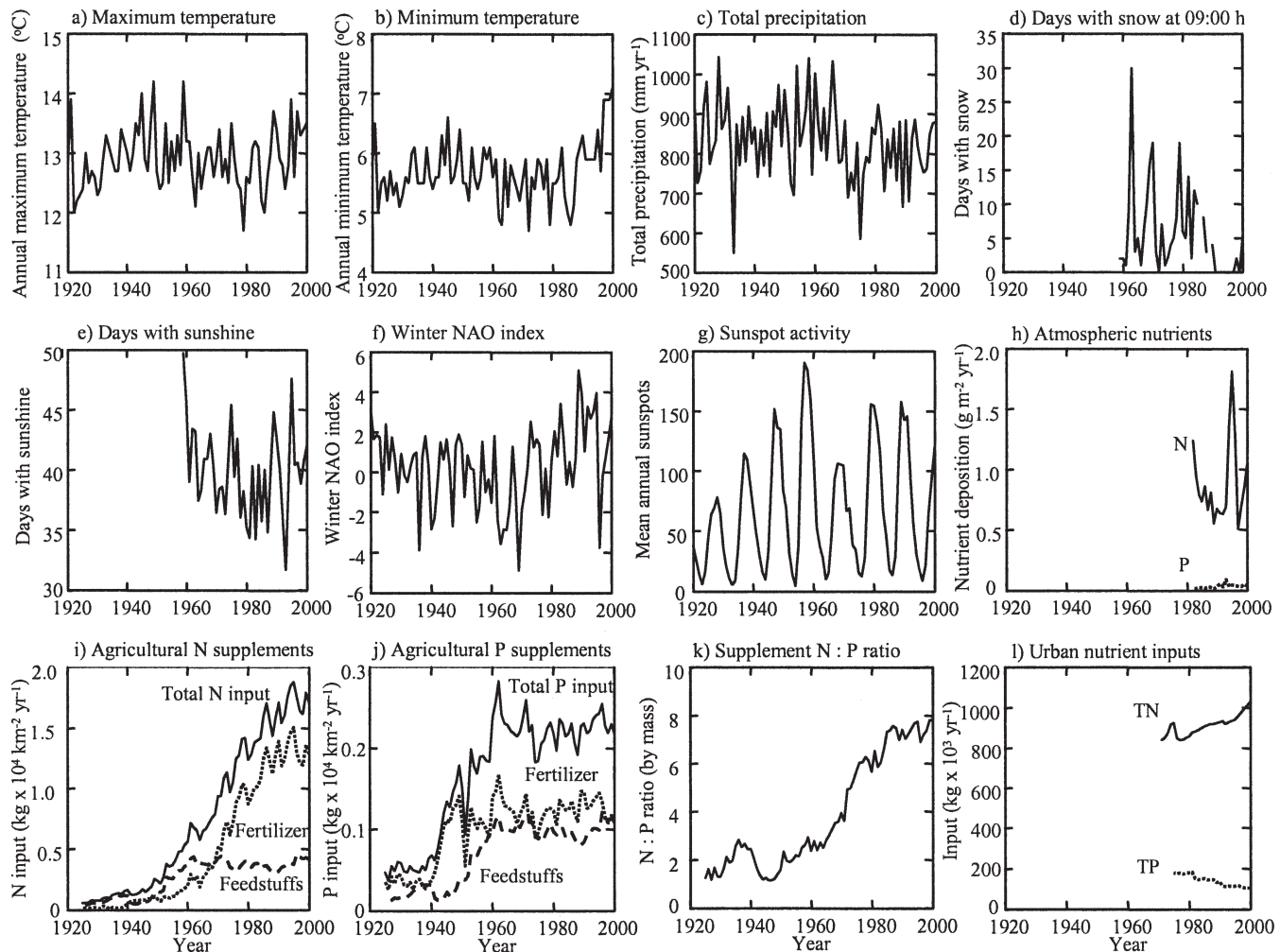


Fig. 2. Long-term data for the Lough Neagh catchment area. Annual historical records include climatic variables such as (a) maximum temperature, (b) minimum temperature, (c) total precipitation, (d) number of days with snow at 09:00 h, (e) number of days with sunshine, (f) winter NAO index, and (g) sunspot activity; resource use variables include (h) atmospheric deposition of N and P, (i) N inputs to agricultural lands, (j) P inputs to agricultural lands, and (k) their mass ratios; and urban factors include (l) N and P inputs to Lough Neagh from urban sewage. Further time-series details are given in Methods and materials.

were estimated from urban population data and assumed per capita P and N values. Annual total P and N inputs ( $\text{kg yr}^{-1}$ ; 1971–1995) from septic tanks in the catchment were estimated from rural population data, assumed per capita P and N values, and a connectivity factor (Foy and Lennox 2006; R. H. Foy, DARDNI, pers. comm.; Fig. 2l).

Finally, annual records of limnological variables (Fig. 3) were obtained from the Agricultural and Environmental Science Division of DARDNI for lake transparency (secchi depth, m; 1968–1995), concentrations ( $\mu\text{g L}^{-1}$  or  $\text{mg L}^{-1}$ ) of total P (TP; 1969–1995), dissolved organic phosphorus (1974–1995), dissolved reactive phosphorus (1974–1995), and particulate phosphorus (1974–1995), dissolved nitrate ( $\text{NO}_3$ ; 1969–1995), dissolved ammonium ( $\text{NH}_4$ ; 1974–1995), dissolved silica ( $\text{SiO}_2$ ; 1971–1995), and Chl *a* (1968–1995). In addition, mean annual biovolumes ( $\text{mm}^3 \text{L}^{-1}$ ) were estimated for the major phytoplankton during 1969–1995, including *Limnithrix redekei* (Van Goor), *P. agardhii* (Komárek) Anagnostides, *Stephanodiscus astraera* (Ehr.)

Kützing (now *S. neoastraera* Håkansson and Hickel), *Aulacoseira subarctica* (O. Müller) Haworth, *Aphanizomenon flos-aquae* fa *gracile* Lemm., and *Anabaena* spp. (Gibson et al. 2000). Limnological variables were quantified using standard methodologies (Wood and Smith 1993) for depth-integrated samples collected from the center of Lough Neagh during 1969 to 1992 (weekly) and 1993 to 1995 (biweekly).

## Results

**Sediment chronology**—The  $^{210}\text{Pb}$  activity declined linearly with depth in Lough Neagh sediments (Fig. 4a). Comparison of chronological models (Gallagher 2003) indicated that the CRS approach provided the best fit to  $^{210}\text{Pb}$  activities, with excellent agreement with other radioisotopes (Fig. 4b), including mid-1960s maxima in  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  activities (ca. 155 cm) corresponding to peak atmospheric nuclear tests and a maximum in  $^{137}\text{Cs}$  activity

