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Changes in amorphous silica sequestration with eutrophication of riverine impoundments

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Abstract The effect of eutrophication on particulate amorphous silica (ASi) sequestration was isolated and quantified in Lake St. Croix and Lake Pepin, two natural, human-impacted impoundments of the upper Mississippi River. In contrast to impoundments behind engineered dams, where silica (Si) fluxes may be changed by various aspects of dam construction, these two riverine lakes have long (9,000+ years) sedimentary sequences that record the entire span of cultural eutrophication and the resulting silica sequestration. The concentrations of dissolved silicate (DSi) and ASi in the lake inflows were measured for 1 year to obtain the total flux of bioavailable silica ($TSi_b = DSi + ASi$) to each impoundment. Historical rates of Si sequestration in each lake were determined using ASi burial in multiple sediment cores and modeled estimates of historical TSi_b fluxes. The Si trapping efficiency of each lake was found to have increased exponentially with cultural eutrophication (estimated two- to five-fold increase in Lake St. Croix and 9- to 16-fold increase in Lake Pepin over the last 100 years), indicating the degree to which eutrophication of impoundments can reduce silica export to downstream coastal and marine ecosystems. Because these two lakes presently exhibit different degrees of eutrophication, together they depict a relationship between phosphorus concentration and Si trapping efficiency that may be applied to other impoundments, including human-made reservoirs.

Keywords Biogenic silica · Trapping efficiency · Mississippi River · Eutrophication · Riverine lake

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Introduction

The eutrophication of the world's rivers has impacted both the riverine ecosystems and the coastal marine environment near the mouths of rivers (Caraco 1993; Meybeck 2002). In particular, depletion of dissolved silicate (DSi) in coastal waters has led to relatively fewer diatoms and more flagellated algae and coccolithophores, for example in the Gulf of Mexico (Turner et al. 1998) and the Black Sea (Humborg et al. 2000), thereby potentially damaging fisheries that are dependent on diatom-feeding copepods. Rivers are the primary exporters of Si to the oceans, so the biogeochemical cycling of Si in river systems is of major importance to coastal marine ecosystems.

Depletion of DSi in the coastal oceans can be the result of relative increases in total phosphorus (TP) and nitrogen (TN) concentrations, which changes the stoichiometric balance of nutrients available to organisms. Agricultural, municipal, and industrial processes add phosphorus and nitrogen to the environment in large quantities (Howarth and Marino 2006), while relatively few anthropogenic activities actually enhance silica export (Conley et al. 2008; Sferratore et al. 2006). Thus, increases in TP and TN, and a relative decrease in Si, puts diatoms at a disadvantage and allows other, non-siliceous algae to proliferate and dominate.

Another major cause of coastal Si depletion is the damming of rivers, which may decrease riverine Si fluxes in two ways. First, filling reservoirs behind dams inundates new land and may decrease the rates of silicate weathering and DSi flux out of the riparian zone (Humborg et al. 2002). Second, reservoirs create new depositional areas in which particulate amorphous silica (ASi), primarily of biologic origin such as diatom frustules and/or phytoliths, can settle out of the water column and be buried in sediments rather than continue downstream to be dissolved and recycled (Conley 1997). Diatoms may flourish in the low turbidity environment of a reservoir, transforming more DSi to ASi for eventual burial in the sediments. In addition, the ubiquitous eutrophication of rivers, lakes and reservoirs by human activity accelerates ASi production and, consequently, ASi burial. Because approximately 60% of riverine flow now goes through human-made impoundments (Vorosmarty et al. 1997), the “artificial lake effect” has in recent decades become a larger component of the global Si cycle (Conley and Schelske 1993; Conley et al. 2000).

Several important datasets demonstrate a decrease of DSi in a river before and after damming, but none of these studies separates the effect of eutrophication on Si sequestration. For instance, Wahby and Bishara (1980) observed that DSi concentrations in the Nile River decreased by 200 $\mu g\ l^{-1}$ after the construction of the High Dam at Aswan, but that depletion was likely caused by reservoir eutrophication as well as the inundation of new land and the creation of new depositional areas. Similarly, DSi monitoring in the Black Sea showed a 60% decrease in wintertime DSi concentration after the construction of the Iron Gates dams and dams on other tributaries (Humborg et al. 2000), a cumulative impact of a variety of dam effects (Humborg et al. 2006). Although there are no pre-dam DSi data for Scandinavian rivers flowing into the Baltic Sea, those rivers without dams currently have significantly higher DSi concentrations than do similar rivers nearby that are dammed (Humborg et al. 2002).

In addition, most dams were built after human activities in the watershed had already begun to increase nutrient concentrations, so monitoring data will not necessarily characterize the natural, pre-impact river water quality. Thus, reservoir sediments cannot be used to characterize natural conditions because they inherently do not extend before the first anthropogenic impacts to the system. It is also difficult to use reservoir sediments to quantify recent environmental changes because they are often difficult to date using radioisotopic methods, and sediment accumulation rates are often extremely high.

Here we present data from two natural impoundments on the upper Mississippi River, Lake St. Croix and Lake Pepin, which contain long, dateable sediment records of the history of eutrophication. Lake St. Croix is located at the terminus of the St. Croix River, a relatively pristine tributary of the Mississippi River (Fig. 1). In contrast, Lake Pepin is on the Mississippi River mainstem downstream of several large cities and the most intensively farmed areas of Minnesota. Thus, the two lakes depict contrasting stages of eutrophication. ASi and DSi concentrations were measured in the inflows of each lake from April 2004–March 2005, and were multiplied by river discharge to determine ASi and DSi fluxes (as t year^{-1}). Total bioavailable silica (TSi_b) fluxes were calculated as the sum of ASi fluxes and DSi fluxes for the year. Dated lake sediment cores were then used to quantify the ASi accumulation rate in Lakes St. Croix and Pepin through time, beginning before Euro-American settlement in the 1800s. We evaluate the effect of eutrophication on Si sequestration in lakes St. Croix and Pepin and quantify the progression of eutrophication and ASi sequestration since Euro-American settlement.

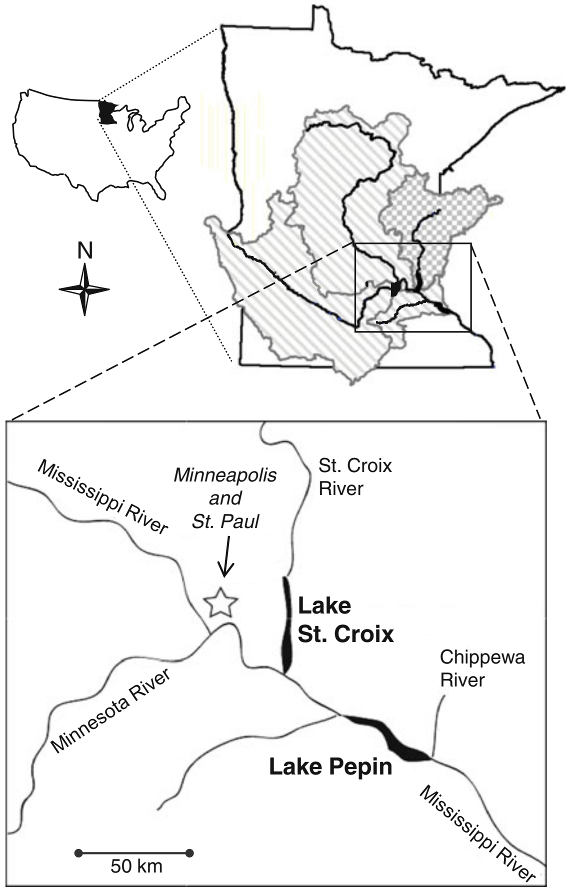


Fig. 1 Map of Lake St. Croix and Lake Pepin. The St. Croix River watershed (*checkered*) and the Lake Pepin watershed (all *cross-hatched* and *checkered*) are shown on the state map of Minnesota

Site descriptions

Lakes St. Croix and Pepin formed over 9,000 years ago when meltwater from Glacial Lakes Agassiz and Duluth ceased flowing through the Mississippi River. The flow reduction allowed deltaic sediment from the Chippewa River (Fig. 1) to partially dam the Mississippi River, creating a long Y-shaped lake reaching up the Mississippi and St. Croix valleys. A delta at the head of the Mississippi arm grew relatively rapidly at first, prograding across the St. Croix confluence and splitting the St. Croix arm from the main body of Lake Pepin. The continued migration of the Mississippi delta during the Holocene has displaced the present-day head of Lake Pepin some 24 km downstream of the St. Croix confluence (Blumentritt et al. 2009).

