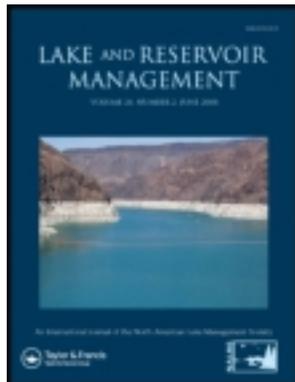


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### Long-term Changes in Iron and Phosphorus Sedimentation in Vadnais Lake, Minnesota, Resulting from Ferric Chloride Addition and Hypolimnetic Aeration

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# Long-term Changes in Iron and Phosphorus Sedimentation in Vadnais Lake, Minnesota, Resulting from Ferric Chloride Addition and Hypolimnetic Aeration

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## Abstract

Engstrom, D. R. 2005. Long-term changes in iron and phosphorus sedimentation in Vadnais Lake, Minnesota, resulting from ferric chloride addition and hypolimnetic aeration. *Lake and Reserv. Manage.* 21(1):96-106.

Changes in iron (Fe) and phosphorus (P) cycling in Vadnais Lake, Minnesota, resulting from ferric chloride addition and hypolimnetic aeration are evaluated by repeat sampling of bottom sediments over a 13-year period: in 1985 (pre-treatment), and in 1990 and 1998 (post-treatment). Lead-210 derived accumulation rates for Fe, Mn, total-P, and P-fractions are combined with input/output monitoring to construct chemical mass-balances for each of the three time periods. Iron injections/aeration caused large and sustained reductions in water-column total-P by increasing phosphorus removal to the sediments and preventing its recycling during stratification. Annual whole-lake phosphorus sedimentation rose from 1.26 to 1.52 t between 1985 and 1990, equivalent to a doubling of in-lake retention of external P loads (from 19% to 38%). Most of the increase is represented in the labile Fe-bound fraction. The measured sedimentary fluxes for 1985 and 1990 are similar to those calculated by difference from inflow/outflow data, whereas measured P sedimentation in 1998 ( $2.43 \text{ t-yr}^{-1}$ ) is three times higher than that estimated from input/output calculations. These results suggest surface enrichment by upward P diffusion within the sediment column. Present-day Fe accumulation rates ( $24 \text{ t-yr}^{-1}$ ) are 33% greater than those immediately preceding treatment and 14% greater than pre-settlement fluxes ( $21 \text{ t-yr}^{-1}$ ). The  $6 \text{ t-yr}^{-1}$  increase in Fe accumulation between 1985 and 1998 is roughly equal to the rate of iron injection to Vadnais Lake. Fifty-four tons of iron addition to the Lambert Creek tributary between 1990 and 1998 have also enriched littoral sediments in Fe, P, and Mn near the creek's outfall. These engineering solutions have substantially improved water quality in Vadnais Lake, but continued hypolimnetic aeration will be required to prevent internal phosphorus loading from the large reservoir of labile sedimentary P that has accumulated since treatment began.

**Key Words:** Iron addition, hypolimnetic aeration, sedimentation, phosphorus inactivation, internal loading.

Chemical addition to lakes and reservoirs to regulate internal phosphorus (P) cycling is an important management tool for controlling nuisance algal blooms. The purpose is to enhance P removal from the water column and to retard its release from the sediments. The most widely used additives, aluminum sulfate (alum) and/or sodium aluminate, have been shown to be moderately to highly effective in numerous case studies (Cooke *et al.* 1993, Smeltzer *et al.* 1999, Welch & Cooke 1999). A potentially viable alternative, iron (Fe) addition (as ferric chloride or ferric sulfate) has been used only infrequently, and in most cases with limited success, largely because of the need to maintain oxygenated conditions during stratification and so prevent redox mobilization of the ferric hydroxide-phosphorus complex. However, iron does not exhibit the pH-related toxicity of Al, and so might be prefer-

able in poorly buffered waters and for long-term continuous applications such as municipal water supplies.