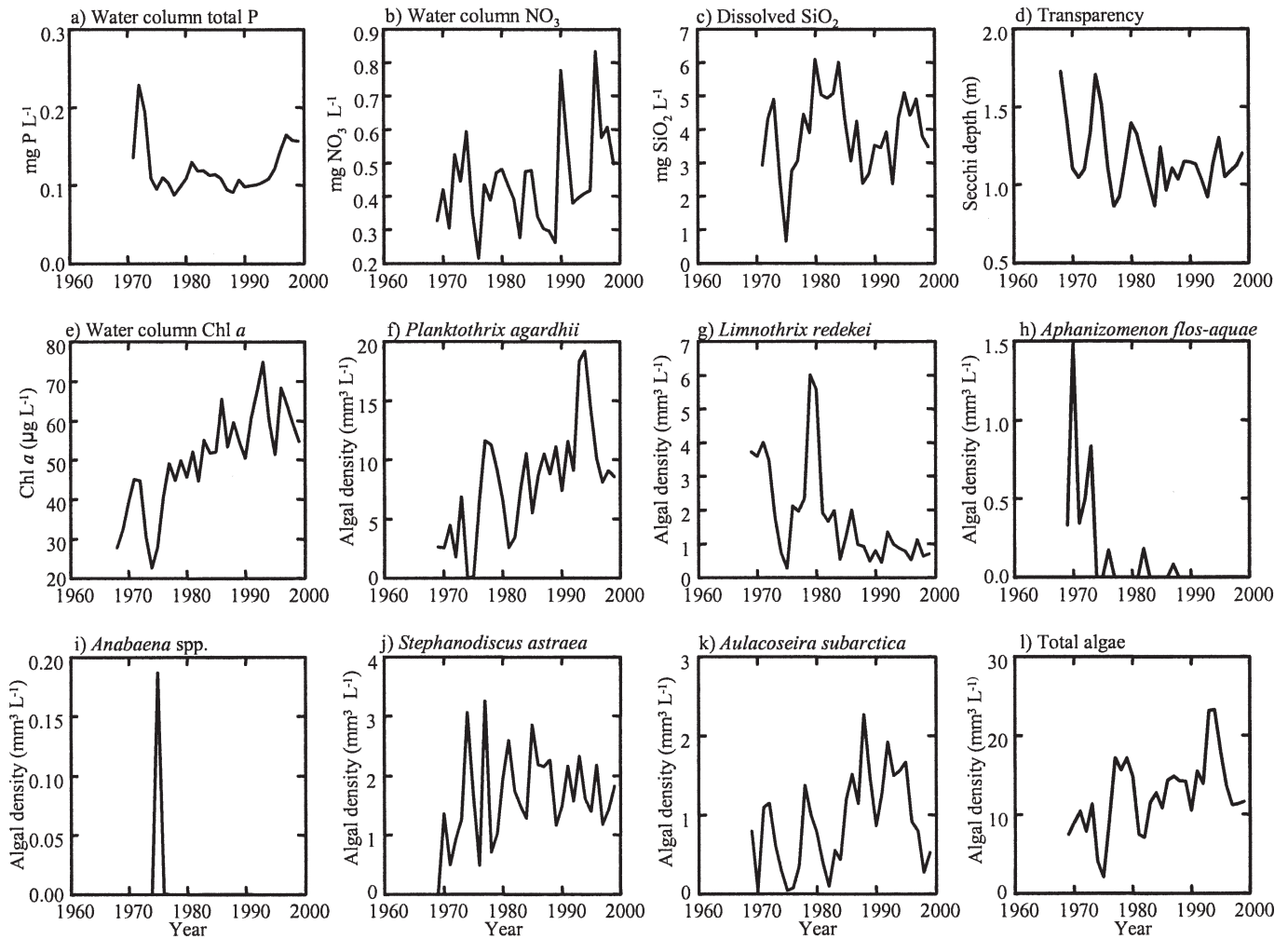


Fig. 3. Long-term limnological monitoring data for Lough Neagh. Records include water-column concentrations of (a) total P, (b) dissolved  $\text{NO}_3$ , (c) dissolved  $\text{SiO}_2$ , (d) secchi depth transparency, (e) Chl *a*, (f) *Planktothrix agardhii*, (g) *Limnothrix redekei*, (h) *Aphanizomenon flos-aquae*, (i) *Anabaena* species, (j) *Stephanodiscus astraea*, (k) *Aulacoseira subarctica*, and (l) total algae. Units of each plot presented on respective y-axis.

(ca. 55 cm) from the 1986 Chernobyl nuclear accident. Application of the CRS calculation also showed that sediment accumulation rates were extremely high and constant ( $5.4 \text{ cm yr}^{-1}$ ), consistent with prior radioisotopic analysis of this coring site (Gallagher 2003). As a consequence of such high sedimentation rates, the 330-cm core encompassed a 62-yr period (1933–1995) with annual resolution of fossil records.

**Biostratigraphic zonation**—Stratigraphically constrained cluster analysis identified five distinct units distributed into two principal zones (Fig. 5). The most significant changes in geochemical ( $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$ , %N, %C) and algal (pigments, microfossils) assemblages occurred ca. 1955 and separated Zone I (ca. 1933–1955) from Zone II (ca. 1955–1995). Zone I was further divided into two main subzones, whereas three subclusters were identified within Zone II.

Zone Ia (ca. 1933–1939) was defined by low and constant  $\delta^{15}\text{N}$  ( $\sim 6.5\%$ ), C ( $\sim 5\%$ ), and N ( $\sim 0.5\%$ ) contents and relatively enriched  $\delta^{13}\text{C}$  signatures (ca.  $-28.5\%$ ) (Fig. 5a–

d). During this interval, fossil pigment concentrations were low and stable, with the exception of oscillaxanthin from the Oscillatoriaceae (Fig. 5e–m). Chlorophyte microfossils were abundant and diverse ( $>20$  species) throughout this zone (Fig. 5o–t). In contrast, fossils from several cyanobacterial taxa were rare or absent (*Anabaena*, *Aphanizomenon*), while those from *Gloeotrichia* and nonspecific heterocysts were present throughout Zone Ia (Fig. 5u–x).

Signatures of  $\delta^{15}\text{N}$  increased during Zone Ib (ca. 1939–1955), while those of  $\delta^{13}\text{C}$  declined steadily from ca.  $-28.5\%$  to ca.  $-29.5\%$  (Fig. 5a,c). In addition to an overall increase in N and C content, abundances of both elements peaked during the early 1940s (Fig. 5b,d). However, concentrations of pigments from total algae ( $\beta$ -carotene), Oscillatoriaceae (oscillaxanthin), and chlorophytes (pheophytin *b*) remained stable during this interval, while those from colonial cyanobacteria (aphanizophyll, myxoxanthophyll, canthaxanthin), bloom-forming algae (lutein-zeaxanthin), and cryptophytes (alloxanthin) increased throughout this zone, and those from diatoms

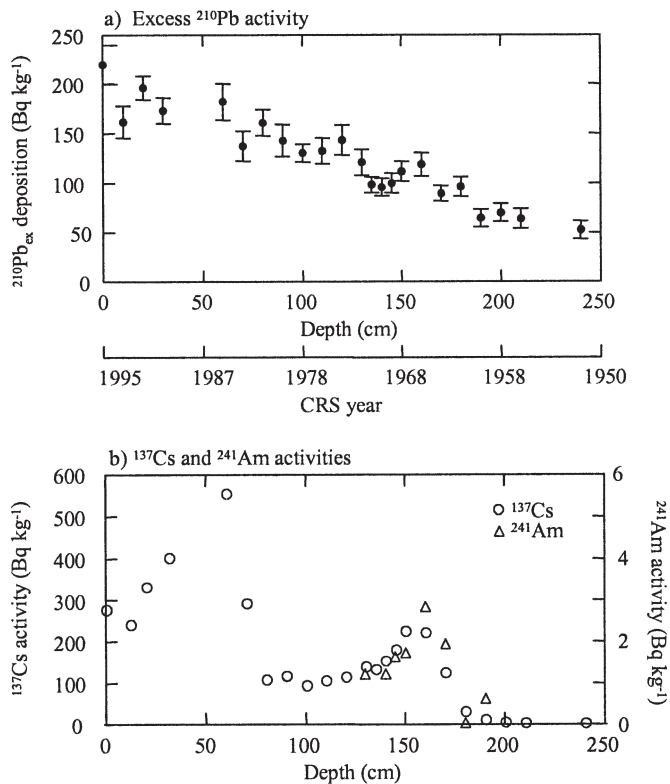


Fig. 4.  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ , and  $^{241}\text{Am}$  profiles in sediments of Lough Neagh, Northern Ireland. (a) Excess  $^{210}\text{Pb}$  activity (Bq g $^{-1}$  dry mass) as a function of sediment depth and age estimated from  $^{210}\text{Pb}$  profiles using the CRS calculation. (b) Activities of  $^{137}\text{Cs}$  (left axis) and  $^{241}\text{Am}$  (right axis) as a function of sediment depth and CRS age.

(diatoxanthin) increased after ca. 1945 (Fig. 5e–m). Microfossil concentrations of total algae and chlorophytes, including *Pediastrum*, *Tetraëdron*, *Celastrum*, *Botryococcus*, and *Staurastrum*, were greatly elevated in Zone Ib (Fig. 5n–t). In contrast, microfossils of *Anabaena* and *Aphanizomenon* were largely absent from this zone, while those of nonspecific heterocysts were sporadically present at reduced concentrations (Fig. 5u–x).