Present-day Lake St. Croix is 37 km long, 0.5–2 km wide and has a mean depth of 9.7 m. The northern portion of the St. Croix watershed is forested while the southern part encompasses substantial agricultural, urban and ex-urban land-use. In 1968 the St. Croix River was designated a National Scenic Riverway because of its environmental quality, beauty and its popularity for recreational pursuits (Table 1).

Lake Pepin is 34 km long, 2–3 km wide and shallower than Lake St. Croix with a mean depth of 5.4 m. In contrast to the St. Croix, the Lake Pepin watershed was highly altered following Euro-American settlement. Large areas of southern and western Minnesota became important agricultural regions that are today dominated by row-crops (corn and soybeans). For example, grain corn production in the Lake Pepin watershed increased 350-fold between 1860 and 1992, while corn production in the St. Croix watershed increased 100-fold during the same period (Mulla and Sekely 2009). In addition, most of the large cities in the state, including the Minneapolis-St. Paul metropolitan area with a population of 3 million in 2007, discharge treated wastewater to the Mississippi River upstream of Lake Pepin. In contrast, the entire St. Croix River watershed had a population of only 406,000 in 1992.

Although the St. Croix River is considered to be relatively unpolluted, recent sediment core studies have shown that water-column total phosphorus concentration (TP) in Lake St. Croix has more than doubled since Euro-American settlement in the mid-1800s to recent values around 0.05 mg l^{-1} (Edlund et al. 2009). Studies of sediment cores from Lake Pepin have shown TP has quadrupled since the early 1800s to recent values around 0.2 mg l^{-1}. In addition, Engstrom et al. (2009) previously determined basin-wide sedimentation rates using a combination of geophysical measurements and ^{210}Pb-dated sediment cores, providing a unique opportunity to examine changes in whole-lake elemental accumulation rates. The whole-lake sediment accumulation rate in Lake Pepin has increased more than tenfold since Euro-American settlement. Although Native Americans had lived in these watersheds for thousands of years before Europeans arrived in the Americas, they had little measurable impact on the water quality of these large rivers.

The first settlers arrived about the same time in both watersheds, but population growth and land-use disturbance was more rapid and extensive in the Lake

Table 1 Key differences between Lake St. Croix (St. Croix River) and Lake Pepin (Mississippi River)

	Lake St. Croix	Lake Pepin
Average inflow in 2004 (m^3 s^{-1})	165	558
Watershed area (km^2)	19,900	122,000
Lake area (km^2)	35	103
Mean lake depth (m)	9.7	5.4
Water residence time (days)	20–50	6–45
Average TP concentration (μg l^{-1})	50	200
Trophic state[a]	Mesotrophic	Hyper-eutrophic

Adapted from Triplett et al. (2008)

[a] Trophic state defined by Carlson's trophic state index (Carlson 1977)

Pepin watershed. By the time sanitary sewers were being built in the Twin Cities (Minneapolis and St. Paul, MN) in the late 1800s, TP in Lake Pepin was over 0.10 mg l^{-1}, or twice its natural value, while Lake St. Croix was still near its background (circa 0.03 mg l^{-1}). The eutrophication of Lake Pepin progressed rapidly in the following decades. TP in both lakes increased again after World War II when the use of chemical fertilizers became widespread and agriculture in general became more industrialized. Mulla and Sekely (2009) showed that TP concentrations in Lake Pepin inflow are significantly correlated to increased population (largely in cities), total acreage in row cropping, river flow and total phosphorus fertilizer application.

Methods

Water samples used to measure modern DSi and ASi concentrations were collected at 1 m depth below the surface of the Lake St. Croix and Lake Pepin inflows approximately weekly from 5 April 2004 to 24 March 2005, as described in Triplett et al. (2008). Filtered water was analyzed for DSi, and ASi concentrations were determined by digesting the filters in NaOH following the methods of Krausse et al. (1983). Concentrations of DSi in the filtrates (river water DSi) and in the filter digestion solutions (river water ASi) were measured as SiO_2 on a Lachat QuikChem 8000 colorimeter as molybdate-reactive silica (McKnight 1991).

River discharges were measured by the U.S. Geological Survey and U.S. Army Corps of Engineers. To calculate the flux of total bioavailable silica (TSi_b) into each lake, ASi and DSi concentrations for each monitoring date were summed then multiplied by the appropriate river discharge.

As part of earlier studies, 24 sediment cores were collected from Lake St. Croix (Triplett et al. 2009) and 25 from Lake Pepin (Engstrom et al. 2009). Selected "primary" cores (8 in Lake St. Croix, 10 in Pepin) were dated using ^{210}Pb, ^{137}Cs and ^{14}C methods, and core-specific sediment accumulation rates were calculated. To extrapolate these accumulation rates to the entire lake, the depositional areas of the lakes were divided into sections, each of which was represented by one or more of the dated cores. Whole-lake sediment accumulations were calculated as the sum of sediment accumulation in the depositional areas.

Sediment ASi concentrations were measured using a time-step digestion (Conley and Schelske 2001; DeMaster 1981). ASi was previously referred to as biogenic silica (BSi), however, with the recognition that there are also inorganic ASi compounds present in soil (Saccone et al. 2007) the term amorphous silica (ASi) is probably more representative of silica found in rivers and the sediments of rivers. Freeze-dried subsamples (0.03 g) were digested in 1% Na_2CO_3 for 5 h in an 85°C water-bath shaker. The solutions were sub-sampled at 3-, 4- and 5-h time steps to chart the progressive silica dissolution over time and thereby correct for DSi contributed by mineral silicates. Sediment ASi concentrations were multiplied by the sediment accumulation rate to produce core-specific rates of ASi deposition that were then converted to whole-lake ASi accumulation rates as described above. Because conversion of core-specific accumulation rates requires combining the dating models of multiple cores, data were compiled as 10-year averages from 1930 to 2000 and as 20- or 30-year averages from the time of Euro-American settlement (1830 for Lake Pepin and 1850 for Lake St. Croix) to 1930. The pre-Euro-American settlement values are averages of several samples over a period of 100–1000 years before settlement, to account for natural variability.