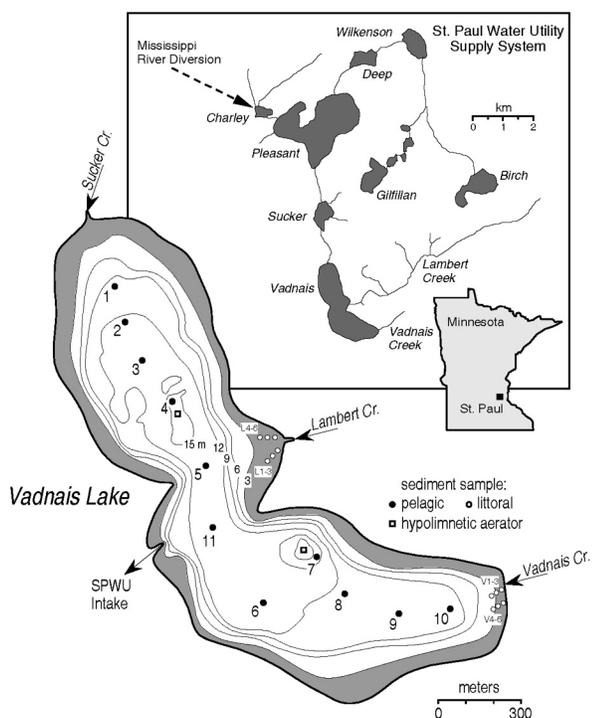
Cooke *et al.* (1993) reviewed a handful of case studies involving iron additions and concluded that none demonstrated long-term control of internal P loading. They cited as promising a design by Walker *et al.* (1989) to use hypolimnetic aeration in tandem with iron additions in the chain of lakes supplying water to the city of St. Paul, Minnesota. That design has now been in near-continuous operation for over a decade, and the results in terms of reduced water-column phosphorus and algal blooms have been remarkable (Walker 2000). However, questions remain regarding the fate of the added iron as well as the removed phosphorus: how has this long-term treatment affected Fe and P cycling within

the water-column and sediments; how have sedimentary concentrations and fluxes of Fe and P changed; and how do present-day Fe and P budgets compare with pre-treatment conditions? These questions are important not only in terms of understanding the processes involved, but also because of regulatory concerns about both the effectiveness and potential impacts of this type of lake treatment.

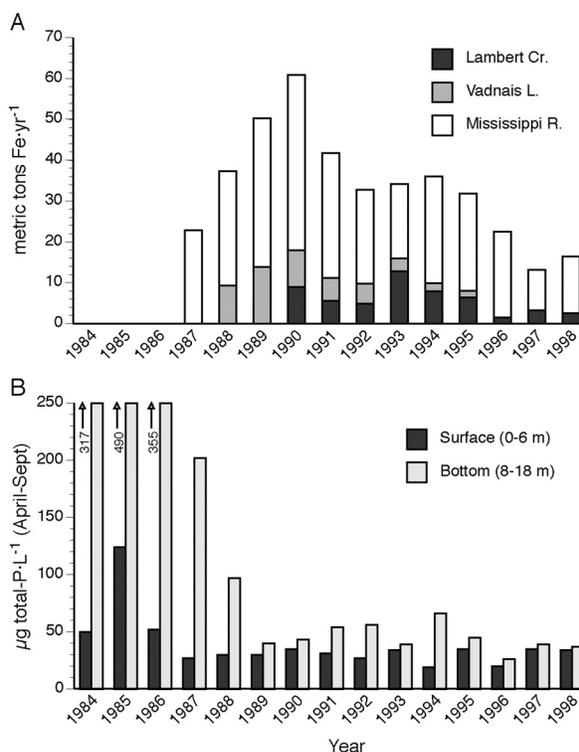
This long-term study quantifies the changes in iron and phosphorus budgets of Vadnais Lake – the terminal reservoir in the St. Paul water supply system – by comparing iron and phosphorus sedimentation before and after iron treatment commenced. Iron (as  $\text{FeCl}_3$ ) has been injected through hypolimnetic aerators, in operation in Vadnais Lake since 1987, and added to inlet streams, principally Lambert Creek. The study compares recent (1998) P and Fe sedimentation rates to those measured in 1990 (after several years of Fe addition) and 1985 (prior to Fe addition) and uses a similar sampling and analytical strategy throughout its course. It also employs data from long-term hydrological and chemical monitoring of the Vadnais Lake chain to develop iron and phosphorus mass-balances under both past and present-day management practices.

## Study Site

The St. Paul Water Utility (SPWU) obtains source water from a chain of lakes and impoundments supplied primarily by diversion from the Mississippi River and seasonally by runoff from local watersheds (Fig. 1). The system consists of three primary reservoirs that flow downstream from Pleasant Lake through Sucker Lake and finally to Vadnais Lake, from which the water is pumped to the SPWU filtration plant. The quality of the water delivered to the SPWU has been impaired historically by inputs of excess nutrients, particularly phosphorus, from changes in land-use in the contributing watersheds. As the terminal reservoir in the chain, Vadnais Lake exerts considerable influence on nutrient dynamics, algal productivity, and ultimately the presence of taste and odor problems that have until recently plagued St. Paul water supplies. Vadnais Lake is a moderately deep (mean depth = 8 m), 159 ha natural reservoir with an average residence time of 0.24 yr. Water enters the lake primarily through Sucker and Lambert Creeks and outflows almost entirely through the SPWU pumping station (Fig. 1). The basin itself is steep sided with only a modest littoral area and a relatively large flat profundal region; roughly 50% of the lake bottom is between 9 and 12 meters deep. Fine-grained



**Figure 1.**—Bathymetry and locations of sample sites and hypolimnetic aerators in Vadnais Lake, the terminal basin in the St. Paul Water Utility's supply system. The shaded region above the 3-m contour is non-depositional for fine-grained sediments.