Zone IIa (ca. 1955–1964) marked the major transition in fossil assemblages (Fig. 5). During this interval, the N and C content of sediments increased sharply, the N isotopic ratio continued to increase, while  $\delta^{13}\text{C}$  values declined further (Fig. 5a–d). This zone was also characterized by increased pigment abundances from colonial cyanobacteria (aphanizophyll, myxoxanthophyll, canthaxanthin), chlorophytes (pheophytin *b*), and diatoms (diatoxanthin) and by significant declines in carotenoids from Oscillatoriaceae (oscillaxanthin) (Fig. 5e–m). Although total algal microfossil concentrations were lower in Zone IIa than in Zone Ib, microfossils from several cyanobacteria were present at greatly elevated densities (e.g., *Anabaena*, *Aphanizomenon*, *Gloetrichia*; Fig. 5u–w), as were nonspecific heterocysts and microfossils from the green algae *Botryococcus* and *Staurastrum* (Fig. 5x,s,t). In contrast, concentrations of most other chlorophyte taxa declined greatly during this period (Fig. 5o–r).

Zone IIb (ca. 1964–1991) was the longest of the five subzones and encompassed sediments with the most extreme variation in stable isotope, pigment and microfossil contents (Fig. 5). Specifically,  $\delta^{15}\text{N}$  increased  $\sim 2\text{‰}$  from ca. 1964 ( $\sim 8\text{‰}$ ) to the mid-1970s ( $>10\text{‰}$ ), while  $\delta^{13}\text{C}$  signatures declined nearly  $1\text{‰}$  after ca. 1980 (Fig. 5a,c). Similarly, concentrations of most pigment biomarkers increased rapidly throughout Zone IIb, with the exception of that from Oscillatoriaceae (oscillaxanthin), which declined to constant abundance by ca. 1970 (Fig. 5e–m). Overall concentrations of algal microfossils were low and declined throughout this zone (Fig. 5n), reflecting continued losses of most chlorophytes and dramatic reductions of the cyanobacteria *Anabaena*, *Aphanizomenon*, and *Gloetrichia* (Fig. 5o–x).

Finally, Zone IIc (ca. 1991–1995) was defined by maxima of  $\delta^{15}\text{N}$  signals and many fossil pigment concentrations as well as a  $\delta^{13}\text{C}$  minimum and continued declines in abundances of most algal microfossils (Fig. 5). Specifically, pigment concentrations from diatoms (diatoxanthin), cryptophytes (alloxanthin), chlorophytes (pheophytin *b*), bloom-forming algae (lutein-zeaxanthin), and colonial cyanobacteria (aphanizophyll, myxoxanthophyll, canthaxanthin) all reached core-wide maxima during this zone (Fig. 5e–m). In contrast, most microfossils from chlorophytes and cyanobacteria either were absent (e.g., *Celastrum*, *Anabaena*) or were present at only trace levels (e.g., *Pediastrum*, *Tetraëdron*, *Scenedesmus*, *Botryococcus*, *Aphanizomenon*, *Gloetrichia*) (Fig. 5n–x).

*Correlations of fossil and historical data*—Sedimentary  $\delta^{15}\text{N}$  values in Lough Neagh were strongly correlated ( $r^2 = 0.916$ ,  $p < 0.0001$ ) with total supplements of N to agricultural catchments within NI (Fig. 6a). Similarly, over 87% of the variance in sedimentary  $\delta^{15}\text{N}$  could be explained by a linear relationship with the annual mass of N applied as chemical fertilizers alone (analysis not shown). Fossil concentrations of pigments from colonial cyanobacteria (myxoxanthophyll) ( $r^2 = 0.837$ ,  $p < 0.0001$ ) and from total algae ( $\beta$ -carotene) ( $r^2 = 0.388$ ,  $p < 0.0001$ ) were also significantly correlated with N supplements to farmland in NI (Fig. 6g,i) as well as to changes in fossil  $\delta^{15}\text{N}$  signatures ( $r^2 = 0.750$  and  $0.326$ , respectively,  $p < 0.0001$ ). Regression analysis of limnological data revealed that both concentrations of water-column Chl *a* ( $r^2 = 0.666$ ,  $p < 0.0001$ ), and densities of the predominant phytoplankton *P. agardhii* ( $r^2 = 0.566$ ,  $p < 0.0001$ ) were strongly correlated with annual N inputs to NI agriculture during 1969–1995 (Fig. 6c,e) and with direct measurements of N influx to the lake ( $r^2 = 0.424$ ,  $p = 0.002$ ) during 1975–1987 (data from Gibson et al. 1992) but not with annual N additions from either urban ( $r^2 = 0.106$ – $0.173$ ,  $p = 0.105$ – $0.182$ ; 1971–1996) or atmospheric sources (both  $r^2 = 0.000$ ,  $p > 0.50$ ; 1982–1996) (both analyses not shown).

Regression analyses showed that P supplements to agriculture were significantly correlated with past changes in the abundance of colonial cyanobacteria (as myxoxanthophyll,  $r^2 = 0.296$ ,  $p < 0.0001$ ), modern *P. agardhii* concentrations ( $r^2 = 0.151$ ,  $p = 0.031$ ), and modern total algal biomass (as Chl *a*;  $r^2 = 0.152$ ,  $p = 0.027$ ); however,

