

Landscape-scale effects of urban nitrogen on a chain of freshwater lakes in central North America

Peter R. Leavitt,¹ Curtis S. Brock, Courtney Ebel, and Alain Patoine

Limnology Laboratory, Department of Biology, University of Regina, Regina, Saskatchewan S4S 0A2, Canada

Abstract

We measured nitrogen (N) transport to and storage in nine lakes linked by the Qu'Appelle River, Saskatchewan, Canada, to quantify the unique effects of N on the eutrophication of phosphorus (P)-replete lakes. Stable isotope content ($\delta^{15}\text{N}$) was measured for dissolved N, periphyton, particulate organic matter (POM), and sediment samples collected at 10 stations along Wascana Creek and the Qu'Appelle River, lotic ecosystems that receive wastewaters from the City of Regina and that drain into Pasqua Lake. Urban effluent ($\delta^{15}\text{N} \sim 16 \pm 2\text{‰}$) enriched dissolved N isotope ratios of river water by up to 15‰ but was not stored in lotic sediments. Instead, urban N increased $\delta^{15}\text{N}$ signatures of lotic periphyton and POM by 10–15‰ and was transported to Pasqua Lake, where sedimentary $\delta^{15}\text{N}$ values increased from $\sim 6.5\text{‰}$ during the 19th century to 14.0‰ by the 1990s. This increase was linearly correlated both to the mass of dissolved N released from Regina ($r^2 = 0.84$, $p < 0.0001$) and to a 300% increase in the production of Pasqua Lake (as fossil pigments) since ca. 1880 ($r^2 = 0.69$, $p < 0.0001$). Similar isotopic enrichment was recorded in five downstream lakes, but not three reference ecosystems, although the degree of downstream enrichment declined rapidly, mainly as a result of sequestration of urban N in lake sediments. Together, these patterns demonstrate that urban N can directly degrade surface waters of P-sufficient lakes, but that these ecosystems can eliminate urban effects through permanent storage of wastewater N in their sediments.

Eutrophication of surface waters by point and diffuse sources of nutrients remains a potent cause of aquatic ecosystem degradation despite decades of intensive study (Carpenter et al. 1998; Smith 2003). In general, phosphorus (P) supply is thought to regulate algal production in freshwater lakes (Schindler 1977), whereas nitrogen (N) supply is the predominant control in many estuaries and shallow marine environments (Vitousek et al. 1997; Rabalais 2002). However, to date, few studies have investigated the unique effects of N loading on freshwater ecosystems during eutrophication (Kilinc and Moss 2002; James et al. 2003), despite recognition that many phytoplankton communities can exhibit N limitation (Elser et al. 1990), particularly if lakes lie in catchments with P-rich soils (e.g., Hall et al. 1999b). Further, it is increasingly evident that long-term agricultural practices can saturate soils with P (Bennett et al. 1999; Foy et al. 2002), thereby increasing P export to surface waters (Bennett et al. 2001)

and creating conditions in which diffuse and point sources of N degrade water quality (Bunting et al. 2005). Unfortunately, investigators have rarely quantified the degree to which such P-sufficient lakes are degraded by N, nor the ability of these lakes to sequester or eliminate N (sedimentation, ammonia volatilization, denitrification), thereby reducing environmental effects of N on downstream lakes or estuaries.

Eutrophication arising from N influx may be particularly severe in lakes of the northern Great Plains, sites often characterized by high nutrient content, low N : P ratios, surface blooms of N_2 -fixing cyanobacteria, and periodic fish kills (Hammer 1971; Haertel 1976). In many cases, supply of P from glacial tills and soils is great (Allan and Kenney 1978; Klassen 1989), leading to poor predictive relationships between P fluxes and algal abundance (Allan 1980; Campbell and Prepas 1986). Instead, recent paleoecological evidence suggests that changes in N influx from urban and agricultural sources are correlated with increased lake production and biological change during the 20th century (Hall et al. 1999b; Dixit et al. 2000; Quinlan et al. 2002). However, because agricultural and urban development has often been simultaneous, such retrospective analyses have been incapable of distinguishing among the effects of diffuse and point sources of N. Fortunately, analysis of stable isotopes can provide a means of differentiating among urban and agricultural sources of N, provided that their isotopic signatures can be distinguished (e.g., Wayland and Hobson 2001; deBruyn et al. 2003; Anderson and Cabana 2005). Further, when combined with paleolimnological analyses of past lake production, it is possible to quantify how ecosystem production and community composition have varied in response to changes in N loading (e.g., Schindler et al. 2005).

¹ Corresponding author (Peter.Leavitt@uregina.ca).

Acknowledgments

This work was supported by an NSERC Discovery Grant, the Canada Research Chair program, Canada Foundation for Innovation, Saskatchewan Learning, and Environment Canada Science Horizons Youth Internship Program. We thank Roland Hall, Nicole Knezacek, Suzanne McGowan, Murray Hildeman, and Jeff Hovdebo for assistance with sediment core collection and processing, Samantha Dietrich and Mark Graham for Wascana Creek isotope sample collection, Dunling Wang, Nicole Knezacek, and Richard Hughes for stable isotope analyses, and Mark Graham and Nicole Knezacek for fossil pigment analyses. Terry Chamulak (Saskatchewan Watershed Authority) and Gary Nieminen (City of Regina) provided raw hydrologic and effluent data, respectively. We thank Lynda Bunting for insightful discussions concerning N limitation of lake production.

Stable isotopes of N have proven particularly valuable in identifying sources and distribution of urban wastewater (e.g., McClelland et al. 1997; Wayland and Hobson 2001), although the precise isotopic signature of effluent depends on the sewage treatment procedures employed. For example, only large particles and lipids are removed during primary treatment, consequently colloid and total solid concentrations remain high and final effluent is only moderately enriched with ^{15}N (3–8‰) (Heikoop et al. 2000; deBruyn et al. 2003; Gaston and Suthers 2004). In contrast, secondary (colloid removal, microbial processing) and tertiary (chemical flocculation of P) treatment favors sedimentation, ammonia volatilization, and denitrification in clarifying tanks, processes that both greatly enrich ^{15}N content of dissolved N and reduce particle and colloid loads. Under these conditions, $\delta^{15}\text{N}$ of final effluent can exceed 20‰ (Bedard-Haughn et al. 2003). Finally, during biological nutrient removal (BNR) protocols, microbial denitrification can lead to final wastewater $\delta^{15}\text{N}$ values greater than 30‰ (e.g., Savage et al. 2004). However, because the main mechanisms regulating the degree of ^{15}N enrichment (NH_3 volatilization, denitrification) can also occur in terrestrial soils, particularly in the presence of manure (e.g., Anderson and Cabana 2005), and because background $\delta^{15}\text{N}$ values vary greatly among recipient ecosystems (Bedard-Haughn et al. 2003), unambiguous identification of urban N sources is most effective when stable isotopes analyses are conducted at a watershed or landscape level (e.g., McClelland et al. 1997; Steffy and Kilham 2004).

Here, we directly measured the stable isotope signature of urban effluent at all stages of sewage processing, as well as $\delta^{15}\text{N}$ values for dissolved N, periphyton, particulate organic matter (POM), and sediments from lotic ecosystems that delivered wastewaters to lakes. Our main objectives were to quantify how urban N is transported through a chain of nine prairie lakes and to evaluate how this N regulates landscape patterns of algal production. Because algal production in these lakes is known to be regulated by N supply (Hall et al. 1999b), we hypothesized that water quality degradation would be a linear function of N supplies from cities. Further, because algal sedimentation is known to be the main mechanism removing N from these lakes (Patoine et al. 2006), we hypothesized that urban effects would decline rapidly because of sequestration of urban N in lake sediments. When combined with paleolimnological reconstructions of lake production using chemically stable fossil pigments (reviewed in Leavitt and Hodgson 2001), our isotopic analysis sought to demonstrate both that lake eutrophication could arise from N pollution and that such P-sufficient lakes had substantial capabilities to ameliorate degradation of downstream ecosystems, such as has been suggested for wetlands and storm-water retention ponds (e.g., Gerke et al. 2001).

Material and methods

Study area—The Qu'Appelle River drains ~52,000 km² (50°00'–51°30'N, 101°30'–107°10'W) of mixed-grass Prai-

rie in southern Saskatchewan, Canada. Over 75% of the drainage area is composed of agricultural fields (wheat, barley, canola), pastures (cattle, swine), or natural mixed grasslands (~12%); the cities of Regina and Moose Jaw are the main urban centers (Fig. 1). Ten connected water bodies (0.5–552 km²) lie within the central Qu'Appelle catchment, including three headwater reservoirs and seven natural lakes (Table 1). Reservoirs were created by impoundment of the South Saskatchewan River (1968; Lake Diefenbaker), Wascana Creek (1883, deepened 1931; Wascana Lake), and the outflow of Buffalo Pound Lake (1952). Under natural conditions, the Qu'Appelle River flows from near Eyebrow Lake, Saskatchewan, through Buffalo Pound Lake, a central chain of four basins (Pasqua, Echo, Mission, Katepwa lakes), and two downstream lakes (Crooked, Round). Water from Last Mountain Lake and the Wascana Lake reservoir flow into the Qu'Appelle River via Last Mountain Creek and Wascana Creek, respectively (Fig. 1). Since 1968, flow of the Qu'Appelle River has been supplemented with water from the Lake Diefenbaker. Control structures are used to regulate water levels of most lakes, as well as to supply water to Last Mountain Lake during the spring river-discharge maximum.

Lakes receiving water from the Qu'Appelle River form a natural gradient of production from mesotrophic Lake Diefenbaker in the west to eutrophic Katepwa and Crooked lakes in the central and eastern reaches (Table 1). Specifically, limnological monitoring during summers (calendar day of year [DOY], 121–245) during 1994–2004 reveals that mean concentrations of total dissolved phosphorus (P) and chlorophyll *a* (Chl *a*) generally increase from west to east, while Secchi-depth transparency and ratios of total dissolved N : P decline in lakes not directly receiving urban wastewaters (Soranno et al. 1999). Cyanobacteria are present in all Qu'Appelle lakes, with intense surface blooms of colonial and N_2 -fixing taxa during mid- to late summer (McGowan et al. 2005). The presence of these algae, combined with declining N : P ratios, results in a strong landscape gradient of biological N_2 fixation, with elevated levels in eastern downstream lakes (Patoine et al. 2005). Quantification of sedimentary pigments unique to N_2 -fixing cyanobacteria (aphanizopyll) shows that these cyanobacteria are present naturally in Qu'Appelle lakes (Hall et al. 1999b; Dixit et al. 2000); however, their importance as an N source increases from West to East and with lake catchment area (Patoine et al. 2006).