**Figure 2.**—(A) Ferric chloride usage by the St. Paul Water Utility, and (B) mean (April-Sept) total-phosphorus concentrations in surface and bottom waters of Vadnais Lake, 1984-1998.

organic-rich sediments accumulate throughout the deeper parts of the lake (> 3 meters), while coarse sandy materials and rocky substrates dominate the littoral fringe.

In 1984 the SPWU began a comprehensive monitoring and engineering program aimed at understanding and improving water quality in the Vadnais chain of lakes (Schuler 1996). A system of 22 stream-flow and reservoir sampling stations was established to gain understanding of the supply system dynamics and to provide a mass-balance quantification of nutrient loading sources. In 1987 a ferric chloride feed system was added to the Mississippi River pumping station, and two hypolimnetic aerators were installed in Vadnais Lake. The injected iron scavenges dissolved P from the river water and precipitates it to the sediments of Charley and Pleasant lakes, while the hypolimnetic aerators introduce both air and ferric chloride to the bottom waters of Vadnais Lake to inhibit internal P loading during summer stratification. Direct Fe injection into Vadnais Lake ended in 1995, although hypolimnetic aeration continued. In 1990 a ferric chloride injection system was also installed just above the outfall of Lambert Creek into Vadnais Lake, and in 1994 two formerly-drained wetlands in the Lambert flowage were re-impounded to increase upstream retention of phosphorus. The history of  $\text{FeCl}_3$  usage by the SPWU is shown in Figure 2.

Phosphorus levels in Vadnais Lake responded dramatically to these engineering changes. With the onset of hypolimnetic aeration in 1987, surface water total-P declined from mean (April-Sept) values in excess of  $50 \mu\text{g}\cdot\text{L}^{-1}$  to about  $30 \mu\text{g}\cdot\text{L}^{-1}$ ; bottom-water improvements were even more pronounced with total-P decreasing from  $>300 \mu\text{g}\cdot\text{L}^{-1}$  to  $< 50 \mu\text{g}\cdot\text{L}^{-1}$  between 1986 and 1989 (Fig. 2). The treatments largely eliminated mid-summer phosphorus spikes and their associated algal blooms by increasing phosphorus removal to the sediments and preventing its recycling during thermal stratification. Reductions in upstream loads by iron treatment of the Mississippi River intake at Charley Lake, aeration of Pleasant Lake (1994), and iron injections at the Lambert Creek outfall also contributed to the sustained improvement of water-quality conditions in Vadnais Lake. A detailed evaluation and history of the SPWU water-quality controls is given by Walker (2000).

## Methods

### *Sediment Sampling*

The surface sediments of Vadnais Lake were sampled from a set of fixed stations (Fig. 1) in October-1985, May-1990, and October-1998 by means of a gravity corer operated by line from the lake surface. The sampler was fitted with a 4-cm diameter polycarbonate core barrel and typically collected the upper 10-20 cm of soft sediment. The sediments were extruded from the top of the core tube and the uppermost 3

cm of material were retained for analysis. In 1985 and 1990 the extruded core lengths were not measured precisely, but were calculated later from sediment wet density and the cross-sectional area of the core barrel. In 1998 a calibrated extrusion device was used, and core lengths were measured directly. Sample stations were located by visual approximation to shoreline features and confirmed by measured lake depth.

The number of sample stations was increased incrementally on each subsequent visit, so that some stations are not represented by the earlier dates. In 1990 two new sample sites (S-4 and S-7) were located 10-15 meters from the recently installed hypolimnetic aerators, and in 1998 a transect of three cores was collected at approximately 15, 30, and 45 meters from the aerators in the vicinity of S-4 (S-4a, 4b and 4c) and S-7 (S-7a, 7b and 7c). Littoral sediments were also sampled for the first time in 1998 near the outfalls of Lambert and Vadnais creeks (Fig. 1). In each of these two areas, three short cores (2-cm in length) were collected along each of two transects at locations approximately 10, 20, and 30 meters from the shore in water depths ranging from 0.50 to 1.85 m.