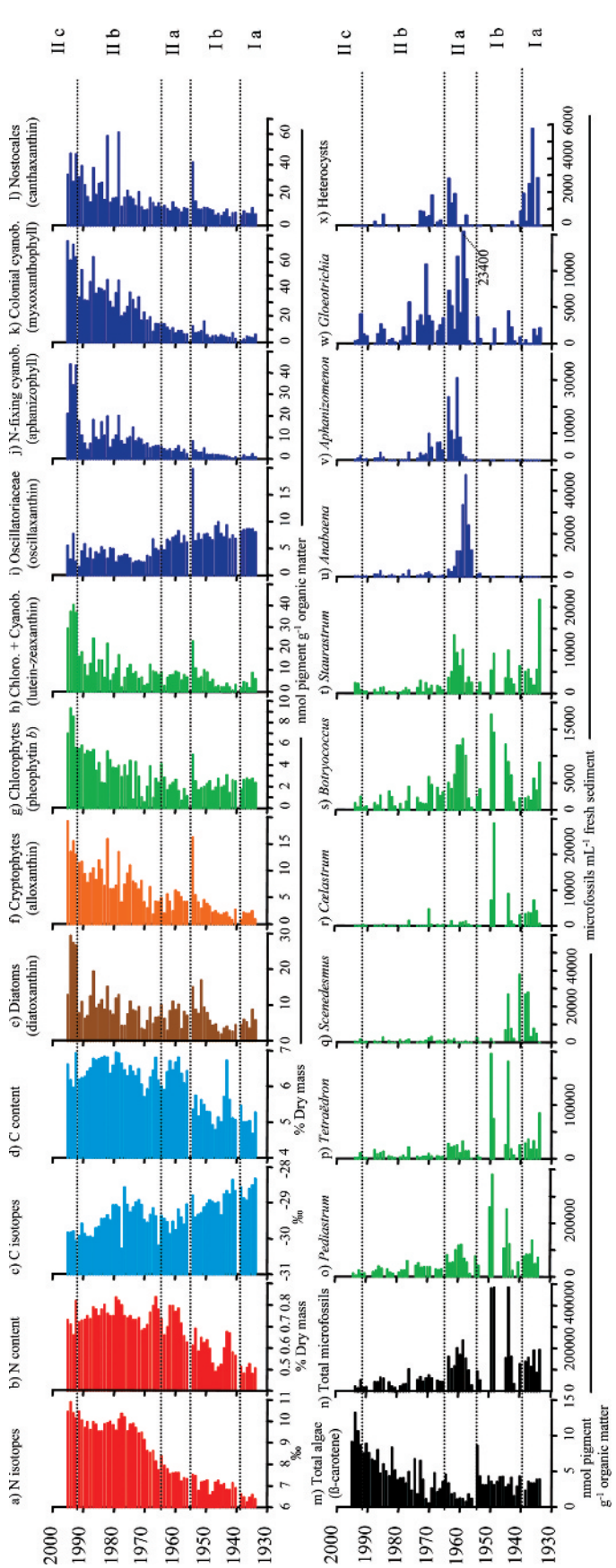


Fig. 5. Temporal changes in geochemistry and fossil assemblages in the sediment core from Lough Neagh, Northern Ireland. Stratigraphic profiles of geochemistry include (a) N isotope ratios, (b) N content, (c) C isotope ratios, and (d) C content. Fossil pigment profiles include compounds from (e) diatoms (diatoxanthin), (f) cryptophytes (alloxanthin), (g) chlorophytes (pheophytin b), (h) chlorophytes and cyanobacteria (lutein-zeaxanthin), (i) Oscillatoriae (oscillaxanthin), (j) potentially N<sub>2</sub>-fixing cyanobacteria ("aphanizophyll"), (k) colonial cyanobacteria (myxoxanthophyll), (l) Nostocales cyanobacteria (canthaxanthin), and (m) total algae (β-carotene). Algal microfossil profiles include (n) total algae, (o) *Pediastrum*, (p) *Tetraëdron*, (q) *Scenedesmus*, (r) *Ceclastrum*, (s) *Botryococcus*, (t) *Staurastrum*, (u) *Anabaena*, (v) *Aphanizomenon*, (w) *Gloeotrichia*, and (x) nonspecific heterocysts. Dotted lines indicate the boundaries of the zones identified by stratigraphically constrained cluster analysis. All fossil pigments as nmol pigment g<sup>-1</sup> organic matter, whereas algae as microfossils mL<sup>-1</sup> fresh sediment.

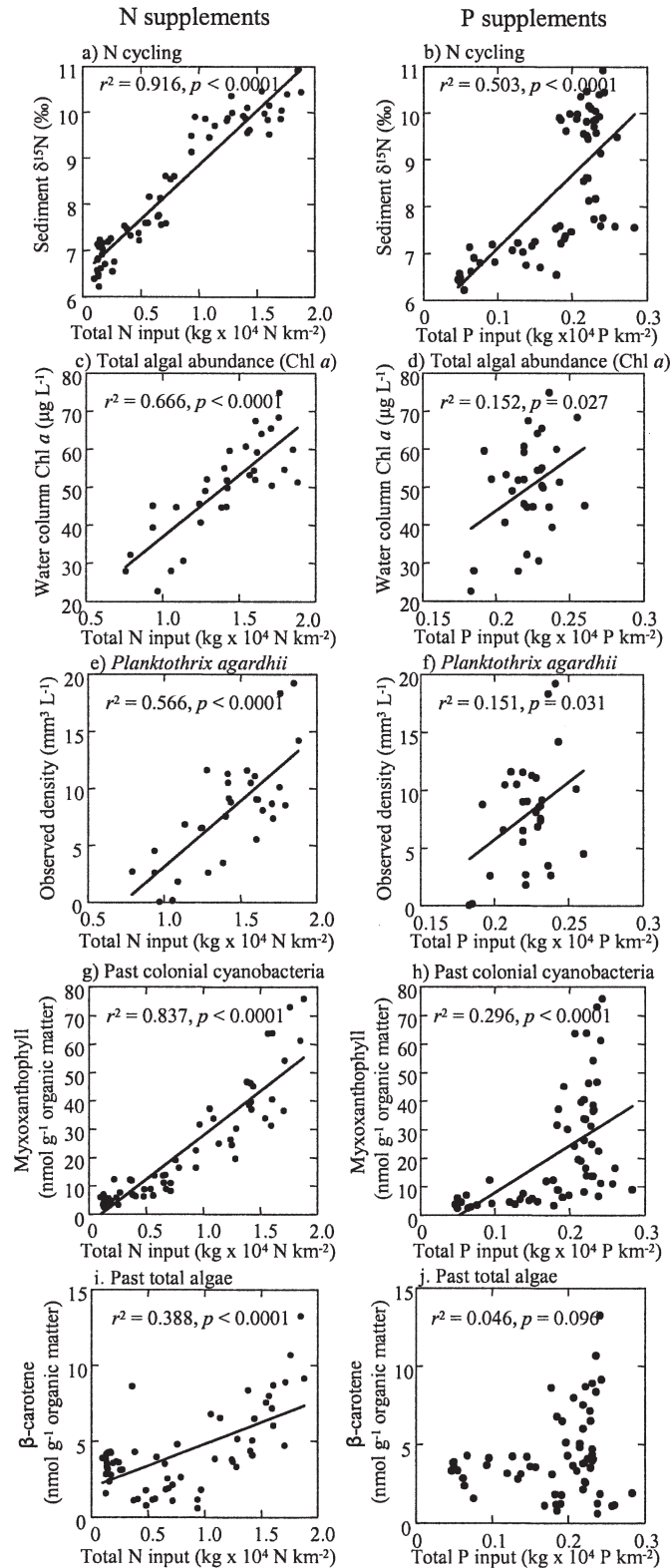


Fig. 6. Relationships between annual supplements of N (a,c,e,g,i) and P (b,d,f,h,j) to Northern Irish farms (both  $\text{kg} \times 10^4 \text{ km}^{-2} \text{ yr}^{-1}$ ) and (a,b) changes in sedimentary  $\delta^{15}\text{N}$  (‰), (c,d) modern water-column Chl *a* ( $\mu\text{g L}^{-1}$ ), (e,f) modern densities of *Planktothrix agardhii* ( $\text{mm}^3 \text{L}^{-1}$ ), (g,h) fossil colonial cyanobacterial pigments ( $\text{nmol myxoxanthophyll g}^{-1}$  organic matter), and (i,j) fossil ubiquitous algal pigments ( $\text{nmol } \beta\text{-carotene g}^{-1}$  organic

these regressions explained  $<50\%$  as much variance as did those based on past annual N use by farms (Fig. 6h,f,d). Further, correlations were substantially weaker when animal feed supplements were excluded and regressions were restricted to P derived from inorganic fertilizers (analysis not shown). Comparison of time series of N and P inputs to farmland in NI suggested that differences in correlation strength reflected the fact that most increases in P supplementation occurred during ca. 1933–1965 (Fig. 2j) rather than during the latter half of the sedimentary record, when rates of algal community change were greatest (Fig. 5). Regardless, correlations were not improved by lagging or advancing P time series by up to 25-yr during cross-correlation analysis to account for decadal lags in P release from soils (Foy and Lennox 2006). In contrast to N-based analyses, changes in modern Chl *a* concentration and *Planktothrix* abundance were not well correlated with annual P flux from other sources, exhibiting negative correlations with P from cities ( $r^2 = 0.393\text{--}0.528$ ,  $p < 0.002$ ; 1975–1996) and weak positive correlations with atmospheric inputs of P ( $r^2 = 0.337\text{--}0.392$ ,  $p < 0.025$ ; 1982–1996) despite the fact that atmospheric deposition represented  $<1\%$  of total P inputs.

Climatic variation during the 20th century did not explain a substantial amount of historical variation in sedimentary geochemical, pigment, and nonsiliceous microfossil contents. In fact, regression analyses of all climatic and fossil variables revealed only one significant correlation, that between winter NAO index and the abundance of colonial cyanobacteria (myxoxanthophyll) ( $r^2 = 0.192$ ,  $p < 0.0001$ ). In all other cases,  $<10\%$  of variance in fossil time series could be explained by changes in common meteorological features.

Regression analysis confirmed that fossil metrics accurately recorded observed changes in algal abundance during the long-term monitoring period (Fig. 7). For example, fossil densities of *A. flos-aquae* were highly correlated ( $r^2 = 0.743$ ,  $p < 0.0001$ ) with microscopic estimates of abundance of this species during the period since 1969 (Fig. 7a). Similarly, fossil concentrations of myxoxanthophyll (colonial cyanobacteria) were correlated with water-column Chl *a* abundances ( $r^2 = 0.355$ ,  $p = 0.001$ ; Fig. 7d) and observed densities of *P. agardhii* ( $r^2 = 0.367$ ,  $p = 0.001$ ; Fig. 7c), a cyanobacterial species that composes  $>70\%$  of phytoplankton biomass and that is itself strongly correlated with observed Chl *a* concentrations ( $r^2 = 0.472$ ,  $p < 0.0001$ ; Fig. 7b). In addition, variations in total algal abundance determined from ubiquitous fossil  $\beta$ -carotene and water-column Chl *a* concentrations were significantly correlated ( $r^2 = 0.286$ ,  $p = 0.003$ ; Fig. 7e), as were variations in the fossil abundances of total algae ( $\beta$ -carotene) and colonial cyanobacteria (myxoxanthophyll) ( $r^2 = 0.573$ ,  $p < 0.0001$ ; Fig. 7f). Unfortunately, further comparisons of fossil and monitoring time series were not

←

matter). Historical regressions are based on data from 1933–1995, whereas modern limnological data encompass the period 1971–1995.