Paleolimnological analysis of fossil diatoms, pigments, and chironomids reveals that urban and agricultural activities have degraded water quality and altered aquatic community composition at several Qu'Appelle sites during the past 125 years despite naturally high lake production (Hall et al. 1999b; Dixit et al. 2000; Quinlan et al. 2002). For example, comparison of fossil records with century-long historical time series of climate, land use, and urbanization using variance partitioning analysis demonstrates that 300% increases of algal abundance since ca. 1880 are correlated with N influx from the City of Regina to Pasqua Lake, the first site to regularly receive urban wastewater (Hall et al. 1999b; Dixit et al. 2000). However,

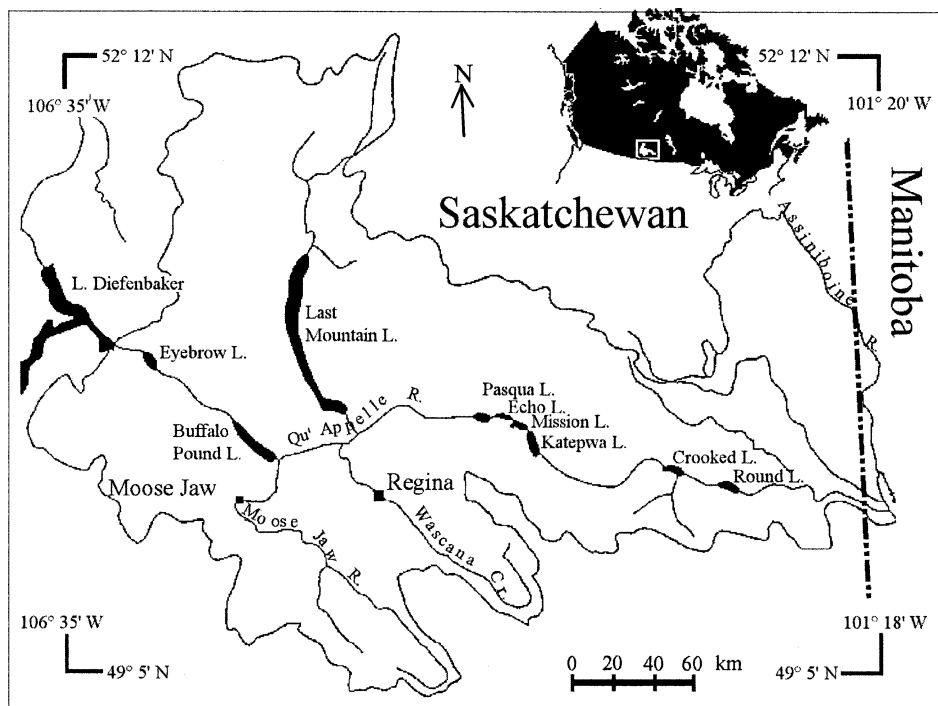


Fig. 1. Map of the drainage basin of the Qu'Appelle River, Saskatchewan, Canada. Under natural conditions, flow arises near Eyebrow Lake and passes through Buffalo Pound, Pasqua, Echo, Mission, Katepwa, Crooked, and Round Lakes. Last Mountain Lake and Wascana Lake drain into the Qu'Appelle River via Last Mountain and Wascana Creeks, respectively. In addition, water is transferred into the catchment from the Lake Diefenbaker reservoir and is occasionally forced into Last Mountain Lake during the spring discharge maximum. The City of Regina (pop. ~180,000) discharges tertiary-treated wastewater into Wascana Creek downstream of Wascana Lake, while urban wastes from Moose Jaw (pop. ~45,000) are diverted entirely from surface waters during most years.

because water quality changes are also influenced by climatic variability, agricultural activities, and lake management strategies, it has proven difficult to identify the unique effects of urban wastes on downstream lakes, or to evaluate how intervening depositional basins might eliminate urban effects by sequestering diffuse and point-source nutrients (cf. Dixit et al. 2000). Fortunately, recent technological developments have allowed the use of stable isotopes to quantify N inputs from urban wastewaters and therefore identify the timing and extent of their effects on recipient ecosystems (McClelland and Valiela 1998; Voss et al. 2000; Costanzo et al. 2001).

Field and laboratory methods—Wastewater samples were collected approximately bimonthly (2001–2002) from the City of Regina sewage treatment plant (STP) at three points during the treatment process (postprimary, post-secondary, posttertiary) to quantify how N and C isotopic signatures of effluent varied through time and in response to sewage treatment procedures. At the same time, water samples were collected from Wascana Creek at a station immediately downstream of the STP (Sta. 3, Fig. 2) to quantify temporal variation in $\delta^{15}\text{N}$ of water arising from dilution of effluent by lotic discharge. Finally, whole-water, periphyton, suspended POM, and sediment (bulk matrix)

samples were collected biweekly during summer 2002 (DOY 165–248) from 10 locations along Wascana Creek, the Qu'Appelle River and Pasqua Lake to quantify spatial patterns of N isotope distribution and transportation of urban N to downstream Pasqua Lake (Fig. 2).

Whole-water and effluent samples were prepared for stable isotope analysis following the procedures of Jones et al. (2004). In brief, liquid samples were passed sequentially through GF/C glass-fiber filters and 0.45- μm pore membrane filters before freeze-drying completely to a solid residue at 0.1 Pa. This dry matrix includes dissolved organic and inorganic (nitrate, nitrite, ammonia) sources of N. Experimental alteration of pH within the range 6.0–10.5 revealed that the $\delta^{15}\text{N}$ signal of dissolved substances was insensitive to alkalinity of stream water, and hence potential loss of volatile NH_3 . In contrast, POM samples for $\delta^{15}\text{N}$ analysis were isolated from GF/C filters (above) with forceps after complete drying of filters at 40°C. Similarly, periphyton samples were collected by scraping the algal matrix, usually containing filamentous chlorophytes and diatoms, from rocks collected in 0.1–0.25 m of water with clean bristle brushes. Excess water was removed, and concentrated periphyton suspensions were freeze dried before isotopic analyses. Finally, stream and littoral lake sediments (~0–10-cm burial depth) were collected by

Table 1. Morphometric and limnological characteristics of study lakes within the Qu'Appelle drainage basin. Limnological variables are means of the summer sampling period (DOY 130–248). Data from Hall et al. (1999a), Quinlan et al. (2002), Patoine et al. (2006), and unpubl. data. See Fig. 1 for lake location.

Lake	Longitude (°W)	Area (km ²)	Volume (m ³ × 10 ⁶)	Mean depth (m)	Conductivity (µS cm ⁻¹)	pH	Dissolved N (µg L ⁻¹)	Dissolved P (µg L ⁻¹)	N : P		Secchi depth (m)	Water residence (yr)
									(dissolved, by mass)	Chl <i>a</i> (µg L ⁻¹)		
Diefenbaker	106.63	430.0	9,400	21.9	510	8.4	331	28.2	29.7	5.0	3.4	1.5
Buffalo	105.30	29.1	87.5	3.0	602	8.5	524	33.9	20.3	29.5	1.1	0.7
Pound												
Last	105.14	226.6	1,807.2	7.9	1,844	8.7	874	57.8	31.5	13.3	2.2	12.6
Mountain												
Wascana	104.67	0.5	0.7	1.4	929	9.0	1449	360.0	6.5	42.4	0.9	0.05
Pasqua	104.00	20.2	120.8	6.0	913	8.9	1012	147.6	6.9	28.5	1.1	0.7
Echo	103.49	12.5	122.1	9.8								0.7
Mission	103.44	7.7	62.9	8.2								0.4
Katepwa	103.39	16.2	233.2	14.4	1,128	8.7	911	166.3	7.7	23.0	1.8	1.3
Crooked	102.44	15.0	120.9	8.1	1,189	8.7	881	117.0	12.1	28.4	1.5	0.5
Round	102.22	10.9	83.9	7.7								

Ekman grab sampler from 0.1–0.25 m of water, homogenized, and freeze-dried before quantification of N isotope content.

Historical changes in the $\delta^{15}\text{N}$ content of whole sediments from Qu'Appelle lakes were quantified by isotopic analysis of annually resolved cores collected in 1995, as well as from a new core collected from Wascana Lake in 2004. Detailed procedures for core collection, estimation of sediment age, and sediment storage are presented in Hall et al. (1999a,b), Dixit et al. (2000), and Quinlan et al. (2002). Briefly, sediments were collected by freeze corer and were analyzed for radioisotope activity (^{210}Pb) to establish core chronology. However, for the Wascana Lake reservoir, sediments were collected by piston corer, and ages were estimated as a linear function of burial depth and time since final reservoir inundation (1931), as marked by the presence of terrestrial plant roots in basal core sediments. Finally, a series of 62 gravity cores were collected from a predetermined grid within Pasqua Lake to quantify spatial variability of N and C isotopic ratios within the uppermost 10 mm of profundal lake sediment. In all cases, isotopic analyses were conducted on freeze-dried whole sediments.

Stable isotope content of all samples was quantified following Savage et al. (2004). All isolated samples were redried completely at 40°C before analysis and ~2 mg dry mass were packed into tin capsules before combustion in a NC2500 Elemental Analyzer (ThermoQuest, CE Instruments) and introduction of gases into a Thermoquest (Finnigan-MAT) Delta Plus^{XL} isotope ratio mass spectrometer. Nitrogen and carbon stable isotope ratios (precision $\pm 0.1\%$) are reported in the conventional δ notation with respect to atmospheric N ($\delta^{15}\text{N}$) or organic C reference material ($\delta^{13}\text{C}$).

Historical changes in algal abundance and gross community composition since ca. 1800 were quantified previously by analyzing fossil algal pigment concentrations in annually resolved cores of sediments from all Qu'Appelle lakes except Diefenbaker (Hall et al. 1999a,b; Dixit et al. 2000). Briefly, concentrations of carotenoid, Chl and derivative pigments were estimated with Hewlett-Packard models 1050 and 1100 high-performance liquid chromatography systems following the standard procedures detailed in Leavitt and Hodgson (2001). Biomarker concentrations (nmol pigment g⁻¹ organic matter) were calculated for pigments characteristic of total algal abundance (Chl *a*, pheophytin *a*, β -carotene), siliceous algae and some dinoflagellates (fucoxanthin), mainly diatoms (diatoxanthin), cryptophytes (alloxanthin), chlorophytes (Chl *b*, pheophytin *b*), chlorophytes and cyanobacteria (lutein-zeaxanthin), total cyanobacteria (echinenone), colonial cyanobacteria (myxoxanthophyll), *Nostocales* (canthaxanthin), and potentially N₂-fixing cyanobacteria (aphanizophyll). In this high-performance liquid chromatography system, carotenoids from *Aphanizomenon* (aphanizophyll), *Anabaena* (4-keto-myxoxanthophyll) and the Oscillatoria-ceae (oscillaxanthin) were incompletely resolved and were presented together as "aphanizophyll" (Hall et al. 1999b). Similarly, lutein (chlorophytes, higher plants) and zeaxanthin (cyanobacteria) were not separated and are pre-

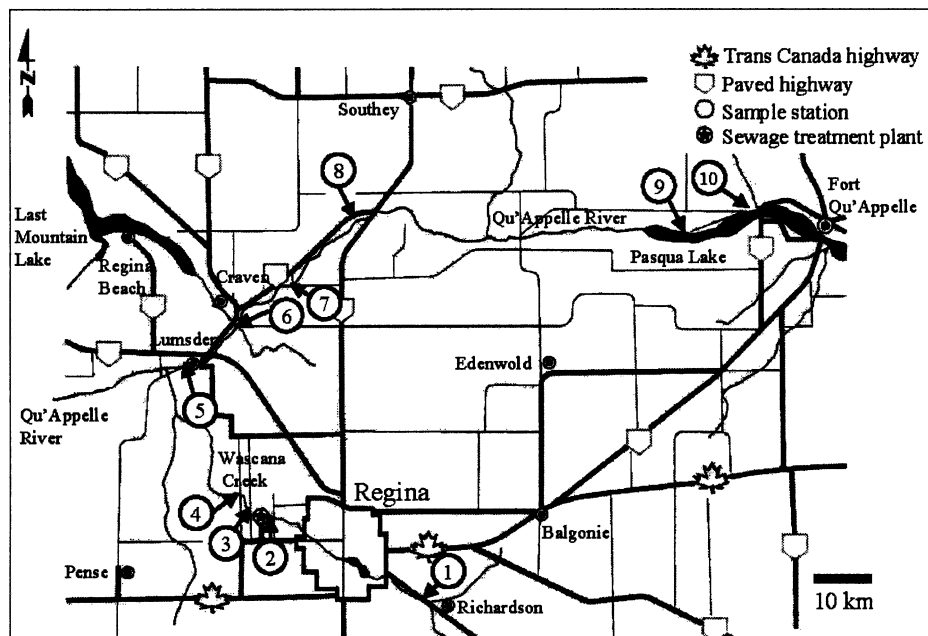


Fig. 2. Sampling locations (open circles 1–10) for isotopic analysis of dissolved N, periphyton, POM, and bulk sediments in Wascana Creek (Sta. 1–4), the Qu'Appelle River (Sta. 5–8), and Pasqua Lake littoral zone (Sta. 9–10) during summer of 2002. The STP (solid circle) is located northwest of Regina, between Sta. 2 and 3. Station 3 was also sampled approximately bimonthly during 2001.

sented together as lutein–zeaxanthin (“bloom-forming algae”).