In 1990 a 1-m long core was collected from site S-11 using a piston corer operated from the lake surface by light-weight magnesium drill rods. The core was maintained in vertical position and extruded in the field at fixed increments of 1-5 cm in length. In 1998 the upper 15 cm of three surface cores (S-2, S-7b, and S-11) were sectioned into five contiguous depth increments, each section 3-cm in length. Based on  $^{210}\text{Pb}$  sedimentation rates (see below), these short cores encompass sediment intervals that had been at the surface at the time the sites were sampled in 1985 and 1990. All core samples were initially stored in polypropylene jars under refrigeration ( $4^\circ\text{C}$ ), but were subsequently dried for chemical analysis; 1985 and 1990 samples were oven dried at  $90^\circ\text{C}$  while 1998 sediments were freeze dried.

### *Loss-on-Ignition*

Dry-density (dry mass per volume of fresh sediment), water content, organic content, and carbonate ( $\text{CaCO}_3$ ) content of Vadnais sediments were determined by standard loss-on-ignition techniques (Dean 1974). Sediment samples of 1-2 g were dried overnight at  $100^\circ\text{C}$  and ignited at  $550^\circ$  and  $1000^\circ\text{C}$  for 1 hr each. Mass measurements were made of the wet samples and after each heating on an electronic analytical balance. Dry density was calculated from water content and fixed densities for organic, carbonate, and non-carbonate inorganic fractions.

### Lead-210 Dating

Surface sediments and core samples from all three collection years were analyzed for  $^{210}\text{Pb}$  activity to determine sediment ages and accumulation rates. Lead-210 was measured through its grand-daughter product  $^{210}\text{Po}$ , with either  $^{208}\text{Po}$  (1985 and 1990 samples) or  $^{209}\text{Po}$  (1998 samples) added as an internal yield tracer. The polonium isotopes were distilled from 0.5 - 4.0 g dry sediment at 550° C following pretreatment with concentrated HCl and plated directly onto silver planchets from a 0.5 N HCl solution (Eakins & Morrison 1978). Activity was measured for 1-7 days with ion-implanted or Si-depleted surface barrier detectors and an Ortec alpha spectroscopy system. Unsupported  $^{210}\text{Pb}$  was calculated by subtracting supported activity from the total activity measured at each level; supported  $^{210}\text{Pb}$  was estimated from the asymptotic activity at depth in the 1990 core from S-11. Dates and sedimentation rates for the S-11 long core were determined according to the c.r.s. (constant rate of supply) model (Appleby & Oldfield 1978) with confidence intervals calculated by first-order error analysis of counting uncertainty (Binford 1990).

A  $^{210}\text{Pb}$  dilution model that assumes a constant flux of  $^{210}\text{Pb}$  to the profundal region of the lake (Binford & Brenner 1986) was used to calculate sedimentation rates for the surface samples and ages for the deeper strata in each of the three short cores, S-2, S-7b, and S-11 (1998). According to this derivative of the c.r.s model, the sediment accumulation rate ( $r$ ) for any surface sample can be estimated by:

$$r = \lambda \cdot D / \ln \left( \frac{F}{F - \lambda \cdot A} \right)$$

where:  $\lambda$  = the decay constant for  $^{210}\text{Pb}$  ( $0.03114 \cdot \text{yr}^{-1}$ )  
 $D$  = the cumulative dry mass in the core interval ( $\text{g} \cdot \text{cm}^{-2}$ )  
 $F$  = the flux of unsupported  $^{210}\text{Pb}$  to the core site ( $\text{pCi} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$ )  
 $A$  = the inventory of unsupported  $^{210}\text{Pb}$  in the core interval ( $\text{pCi} \cdot \text{cm}^{-2}$ ).

The values for  $D$  and  $A$  are measured directly for each surface sample, while  $F$  is estimated from the rate of atmospheric  $^{210}\text{Pb}$  deposition with correction for sediment focusing. Because fine-grained sediments (with which  $^{210}\text{Pb}$  is associated) are eroded (focused) by wave action into deeper parts of the basin, the  $^{210}\text{Pb}$  flux to most sample sites should exceed the atmospheric rate. A  $^{210}\text{Pb}$  flux of  $0.9 \text{ pCi} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$  is assumed for all sites located below the 12-m depth contour, while a rate of  $0.6 \text{ pCi} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$  is applied to the three sites located

above 12 m (S-1, S-9, and S-10). These fluxes (weighted by their respective depth contours) are equivalent to an average lake-wide  $^{210}\text{Pb}$  flux of  $0.5 \text{ pCi} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$  (the atmospheric flux for this region) and a focusing factor of about 2 for sites below the 12-m contour—a value consistent with the inventory of unsupported  $^{210}\text{Pb}$  in the 1990 long core from site S-11 ( $37 \text{ pCi} \cdot \text{cm}^{-2}$ ). The assumption of uniform rates of  $^{210}\text{Pb}$  deposition to the profundal region of the lake is reasonable in light of the lake's simple morphometry.