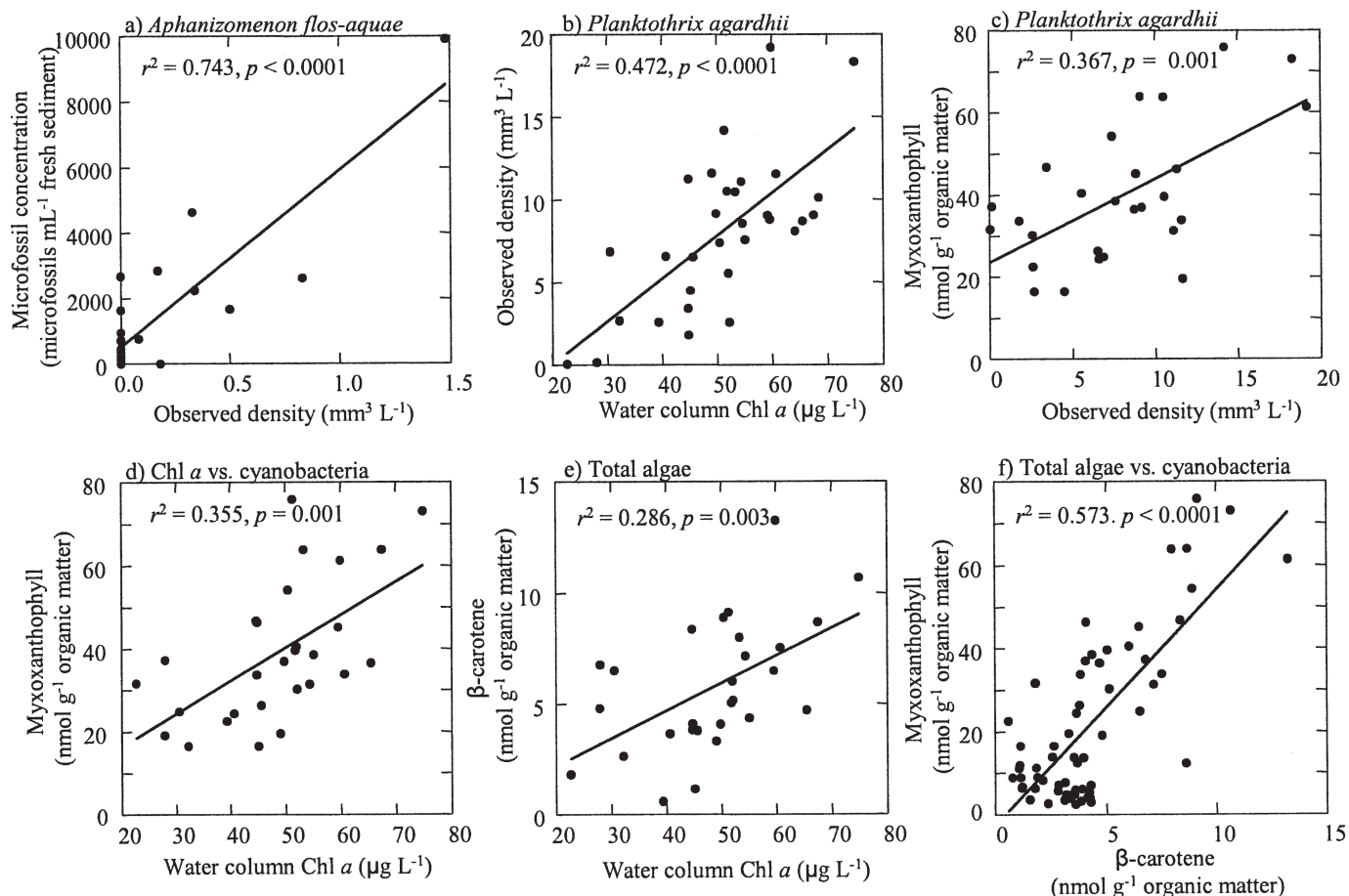


Fig. 7. Relationships between modern and fossil metrics of algal abundance in Lough Neagh, Northern Ireland. Regressions are based on data from 1969–1995 and include (a) observed (mm<sup>3</sup> L<sup>-1</sup>) and fossil densities (microfossils mL<sup>-1</sup> fresh sediment) of *Aphanizomenon flos-aquae*, (b) water-column concentrations of Chl *a* (μg L<sup>-1</sup>) and *Planktothrix agardhii* (mm<sup>3</sup> L<sup>-1</sup>), (c) observed density of *Planktothrix agardhii* (mm<sup>3</sup> L<sup>-1</sup>) and fossil myxoxanthophyll from colonial cyanobacteria (nmol pigment g<sup>-1</sup> organic matter), (d) fossil myxoxanthophyll and water-column Chl *a*, (e) water-column Chl *a* and ubiquitous fossil algal pigments (nmol β-carotene g<sup>-1</sup> organic matter), and (f) fossil myxoxanthophyll (colonial cyanobacteria) and β-carotene (all algae).

possible because other common algal taxa were not preserved in sediments (*Limnothrix redekei*), fossil diatoms were not enumerated (*S. neoastraea*, *A. subarctica*), and phytoplankton enumeration did not include subdominant species or those from nonpelagic habitats.

## Discussion

Analysis of annually resolved fossil records of N input, aquatic production, and algal abundance and gross community composition revealed that water quality degradation in Lough Neagh during the 20th century was strongly correlated to agricultural inputs of N to NI farmland, weakly correlated to P inputs to NI farmland, and uncorrelated to most measures of climatic variability or to N and P loading from urban or atmospheric sources (Fig. 6). Strong correlations between water-column densities of important algal taxa and sedimentary records of their occurrence (Fig. 7) also allowed unambiguous interpretation of past changes in algal production and community composition, as has been demonstrated in whole-lake experiments (Leavitt 1993; Leavitt and Findlay 1994) and

mass balance studies (Leavitt and Carpenter 1990). Similarly, strong correlations between aquatic δ<sup>15</sup>N signatures and agricultural activities have been demonstrated recently for 13 catchments in Canada (Anderson and Cabana 2005) as well as for sedimentary records of allochthonous N influx (Elliott and Brush 2006; Leavitt et al. 2006). Instead, this investigation of Lough Neagh represents the first combination of detailed historical records, catchment-level nutrient mass balances, annually resolved fossil records, and novel analysis of the remains of nonsiliceous algae to demonstrate that the timing and extent of lake eutrophication is most closely related to agricultural use of N. Below, the sedimentary and historical time series are combined to produce a synthetic record of lake eutrophication, evaluate the reliability of fossil records, and identify potential causes of water quality degradation for use in improved lake management strategies.