Numerical analysis—Statistical analyses were restricted to simple linear regressions of predictor and response variables, following appropriate transformation (usually not needed) to normalize variance.

Lake-specific N mass-balance budgets were developed for Pasqua, Echo, Mission, and Katepwa lakes to determine whether these sequential basins (Fig. 1) were capable of sequestering sufficient N through sedimentation to ameliorate effects of urban wastewaters. Details of our mass-balance approach and its assumptions are presented in Patoine et al. (2006) as the maximum net N fixation method and are reviewed briefly below. Unless otherwise noted, rate estimates for the summer sampling period (DOY 130–234) were calculated with mean values from the past 2–10 years.

Maximum net N fixation in Pasqua and Katepwa lakes was estimated from basin-specific estimates of standing stock of total N (TN) in spring and from changes in $\delta^{15}\text{N}$ -POM. This approach assumes that seasonal declines in $\delta^{15}\text{N}$ resulted solely from the inputs of atmospherically derived N_2 with an isotopic signature ($\leq 0\text{‰}$) distinct from that of other local N sources (~ 10 – 15‰ ; Patoine et al. 2006). Relative rates of N_2 fixation (as % TN inputs) for Echo and Mission Lakes, sites that lacked detailed isotopic data, were interpolated from measurements of Pasqua Lake (0% TN fixed) and Katepwa Lake (41% TN fixed). Nitrogen loss through sedimentation was computed for each lake using previously published, lake-specific estimates of permanent sediment accumulation ($\text{g cm}^{-2} \text{ yr}^{-1}$) and N content of

sediments (% dry mass) (Hall et al. 1999a,b; Quinlan et al. 2002) and lake area (km^2). Nitrogen loss through river outflow was estimated as the product of mean concentrations of TN standing stocks (mg N L^{-1}) and mean outflow river discharge rates ($\text{m}^3 \text{ s}^{-1}$). In contrast, N gains through river inflow were estimated directly from mean measurements of TN concentrations (mg N L^{-1}) and river inflow rates ($\text{m}^3 \text{ s}^{-1}$). Other unmeasured inputs of N were estimated by mass difference so that total gains (N_2 fixation, river inflow, other sources) and losses (sedimentation, outflow) were balanced for each lake.

Finally, a modified version of the two-box mixing model of Tucker et al. (1999) was used to estimate the proportion of N in Pasqua Lake derived from the City of Regina following Savage et al. (2004). However, to avoid bias associated with unmeasured differences in N isotope ratios among individual pools of dissolved (nitrate, nitrite, organic) and particulate N (POM, periphyton), calculations were based mainly on sedimentary $\delta^{15}\text{N}$ values from Pasqua Lake and unimpacted headwater sites. In this approach, we assumed that the average $\delta^{15}\text{N}$ of filtered effluent after tertiary treatment in 2002 ($16.2 \pm 2.0\text{‰}$) was representative of all urban N loading during the 20th century, as suggested by direct comparison of dissolved $\delta^{15}\text{N}$ values after primary, secondary, and tertiary wastewater treatment (see below). We further assumed that background $\delta^{15}\text{N}$ values were $\sim 6.5\text{‰}$, the value recorded in organic lake sediments from Pasqua Lake before European colonization, sedimentary $\delta^{15}\text{N}$ signals of headwater reference lakes during the 20th century (Last Mountain, Buffalo Pound, Wascana), and in periphyton and POM samples from Wascana Creek upstream of the Regina STP

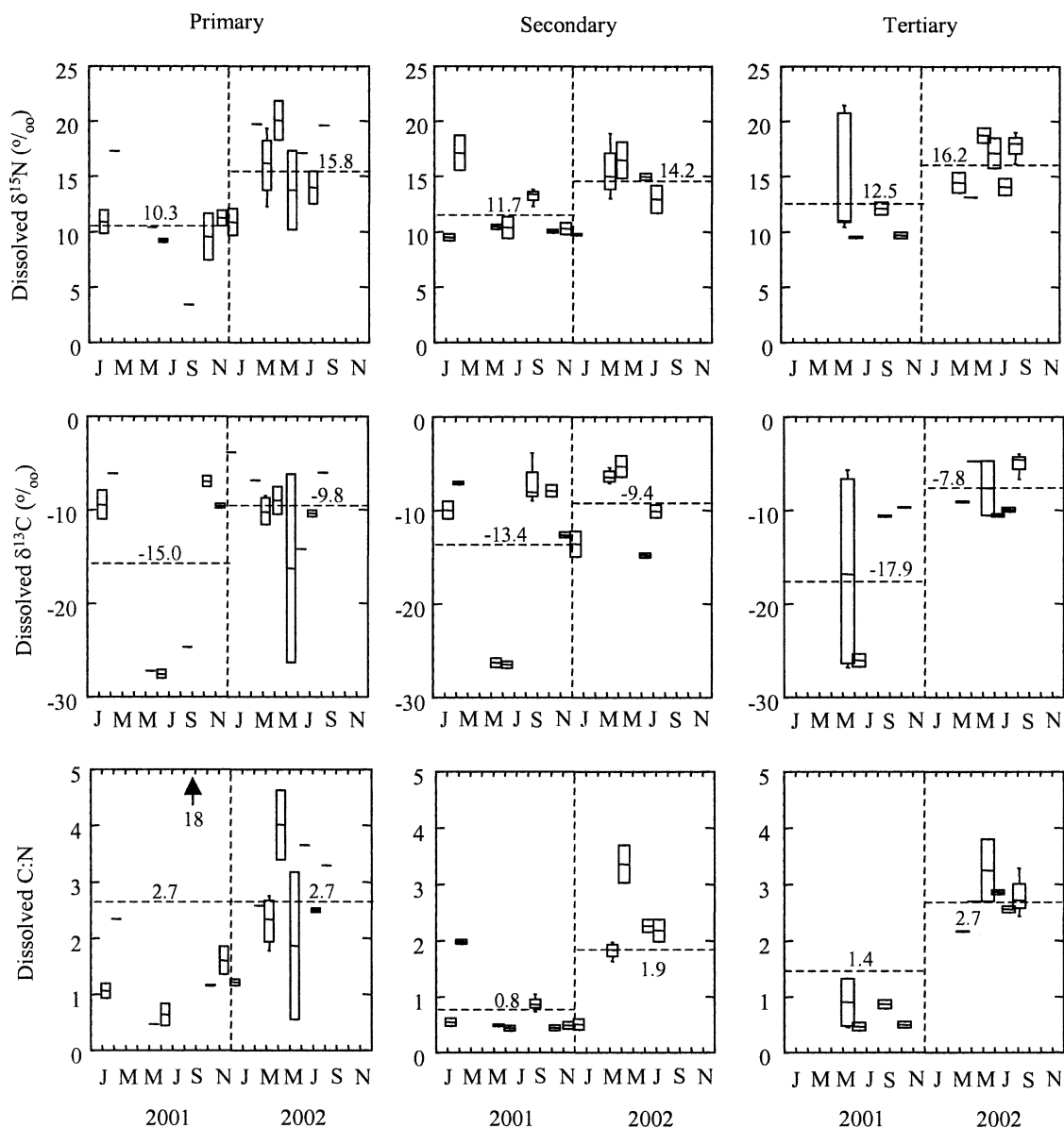


Fig. 3. Box-whisker plots for mean (horizontal line) and standard deviation (box) of $\delta^{15}\text{N}$ (top row), $\delta^{13}\text{C}$ (middle row), and elemental C : N mass ratios (bottom row) of dissolved substances in effluent subject to primary (left column), secondary (center column) and tertiary (right column) wastewater treatment. Annual averages are labeled with dashed lines; outliers are usually omitted.

outfall. However, because $\delta^{15}\text{N}$ of the principal inputs to the model (effluent, background, impacted lake sediment) varied 1–2‰ among years or sites (*see below*), output of mixing models was also presented as a range of estimates calculated using extreme values for each model parameter (e.g., effluent range 14.2–18.2‰).

Results

Transport of urban N—Stable isotope ratios and elemental composition of filtered wastewater exhibited consistent variation among years, but were unaffected by the degree to which effluent had been treated (Fig. 3). On average ($\pm\text{SD}$), $\delta^{15}\text{N}$ values were $3.9 \pm 1.5\text{‰}$ greater in

2002 than in 2001, although intra-annual variation was equally great in both years. Similarly, $\delta^{13}\text{C}$ was enriched an average of $6.4 \pm 3.2\text{‰}$ in 2002 relative to the preceding year, whereas elemental ratios of dissolved C : N were generally low (1–3, by mass) and variable in both years. Despite relatively high variation within individual years, effluent analyses revealed no evidence of pronounced seasonal cycles in isotopic signatures or elemental composition of dissolved materials (Fig. 3). In contrast, $\delta^{15}\text{N}$ of dissolved materials in Wascana Creek immediately downstream ($\sim 4\text{ km}$) of the STP outfall showed obvious seasonality, with depleted values ($\sim 2\text{--}5\text{‰}$) during winter, and early spring and elevated ($\sim 12\text{--}22\text{‰}$) signatures thereafter (Fig. 4a). Although dissolved $\delta^{15}\text{N}$ values varied

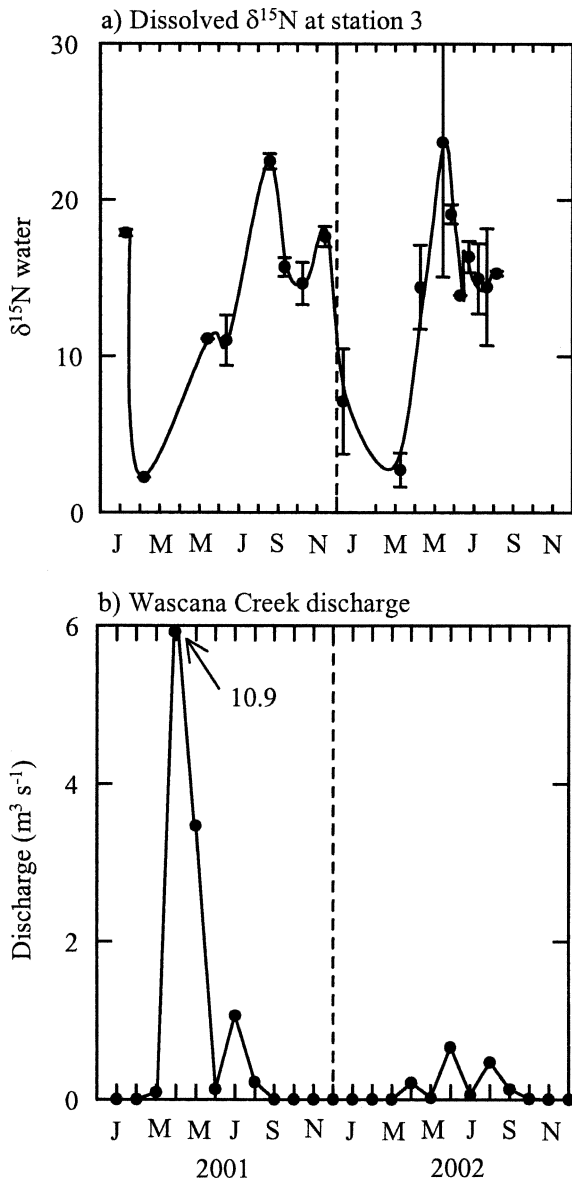


Fig. 4. (a) Seasonal variability of $\delta^{15}\text{N}$ from dissolved substances in Wascana Creek water at Sta. 3 (Fig. 2), immediately downstream of the City of Regina STP, and (b) of Wascana Creek discharge between Sta. 2 and 3 during 2001 and 2002. Mean values and standard deviations are indicated.

inversely with river discharge in 2001, there was little obvious relationship with hydrology during 2002 (Fig. 4b).