Whole-basin sediment accumulation rates were estimated by weighting the sediment flux at each sample site by bathymetric depth contour and summing the values lakewide. Thus the average sedimentation rates for sites S-1, S-9, and S-10 were multiplied by the area of the lake bottom lying between the 3-m and 12-m depth contours (40 ha), sites S-2, S-3, S-5, S-6, S-8, and S-11 were weighted by the lake area between 12 and 15 m (75 ha), and the deepest sites, S-4 and S-7 were applied to depths below 15 m (4 ha). Lake depths above 3-m were considered to be non-depositional for fine-grained sediments, as only sand and coarser material were found in these shallow regions.

### Phosphorus and Iron Analysis

Sediments were extracted for phosphorus and metal determinations according to fractionation procedures adapted from Williams *et al.* (1971, 1976) and Engstrom and Wright (1984). The extraction procedure permits the estimation of three forms of sediment phosphorus:

*NAI-P* (Non-Apatite Inorganic Phosphorus) represents the inorganic phosphorus associated with iron/aluminum oxyhydroxides and that dissolved in sediment pore-fluids.

*Organic-P* is phosphorus bound to particulate organic matter. Microbial decay may convert some organic phosphorus into inorganic forms (NAI-P), which are subsequently bound to sediments or released into the water column.

*Apatite-P* represents phosphorus bound to mineral particles, especially calcium-carbonates. This form is relatively stable and is not readily recycled into the water column.

Total phosphorus was measured as the ortho-P extracted by sequential digestion with 30% hydrogen peroxide (1 hr at 85°C) followed by 0.5 M HCl (0.5 hr at 85°C). Non-apatite inorganic phosphorus (NAI-P) was measured by extracting a second subsample in 0.22 M sodium citrate/0.11 M sodium dithionite/0.11 M sodium bicarbonate (CDB) for 15 min. at 85°C; The sediment residue from the CDB extraction was further treated with 0.5 M HCl (16 hr at 25°C) to determine apatite phosphorus. A third subsample was also treated with

0.5 M HCl (16 hr at 25°C), but without the CDB step, to determine inorganic-P; Non-apatite inorganic P was estimated as the difference between the inorganic-P and apatite-P. Finally the residual (organically-bound) phosphorus was estimated from the difference between the total-P and the inorganic-P. The average relative difference for replicated extractions of five deep-water samples was 2% for total-P, 4% for apatite-P, and 6% for inorganic-P. Extracts were analyzed colorimetrically by spectrophotometer (1985 and 1990 samples) and Lachat Autoanalyzer (1998 samples). Independent measurements of total-P by ICP-MS for 1998 samples were almost identical to colorimetric determinations with an average relative difference of 1.5%.

Acid-extractable Fe and Mn and a suite of six other major elements (Al, Si, P, Mg, Ca, K) were analyzed from the same H<sub>2</sub>O<sub>2</sub>/HCl extract as that used for Total-P determinations. Concentrations were measured on a Perkin-Elmer ELAN-5000 inductively coupled plasma mass spectrometer (ICP-MS); all samples were measured at least five times; samples and standards were spiked with Rh and Sc to correct for instrument drift. Replicated extractions of four samples had an average relative difference of 5% for Fe and 8% for Mn.