*History of water quality change*—Analyses of sedimentary geochemical and algal fossil assemblages identified five phases of lake eutrophication since ca. 1933 (Fig. 5). The first phase (Zone Ia, ca. 1933–1939) was marked by the

lowest primary production of the 20th century, as indicated by low levels of  $\delta^{15}\text{N}$ , reduced concentrations of fossil pigments and sedimentary C and N, enriched  $^{13}\text{C}$  isotope content, and diverse microfossils from mesotrophic chlorophyte algae. Absolute values of stable isotope ratios can be site specific and difficult to interpret because they reflect the mass-weighted mixture of N from all sources, often each with its own distinct  $\delta^{15}\text{N}$  signature. Fortunately, elevated  $\delta^{15}\text{N}$  of dissolved and particulate N in aquatic ecosystems usually reflect inputs of  $^{15}\text{N}$ -enriched matter (e.g., McClelland and Valiela 1998; Voss et al. 2000). In agricultural systems, such enrichment occurs because  $^{14}\text{N}$  is lost preferentially through  $\text{NH}_3$  volatilization, nitrification of soil  $\text{NH}_3$ , and microbial denitrification, all processes that fractionate 10–15‰ when excess N is present (Anderson and Cabana 2005). Although low  $\delta^{15}\text{N}$  signals can also arise from inputs of atmospheric N ( $\sim 0\text{‰}$ ) fixed by biological or industrial processes, both aquatic (Fig. 5u–x) and terrestrial  $\text{N}_2$ -fixing taxa (Stewart and Corry 1938) were rare during the 1930s, as was application of industrially derived  $\text{NH}_3$  fertilizer. Therefore, comparatively low sedimentary  $\delta^{15}\text{N}$  values and N contents suggest low inputs of N to the catchment (1,000–1,500 kg N km $^{-2}$  yr $^{-1}$ ; Fig. 2i) and only modest isotopic fractionation.

Low concentrations of fossil pigments during Zone Ia demonstrated that algal production was at a minimum during the 1930s (Fig. 5e–m). Strong correlations between fossil pigment abundances and both water-column Chl *a* (Fig. 7d) and *P. agardhii* (Fig. 7c) concentrations during 1969–1995 were similar to those recorded in other lakes (e.g., Leavitt 1993; Leavitt and Findlay 1994) and likely reflect the fact that the main processes that regulate algal deposition and fossil preservation (lake depth, thermal stratification, deep-water oxygen content; Cuddington and Leavitt 1999) did not vary substantially during the study period (see Site description). Similarly, estimates of algal community composition derived from enumeration of nonsiliceous microfossils (Fig. 5n–x) were consistent with direct observations during the early 20th century that revealed diverse desmid assemblages despite the presence of colonial cyanobacteria (West and West 1902; Dakin and Latache 1913). Together, these patterns suggest that algal abundance during Zone Ia was at least threefold lower than at present.

Despite apparently low algal production during the early 20th century, nutrient enrichment of the Lough began  $\sim 1700$  with forest clearance and expansion of farming and increased after ca. 1900 with urbanization and agricultural intensification (Carter 1977; Battarbee 1978). For example, expansion of phosphate production by the fertilizer industry in Ireland since ca. 1850 (Cooper 1999) increased inputs of P to agricultural land and resulted in substantial nutrient imbalances in which  $\sim 78\%$  of imported P and  $\sim 48\%$  of N was retained within catchment soils (Foy et al. 2002). Such imbalances would be expected to increase nutrient accumulation in farmed soils as well as runoff to the Lough (Bennett et al. 1999, 2001; Carpenter 2005). Initially, such export should favor P losses to the lake because mineral imbalances of this element were greater

than those of N (Foy et al. 2002) and maintenance of crop production requires substantially more N than P. Consistent with this hypothesis, diazotrophic cyanobacterial heterocysts were common throughout this interval (Fig. 5x), and *Anabaena* spp. were present in historical collections from 1900 to 1911 (West and West 1902; Dakin and Latache 1913), suggesting that algal communities were N limited during the early 20th century.

The second phase of eutrophication (Zone Ib, ca. 1939–1955) was marked by twofold increases in fossil pigments from colonial cyanobacteria (aphanizophyll, myxoxanthophyll, canthaxanthin) and cryptophytes (alloxanthin), abundant chlorophyte microfossils, and few  $\text{N}_2$ -fixing cyanobacteria (Fig. 5f,j–l,o–x). Depleted sedimentary  $\delta^{13}\text{C}$  was consistent with increased production and uptake of respired  $\text{CO}_2$  by algae (Brock et al. 2006). Coeval 1‰ increases in  $\delta^{15}\text{N}$  (Fig. 5a) were consistent with sedimentary  $\delta^{15}\text{N}$  records from a diverse range of lotic systems that have experienced increased N flux from anthropogenic nutrient sources (Elliott and Brush 2006; Leavitt et al. 2006) and with historical records that show that application of N to farmland in NI increased from 1,040 kg N km $^{-2}$  in 1939 to 3,700 kg N km $^{-2}$  in 1955, while that of P increased from 550 to 1,690 kg P km $^{-2}$  (Fig. 2i,j). Together, these changes led to mineral surpluses in soils of 2,390 kg N km $^{-2}$  yr $^{-1}$  and 1,430 kg P km $^{-2}$  yr $^{-1}$  (Foy et al. 2002) that may have been transported to Lough Neagh during the “plow-up campaign” of World War II (1939–1945). During this era, cereal cultivation increased from 1,906 km $^2$  in 1939, to 3,444 km $^2$  in 1943, before declining to 2,837 km $^2$  in 1946 (Symons 1963). Such soil disturbance apparently accelerated soil erosion into the Lough, as recorded in the sediment by both elevated rates of cereal pollen deposition (O’Sullivan et al. 1973) and variability in C and N content during the 1940s (Fig. 5b,d).

Analysis of algal microfossils suggests that primary production during Zone Ib may have been limited more by P than by N fluxes (Fig. 5n–x). In particular, heterocysts from diazotrophic cyanobacteria were largely absent (Fig. 5x), although the abundance of *Gloeotrichia* increased slightly (Fig. 5w). Instead, most chlorophyte taxa reached historical maxima during this period (Fig. 5o–t), similar to increases seen in other European lakes undergoing eutrophication due to P inputs (Jeppesen et al. 2005). Overall, nutrient influx to Lough Neagh may have increased during this period as a consequence of the expansion of urban sewerage systems and the introduction of P-rich household detergents (Battarbee 1978; Foy et al. 2003).

Striking reductions in the main chlorophyte genera (Fig. 5o–t), combined with marked increases in diazotrophic cyanobacteria (Fig. 5u–x), suggest that intense N limitation of algal growth developed during Zone IIa (ca. 1955–1964). Consistent with this hypothesis, N and P amendments to NI farms increased by 55.1% (to 5,740 kg N km $^{-2}$  yr $^{-1}$ ) and 36.7% (to 2,310 kg P km $^{-2}$  yr $^{-1}$ ), respectively, while N:P ratios of supplements (Fig. 2k) remained low ( $\sim 3$ ) and constant (Foy et al. 2002), and water-column P concentrations increased (Battarbee 1978; Foy et al. 2003). Replacement of chlorophytes by  $\text{N}_2$ -fixing

cyanobacteria was observed in Lough Neagh (Fig. 5), is common in P-replete lakes (Schindler 1977), and has been recorded elsewhere by analyses of fossil pigments (Leavitt and Findlay 1994) and nonsiliceous algal microfossils (van Geel et al. 1996). Interestingly,  $\delta^{15}\text{N}$  signals remained enriched during this period, indicating little influence of fixed  $\text{N}_2$  ( $\sim 0\text{‰}$ ) on ecosystem N budgets (Patoine et al. 2006).

Zone IIb (ca. 1964–1991) was defined by large changes in stable isotope signatures ( $+2\text{‰}$   $\delta^{15}\text{N}$ ,  $-1\text{‰}$   $\delta^{13}\text{C}$ ), greatly increased concentrations of most fossil pigments, and sharp declines in microfossils from diazotrophic cyanobacteria, patterns that together suggest a substantial increase in N loading to a N-limited lake (Fig. 5). Consistent with this view, total N supplementation to NI farms increased  $>160\%$  between 1964 and 1991 (Fig. 2i), whereas those of P remained unchanged (Fig. 2j), and urban P inputs decreased 58% from 1983 to 1991 as a result of tertiary treatment of wastewater (Foy et al. 1995). These trends occurred because formal agricultural assessments revealed that farmland soils in NI were P sufficient (Foy et al. 2002) and because European Union (EU) subsidies enacted after 1973 favored the production of grasses for livestock rather than cereal cultivation. In contrast to cereal production, high yields of grass require extensive fertilization with N rather than P (Watson et al. 1992). Not surprisingly, N:P ratios of agricultural supplements increased from  $\sim 2.5$  in 1964 to  $>7.0$  in 1991 (Fig. 2k). Further, because the efficiency of N export from agricultural soils was relatively constant at 12–13% of catchment N additions (Smith and Stewart 1989; Watson et al. 2000), increased supplementation delivered  $\sim 300\%$  more N to Lough Neagh than during the first half of the 20th century, thereby reducing algal reliance on atmospheric N.