In order to compare pre-eutrophication ASi fluxes to later ASi fluxes, we defined a term called the ASi flux ratio:

$$\text{ASi flux ratio} = \frac{(\text{ASi flux to sediment})_{\text{Time X}}}{(\text{ASi flux to sediment})_{\text{Pre-eutrophication}}} \quad (1)$$

using an average pre-eutrophication ASi flux. The ASi trapping efficiency is the ratio of a water body's potential to sequester silica in its sediments and thereby make it unavailable to biota downstream. The modern ASi trapping efficiency for each lake was calculated as the average annual ASi flux to lake sediments in the 1990s divided by the inflowing TSi_b flux as measured in 2004–2005:

$$\text{ASi trapping efficiency (\%)} = \frac{\text{ASi flux to sediment}}{\text{Inflow TSi}_b\text{ flux}} \quad (2)$$

Historical ASi trapping efficiencies could not be directly calculated because there are no historical monitoring data of inflow TSi_b flux to these lakes, or for any other river in the world, for that matter. Furthermore, Conley et al. (2008) have shown that vegetation changes such as deforestation can have major impacts on the flux of DSi from a landscape into rivers, because terrestrial plants make up a significant component of the global silica cycle (Conley 2002). Therefore, it could not be assumed that TSi_b loading has been constant since Euro-American settlement in the 1800s. Instead, the historical TSi_b flux to each lake was estimated based on the measured 2004–2005 TSi_b flux and three scenarios of possible inflowing TSi_b flux in the past. In Scenario 1, the TSi_b flux from each river to its lake was held constant (at the 2004–2005 level) from 1800 to the present. In Scenario 2, TSi_b fluxes doubled immediately following Euro-American settlement and were kept at that higher (2004–2005) level to the present. In Scenario 3, TSi_b fluxes doubled following settlement then were decreased by one-third in the 1970s, after which they were held constant to the present (2004–2005 level). Scenarios 2 and 3 approximate the only direct observations of the impact of land-use change on silica flux, which were made at the Hubbard Brook Experimental Forest (New Hampshire) where DSi concentration in a stream increased 37% following deforestation (Likens et al. 1970).

Historical water-column TP concentrations were reconstructed using diatom analysis as described in Edlund et al. (2009, Lake St. Croix) and Engstrom et al. (2009, Lake Pepin). In brief, diatom remains were identified and counted in sediment samples from dated cores. Lake-water TP was reconstructed from fossil diatom assemblages using diatom-P calibration models. For the Lake St. Croix study, Edlund et al. (2009) used a calibration set of 55 Minnesota lakes (Ramstack et al. 2003). For the Lake Pepin study, Engstrom et al. (2009) used two calibration sets: one based on 31 southeast English lakes (Bennion 1994) because they had high TP levels comparable to Lake Pepin, and one based on 59 British Columbian lakes to provide additional species optima missing from the first set (Reavie et al. 1995).

Results

The seasonal and spatial variations in ASi and DSi concentrations flowing into the two lakes are described in detail elsewhere (Triplett et al. 2008). Briefly, ASi concentrations in both lakes were highest in the summer and lowest in the winter, while DSi concentrations were highest in the winter and lowest in the summer (Fig. 2). The annual flux of DSi into Lake St. Croix during 2004–2005 (53,000 t) was ten times the ASi flux into the lake (4500 t), while the annual DSi flux into Lake Pepin (213,000 t) was four times the ASi flux into that lake (49,500 t) (Table 2). ASi was a larger proportion of the TSi_b load to Lake Pepin (19%) than to Lake St. Croix (8%). Furthermore, Lake Pepin received much higher fluxes of both DSi and ASi than Lake St. Croix, so the flux of total bioavailable silica (TSi_b), the sum of the DSi and ASi fluxes, was almost five times higher to Pepin (263,000 t) than St. Croix (58,000 t). Results from the 2004–2005 monitoring also showed that diatom frustules were the dominant component (>80%) of the microscopy-determined ASi in the inflows and Lakes St. Croix and Pepin.

Sediment ASi concentrations before Euro-American settlement varied from 26 to 79 mg g^{-1} in Lake St. Croix and from 35 to 50 mg g^{-1} in Lake Pepin with no strong trends from upstream to downstream (Figs. 3, 4).

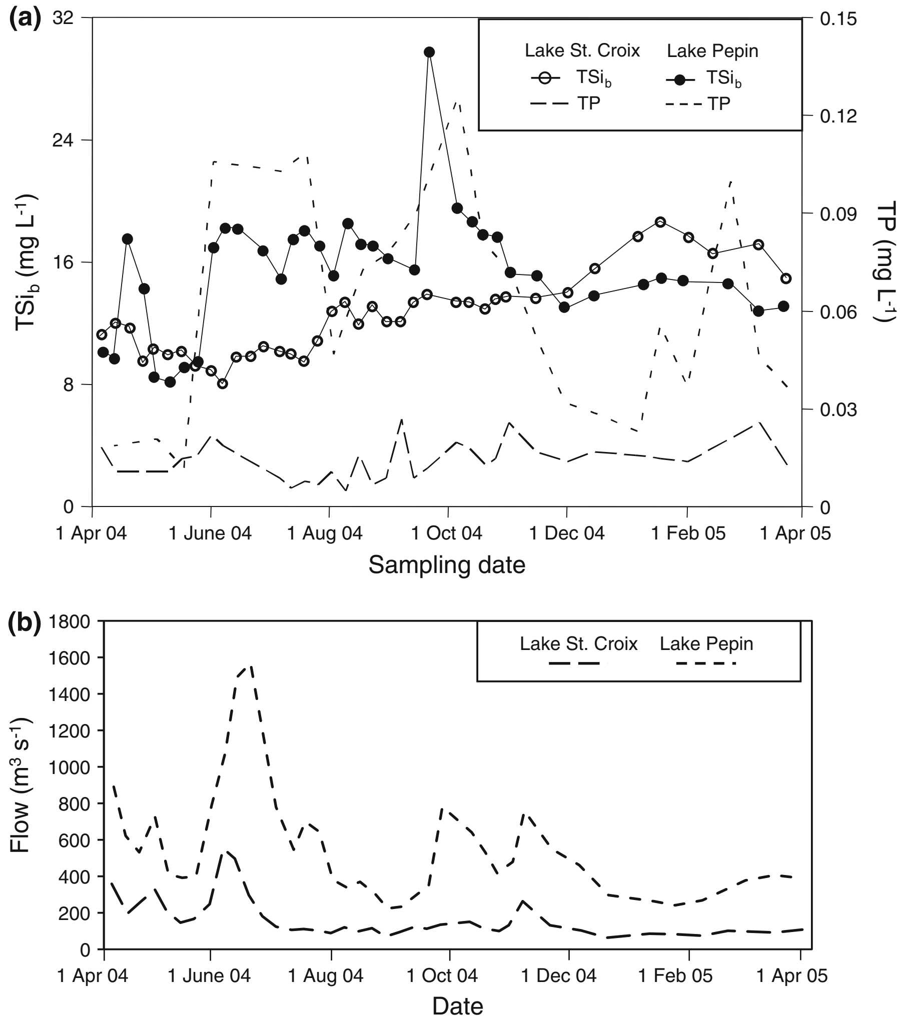


Fig. 2 **a** Total bioavailable silica (TSi_b) concentrations and total phosphorus (TP) concentrations in the Lake St. Croix and Lake Pepin inflows measured biweekly from April 2004 to March 2005. **b** River discharge flowing into Lake St. Croix and Lake Pepin over same time period