Enriched N isotopes from the Regina STP rapidly labeled the dissolved N pool within Wascana Creek (Fig. 5a). Dissolved $\delta^{15}\text{N}$ values ranged 0.2–11‰ (mean \pm SD 7.5 ± 2.6 ‰) at sites upstream of the STP (dashed line), but increased by an additional 10–15‰ immediately downstream of the effluent outfall. In general, the degree of enrichment was greatest in midsummer, when creek flow was low (Fig. 4b) and composed mainly of urban wastewater. Similar patterns of enrichment were noted for periphyton (Fig. 5b), although substantial downstream enrichment with ^{15}N was not recorded until nearly 100 km downstream of the STP. Maximal isotopic ratios

of POM were delayed even further, usually reaching greatest values at locations within Pasqua Lake (>150 km; Fig. 5c). Although $\delta^{15}\text{N}$ signatures of periphyton (6.3 ± 2.4 ‰) and POM (5.5 ± 2.2 ‰) were similar at stations upstream of the STP, POM was less enriched (8.1 ± 5.5 ‰) than periphyton (13.0 ± 6.1 ‰) at downstream locations within Wascana Creek and the Qu'Appelle River (Sta. 5–8; 50–150 km from STP). Similarly, there was little enrichment of sediment substrates within either Wascana Creek (Sta. 3–4) or the Qu'Appelle River. Instead, only the littoral sediments of Pasqua Lake revealed elevated $\delta^{15}\text{N}$ values (9.9 ± 2.3 ‰) relative to those at stream headwater locations (Fig. 5d).

Historical changes of sedimentary $\delta^{15}\text{N}$ —Sedimentary $\delta^{15}\text{N}$ increased from background levels of ~ 6.5 ‰ before 1900 to ~ 14.0 ‰ during the 1990s at Pasqua Lake, the first basin downstream of the City of Regina (Fig. 6a). In contrast, upstream reference lakes not receiving urban effluent either declined ~ 1 ‰ during ca. 1925–1950 (Last Mountain, Buffalo Pound), or remained stable during the 20th century (Wascana). Sediments in lakes downstream of Pasqua Lake also exhibited significant enrichment with ^{15}N , although the extent of $\delta^{15}\text{N}$ increase declined along a gradient from west to east (Fig. 6b). Most of this reduction occurred within the central chain of four “Fishing Lakes” (Pasqua, Echo, Mission, Katepwa), such that the sedimentary $\delta^{15}\text{N}$ signature of easternmost Round Lake exhibited little historical change since 1850 (Fig. 6b) and had a modern isotopic signal characteristic of headwater basins (Fig. 6c). Consistent with this observation, mass-balance calculations (Table 2) showed that 41–80% of TN inputs to the Fishing Lakes were retained in the sediments of each basin, while biological fixation ($\delta^{15}\text{N} \leq 0$ ‰) added 0–41% of TN inputs to each basin.

Spatial analysis of surficial (0–10 mm) sediments within Pasqua Lake suggested that isotopic signatures were consistently elevated (12.5 ± 1.5 ‰) in deep-water regions (>8 m) of the eastern half of the lake, but were depleted to ~ 7 ‰ in shallow portions (<4 m) of western subbasins (Fig. 7). For example, sedimentary $\delta^{15}\text{N}$ exhibited values characteristic of upstream riverine sediments (Fig. 5d) throughout the westernmost basin of Pasqua Lake, a region of <2 m depth, low organic matter content (~ 4 % total C) and low concentrations of fossil pigments (data not shown). In contrast, enriched $\delta^{15}\text{N}$ (Fig. 7a) and $\delta^{13}\text{C}$ values (Fig. 7b) were recorded for littoral sediments of the south shore of the central basin ($\sim 104.00^\circ\text{W}$). Here, repeated Ekman grab samples contained virtually nothing but large (10–15 cm), disarticulated bivalve shells (species unknown), suggesting that benthic deposits had been modified extensively by burrowing fauna. However, despite inhomogeneities associated with shallow waters, sedimentary isotopic values for both C and N varied by only ~ 1 ‰ throughout much of the profundal region.

Sources and consequences of N loading—Changes in sedimentary $\delta^{15}\text{N}$ of Pasqua Lake during the 20th century were strongly and positively correlated ($r^2 = 0.84$, $p < 0.0001$) with the total dissolved N released by the City of

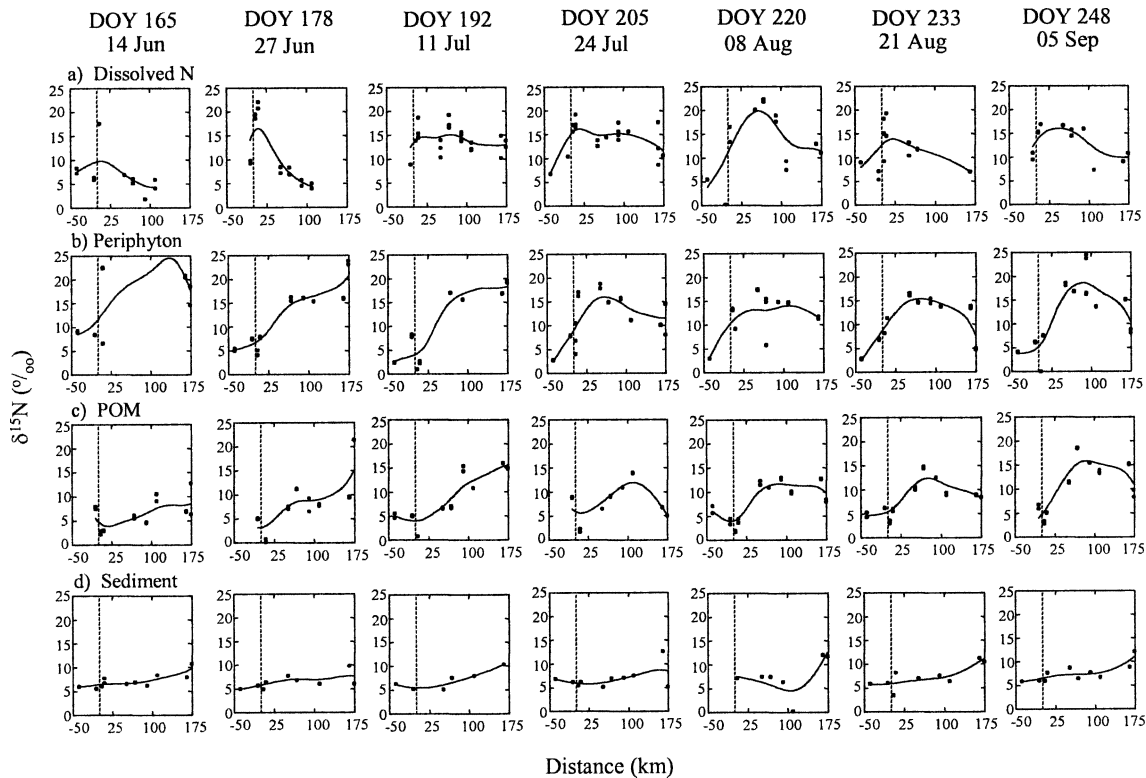


Fig. 5. Spatial variability of $\delta^{15}\text{N}$ from (a) dissolved N, (b) periphyton, (c) POM, and (d) stream or lake sediments in 0.1–0.25 m of water during 2002. Vertical dashed line at 0 km represents the Regina STP. Sites from -50 to 50 km are located on Wascana Creek, those 50 – 150 km are within the Qu'Appelle River, and those >150 km are within Pasqua Lake. See Fig. 2 for precise sampling locations. Samples were collected approximately biweekly between DOY 165 and 248. Duplicate samples were collected and analysis attempted for all stations and dates. Distance-weighted least squares regression lines were used to identify overall spatial trends.

Regina STP to Wascana Creek (Fig. 8a). Overall, variability around the linear regression was greatest at elevated N loadings, suggesting that the data could also be fit with a parabolic function whose asymptote was equivalent to the $\delta^{15}\text{N}$ signature of wastewater N. Alternately, variation around the regression may have arisen from inter-annual changes in effluent $\delta^{15}\text{N}$ signature (Fig. 4) or from variable dilution within streams (Fig. 3a) during recent decades of elevated urban N loading (Fig. 5). Regardless, historical changes in the abundance of bloom-forming chlorophyte and cyanobacterial algae in Pasqua Lake (as lutein-zeaxanthin) were linearly correlated with both urban N loading since ca. 1880 (log transformed; $r^2 = 0.46$, $p < 0.0001$) and with changes in sedimentary $\delta^{15}\text{N}$ since ca. 1800 (Fig. 8b), but not with historical inputs of P from cities or farms (Hall et al. 1999b). Similarly, total algal abundance (as β -carotene) has increased nearly 300% in Pasqua Lake relative to levels seen before intensive European colonization (Fig. 8c). As was the case with sedimentary $\delta^{15}\text{N}$ values (Fig. 6b), large historical changes in total algal abundance were limited to the Fishing Lakes chain ($\sim 104.0^\circ\text{W}$).

Analysis of sedimentary stable isotope ratios using a two-box mixing model showed that inputs of urban wastewater accounted for an average of 71.1% of total ecosystem N in Pasqua Lake, the first site to receive wastewater from the City of Regina. This proportion was based on the

assumptions that tertiary-processed effluent had a consistent $\delta^{15}\text{N}$ signature of $16.2 \pm 2.0\text{‰}$ (Fig. 3), that background $\delta^{15}\text{N}$ values were $\sim 6.5 \pm 1.0\text{‰}$ (Figs. 5, 6), and that modern isotopic ratios in Pasqua Lake have averaged $13.4 \pm 0.9\text{‰}$ since 1975 (Fig. 6c). The approach also assumed that the $\delta^{15}\text{N}$ of effluent was assimilated into organic (particulate) matter without substantial fractionation, as confirmed by comparison of mean $\delta^{15}\text{N}$ values of dissolved N ($13.0 \pm 4.8\text{‰}$) and periphyton ($14.4 \pm 5.3\text{‰}$) in rivers downstream of the STP outfall, and of dissolved N ($11.7 \pm 2.8\text{‰}$) and POM (mainly algae; $10.5 \pm 4.1\text{‰}$) values within Pasqua Lake. Similarly, using extreme values for each model parameter produced a range of potential N contributions from urban sources of 46.7–100% of total ecosystem N. However, despite such large proportions, these estimates may underestimate the importance of urban N because the mixing models do not include estimates of biological fixation of atmospheric N_2 , which is depleted ($\leq 0\text{‰}$) relative to other N inputs (Patoine et al. 2005).