The fifth phase of the eutrophication of Lough Neagh encompassed ca. 1991–1995 and was defined by extremes of  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  signals, C and N content, fossil pigment concentrations, and algal microfossil densities (Fig. 5). Although nutrient supplementation to NI agriculture ( $\sim 2,300$  kg P  $\text{km}^{-2}$   $\text{yr}^{-1}$ ,  $\sim 16,000$  kg N  $\text{km}^{-2}$   $\text{yr}^{-1}$ ) and nutrient surpluses in farmland soils ( $\sim 1,600$  kg P  $\text{km}^{-2}$   $\text{yr}^{-1}$ ,  $\sim 14,000$  kg N  $\text{km}^{-2}$   $\text{yr}^{-1}$ ) were relatively constant during this period (Fig. 2i,j), water-column concentrations of both  $\text{NO}_3$  and Chl *a* (Fig. 3b,e) were much greater during the 1990s than at any time during the preceding 21 years, suggesting that inputs of limiting N were at an historical maximum. Consistent with this hypothesis, concentrations of fossil pigments from colonial cyanobacteria (aphanizophyll, myxoxanthophyll, canthaxanthin; Fig. 5j–l) and densities of the predominant algal taxon *Planktothrix agardhii* (Fig. 3f) reached historical maxima during the 1990s. Similar increases in this species have been recorded in other eutrophic lakes in Europe (Wiedner et al. 2002; Willame et al. 2005), suggesting that it is a reliable indicator of water quality degradation, especially under conditions of high P (Wiedner et al. 2002) and low water-column transparency (Mur et al. 1978). However, as detailed later in this paper, the continued rise of *Planktothrix* in Lough Neagh is most closely correlated with the use of N as an agricultural

supplement rather than with P inputs as previously supposed.

*Reliability of the fossil record*—Identification of the causes of ecosystem change from fossil records requires both that sedimentary deposits accurately record known changes in limnological conditions and that the correlates of fossil time series are sufficiently well distinguished to allow evaluation of competing hypotheses concerning potential mechanisms underlying observed historical variations. Fortunately, the presence of a continuous 27-yr record of water chemistry, algal abundance, and phytoplankton community composition allowed direct calibration, often for the first time, of widely used fossil metrics with their limnological equivalents. In addition, the exceptional availability of annual mass balances for the major nutrient fluxes in NI agriculture during the 20th century (Foy et al. 2002), as well as concomitant records of climatic variability and nutrient inputs from atmospheric and urban sources, allowed quantitative evaluation of the relative importance of these factors as causes of eutrophication.

Stratigraphic changes in fossil pigment concentrations accurately captured the main historical trends in algal abundance and gross community composition (Fig. 5e–m). At present, the hypertrophic state of Lough Neagh is characterized most obviously by the abundance of *Planktothrix agardhii* (Gibson et al. 2000). Although closely related to other Oscillatoriaceae, *P. agardhii* lacks the diagnostic indicator carotenoid oscillaxanthin, instead producing myxoxanthophyll as its main accessory pigment (Leavitt and Brown 1988). Given this fact, the strong correlations between water-column densities of *P. agardhii* and coeval concentrations of fossil myxoxanthophyll ( $r^2 = 0.367$ ,  $p = 0.001$ ; Fig. 7c), between epilimnetic *P. agardhii* and Chl *a* concentrations ( $r^2 = 0.472$ ,  $p < 0.0001$ ; Fig. 7b), and between fossil myxoxanthophyll and observed water-column Chl *a* abundances ( $r^2 = 0.355$ ,  $p = 0.001$ ; Fig. 7d), all demonstrate clearly that sedimentary deposits accurately recorded known changes in the abundance of this predominant algae. Further, given the importance of *Planktothrix* in Lough Neagh, it is not surprising that total algal abundance measured as ubiquitous, chemically stable  $\beta$ -carotene (Leavitt and Hodgson 2001) was correlated with both water-column estimates of total algal biomass as Chl *a* ( $r^2 = 0.286$ ,  $p = 0.003$ ; Fig. 7e) and past estimates of colonial cyanobacterial concentration (myxoxanthophyll) ( $r^2 = 0.573$ ,  $p < 0.0001$ ; Fig. 7f).

As in other lakes, fossil concentrations were closely related to annual average standing crops of algae rather than estimates of primary productivity (reviewed in Leavitt 1993; Leavitt and Hodgson 2001). Interestingly, pigment–plankton correlations observed for Lough Neagh were often stronger than those recorded in other calibration exercises, including those in lakes with annually laminated sediments (Leavitt and Findlay 1994). Such high correlations likely reflect the fact that water transparency is low in Lough Neagh (mean secchi depth  $\sim 1.1$  m; Fig. 3d) because of both high Chl *a* concentrations (Fig. 3e) and DOC inputs from catchment peat deposits ( $K_d = 0.925$   $\text{m}^{-1}$ ;

Gibson et al. 2000). As shown elsewhere, poor plankton–fossil correlations can arise when algal production is concentrated on benthic surfaces or in metalimnetic regions, habitats that are represented well within the sedimentary record but that are rarely sampled during limnological monitoring programs (Cuddington and Leavitt 1999).

Analysis of Lough Neagh allowed the first quantitative calibration of nonsiliceous algal microfossils with long-term records of phytoplankton community change (Fig. 7a). Although it has been known for more than 100 years that nonsiliceous algae are preserved in many lake sediments (reviewed in Cronberg 1986; van Geel 2001), previous studies have attempted only qualitative comparisons of modern and past populations (e.g., Livingstone and Cambray 1978). In contrast, the strong linear correlation between observed and fossil populations of *A. flos-aquae* ( $r^2 = 0.743$ ,  $p < 0.0001$ ) in Lough Neagh is the first direct demonstration that historical variations in past abundance of some algal taxa can be reconstructed from nonsiliceous microfossil concentrations. However, it should also be noted that because many important algal species do not produce recognizable morphological fossils in Lough Neagh (e.g., *Planktothrix agardhii*), such remains cannot be used to evaluate past trends in total algal abundance (e.g., total algal microfossils vs.  $\beta$ -carotene; Fig. 5n vs. 5m). Instead, nonsiliceous algal microfossils appear to be most useful for identifying the presence and abundance of specific taxa as well as for improving interpretation of sedimentary pigment profiles.

*Identifying causes of water quality change*—Regression analyses showed that recent degradation of Lough Neagh water quality was correlated most closely with agricultural use of N during the 20th century (Fig. 6). For example, both modern ( $r^2 = 0.566$ ,  $p < 0.0001$ ; 1969–1995) and fossil ( $r^2 = 0.837$ ,  $p < 0.0001$ ; 1933–1995) measures of colonial cyanobacterial standing crop were strongly correlated with N supplements to NI farms, as were modern ( $r^2 = 0.666$ ,  $p < 0.0001$ ) and fossil ( $r^2 = 0.388$ ,  $p < 0.0001$ ) indices of total algal biomass (Fig. 6). In contrast, similar regressions using NI agricultural P inputs explained <50% of the variance in past algal abundance than did those conducted using agricultural N inputs (Fig. 6), even when time series were cross correlated up to 25 yr to account for known lags in P release from soils (Foy and Lennox 2006). Further, because annual N use by NI agriculture (or sedimentary  $\delta^{15}\text{N}$ ) was a much better predictor of colonial cyanobacterial abundance ( $r^2 = 0.837$ ,  $p < 0.0001$ ) than of total algal biomass ( $r^2 = 0.388$ ,  $p < 0.0001$ ) during 1933–1995 but regressions were of similar magnitude ( $r^2 = 0.566$  and  $0.666$ , respectively) during the monitoring period (1969–1995), when *Planktothrix agardhii* dominated phytoplankton assemblages, it can be inferred that N mainly stimulated prokaryotic algae.