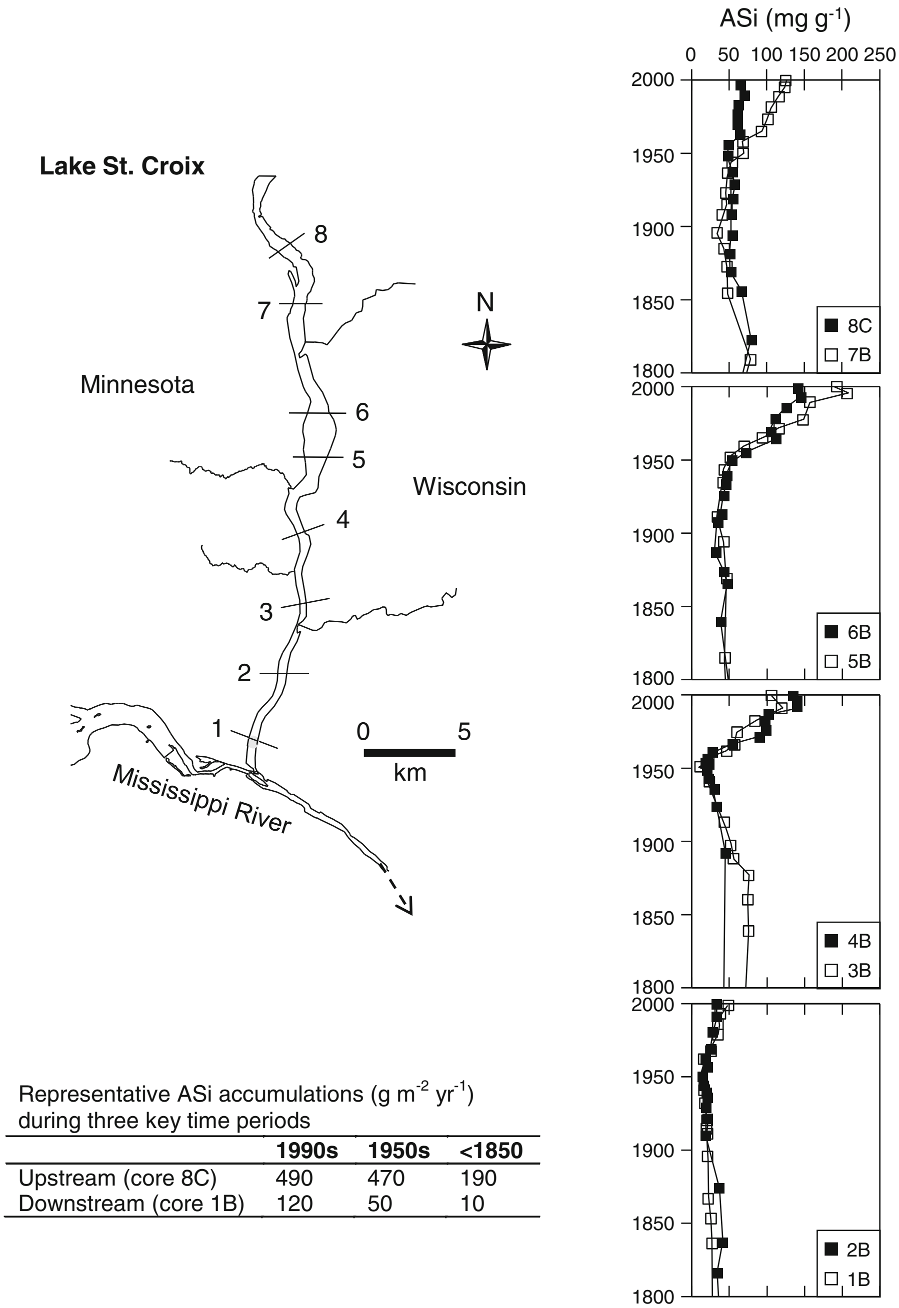
Table 2 Annual fluxes of amorphous silica (ASi), dissolved silicate (DSi) and total bioavailable silica (TSi_b) in the inflows of Lake St. Croix and Lake Pepin during April 2004–March 2005

Lake	ASi flux (t year^{-1})	DSi flux (t year^{-1})	TSi_b* flux (t year^{-1})	TSi_b flux (t year^{-1} km^{-2})	Percent TSi_b as ASi
St. Croix	4500 (±1,100)	53,000 (±10,000)	58,000 (±10,000)	2.9	8% (+5%, −3%)
Pepin	49,500 (±11,000)	213,000 (±37,000)	263,000 (±39,000)	2.2	19% (+8%, −6%)

Error terms (in parentheses) represent ±1SD as determined in Triplett et al. (2008)

* TSi_b = ASi + DSi

Sediment ASi concentrations in both lakes peaked in the 1990s, ranging from 33 to 208 mg g^{-1} in Lake St. Croix and from 38 to 67 mg g^{-1} in Lake Pepin (Triplett et al. 2008). In Lake St. Croix, ASi accumulation rates before Euro-American settlement were highest in core 8C (185 g m^{-2} year^{-1}), which also had the highest sediment accumulation rate, and lowest in cores 5B and 4B (10 g m^{-2} year^{-1} in both). Cores 8C, 7B, 3B and 2B had ASi accumulation rate peaks in the 1950s or 1960s (between 310 and 650 g m^{-2} year^{-1}) because of extremely high sediment accumulation rates, and in the 1990s core 8C and 3B had the highest accumulation



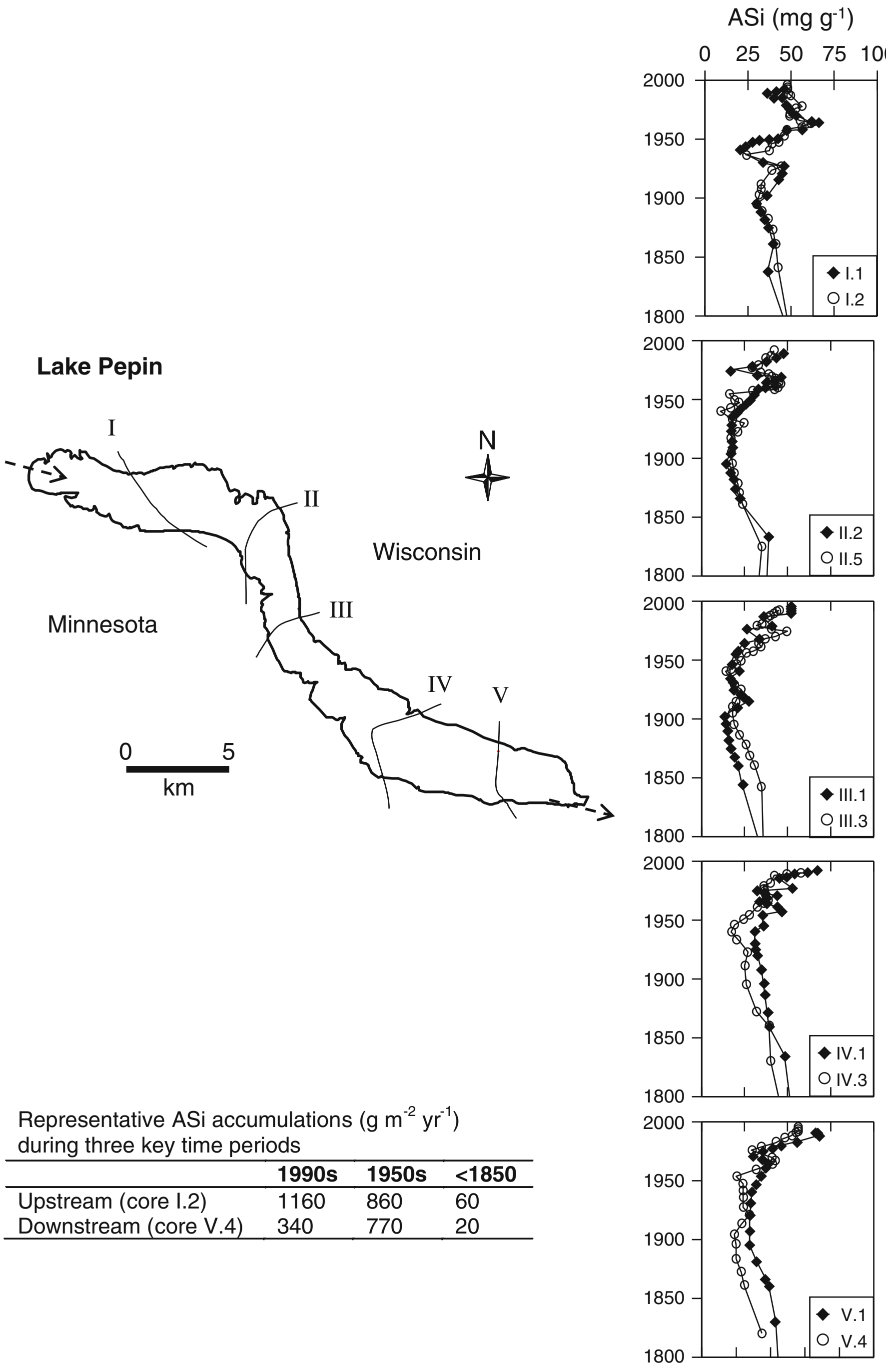
Representative ASi accumulations (g m^{-2} yr^{-1}) during three key time periods