## Results and Discussion

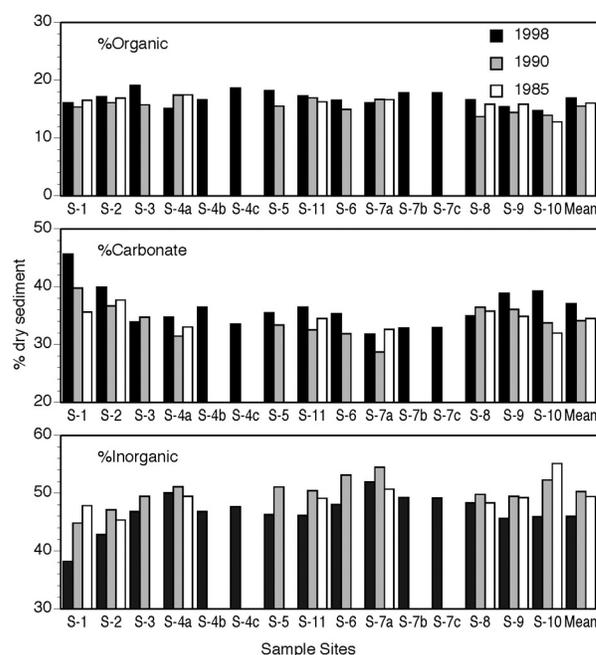
### Surface-Sediment Composition

The surficial sediments from the deep-water regions of Vadnais Lake are of fairly uniform composition (Fig. 3). Organic content averages  $16.3 \pm 1.4\%$  (s.d.), carbonate (CaCO<sub>3</sub>) is  $35.1 \pm 3.1\%$ , and non-carbonate inorganic materials make up the remaining  $48.6 \pm 3.3\%$ . There is no discernable pattern across the lake basin, and differences between 1985 and 1990 are small and variable among sample sites. However, samples from 1998 are significantly higher in organic matter and carbonates and lower in inorganic content (about 4% on average) than the 1985 ( $p = .015$ ) and 1990 ( $p < .0001$ ) collections (paired t-tests).

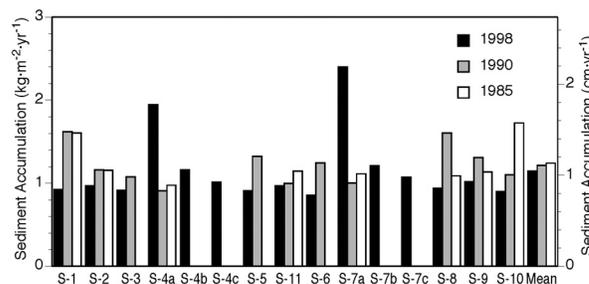
Sediment accumulation rates are likewise similar among sampling sites and from year to year, averaging  $1.2 \pm 0.3$  kg·m<sup>-2</sup>·yr<sup>-1</sup> (approximately 1.1 cm·yr<sup>-1</sup>) (Fig. 4). Only the two sites nearest the hypolimnetic aerators in 1998 (S-4a and S-7a) stand out with substantially elevated sediment fluxes (about twice the 1998 mean). These high accumulation rates proximal to the aerators are likely an artifact of low <sup>210</sup>Pb deposition caused by bottom turbulence and winnowing of fine-grained sediments away from the immediate vicinity of the aerators. This sediment winnowing is also seen in the concentration data for Fe, Mn, and P, all of which are associated with fine-grained particulates (see below). But even if the <sup>210</sup>Pb deposition rates for S-4a and S-7a are erroneously high, the effect on calculations of whole-lake accumulation is trivial (<1% difference), given the small portion of the lake

bottom represented by these core sites.

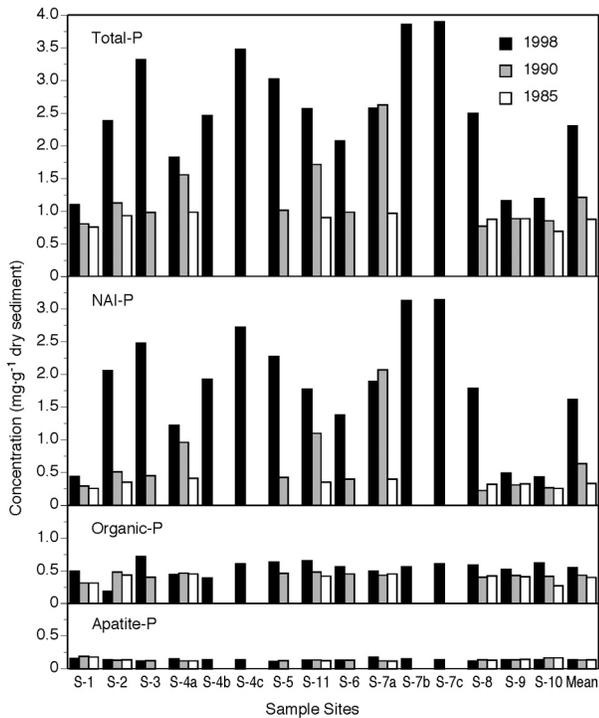
Phosphorus concentrations, on the other hand, show striking changes between collection years (Fig. 5). In 1985 deep-water sediments were spatially uniform in total-P ( $0.88 \pm 0.09$  mg·g<sup>-1</sup> dry mass) and similar in proportion of the three major fractions (38% NAI-P, 16% apatite-P, and 46% organic-P). In 1990 several sites, especially those near the aerators (S-4 and S-7), showed significant increases in total-P, so that the lake-wide mean rose to  $1.21 \pm 0.56$  mg·g<sup>-1</sup>. Virtually all of this increase was in the NAI-P fraction, as apatite-P and organic-P remained unchanged. By 1998 total-P concentrations had risen markedly at all sites below