Identification of agricultural N as the principal control of eutrophication requires that there is a positive correlation between nutrient supplementation to NI farmland and N runoff to Lough Neagh. Fortunately, four lines of evidence suggest that this assumption is valid. First,

detailed mineral balances demonstrate that soils in NI exhibited N surpluses throughout the period of study (Foy et al. 2002), a prerequisite for persistent nutrient export. Second, two independent estimates suggest that a constant fraction (~12–13%) of applied N has been exported from NI agricultural lands into rivers leading to Lough Neagh during 1971–2000, despite nearly threefold increases in soil N surplus between 1970 (~6,000 kg N km<sup>-2</sup>) and 1995 (~16,000 kg N km<sup>-2</sup>) (Smith and Stewart 1989; Watson et al. 2000). Third, the very strong correlation between sedimentary  $\delta^{15}\text{N}$  and total annual N supplementation to NI agriculture since 1933 ( $r^2 = 0.916$ ,  $p < 0.0001$ ; Fig. 6a) is consistent with other studies that demonstrate a linear relationship between fossil N isotope signatures and N loading to aquatic ecosystems from the catchment ( $r^2 = 0.84$  in Leavitt et al. 2006;  $r^2 = 0.86$  in Elliott and Brush 2006) or agricultural intensity and aquatic  $\delta^{15}\text{N}$  signals ( $r^2 = 0.69$  in Anderson and Cabana 2005). Fourth, observed increases in the predominant algal species, *Planktothrix agardhii*, were correlated equally well with N inputs to NI farms during 1969–1995 ( $r^2 = 0.565$ ,  $p < 0.0001$ ; Fig. 6e) as with directly measured NO<sub>3</sub> influx (g N m<sup>-2</sup> yr<sup>-1</sup>) to Lough Neagh during 1975–1987 ( $r^2 = 0.424$ ,  $p = 0.016$ ; data from Gibson et al. 1992) but were uncorrelated with influx of total or dissolved reactive P to the lake ( $r^2 = 0.000$ – $0.132$ ,  $p > 0.075$ ; data from Foy and Lennox 2006).

Limitation of algal production by N since 1933 may have arisen because of saturation of algal demand for P early in the 20th century. For example, analysis of fossil diatoms suggests that lake eutrophication occurred as early as ca. 1700 (Battarbee 1978; Foy et al. 2003). Similarly, nutrient balances for NI suggest that P surpluses date to at least 1905, if not earlier, possibly reflecting development of the P fertilizer industry during the preceding century (Cooper 1999). Thus, while total P inputs to farmland increased from 550 kg km<sup>-2</sup> in 1933 to 2,430 kg km<sup>-2</sup> in 1995 and largely saturated soil-binding capacity for P (Foy et al. 2002), both paleoecological and historical evidence suggest that P supply was sufficient for algal growth and that modest N limitation was evident early in the 20th century.

Although urban wastewaters cause widespread eutrophication of lakes (Schindler 2006; Smith 2006), point sources of N do not appear to have had substantial effects on algal production in Lough Neagh during the 20th century. For example, mass balances for 1971–1995 indicate that mean annual urban N accounted for only 10–20% of annual N loading to Lough Neagh (Smith 1977; R. H. Foy unpubl. data). Further, because inputs of urban nutrients are correlated to human population density (see Methods and materials) and because human population density is correlated also to inputs of N to agricultural lands ( $r^2 = 0.874$ ,  $p = 0.004$ ; Bunting 2004), it can be inferred that the proportion of N derived from cities has been relatively constant since 1933. Similarly, initiation of tertiary wastewater treatment by most WWTWs in 1981 eliminated ~60% of P from urban sources (Foy et al. 1995) yet did not result in sustained declines of Chl *a* concentration or phytoplankton biovolume (Fig. 3). Therefore, although urban nutrient sources could have combined with land-use practices to enrich Lough Neagh prior to 1933

(Battarbee 1978; Foy et al. 2003), our analyses suggest that they did not contribute substantially to water quality degradation thereafter.

Finally, despite the availability of detailed meteorological records throughout the 20th century, there is little evidence of direct climatic regulation of Lough Neagh water quality. With the exception of a modest statistical relationship between winter NAO index and fossil myxoxanthophyll ( $r^2 = 0.192$ ,  $p = 0.005$ ), all regressions between fossil and climatic variables were nonsignificant. Weak correlations of past algal abundance with the NAO contrast with analyses of other European lakes (e.g., Straile 2002) and suggest that climatic effects on algal communities in Lough Neagh were overwhelmed by land-use practices, such as has been seen in other regions with intensive agriculture (e.g., Hall et al. 1999).

*Management implications*—Quantitative comparison of historical and fossil time series demonstrated that colonial cyanobacterial development (Fig. 6e,g), total algal production (Fig. 6c,i), and water quality degradation since 1933 were associated most closely with inputs of N to NI farmlands. We hypothesize that strong N limitation of phytoplankton growth may have developed because soils of agroecosystems were sequentially saturated with P then N. In this mechanism, export of surplus P from the catchment starting in 1700 initially stimulated production of diatoms (Battarbee 1978; Foy et al. 2003) and diverse chlorophytes (Fig. 5o–t) but eventually led to P sufficiency as soil capacity for P storage was saturated. Once established, such diffuse inputs of P may persist for over 1,000 yr (Carpenter 2005) and can create conditions in which water quality loss is linked with N influx to P-replete lakes. This scenario is similar to that seen in polymictic lakes of central North America where abundant P supply from glacial tills and soils has favored hypertrophic conditions, strong N limitation, and extensive blooms of cyanobacteria (Leavitt et al. 2006). These patterns also allow us to make specific recommendations to watershed managers.

First, our analyses suggest that short-term management strategies should reduce both diffuse and point source inputs of N to Lough Neagh. As shown by both limnological and paleoecological time series (Fig. 6), growth of colonial cyanobacteria, especially *Planktothrix agardhii*, is strongly correlated with influx of N rather than P. However, strains of this and related species of *Planktothrix* commonly produce toxic microcystins (Hisbergues et al. 2003; Briand et al. 2005), especially in shallow or polymictic lakes (Wiedner et al. 2002; Janse et al. 2005). Further, recent evidence demonstrates that production of microcystin by algae is positively correlated with N availability (Giani et al. 2005; Rolland et al. 2005). As a consequence, management to reduce N loading may not only shift phytoplankton communities from *Planktothrix* to the nontoxic *Limnithrix* species characteristic of the early 1970s (Gibson et al. 2000; Fig. 3f,g) but also reduce the potential toxicity of those *Planktothrix* that remain.

Second, long-term management strategies must determine whether soil surpluses of P are sufficient to saturate algal demand under future economic scenarios (e.g., Foy

and Lennox 2006). Once P replete, soils can supply excess P to lakes for many centuries (Carpenter 2005), depending on climatic, hydrologic, edaphic, geologic, and economic conditions. Under present conditions of polymixis and poor transparency (mean secchi depth  $\sim 1.1$  m;  $K_d = 0.925$  m $^{-1}$ ), low light availability may limit N<sub>2</sub> fixation by cyanobacteria and favor nondiazotrophic taxa (Mur et al. 1978; Wiedner et al. 2002). However, reduced N loading would be expected to reduce interception of light by algae, possibly favoring surface blooms of heterocystous cyanobacteria (e.g., Fig. 5, Zone IIa). Such a perverse response is most likely under conditions in which P release from soils cannot be reduced sufficiently to induce P limitation of algal production but should be avoidable if soil stores of P can be depleted more rapidly than those of N.

With the enactment of EU Water Framework Directive (2000/60/EC), it is more essential than ever to identify and mediate the factors that degrade surface waters. Consequently, similar paleoecological studies should be conducted in Europe to quantify the spatial extent of water quality degradation by diffuse N inputs. In this regard, research by Kilinc and Moss (2002) and James et al. (2003) suggests that algal production in lakes of the west Midlands in England may also be N limited. Similar patterns may be expected throughout western Europe, southern Scandinavia, and New Zealand, where agricultural production has increased during the 20th century through the use of nutrient supplements. Such analysis should also consider the factors that induce farmers to use excess fertilizer (e.g., farm income support, market subsidies) because the magnitude of nutrient supplementation may be under complex economic and social controls.

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Received: 18 March 2006

Accepted: 13 August 2006

Amended: 18 August 2006