	1990s	1950s	<1850
Upstream (core 8C)	490	470	190
Downstream (core 1B)	120	50	10

Fig. 3 Amorphous silica (ASi) concentrations in eight dated sediment cores from Lake St. Croix. Cores are labeled by the lake transect that they represent (e.g., Core 8C is the dated core from transect 8)

rates (490 and 390 g m^{-2} $year^{-1}$, respectively). In Lake Pepin, ASi accumulation rates before Euro-American settlement were highest in the upstream cores (90 and 60 g m^{-2} $year^{-1}$ in cores I.2 and I.3). ASi accumulation peaked in all Lake Pepin cores in the 1990s, with upstream cores receiving the most ASi (1160 and 770 g m^{-2} $year^{-1}$ in cores I.2 and I.3) and downstream cores receiving the least (280 and 340 g m^{-2} $year^{-1}$ in cores V.1 and V.4).

Before Euro-American settlement, the whole-lake ASi accumulation rate in Lake St. Croix was 1060 t $year^{-1}$ and in Lake Pepin was 3300 t $year^{-1}$



Representative ASi accumulations (g m^{-2} yr^{-1}) during three key time periods

	1990s	1950s	<1850
Upstream (core I.2)	1160	860	60
Downstream (core V.4)	340	770	20

Fig. 4 Amorphous silica (ASi) concentrations in ten dated sediment cores from Lake Pepin. Cores are labeled by the lake transect that they represent (e.g., Cores I.1 and I.2 are the dated cores from transect I)

(Fig. 5). In Lake St. Croix, ASi accumulation rates increased gradually through the 1930s and then rapidly until about 1960 from the 1960s through the 1990s ASi accumulation rates were fairly constant (c. 5200 t $year^{-1}$). In Lake Pepin, ASi accumulation rates increased after 1940 and plateaued from the 1960s to the 1980s (c. 28,000 t $year^{-1}$). In the 1990s, the whole-lake ASi accumulation rates peaked, in

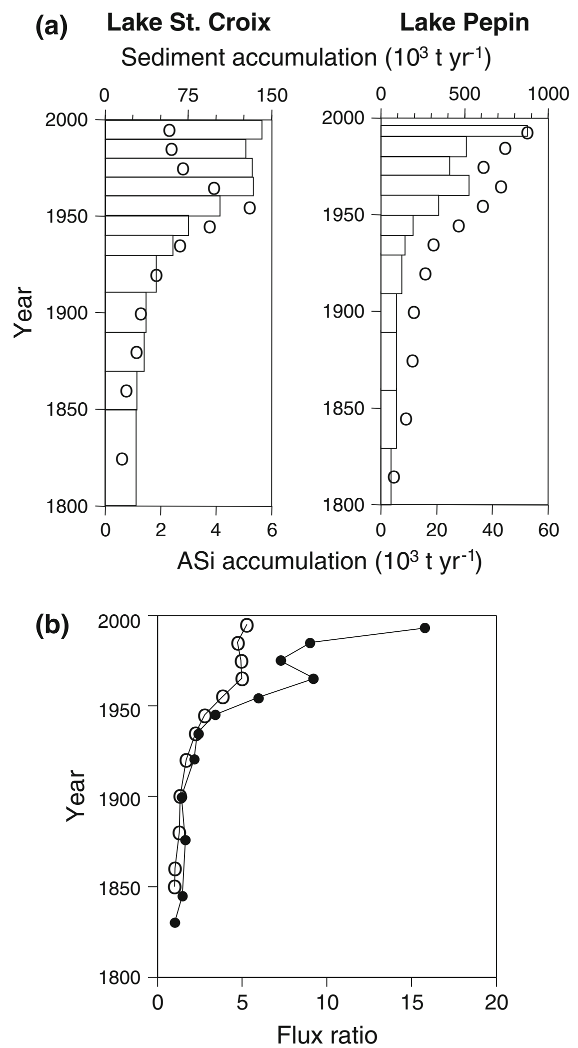


Fig. 5 **a** Whole-lake amorphous silica (ASi) accumulation rates (*bar graphs*) and whole-lake sediment accumulation rates (*open circles*) in Lake St. Croix and Lake Pepin, 1800–2000 **b** Whole-lake ASi flux ratios, calculated as the ratio of flux at each time period to the flux before Euro-American settlement, in Lakes St. Croix and Pepin

Lake St. Croix reaching 5590 t year^{-1}, a fivefold increase from background (pre-Euro-American settlement) conditions, and in Lake Pepin reaching 52,300 t year^{-1}, a 16-fold increase from background conditions. For comparison, the whole-lake sediment accumulation rate in Lake St. Croix in the 1990s was less than threefold higher (Triplett et al. 2009) and in Lake Pepin tenfold higher than rates prior to Euro-American settlement rates (Engstrom et al. 2009).

TP concentrations in the water-column of Lake St. Croix increased slightly after Euro-American settlement then rapidly after 1950, peaking in the 1990s at twice the lake's background concentration (Edlund et al. 2009). The TP concentrations in Lake Pepin also increased most rapidly after 1950 and were still increasing in the 1990s to more than four times pre-settlement values (Engstrom et al. 2009).

Trapping efficiency

The peak ASi flux ratios (modern:pre-settlement) in both lakes were calculated in sediments from the 1990s: 5.2 and 16 for Lake St. Croix and Lake Pepin, respectively.

The ASi trapping efficiency of Lake St. Croix in 2004–2005 was 9.7% and that of Lake Pepin was 19.8%. Lake St. Croix exported about 90% of the TSi_b that entered its upstream end to the Mississippi River, while Lake Pepin exported 80% of its TSi_b load downstream; the remainder was trapped in the sediments of the two impoundments.

The three scenarios used to reconstruct historical ASi trapping efficiencies for the lakes estimated inflowing TSi_b along a range, from equivalent to modern-day TSi_b inflow to account for enhanced DSi transport with forest removal and soil disturbance (Conley et al. 2008). All three scenarios produced low background (pre-Euro-American settlement) efficiencies for both lakes. For Lake St. Croix, Scenario 1 (inflow TSi_b held constant) produced the lowest trapping efficiency of 1.8% and Scenario 2 (inflow TSi_b doubled after Euro-American settlement) gave the highest ASi background trapping efficiency of 3.7% (Fig. 6). Scenario 3 (inflow TSi_b increased then decreased) produced an intermediate pre-settlement value of 2.8%. Similarly, for Lake Pepin, Scenario 1 produced the lowest background trapping efficiency of 1.1%, and Scenario 2 the highest efficiency of 2.3%, and Scenario 3 an intermediate value of 1.7% (Fig. 6).

Discussion

ASi burial

Measured TSi_b fluxes show that the larger, nutrient-rich Mississippi River delivers more Si to Lake Pepin (262,000 t year^{-1}) than does the mesotrophic St. Croix River to Lake St. Croix (57,500 t year^{-1}).