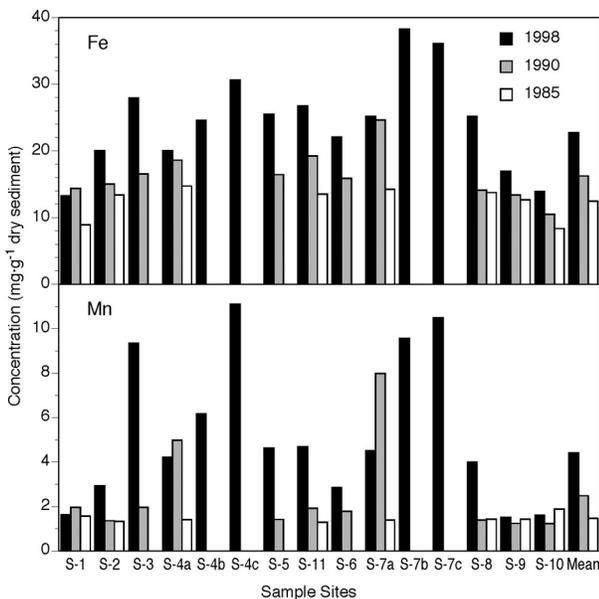
**Figure 3.**—Composition of Vadnais Lake surface sediments from loss-on-ignition analysis.



**Figure 4.**—Sediment accumulation rates at sample sites determined by <sup>210</sup>Pb dating. Linear accumulation rates are an approximation based on a mean bulk density of 0.11 g dry mass · cm<sup>-3</sup> wet sediment.



**Figure 5.**-Concentrations of total-phosphorus and P-fractions in surface sediments from Vadnais Lake.



**Figure 6.**-Iron and manganese concentrations in surface sediments from Vadnais Lake.

the 12-m depth contour (but less so at the shallower sites, S-1, S-9, and S-10), owing again to increased levels of NAI-P. P concentrations also increased with distance along the transect of sites away from the two aerators, S-4 (a-c) and S-7 (a-c), most likely a consequence of bottom turbulence and sediment winnowing (as noted for  $^{210}\text{Pb}$  above). In these most recent (1998) collections, total-P averaged  $2.35 \pm 0.92 \text{ mg}\cdot\text{g}^{-1}$  (almost 3x 1985 values), and 71% was in the NAI-P fraction.

The changes in iron and manganese concentrations between collection years mirror those exhibited by total-P and NAI-P (Fig. 6). In 1985, Fe concentrations averaged  $12.5 \pm 2.4 \text{ mg}\cdot\text{g}^{-1}$ , by 1990 they had risen to  $16.3 \pm 3.7 \text{ mg}\cdot\text{g}^{-1}$ , and in 1998 they were at  $23.1 \pm 7.2 \text{ mg}\cdot\text{g}^{-1}$ . Mn concentrations averaged  $1.5 \pm 0.2 \text{ mg}\cdot\text{g}^{-1}$  in 1985,  $2.5 \pm 2.1 \text{ mg}\cdot\text{g}^{-1}$  in 1990, and  $4.6 \pm 3.3 \text{ mg}\cdot\text{g}^{-1}$  in 1998. Iron increases between 1985 and 1990 were fairly uniform among sample sites, whereas those for Mn were largely restricted to the aerator sites, S-4 and S-7. By 1998 Mn as well as Fe had increased markedly at all sites below the 12-m depth contour, and like phosphorus, both elements showed higher concentrations along the transect of sites away from the two aerators. The Fe increases from 1990 to 1998 were smaller relative to those for P or Mn, so that Fe/P ratios decreased from a lakewide average of 14.3 in 1985 and 1990 to 10.4 in 1998; Fe/Mn ratios fell from an average of 8.6 to 6.4 during this same period.

### *Sediment Fluxes and Mass Balance*

The rising sedimentary concentrations of P, Fe, and Mn between collection years coupled with steady lake-wide sedimentation rates has resulted in a marked increase in burial of these elements in the sediments of Vadnais Lake (Fig. 7). Lake-wide total-P fluxes - estimated by weighting the P flux at each sample site by the portion of the depositional basin it represents (see methods) - were 1.26 metric tons ( $\text{t}\cdot\text{yr}^{-1}$ ) in 1985, 1.52  $\text{t}\cdot\text{yr}^{-1}$  in 1990, and 2.43  $\text{t}\cdot\text{yr}^{-1}$  in 1998. Virtually all of this increase was in the NAI-P fraction which increased by 40% between 1985 and 1990 and 150% from 1990 to 1998. Present-day (1998) Fe fluxes of 24.2  $\text{t}\cdot\text{yr}^{-1}$  are 7% higher than they were in 1990 (22.6  $\text{t}\cdot\text{yr}^{-1}$ ) and 36% above 1985 values (17.8  $\text{t}\cdot\text{yr}^{-1}$ ). Over this same 13-year time period (but mostly after 1990) Mn sedimentation doubled from 2.18 to 4.27  $\text{t}\cdot\text{yr}^{-1}$ .