Discussion

Analysis of stable isotope ratios in water, periphyton, POM, and sediment demonstrated that N within tertiary-treated urban wastewater was effectively transported to downstream lakes (Fig. 5), where it resulted in a 300% increase in lake production (Fig. 8). Although ^{15}N -enriched

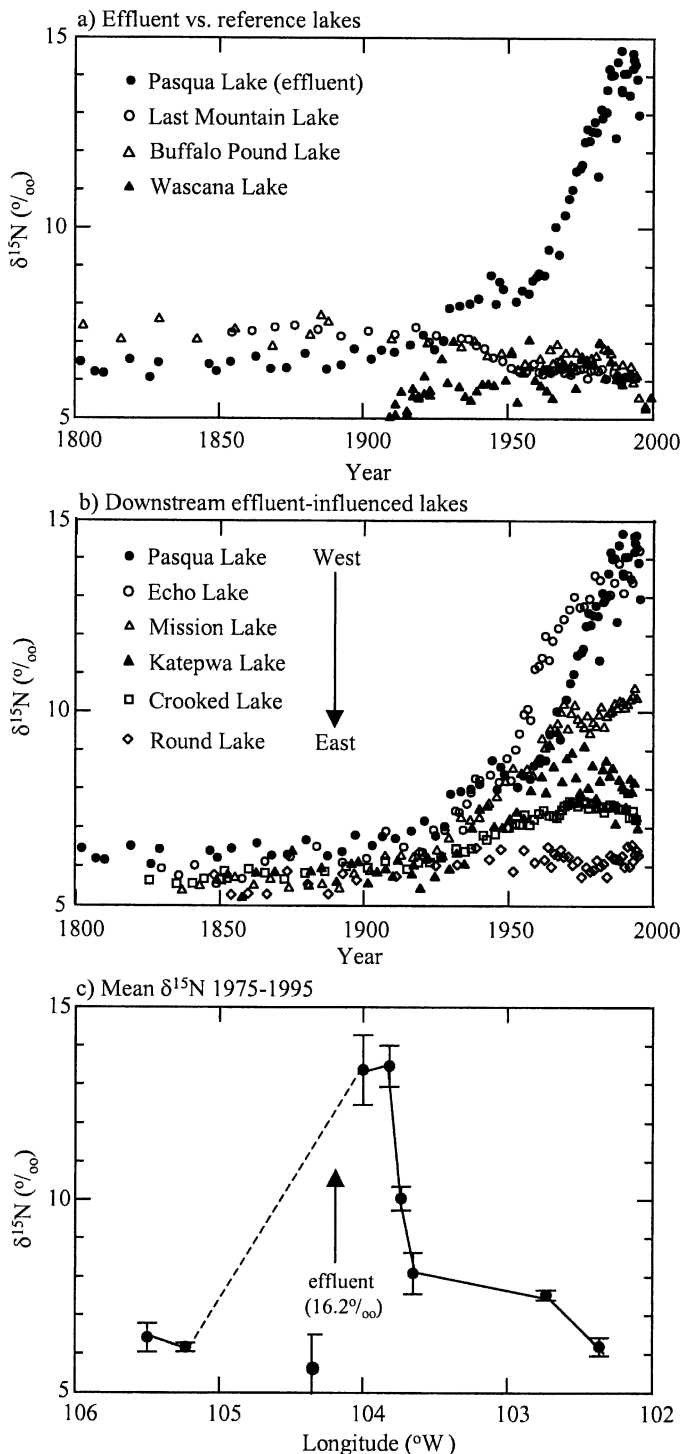


Fig. 6. Historical changes in (a) $\delta^{15}\text{N}$ of bulk sediments from Pasqua Lake and its upstream reference ecosystems, and (b) from Qu'Appelle lakes receiving urban wastewaters. (c) Mean \pm SD $\delta^{15}\text{N}$ values for sediments deposited during 1975–1995.

effluent (Fig. 3) labeled pools of dissolved N, periphyton and, secondarily, POM in flowing waters by 10–15‰ (Figs. 4, 5), urban N was not incorporated into stream sediments (Fig. 5d), suggesting that lotic ecosystems stored little N from wastewaters. Instead, sedimentary $\delta^{15}\text{N}$

signatures and fossil pigment concentrations in downstream Pasqua Lake, but not three upstream reference ecosystems, increased as a linear function of the TN released to lake-inflow streams by the City of Regina (Fig. 8). However, the effect of urban effluent declined rapidly in a chain of downstream lakes (Figs. 7, 8) because up to 80% of N inputs were sequestered permanently within sediments of each lake basin (Table 2). Together, these patterns demonstrate that although urban N can directly degrade water quality, these prairie lakes can eliminate downstream effects of urbanization through storage of wastewater N in their sediments (*see also* Dixit et al. 2000; Quinlan et al. 2002).

Transport of urban N—Isotopic and elemental characteristics of urban effluent varied little as a function of the degree of wastewater treatment, despite exhibiting modest temporal variability within and among years (Fig. 3). In general, $\delta^{15}\text{N}$ values of dissolved N were similar to those recorded for effluent from other STP that use chemical precipitation to remove P (Bedard-Haughn et al. 2003). In these treatment systems, isotopic enrichment of N arises mainly from ammonia volatilization and denitrification during sewage collection and processing, whereas increased $\delta^{13}\text{C}$ values may reflect C-4 plant material in wastes or the presence of carbonates (~ 0 to -10%). Similarly, low C : N ratios are consistent with the chemical treatment process to remove excess P and C, but not N. Presently, N outputs from Regina are at an all-time maximum, whereas P loading to Wascana Creek is similar to levels recorded in the 1930s (*see* fig. 2f in Hall et al. 1999b).

Interannual variability in effluent isotope values likely arose from changes in source material composition, as $\delta^{15}\text{N}$ values were not enriched further after secondary or tertiary treatment (Fig. 3). As shown elsewhere (Heikoop et al. 2000; deBruyn et al. 2003; Gaston and Suthers 2004), these organic fractions can exhibit low ^{15}N content relative to that of dissolved inorganic N, and can lead to low $\delta^{15}\text{N}$ values of whole effluent when organic N is a high proportion of TN levels (e.g., primary-processed sewage). Similarly, newer BNR technologies can increase $\delta^{15}\text{N}$ values of effluent to over 30‰ (e.g., Savage et al. 2004). However, BNR processes are not used by the City of Regina, and therefore the $\delta^{15}\text{N}$ values recorded for effluent during 2001–2002 are likely to be representative of urban waste signatures during much of the 20th century, particularly given that the 175-km flow path to Pasqua Lake may have favored transport of dissolved over suspended particulate N.

Although effluent $\delta^{15}\text{N}$ exhibited little seasonality, analysis of dissolved N isotope ratios within Wascana Creek immediately downstream of the STP revealed pronounced annual cycles of ^{15}N enrichment, with low $\delta^{15}\text{N}$ values during late winter and spring (Fig. 4a). Such variability should be common in many north-temperate lotic ecosystems receiving effluent and likely arise from several simultaneous processes. First, effluent $\delta^{15}\text{N}$ values may have been diluted by inputs of depleted N from background sources, such as inorganic fertilizers ($\sim 0\%$) that are usually lost from upstream farmland during snow

Table 2. Mean N mass balance for the Fishing Lake chain of the Qu'Appelle Valley, Saskatchewan, calculated for DOY 137–233 following Patoine et al. (2006). Nitrogen inflow and outflow was estimated as the product of total N (TN) concentrations 2003–2004 (except Katepwa Lake 1994–2003) and river discharge (1994–2002). Maximum net N₂ fixation was estimated from seasonal changes in $\delta^{15}\text{N}$ -POM (1994–2003) and initial TN standing stocks. Inputs of N unrelated to N₂ fixation or inflow (“other inputs”) were estimated as [total outputs – (N fixed + N inflow)]. Nitrogen sedimentation was estimated as mass accumulation rates \times %N content, 1985–1995. All units are Mg (megagrams) of N. See “Material and methods” for details.

Nitrogen	Pasqua	Echo	Mission	Katepwa
Average seasonal N standing stock, Mg	254	236	88	236
N inflow, Mg (% of total inputs)	151(45%)	157(43%)	171(50%)	93(19%)
Other N inputs, Mg (% of total inputs)	187(55%)	156(43%)	76(22%)	195(40%)
Net N fixation, Mg (% of total inputs)	0(0%)	50(14%)	93(27%)	199(41%)
N sedimentation, Mg (% of total outputs)	139(41%)	180(50%)	207(61%)	391(80%)
N outflow, Mg (% of total outputs)	199(59%)	183(50%)	133(39%)	96(20%)

melt and the spring river-discharge maximum (Fig. 4b). Second, because dissolved organic matter (as dissolved organic carbon [DOC]) concentrations are typically greatest in Wascana Lake immediately near ice-out ($\sim 200\%$ mean summer DOC; Table 1) and because this lake serves as the source of creek water above the STP, seasonal variations in organic N flux may have influenced $\delta^{15}\text{N}$ signatures of the dissolved N pool within the creek. Finally, TN output from the STP varies twofold among months as a result of variability in wastewater volume and raw sewage N content (City of Regina unpubl. data) and thereby alters the relative importance of urban inputs to the overall N budget of Wascana Creek.

Regardless of the precise mechanism that produced low $\delta^{15}\text{N}$ values during spring, isotopic ratios of dissolved N during the remainder of the year were similar to those of processed wastewater. In fact, application of a two-box mixing model using $\delta^{15}\text{N}$ values of dissolved N in upstream water ($6.8 \pm 3.6\text{‰}$), effluent ($16.2 \pm 2.0\text{‰}$), and creek water 4 km downstream of the outfall ($14.8 \pm 2.6\text{‰}$) (Fig. 5a) revealed that urban N accounted for $\sim 85\%$ of total stream N during summer 2002, similar to proportions ($\sim 80\%$) recorded by urban engineers on the basis of TN content of Wascana Creek during October 2004 (City of Regina unpubl. data). In contrast, mixing models suggest that urban N accounts for less than 10% of TN content during spring, consistent with mass balances based solely on effluent volume and hydrologic discharge (Fig. 4b). Such high seasonality of isotopic signatures is rarely recognized in ecological or hydrological studies of N flux, yet can significantly alter outcomes of mixing model analyses.

Comparative analysis of the N isotope contents of dissolved, periphytic, suspended particulate, and sedimentary N pools suggested that these prairie rivers do not permanently store nitrogenous wastes from cities (Fig. 5). Instead, lotic ecosystems apparently act as effective conduits of urban N to downstream ecosystems (Fig. 6). Without quantification of the TN content of each particulate and dissolved pool, it remains difficult to evaluate the relative importance of individual pathways of N transport to Pasqua Lake. However, analysis of

spatial patterns of $\delta^{15}\text{N}$ suggested that N flow into lakes is mainly through dissolved and periphytic vectors. For example, $\delta^{15}\text{N}$ values of dissolved N were usually greatest immediately downstream of the STP, whereas maximal ^{15}N content of lotic periphyton and POM were recorded 50–100 (Fig. 5b) and 75–100 km (Fig. 5c) downstream of Regina, respectively. Such sequential patterns of enrichment, combined with the observation that mean $\delta^{15}\text{N}$ signatures of stream periphyton ($13.0 \pm 6.1\text{‰}$) were greater than those of POM ($8.1 \pm 5.5\text{‰}$) downstream of Regina, suggest that urban N was rapidly accumulated into periphyton, but not suspended matter. Further, because periphyton is removed each year by scouring in spring (e.g., irregular presence during DOY 165–192 in Fig. 5b), and because enriched N isotopes do not accumulate in lotic sediments (Fig. 5d), we infer that wastewater N is transported efficiently to downstream lakes.