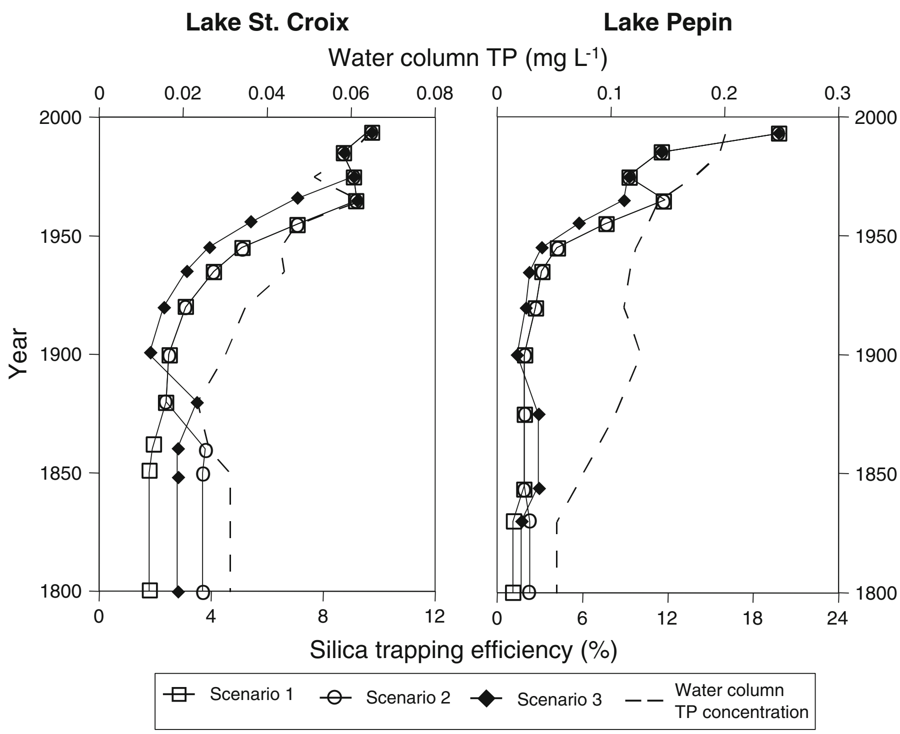


Fig. 6 Amorphous silica (ASi) trapping efficiency is plotted with water column concentration of total phosphorus (TP), as reconstructed by diatom analysis, for Lake St. Croix and Lake Pepin, 1800–2000. ASi trapping efficiency was calculated as the ratio of ASi flux to the sediment versus inflowing bioavailable silica (TSi_b). In Scenario 1, TSi_b has been constant since Euro-American settlement; in Scenario 2, TSi_b doubled after settlement; and in Scenario 3, TSi_b doubled following settlement then declined by one-third in recent decades

However, the ASi sediment concentrations in Lake Pepin are generally lower than those in Lake St. Croix, because the sediment flux to Lake Pepin is much higher, effectively diluting ASi in the sedimentary record. Some of the variability in ASi concentration between proximal cores (e.g. Lake St. Croix cores 8C and 7B) and within single cores (e.g. Lake Pepin core I.1) may also be attributed to different or changing rates of sediment accumulation. In a companion study of the modern silica fluxes in these two systems, Triplett et al. (2008) determined that the export of re-dissolved ASi from the lake sediments back to the water column was a very small component of the Si budgets in both lakes. Modern sediment accumulation rates in Lake St. Croix (1.74 kg m^{-2} $year^{-1}$, Triplett et al. 2009) and Lake Pepin (8.64 kg m^{-2} $year^{-1}$, Engstrom et al. 2009) are high relative to most other non-riverine lakes in Minnesota (median value of 55 lakes: 1.55 kg m^{-2} $year^{-1}$; Engstrom et al. 2007) so sedimented ASi is rapidly buried and isolated from overlying water. (Lake water is undersaturated with respect to ASi, so continued contact would lead to dissolution.) Artificial impoundments on rivers generally have high sediment accumulation rates as well, so ASi recycling from reservoir sediments is also likely a small flux that does little to diminish the trapping of ASi behind dams. Note that, although ASi may or may not be recycled rapidly in freshwater, ASi solubility increases dramatically upon exposure to saline water in coastal areas (Hamrouni and Dhahbi 2001; Icenhower and Dove 2000) and thus should be considered to be bioavailable to marine organisms.

ASi burial through time

The Si flux to Lake Pepin has always been larger than the flux to Lake St. Croix, in part because the Mississippi River is larger than the St. Croix, so ASi accumulation rates have also been higher in Lake Pepin (Fig. 5a). ASi accumulation in both lakes increased in the 1940s and 1950s and has remained high despite a significant reduction in whole-lake sediment accumulation in Lake St. Croix, reflecting the fact that ASi is more tightly coupled to other factors (i.e. TP concentration) than to sediment accumulation. ASi flux ratios show that the rate of ASi sequestration in Lake Pepin has increased more than has the sequestration in Lake St. Croix, relative to pre-eutrophication fluxes to each lake. By the 1990s, the ASi flux ratio in Lake St. Croix was over 5 (relative to a pre-eutrophication ratio of 1.0), but in Lake Pepin the ratio had reached 16 (Fig. 5b).

Another way to interpret temporal changes in ASi flux to the sediment is as the ASi trapping efficiency of a lake through time. ASi trapping efficiency (Eq. 2) measures how much of the riverine TSi_b is sequestered in lake sediments and thus is not exported to marine ecosystems. Also, because ASi trapping efficiency is the ratio of sedimented ASi to incoming TSi_b, it is not merely a function of increased sediment accumulation rates. While historical ASi flux to the sediment was measured directly from lake sediment cores, the only TSi_b data in existence for these two lakes were collected during the one year of this study and it cannot be assumed to represent historical conditions.

The 2004–2005 TSi_b fluxes were collected during an "average" flow year and so represent average TSi_b fluxes that do not capture inter-annual variability. Further uncertainty arises when the modern TSi_b fluxes are used to estimate historical TSi_b fluxes, largely because land use has changed so dramatically in the last century and a half. Biogeochemists once believed that Si flux from land to water was simply a function of weathering rates of rocks and soil minerals. However, recent work by Conley (2002) and Derry et al. (2005), among others, has shown that a large portion of inorganic Si released by weathering goes through a terrestrial biological cycle before reaching surface waters. The importance of terrestrial Si cycling was also apparent at Hubbard Brook, New Hampshire, where DSi export increased by 37% within 5 months of deforestation of a watershed (Likens et al. 1970), and remained elevated for several decades thereafter (Conley et al. 2008). The record from Hubbard Brook represents a unique, long-term dataset with defined experimental manipulations, and no comparable studies have been done in agricultural regions such as Minnesota. Historical land use change over many centuries in Europe led to lowered TSi mobilization through cultivation and depletion of soil ASi pools (Struyf et al. 2010) and it is reasonable to assume that the conversion of millions of hectares of midwestern prairie and forest to row-crop agriculture changed Si fluxes, both DSi and ASi, to the Mississippi River and its tributaries.

The Hubbard Brook study provides the basis for the three scenarios used here to model historical TSi_b fluxes to Lakes St. Croix and Pepin. Scenario 1 represents the simplest case, in which riverine TSi_b inflow has not changed through time. It suggests that either plant uptake of DSi remained constant after land conversion in the Mississippi and St. Croix watersheds, or that a higher rate of DSi export from land to water was counterbalanced by decreased mineral weathering, a potential consequence of hydrological alterations to the landscape such as ditching and drainage. Scenario 2, in which TSi_b fluxes doubled immediately following Euro-American settlement, represents a large sustained enhancement from the wholesale replacement of perennial vegetation by annual row-crops. Scenario 3 most closely mimics the Hubbard Brook data: TSi_b flux increased with vegetation clearance and then decreased many decades later. In both Scenarios 2 and 3, TSi_b flux doubled after clearance, which is more dramatic than the 37% increase observed at Hubbard Brook.