Overall, there was little evidence of substantial net fractionation of N isotopes during transportation within lotic ecosystems. Previous studies have variously shown that uptake of NO₃ and NH₄ by algae, NH₃ volatilization, and denitrification in stream sediments may substantially alter isotopic ratios of dissolved and organic N pools (reviewed in Waser et al. 1998; Robinson 2001; Bedard-Haughn et al. 2003), particularly when dissolved N concentrations are in excess of biotic demands. However, although periphyton $\delta^{15}\text{N}$ values were slightly lower ($6.3 \pm 2.4\text{‰}$) than dissolved N values ($7.5 \pm 2.6\text{‰}$) upstream of the STP, suggesting a preferential uptake of ^{14}N by benthic biota, this pattern was not evident in downstream samples ($13.0 \pm 6.1\text{‰}$, $13.1 \pm 5.1\text{‰}$, respectively), despite a fivefold increase in TN concentration (*see above*). Similarly, although volatilization of NH₃ would be expected to increase $\delta^{15}\text{N}$ of dissolved inorganic N by over 10%, maximal enrichment of dissolved N was recorded near the STP, with reduced values in the lower reaches of Wascana Creek and in the Qu'Appelle River (Fig. 5a). Part of this decline undoubtedly reflects mixing of enriched Wascana Creek water with ^{15}N -depleted water from the Qu'Appelle River headwaters (*see below*) and might compensate partly for enrichment associated with loss of NH₃. However, the

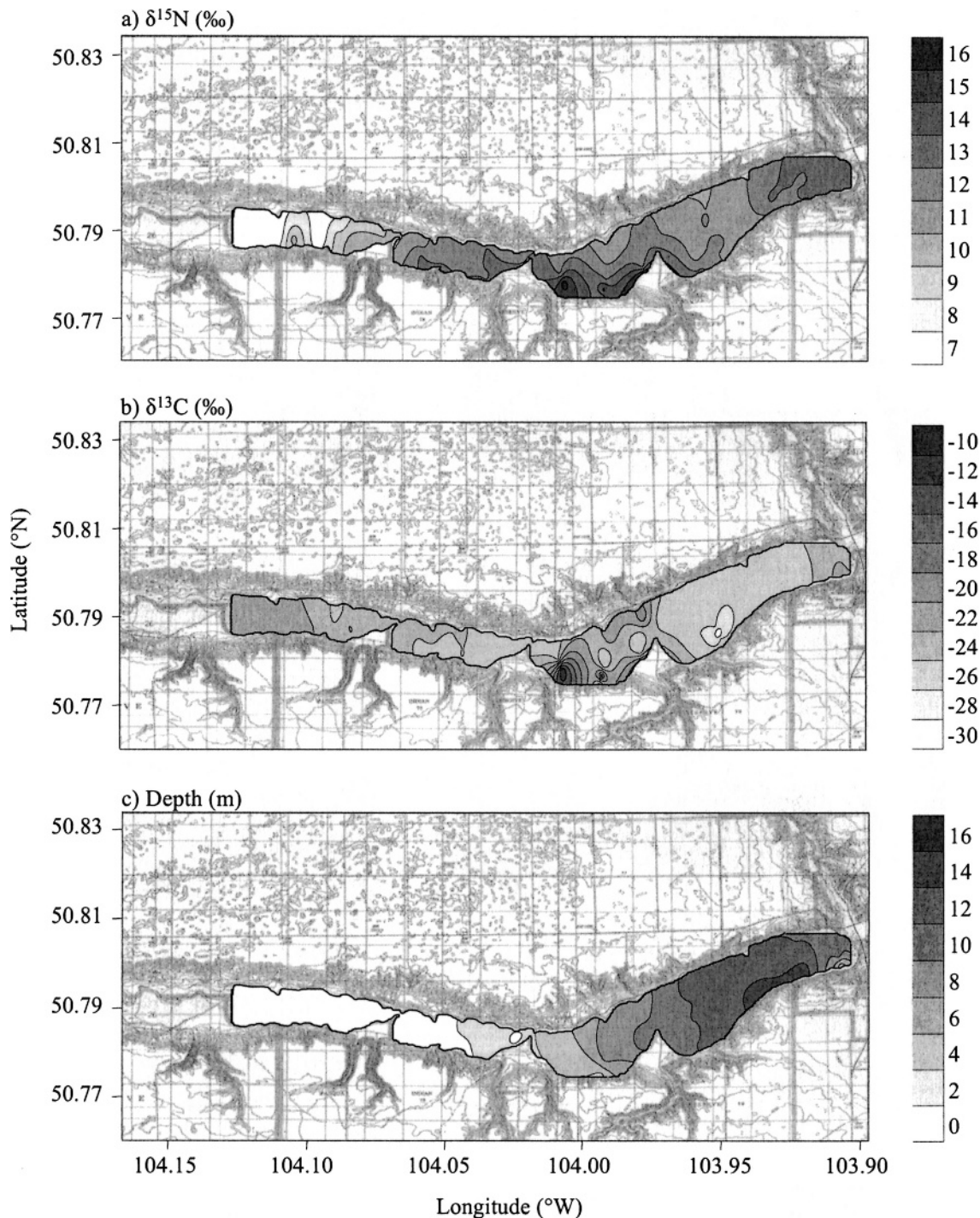


Fig. 7. Spatial variability of (a) surface sedimentary (0–10 cm depth) $\delta^{15}\text{N}$, (b) sedimentary $\delta^{13}\text{C}$, and (c) water-column depth in Pasqua Lake during summer 2001.

short transit time of water in these lotic ecosystems, usually <3 weeks from Regina to Pasqua Lake, likely reduced the importance of NH_3 volatilization relative to discharge as the main export process for the creek. For similar reasons of rapid transit and lack of pronounced increase in periphytic or sedimentary $\delta^{15}\text{N}$ within the Qu'Appelle River (50–150 km from the STP; Figs. 5b, 5d), we also infer that microbial denitrification did not greatly transform N isotope

ratios before reaching Pasqua Lake. Under normal circumstances, denitrification increases $\delta^{15}\text{N}$ of organic matter by 10–20‰ relative to dissolved N pools (Bedard-Haughn et al. 2003). Instead, patterns of ^{15}N enrichment and transportation are more consistent with lotic ecosystems acting as inert conduits of N to downstream lakes.

Several lines of evidence suggest that N within the Qu'Appelle River was not greatly enriched with ^{15}N before

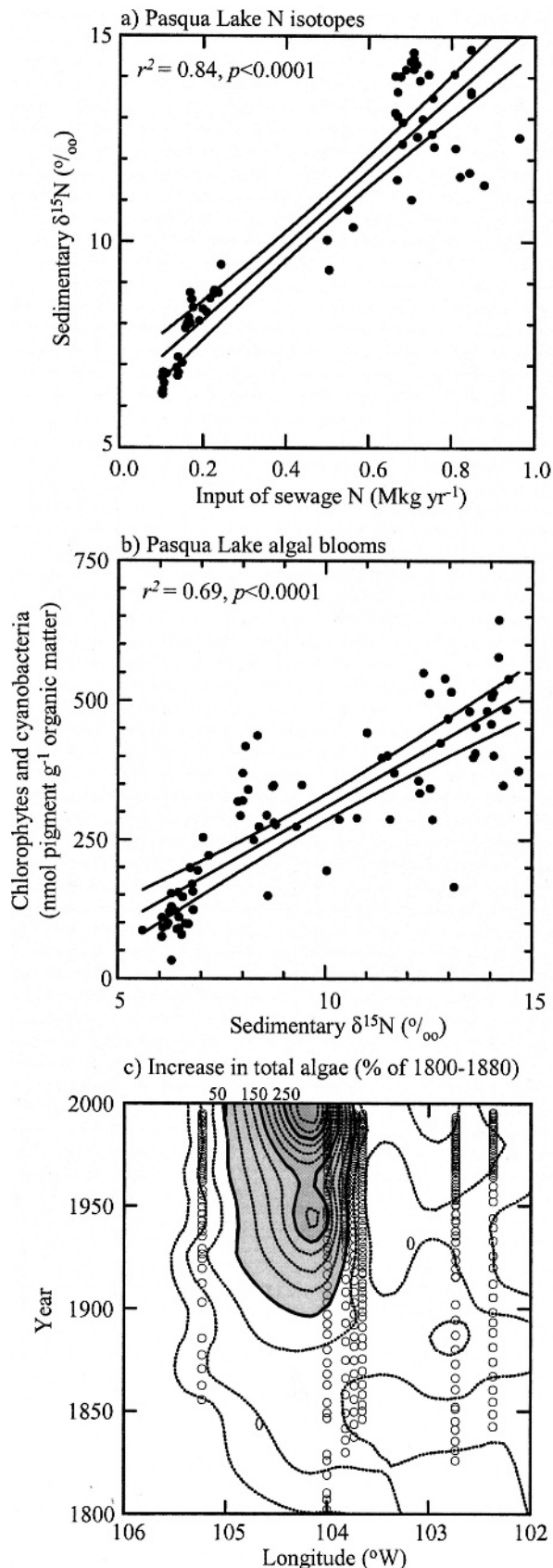


Fig. 8. Linear regression of sedimentary $\delta^{15}\text{N}$ from Pasqua Lake as a function of (a) total N efflux from the City of Regina

confluence with Wascana Creek, such as can occur in other agricultural catchments (Anderson and Cabana 2005). First, analysis of sedimentary N isotopes from Buffalo Pound Lake, the immediate source of water for the Qu'Appelle River (Fig. 1), showed that $\delta^{15}\text{N}$ values declined 1‰ during the 20th century to values ($6.4 \pm 0.4\text{‰}$) typical of unenriched systems, including other undisturbed headwater lakes (Fig. 6a), Wascana Creek upstream of the STP ($7.5 \pm 2.6\text{‰}$; Fig. 5a), and POM collected from Wascana Lake during summers of 1996–2004 ($5.5 \pm 2.0\text{‰}$; Patoine et al. 2006). Second, $\delta^{15}\text{N}$ values of dissolved substances within Wascana Creek usually declined downstream of the river confluence (>50 km; Fig. 5a), especially during spring and early summer when discharge was greatest (Fig. 4b vs. Fig. 5a). Finally, urban wastes from Moose Jaw have been entirely diverted from the Moose Jaw Creek tributary of the Qu'Appelle River (Fig. 1) since the early 1970s, except in late fall, when sewage lagoons reach capacity and exceptional precipitation occurs. Consequently, preliminary analysis of dissolved and periphytic $\delta^{15}\text{N}$ signatures in Moose Jaw Creek during summer 2004 revealed a range of 3–10‰, similar to background values of Wascana Creek.

N sequestration in lake sediments—Past algal abundance and sedimentary $\delta^{15}\text{N}$ values in Pasqua Lake increased as a linear function of TN inputs from the City of Regina (Fig. 8). Overall, the degree of isotopic enrichment and effects on Pasqua Lake were similar to those recorded for other effluent-impacted lakes (Teranes and Bernasconi 2000; Ogawa et al. 2001; Renberg et al. 2001) and estuaries (Risk and Erdmann 2000; Voss et al. 2000; Kauppila et al. 2005), especially those in which algal growth is limited by N supply. As in many prairie lakes (Barica 1987), concentrations of dissolved P are elevated in Qu'Appelle Valley systems (Table 1), reflecting the naturally high P supply from regional soils (Klassen 1989; Kenney 1990). As a result, N : P ratios are often low in downstream lakes (Soranno et al. 1999), especially in late summer, and N_2 -fixing cyanobacteria are both presently (Graham 1997; Patoine et al. 2005) and historically abundant in Qu'Appelle lakes (Hall et al. 1999a,b; Dixit et al. 2000).

Profundal sediments of Pasqua and downstream lakes were likely enriched with ^{15}N because algal growth is N-limited during summer (Hall et al. 1999b; Dixit et al. 2000; Patoine et al. 2005) and because organic matter sedimentation accounts for 41–80% of all N export from these lakes (Table 2). Consistent with such an algal-transport mecha-

←

1875–1995, and (b) as a predictor of past changes in the abundance of bloom-forming algae (chlorophytes, cyanobacteria; as nmol fossil lutein–zeaxanthin g^{-1} organic matter) during 1780–1995. (c) Total algal abundance in Pasqua Lake (as ubiquitous fossil β -carotene at 104.0°W) increased up to 300% above values recorded from sediments that predated substantial European activity (i.e., ca. 1800–1880). Contour lines were interpolated between lakes using distance-weighted least-squares regression in SYSTAT v. 10. Results from Wascana Lake (deepened in 1931) are not presented.

nism, the $\delta^{15}\text{N}$ value of deep-water surface sediments (Fig. 7) was midpoint ($12.8 \pm 1.5\text{‰}$) between mean signatures of POM ($11.1 \pm 4.2\text{‰}$) and periphyton ($14.7 \pm 5.0\text{‰}$) recorded during 2002 (Fig. 5). Further, when it is recognized that invertebrate remains are common in Qu'Appelle sediments (Quinlan et al. 2002), that zooplankton are 2–7‰ more enriched than POM (Patoine et al. 2005), and that POM values during winter and early spring are often greater than those recorded during summer (Patoine et al. 2005), we conclude that sedimentary N isotope ratios reflect the mean isotopic signatures of organic matter within the overlying water column (*see also* Teranes and Bernasconi 2000). Although organic matter degradation can alter $\delta^{15}\text{N}$ values in sediments relative to water-column values (Voss et al. 1997; Lehmann et al. 2002), such transformations do not appear to have been important in Pasqua Lake, much like results from other eutrophic lakes (Lehmann et al. 2004a,b).