Despite the differences in TSi_b fluxes among the scenarios, all results showed that ASi trapping efficiency in both lakes has increased substantially since Euro-American settlement (Fig. 6). The ASi trapping efficiency of Lake St. Croix rose from a background between 1.8% and 3.7–9.8%, a two- to fivefold increase. During the same period, TP concentrations in the water-column increased along a similar trajectory (Edlund et al. 2009). In contrast, the ASi trapping efficiency of Lake Pepin went from a baseline between 1.1% and 2.3–19.8%, a 9- to 16-fold increase. The TP concentrations in Lake Pepin began increasing in the early 1900s (Engstrom et al. 2009), prior to the rise in the ASi trapping efficiency, and peaked in the 1990s at four times background concentration, coincident with the peak ASi trapping efficiency. As shown in Fig. 7, ASi trapping efficiency in the two lakes follows an exponential relationship with TP concentrations; $R^2 = 0.8$ in both cases. For a given DSi flux to the lakes, it would appear that a unit increase in TP leads to more than a unit increase in ASi burial, and that TP may be recycled in the lakes to produce multiple generations of diatoms before it is permanently sedimented or flushed through the outflow. While in-lake recycling of TP might be expected to be higher in the relatively shallow water of Lake Pepin, Triplett et al. (2008) showed that any such effect does not directly correspond to significant increases in

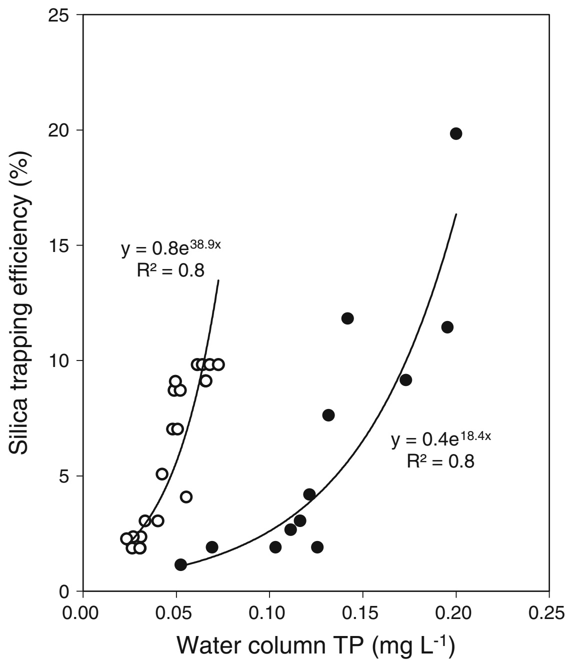


Fig. 7 The relationships between concentration of total phosphorus (TP) in the water column and amorphous silica (ASi) trapping efficiency since 1800. ASi trapping efficiency depicted here is with no change in inflow TSi_b through time (Scenario 1) for Lake St. Croix and Lake Pepin. Historical water column TP values were reported by Edlund et al. (2009) and Engstrom et al. (2009)

diatom production due to other limiting factors in the environment.

Effects of eutrophication

The consistently lower ASi trapping efficiency for Lake Pepin at any given TP (Fig. 7) may be due to the ecosystem effects of eutrophication. First, phosphorus may not be limiting diatom growth in Lake Pepin, so that TP and ASi burial are less tightly coupled in Lake Pepin than in Lake St. Croix. There is strong evidence that primary production in Lake Pepin is light-limited on account of high turbidity from suspended silts and clays and occasionally nitrogen-limited as well (Lafrancois et al. 2009). Also, primary production in Lake Pepin may be dominated by non-siliceous algae (greens and blue-greens), which compete with diatoms for both light and nutrients. Also, the diatom community itself has been significantly altered: Edlund et al. documented that as TP increased in Lake St. Croix, the dominant type of diatom changed from benthic species to planktic species (2009). Similarly, in Lake Pepin benthic species comprised 50% of the diatom population before 1900 to less than 10% by 1940 (Engstrom et al. 2009). All of these ecosystem effects are direct results of land-use change and eutrophication, and are an integral part of the relationship between eutrophication and silica trapping in impacted rivers.

The relatively low ASi trapping efficiency of Lake Pepin may also be due to reductions in the physical capacity of that basin to trap particles as sediment has filled the lake basin; for example, ASi may be more easily resuspended by wave or boat-wake action in the relatively shallow water of Lake Pepin. However, changes in basin morphometry of both lakes, quantified in previous studies, are small. Lake Pepin has lost about 17% of its volume (Engstrom et al. 2009), while Lake St. Croix has lost about 8% of its volume (Triplett et al. 2009) since the 1800s due to sediment infilling. Those volume losses would have only a minor effect on lake residence time and hence on particle trapping dynamics and ASi burial.

The magnitudes of change in TP and ASi accumulation in Lakes St. Croix and Pepin exemplify a range of possible relationships between nutrient loading and ASi trapping. During the past two hundred years, Lake Pepin experienced a larger increase in TP and a larger increase in ASi trapping efficiency than did Lake St. Croix (Fig. 7). Because of intensive agriculture and urbanization, Lake Pepin's TP concentration increased 4× between 1800 and 1996 and ASi trapping efficiency increased between 9× and 16× (depending on the scenario used to model historical TSi_b inflow). Anthropogenic activities have had far less impact on Lake St. Croix, so that it experienced smaller changes in TP concentration and ASi trapping (Table 3).

The region bounded by the Lake St. Croix and Lake Pepin datasets (Table 4) may be used to estimate the change in ASi trapping efficiency in other impoundments with a given change in phosphorus concentration. However, if factors other than eutrophication have strongly affected algal productivity or physical characteristics of the impoundment, the relationship may be different. For example, a lake with a change in TP identical to that of Lake St. Croix might have a smaller change in ASi trapping efficiency if turbidity increased dramatically and severely limited diatom growth.

Table 3 The minimum and maximum rates of sediment accumulation and ASi accumulation in Lake St. Croix and Lake Pepin between 1800 and 2000

Lake	Sediment minimum (t $year^{-1}$)	Sediment maximum (t $year^{-1}$)	ASi minimum (t $year^{-1}$)	ASi maximum (t $year^{-1}$)
St. Croix	16,000 (±1,600)	131,000 (±13,000)	1100 (±100)	5600 (±1,000)
	(<1850)[a]	(1950–1959)	(<1850)	(1990–1999)
Pepin	79,000 (±8,000)	876,000 (±88,000)	3300 (±200)	52,000 (±9,300)
	(<1830)[a]	(1990–1996)[b]	(<1830)	(1990–1996)

The time period of the reported rate is in parentheses. Error terms (in parentheses) represent ±1SD

[a] Euro-American settlement began in around 1850 in the St. Croix River watershed and in 1830 in other parts of the Mississippi River watershed

[b] The Lake Pepin sediment cores were collected in 1996

Table 4 Changes in concentration of total phosphorus (TP) in the water column (from Triplett et al. 2009 and Engstrom et al. 2009) and silica trapping efficiencies since 1800

	Lake St. Croix	Lake Pepin
Increase in water column TP (%)	100	280
Minimum modeled increase in silica trapping efficiency (%)	160	770
Maximum modeled increase in silica trapping efficiency (%)	430	1600

The minimum and maximum changes in silica trapping efficiency are as modeled by Scenario 1 (lake inflow total bioavailable Si (TSi_b) has not changed since 1800) and Scenario 2 (lake inflow TSi_b doubled after Euro-American settlement), respectively

Conclusions

The eutrophication of rivers increases the ASi trapping efficiency of riverine impoundments, thereby decreasing the amount of TSi_b reaching coastal marine ecosystems. In Lakes St. Croix and Pepin, long sediment records provide unique historical perspectives on this subject not usually found in large river systems. Both lakes were very inefficient at trapping ASi prior to eutrophication, both around 2%, indicating that the existence of impoundments would, by itself, trap little ASi. However, the onset of major land-use change and the attendant effects of eutrophication caused the ASi trapping efficiencies of both lakes to significantly increase. Therefore, eutrophication is more important than other dam effects in controlling the ASi trapping efficiency of riverine impoundments, although those effects may ultimately determine the mass of ASi exported from the system.

Furthermore, these two lakes bracket a range of trophic change. The extensive landscape alteration in the Mississippi River watershed has led to a larger change in nutrient concentrations in Lake Pepin than in Lake St. Croix, and thus to a larger change in ASi trapping efficiency. The relationship outlined by the two contrasting lakes may help estimate the effect of eutrophication on other impoundments where multiple dam effects are simultaneously affecting riverine exports of Si to the ocean.

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References

Bennion H (1994) A diatom-phosphorus transfer function for shallow, eutrophic ponds in southeast England. Hydrobiologia 275–276:391–410

Blumentritt DJ, Wright HE Jr, Stefanova V (2009) Formation and early history of Lakes Pepin and St. Croix of the upper Mississippi River. J Paleolimnol 41:541–543

Caraco NF (1993) Disturbance of the phosphorus cycle: a case of indirect effects of human activity. Trends Ecol Evol 8:51–54

Carlson RE (1977) A trophic state index for lakes. Limnol Oceanogr 22:361–369

Conley DJ (1997) Riverine contribution of biogenic silica to the oceanic silica budget. Limnol Oceanogr 42:774–777

Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochem Cycles 16:1121. doi:1110.1029/2002GB001894

Conley DJ, Schelske CL (1993) Potential role of sponge spicules in influencing the silicon biogeochemistry of Florida lakes. Can J Fish Aquat Sci 50:296–302

Conley DJ, Schelske CL (2001) Biogenic silica. In: Smol JP, Birks HB, Last WM (eds) Tracking environmental change using lake sediments. Kluwer, Dordrecht, pp 281–293

Conley DJ, Stalnacke P, Pitkanen H, Wilander A (2000) The transport and retention of dissolved silicate by rivers in Sweden and Finland. Limnol Oceanogr 45:1850–1853

Conley DJ, Likens GE, Buso DC, Saccone L, Bailey SW, Johnson CE (2008) Deforestation causes increased dissolved silicate losses in the Hubbard Brook Experimental Forest. Global Change Biol 14:2548–2554

DeMaster DJ (1981) The supply and accumulation of silica in the marine environment. Geochim Cosmochim Acta 45:1715–1732

Derry LA, Kurtz AC, Ziegler K, Chadwick OA (2005) Biological control of terrestrial silica cycling and export fluxes to watersheds. Nature 433:728–730

Edlund MB, Engstrom DR, Triplett LD, Lafrancois BM, Leavitt P (2009) 20th century eutrophication of the St. Croix River (Minnesota–Wisconsin, USA) reconstructed from the sediments of its natural impoundment. J Paleolimnol 41:641–657

Engstrom DR, Balogh SJ, Swain EB (2007) History of mercury inputs to Minnesota lakes: influences of watershed disturbance and localized atmospheric deposition. Limnol Oceanogr 52:2467–2483

Engstrom DR, Almendinger JE, Wolin JA (2009) Historical changes in sediment and phosphorus loading to the Upper Mississippi River: mass-balance reconstructions from the sediments of Lake Pepin. J Paleolimnol 41:563–588

Hamrouni B, Dhahbi M (2001) Analytical aspects of silica in saline waters—application to desalination of brackish waters. Desalination 136:225–232

Howarth RW, Marino R (2006) Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: evolving views over three decades. Limnol Oceanogr 51:364–386

Humborg C, Conley DJ, Rahm L, Wulff F, Cociasu A, Ittekkot V (2000) Silicon retention in river basins: far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. Ambio 29:45–50

Humborg C, Blomqvist S, Avsan E, Bergensund Y, Smedberg E (2002) Hydrological alterations with river damming in northern Sweden: implications for weathering and river biogeochemistry. Global Biogeochem Cycles 16:12-11–12-12

Humborg C, Pastuszak M, Aigars J, Siegmund H, Morth C-M, Ittekkot V (2006) Decreased silica land-sea fluxes through damming in the Baltic Sea catchment—significance of particle trapping and hydrological alterations. Biogeochemistry 77:265–281

Icenhower JP, Dove PM (2000) The dissolution kinetics of amorphous silica into sodium chloride solutions: effects of temperature and ionic strength. Geochim Cosmochim Acta 64:4193–4203

Krausse GL, Schelske CL, Davis CO (1983) Comparison of three wet-alkaline methods of digestion of biogenic silica in water. Freshw Biol 13:73–81

Lafrancois BM, Magdalene S, Johnson DK (2009) Recent water quality trends and a comparison to sediment-core records for two riverine lakes of the Upper Mississippi River basin: Lake St. Croix and Lake Pepin. J Paleolimnol 41:603–622

Likens GE, Bormann FH, Johnson NM, Fisher DW, Pierce RS (1970) Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. Ecol Monogr 40:23–47

McKnight R (1991) Determination of silica in waters by flow injection analysis, 0.2 to 20.0 mg SiO_2/L. QuikChem method 10-114-27-1-A. Lachat Instruments, Milwaukee

Meybeck M (2002) Riverine quality at the Anthropocene: propositions for global space and time analysis, illustrated by the Seine River. Aquat Sci 64:376–393

Mulla DJ, Sekely AC (2009) Historical trends affecting accumulation of sediment and phosphorus in Lake Pepin, upper Mississippi River, USA. J Paleolimnol 41:589–602

Ramstack JM, Fritz SC, Engstrom DR, Heiskary SA (2003) The application of a diatom-based transfer function to evaluate regional water-quality trends in Minnesota since 1970. J Paleolimnol 29:79–94

Reavie ED, Hall RI, Smol JP (1995) An expanded weighted averaging model for inferring past total phosphorus concentrations from diatom assemblages in eutrophic British Columbia (Canada) lakes. J Paleolimnol 14:49–67

Saccone L, Conley DJ, Koning E, Sauer D, Sommer M, Kaczorek D, Blecker SW, Kelly EF (2007) Assessing the extraction and quantification of amorphous silica in soils of forest and grassland ecosystems. Eur J Soil Sci 58:1446–1459

Sferratore A, Garnier J, Billen G, Conley DJ, Pinault S (2006) Diffuse and point sources of silica in the Seine River watershed. Environ Sci Technol 40:6630–6635

Struyf E, Smis A, Van Damme S, Garnier J, Govers G, Van Wesemae B, Conley DJ, Batelaan O, Frot E, Clymans W, Vandevenne F, Lancelot C, Goos P, Meire P (2010) Historical land use change has lowered terrestrial silica mobilization. Nat Commun 1:129

Triplett LD, Engstrom DR, Conley DJ, Schellhaass SM (2008) Silica fluxes and trapping in two contrasting natural impoundments of the upper Mississippi River. Biogeochemistry 87:217–230

Triplett LD, Engstrom DR, Edlund MB (2009) A whole-basin stratigraphic record of sediment and phosphorus loading to the St. Croix River, USA. J Paleolimnol 41:659–677

Turner RE, Qureshi N, Rabalais NN, Dortch Q, Justic D, Shaw R (1998) Fluctuating silicate:nitrate ratios and coastal plankton food webs. Proc Natl Acad Sci USA 95:13048–13051

Vorosmarty CJ, Meybeck M, Fekete B, Sharma K (1997) The potential impact of neo-Castorization on sediment transport by the global network of rivers. In: Human impact on

erosion and sedimentation: fifth scientific assembly of the IAHS. IAHS, Rabat, pp 261–273
Wahby SD, Bishara NF (1980) The effect of the River Nile on Mediterranean water, before and after the construction of the High Dam at Aswan. In: Martin JM, Burton JD, Eisma D (eds) River inputs to ocean systems. UNEP, IOC, SCOR, United Nations, New York, pp 311–318