Effective sequestration of N by Qu'Appelle lakes rapidly attenuated the effects of urban effluent on water quality in downstream lakes (Figs. 6, 8). For example, although the abundance of total (Fig. 8c) and bloom-forming (Fig. 8b) algae had increased ~300% in Pasqua Lake since 1900, inferred production of Echo Lake rose only 50–100% over the same period, whereas no unique effects of wastewater could be identified for Katepwa Lake, the fourth basin in the Fishing Lakes chain. Such rapid mediation of urban effects is also evident in the fossil diatom (Dixit et al. 2000) and chironomid (Quinlan et al. 2002) records from these lakes, and is consistent with the removal of 41–80% of inflow N by each sequential basin (Table 2). In contrast, mean N isotope ratios in sediments from 1975–1995 declined only 40% over the same spatial scale (Fig. 6c), possibly reflecting inputs of atmospheric N via biological fixation ($\delta^{15}\text{N} \sim 0\text{‰}$). For example, in the absence of fixed N, isotopic signals would be expected to be similar in all Fishing Lakes, mainly because sites share ~90% the same catchment area (Dixit et al. 2000). However, assuming that a linear gradient of net N_2 fixation exists between Pasqua (no fixation) and Katepwa Lakes (~41% of TN inputs) (Table 2), sedimentary isotope ratios would be expected to decline from $13.4 \pm 0.9\text{‰}$ (Pasqua), through 11.5‰ (Echo) and 8.4‰ (Mission) to background levels (~5‰) by Katepwa Lake as a result of sequential dilution of lake-water N with atmospheric N. In general observed isotopic signatures were greater than expected in Echo ($13.4 \pm 0.5\text{‰}$), Mission ($10.0 \pm 0.3\text{‰}$) and Katepwa Lakes ($8.1 \pm 0.5\text{‰}$), suggesting either that rates of N_2 fixation were less than the maximum predicted (*see* Patoine et al. 2006), that ^{14}N was lost via NH_3 volatilization or denitrification, or that ^{15}N may be entering the lakes, possibly from small urban centers (e.g., Fort Qu'Appelle between Echo and Mission Lakes) or from internal sources (Table 2). Although further research will be required to resolve this issue, it remains evident that the spatial scale over which urban effects can be detected differs among fossil pigments (two lake basins) and stable isotopes (>4 basins).

Sedimentary $\delta^{15}\text{N}$ signatures varied relatively little since ca. 1800 in the three reference lakes (Buffalo Pound, Last Mountain, Wascana) and demonstrated that changes in

regional climate and development of European-style land-use practices did not greatly alter N cycles within headwaters of the Qu'Appelle catchment. Rusak et al. (2004) show that sedimentary $\delta^{15}\text{N}$ can increase ~5‰ during decade-long droughts, while the addition of farm fertilizers can either increase (Anderson and Cabana 2005) or potentially reduce $\delta^{15}\text{N}$ of surface waters a similar amount, depending on whether ^{15}N -enriched manure or isotopically depleted inorganic N is added to fields (Bedard-Haughn et al. 2003). In addition, development of intense blooms of N_2 -fixing cyanobacteria may also reduce sedimentary $\delta^{15}\text{N}$ in some highly eutrophic lakes (e.g., Brenner et al. 1999). Unfortunately, because drought frequency has declined in Saskatchewan since 1900 (Rusak et al. 2004), because cyanobacteria are common in our reference systems (Hall et al. 1999a), and because most prairie farmers began using chemical fertilizers ($\delta^{15}\text{N} \sim 0\text{‰}$) since ca. 1950, we cannot clearly identify the causes of observed 1‰ declines of sedimentary $\delta^{15}\text{N}$ at Last Mountain and Buffalo Pound lakes (Fig. 6a).

Management implications—Combined use of stable isotope analyses, paleolimnology, and whole-lake mass balances revealed that urban N degraded water quality of P-rich prairie lakes. Although lotic ecosystems did not appear to store or transform N from cities, sequential lake basins rapidly eliminated urban effects by sequestering N in their sediments, such as occurs in wetlands or storm-water retention ponds (e.g., Gerke et al. 2001). As indicated below, we believe that these patterns will be common to other P-sufficient lakes and, taken together, allow us to make specific recommendations to watershed managers.

First, our analyses suggest that improvements in water quality are linked to reductions in N influx when lakes are replete with P from natural or anthropogenic sources. Nitrogen limitation of algal growth in Qu'Appelle lakes is indicated by the high abundance of N_2 -fixing cyanobacteria (Graham 1997; Patoine et al. 2005) even before European colonization (Hall et al. 1999a,b; Dixit et al. 2000), low N : P ratios in downstream lakes (Table 1), bottle bioassay analyses during summers 1994–2004 (Graham 1997; P. R. Leavitt unpubl. data) and high importance of fixed N relative to TN influx in downstream lakes (Table 2; Patoine et al. 2006). Further, P seems not to regulate algal production in these lakes, as indicated both by empirical models that consistently overestimate summer Chl *a* concentrations on the basis of dissolved P content in spring (Table 1; *see* Campbell and Prepas 1986), and by the observation that diversion of >70% of total P input to Pasqua Lake since 1976 has not reduced algal abundance measured by both long-term monitoring studies (Chambers 1989; Soranno et al. 1999) and paleoecological analyses (Hall et al. 1999b; Dixit et al. 2000). Taken together, these patterns suggest elimination of urban N sources should be the first priority for ecosystem management and that substantial improvements in water quality are expected even though Pasqua Lake is naturally eutrophic (Hall et al. 1999b).

Second, we propose that sewage treatment processes should be upgraded to modern microbial methods if receiving lakes are replete with P. Such BNR procedures

remove up to 90% of total dissolved N load through denitrification (Savage et al. 2004). Concerns that concomitant reductions in N : P ratios of effluent will unduly promote blooms of toxic cyanobacteria are probably unfounded for several reasons. First, populations of colonial cyanobacteria are common in all Qu'Appelle lakes regardless of effluent inputs (McGowan et al. 2005; Patoine et al. 2005). Second, *Microcystis* and other potentially toxic cyanobacteria are already abundant in Pasqua Lake, likely reflecting the naturally low N : P ratios (Table 1). Finally, prior analysis of fossil pigments reveals that the abundance of potentially N₂-fixing cyanobacteria has increased approximately fivefold since 1950 (Dixit et al. 2000), despite a fivefold increase in N : P after onset of tertiary wastewater treatment in 1976 (fig. 2f in Hall et al. 1999b). Instead, our analyses show that a 90% reduction in urban N should decrease algal abundance up to 300% (Figs. 6b, 8c), as well as improve the oxygen content of profundal waters (Quinlan et al. 2002). Further, because BNR processes also provide better P removal from wastewaters than do many strictly chemical approaches, improved effluent treatment is also expected to reduce production of P-limited or N-P colimited algae.

Third, we suggest that watershed managers clearly inform special-interest groups concerning the degree of water quality improvement expected for each lake. For example, paleolimnological analyses show clearly that algal abundance will decline most in Pasqua Lake (Fig. 8c), the first basin to receive urban effluent, but that there is little change expected for Mission or Katepwa Lakes, sites only two basins downstream. Further, because mass-balance analyses suggest that internal sources of N may account for 22–55% of TN inputs to the water column (“other” in Table 2), managers should indicate that recovery of lakes may occur on decadal timescales, such as occurs in P-limited lakes recovering from eutrophication (Battarbee et al. 2005).

Finally, we suggest that improved water quality will result from N diversion in other P-sufficient ecosystems, including those receiving diffuse sources of N. Although effects of terrestrial N on water quality are well documented for estuaries and other N-limited marine environments (e.g., Voss et al. 2000; Savage et al. 2004), recent evidence also suggests that nutrient supplements have saturated the capacity of agricultural soils to retain P, greatly increased terrestrial export of P to lakes, and have created severe N-limitation that favors blooms of cyanobacteria in lakes (e.g., Bennett et al. 2001; Foy et al. 2002). These patterns are especially well developed in lowland Europe (e.g., Ireland, the Netherlands, Denmark) where soil P content is often elevated and where concern over fluxes of N has resulted in European legislation to reduce nitrate loading to surface and ground waters. Under such P-rich conditions, we hypothesize that historical changes in water quality may be more closely linked to influx of N than of P, such as has been suggested by preliminary analyses of sedimentary stable isotopes, pigments, and algae from lakes within P-saturated landscapes (e.g., Bunting et al. 2005).

In conclusion, measurement of N transport to and storage in eight lakes linked by the Qu'Appelle River

demonstrated that N from urban wastewaters was effectively transported to downstream lakes (Fig. 5), where it resulted in a 300% increase in algal production (Fig. 8). Analysis of spatial patterns of $\delta^{15}\text{N}$ within dissolved N, periphyton, POM, and sediments revealed that urban N was not stored or substantially transformed within lotic ecosystems. Instead, sedimentary $\delta^{15}\text{N}$ signatures and fossil pigment concentrations increased in Pasqua Lake as a linear function of urban N flux, although the effects of urban effluent declined rapidly in a chain of downstream lakes and were absent from three reference ecosystems. Together, these patterns demonstrate that although urban N can directly degrade water quality, sequential basins can eliminate downstream effects of urbanization through storage of wastewater N in their sediments.

References

- ALLAN, R. J. 1980. The inadequacy of existing chlorophyll *a* phosphorus concentrations for assessing remedial measures of hypereutrophic lakes. *Environ. Pollut. Ser. B* **1**: 217–231.
- , AND B. C. KENNEY. 1978. Rehabilitation of eutrophic prairie lakes. *Int. Ver. Theor. Angew. Limnol. Vehr.* **20**: 214–224.
- ANDERSON, C., AND G. CABANA. 2005. $\delta^{15}\text{N}$ in riverine food webs: Effects of N inputs from agricultural watersheds. *Can. J. Fish. Aquat. Sci.* **62**: 333–340.
- BARICA, J. 1987. Water quality problems associated with high productivity of prairie lakes in Canada: A review. *Water Qual. Bull.* **12**: 107–115.
- BATTARBEE, R. W., N. J. ANDERSON, E. JEPPESEN, AND P. R. LEAVITT. 2005. Oligotrophication—the combined role of palaeolimnological and observational approaches. *Freshwat. Biol.* **25**: 1772–1780.
- BEDARD-HAUGHN, A., J. W. VAN GROENIGEN, AND C. VAN KESSEL. 2003. Tracing ^{15}N through the landscapes: Potential uses and precautions. *J. Hydrol.* **272**: 175–190.
- BENNETT, E. M., S. R. CARPENTER, AND N. F. CARACO. 2001. Human impact on erodable phosphorus and eutrophication: A global perspective. *BioScience* **51**: 27–234.
- , T. REED-ANDERSEN, J. N. HOUSER, J. R. GABRIEL, AND S. R. CARPENTER. 1999. A phosphorus budget for the Lake Mendota watershed. *Ecosystems* **2**: 69–75.
- BRENNER, M., T. J. WHITMORE, J. H. CURTIS, D. A. HODELL, AND C. L. SCHELSKE. 1999. Stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) signatures of sedimented organic matter as indicators of trophic state. *J. Paleolimnol.* **22**: 205–221.
- BUNTING, L., P. R. LEAVITT, V. HALL, C. E. GIBSON, AND E. J. MCGEE. 2005. Nitrogen degradation of water quality in a phosphorus-saturated catchment: The case of Lough Neagh, Northern Ireland. *Verh. Internat. Verein. Limnol.* **29**: 1005–1010.
- CAMPBELL, C. E., AND E. E. PREPAS. 1986. Evaluating factors related to the unusually low chlorophyll levels in prairie saline lakes. *Can. J. Fish. Aquat. Sci.* **43**: 846–854.
- CARPENTER, S. R., N. F. CARACO, D. L. CORRELL, R. W. HOWARTH, A. N. SHARPLEY, AND V. H. SMITH. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol. Appl.* **8**: 559–568.
- CHAMBERS, P. A. 1989. Reconnaissance study of the Qu'Appelle lakes: Report on the September 1989 evaluation of aquatic macrophyte growth in the Qu'Appelle lakes. Contribution 89080. National Hydrology Research Institute.

- COSTANZO, S. D., M. J. O'DONOHUE, W. C. DENNISON, N. R. LONERAGAN, AND M. THOMAS. 2001. A new approach for detecting and mapping sewage effects. *Mar. Poll. Biol.* **42**: 149–156.
- DEBRUYN, A. M. H., D. J. MARCOGLIESE, AND J. B. RASMUSSEN. 2003. The role of sewage in a large river food web. *Can. J. Fish. Aquat. Sci.* **60**: 1332–1344.
- DIXIT, A. S., R. I. HALL, P. R. LEAVITT, R. QUINLAN, AND J. P. SMOL. 2000. Effects of sequential depositional basins on lake response to urban and agricultural pollution: A palaeoecological analysis of the Qu'Appelle Valley, Saskatchewan, Canada. *Freshwat. Biol.* **43**: 319–337.
- ELSER, J. J., E. R. MARZOLF, AND C. R. GOLDMAN. 1990. Phosphorus and nitrogen limitation of phytoplankton growth in the fresh-waters of North America—a review and critique of experimental enrichments. *Can. J. Fish. Aquat. Sci.* **47**: 1468–1477.
- FOY, R. H., J. S. BAILEY, AND S. D. LENNOX. 2002. Mineral balances for the use of phosphorus and other nutrients by agriculture in Northern Ireland from 1925 to 2000—methodology, trends and impacts of losses to water. *Irish J. Agric. Food Res.* **41**: 247–263.
- GASTON, T. F., AND I. M. SUTHERS. 2004. Spatial variation in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of liver, muscle and bone in a rocky reef planktivorous fish: The relative contribution of sewage. *J. Exp. Mar. Biol. Ecol.* **304**: 17–23.
- GERKE, S., L. A. BAKER, AND Y. XU. 2001. Nitrogen transformations in a wetland receiving lagoon effluent: Sequential model and implications for water reuse. *Water Res.* **35**: 3857–3866.
- GRAHAM, M. D. 1997. Omnivory and selective feeding by zooplankton along a lake production gradient. M.S. thesis, Univ. Regina.
- HAERTEL, L. 1976. Nutrient limitation of algal standing crops in shallow prairie lakes. *Ecology* **57**: 664–678.
- HALL, R. I., P. R. LEAVITT, A. S. DIXIT, R. QUINLAN, AND J. P. SMOL. 1999a. Limnological succession in reservoirs: a paleolimnological comparison of two methods of reservoir formation. *Can. J. Fish. Aquat. Sci.* **56**: 1109–1121.
- , ———, R. QUINLAN, A. S. DIXIT, AND J. P. SMOL. 1999b. Effects of agriculture, urbanization and climate on water quality in the northern Great Plains. *Limnol. Oceanogr.* **43**: 739–756.
- HAMMER, U. T. 1971. Limnological studies of the lakes and streams of the upper Qu'Appelle Valley River system, Saskatchewan, Canada. *Hydrobiologia* **37**: 473–507.
- HEIKOOP, J. M., AND OTHERS. 2000. Nitrogen-15 signals of anthropogenic nutrient loading in reef corals. *Mar. Pollut. Bull.* **40**: 628–636.
- JAMES, C., L. J. FISHER, AND B. MOSS. 2003. Nitrogen driven lakes: The Shropshire and Cheshire meres? *Arch. Hydrobiol.* **158**: 249–266.
- JONES, R. I., L. KING, M. M. DENT, S. C. MABERLY, AND C. E. GIBSON. 2004. Nitrogen stable isotope ratios in surface sediments, epilithon and macrophytes from upland lakes with differing nutrient status. *Freshwat. Biol.* **49**: 382–391.
- KAUPPILA, P., K. WECKSTRÖM, S. VAALGAMAA, A. KORHOLA, H. PITKÄNEN, N. REUSS, AND S. DREW. 2005. Tracing pollution and recovery using sediments in an urban estuary, northern Baltic Sea: Are we far from ecological reference conditions? *Mar. Ecol. Prog. Ser.* **290**: 35–53.
- KENNEY, B. C. 1990. Dynamics of phosphorus in a chain of lakes: The Fishing Lakes. NHRI Paper 44, IWD Scientific Series 176. National Hydrology Institute, Saskatoon.
- KILINC, S., AND B. MOSS. 2002. Whitemere, a lake that defies some conventions about nutrients. *Freshwat. Biol.* **47**: 207–218.
- KLASSEN, R. W. 1989. Quaternary geology of southern Canadian Interior Plains, p. 138–174. *In* R. J. Fulton [ed.], Quaternary geology of Canada and Greenland. Geological Survey of Canada.
- LEAVITT, P. R., AND D. A. HODGSON. 2001. Sedimentary pigments, p. 295–325. *In* J. P. Smol, H. J. B. Birks, and W. M. Last [eds.], Tracking environmental change using lake sediments. V. 3, Terrestrial, algal and siliceous indicators. Kluwer.
- LEHMANN, M. F., S. M. BERNASCONI, A. BARBIERI, AND J. A. MCKENZIE. 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. *Geochim. Cosmochim. Acta* **66**: 3573–3584.
- , ———, ———, M. SIMONA, AND J. A. MCKENZIE. 2004a. Interannual variation of the isotopic composition of sedimenting organic carbon and nitrogen in Lake Lugano: A long-term sediment trap study. *Limnol. Oceanogr.* **49**: 839–849.
- , ———, J. A. MCKENZIE, A. BARBIERI, M. SIMONA, AND M. VERONESI. 2004b. Seasonal variation of the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of particulate and dissolved carbon and nitrogen in Lake Lugano: Constraints on biogeochemical cycling in a eutrophic lake. *Limnol. Oceanogr.* **49**: 415–429.
- MCCLELLAND, J. W., AND I. VALIELA. 1998. Linking nitrogen in estuarine producers to land-derived sources. *Limnol. Oceanogr.* **43**: 577–585.
- , ———, AND R. H. MICHNER. 1997. Nitrogen-stable isotope signatures in estuarine food-webs: A record of increasing urbanization in coastal watersheds. *Limnol. Oceanogr.* **42**: 930–937.
- MCGOWAN, S., A. PATOINE, M. D. GRAHAM, AND P. R. LEAVITT. 2005. Intrinsic and extrinsic controls of lake phytoplankton synchrony. *Verh. Internat. Verein. Limnol.* **29**: 794–798.
- OGAWA, N. O., T. KOITABASHI, H. ODA, T. NAKAMURA, N. OHKOUCHI, AND E. WADA. 2001. Fluctuations of nitrogen isotope ratios of gobiid (Isaza) specimens and sediments in Lake Biwa, Japan, during the 20th century. *Limnol. Oceanogr.* **46**: 1228–1236.
- PATOINE, A., M. D. GRAHAM, AND P. R. LEAVITT. 2006. Spatial variation of nitrogen fixation in lakes of the northern Great Plains. *Limnol. Oceanogr.* **51**: 1665–1677.
- , ———, ———, AND R. HESSLEIN. 2005. Landscape-scale patterns of nitrogen fixation by cyanobacteria. *Verh. Internat. Verein. Limnol.* **29**: 359–364.
- QUINLAN, R., P. R. LEAVITT, A. S. DIXIT, R. I. HALL, AND J. P. SMOL. 2002. Landscape effects of climate, agriculture and urbanization on benthic invertebrate communities of Canadian prairie lakes. *Limnol. Oceanogr.* **47**: 378–391.
- RABALAIS, N. N. 2002. Nitrogen in aquatic ecosystems. *Ambio* **31**: 102–112.
- RENNBERG, I., R. BINDLER, E. BRADSHAW, O. EMTERYD, AND S. MCGOWAN. 2001. Sediment evidence of early eutrophication and heavy metal pollution of Lake Mälaren, central Sweden. *Ambio* **30**: 496–502.
- RISK, M., AND M. V. ERDMANN. 2000. Isotopic composition of nitrogen in stomatopod (Crustacea) tissues as an indicator of human sewage impacts on Indonesian coral reefs. *Mar. Pollut. Bull.* **40**: 50–58.
- ROBINSON, D. 2001. $\delta^{15}\text{N}$ as an integrator of the nitrogen cycle. *Trend. Ecol. Evol.* **16**: 153–162.
- RUSAK, J. A., P. R. LEAVITT, S. MCGOWAN, G. CHEN, O. OLSON, S. WUNSAM, AND B. F. CUMMING. 2004. Millennial-scale relationships of diatom species richness and production in two prairie lakes. *Limnol. Oceanogr.* **49**: 1290–1299.
- SAVAGE, C., P. R. LEAVITT, AND R. ELMGREN. 2004. Distribution and retention of sewage nitrogen in surface sediments of a coastal bay. *Limnol. Oceanogr.* **49**: 1503–1511.

- SCHINDLER, D. E., P. R. LEAVITT, C. BROCK, S. P. JOHNSON, AND P. D. QUAY. 2005. Marine-derived nutrients, commercial fisheries, and the production of salmon and lake algae in Alaska. *Ecology* **86**: 3225–3231.
- SCHINDLER, D. W. 1977. The evolution of phosphorus limitation in lakes. *Science* **195**: 260–262.
- SMITH, V. H. 2003. Eutrophication of freshwater and coastal marine ecosystems—a global problem. *Env. Sci. Pollut. Res.* **10**: 126–139.
- SORANNO, P. A., AND OTHERS. 1999. Spatial variation among lakes within landscapes: Ecological organization along lake chains. *Ecosystems* **2**: 395–410.
- STEFFY, L. Y., AND S. S. KILHAM. 2004. Elevated $\delta^{15}\text{N}$ in stream biota in areas with septic tank systems in an urban watershed. *Ecol. Appl.* **14**: 637–641.
- TERANES, J. L., AND S. M. BERNASCONI. 2000. The record of nitrate utilization and productivity limitation provided by $\delta^{15}\text{N}$ values in lake organic matter—a study of sediment trap and core sediments from Baldeggersee, Switzerland. *Limnol. Oceanogr.* **45**: 801–813.
- TUCKER, J., N. SHEATS, A. E. GIBLIN, C. S. HOPKINSON, AND J. P. MONTOYA. 1999. Using stable isotopes to trace sewage-derived material through Boston Harbor and Massachusetts Bay. *Mar. Environ. Res.* **48**: 353–375.
- VITOUSEK, P. M., AND OTHERS. 1997. Human alteration of the global nitrogen cycle: Sources and consequences. *Ecol. Appl.* **7**: 737–750.
- VOSS, M., B. LARSEN, M. LEIVUORI, AND H. VALLIUS. 2000. Stable isotope signals of eutrophication in Baltic Sea sediments. *J. Mar. Syst.* **25**: 287–298.
- , U. STRUCK, AND J. P. MONTOYA. 1997. Nitrogen stable isotope dynamics in the central Baltic Sea: Influence of deep water-renewal on the N-cycle changes. *Mar. Ecol. Prog. Ser.* **158**: 11–21.
- WASER, N. A. D., P. J. HARRISON, B. NIELSEN, S. E. CALVERT, AND D. H. TURPIN. 1998. Nitrogen isotope fractionations during the uptake and assimilation of nitrate, nitrite, ammonia and urea by a marine diatom. *Limnol. Oceanogr.* **43**: 215–224.
- WAYLAND, M., AND K. A. HOBSON. 2001. Stable carbon, nitrogen, and sulfur isotope ratios in riparian food webs on rivers receiving sewage and pulp-mill effluents. *Can. J. Zool.* **79**: 5–15.

Received: 19 August 2005

Accepted: 18 March 2006

Amended: 28 March 2006