These results provide strong evidence that engineering solutions (hypolimnetic aeration and iron injections) undertaken to increase phosphorus retention in Vadnais sediments have markedly altered the redox environment of the deeper parts of the basin, resulting in more effective burial of the P, Fe, and Mn loads entering the lake. Indeed previous analyses of the phosphorus mass-balance for Vadnais Lake (Walker 1990) arrived at the same conclusions based on direct hydrologic and water-quality monitoring (Fig. 8). Net phosphorus

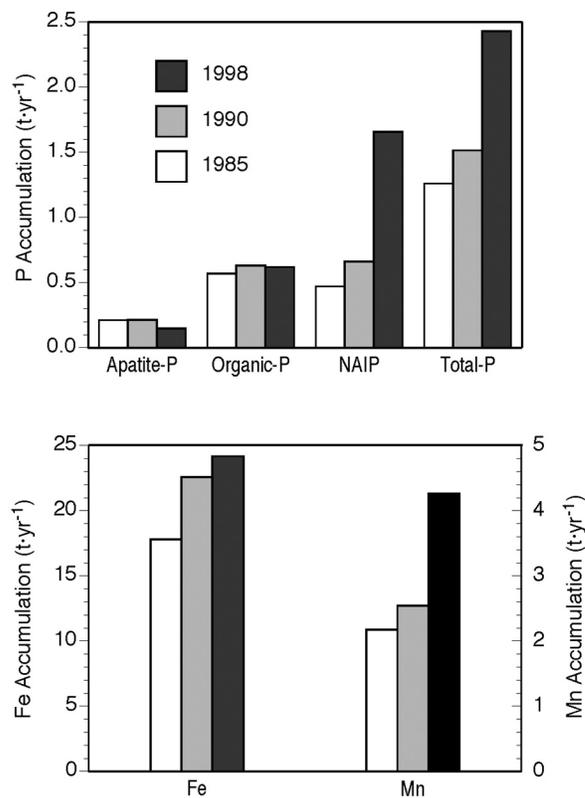
## Long-term Changes in Iron and Phosphorus Sedimentation in Vadnais Lake, Minnesota, Resulting from Ferric Chloride Addition and Hypolimnetic Aeration

sedimentation, estimated by the difference between monthly inflows, outflows, and changes in water-column storage of total-P for 1984-85 (1.26 t·yr<sup>-1</sup>) and 1988-89 (1.45 t·yr<sup>-1</sup>) are almost identical to rates determined for these same intervals by direct analysis of the sediments (Fig. 9). Although the increase in P sedimentation between 1985 and 1990 was small, P inputs declined simultaneously, and in-lake P retention was much enhanced. Both approaches (mass-balance and sediment cores) confirm that in-lake retention (sediment burial) doubled from about 19% to 38% of influent total-P following the onset of hypolimnetic aeration and iron injection.

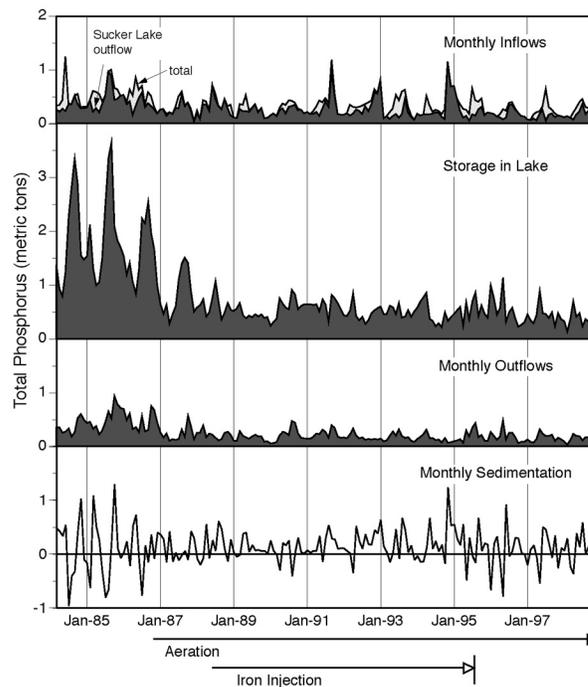
However, the coherence between sediment-core and mass-balance results does not hold for the 1998 sediment collections. Phosphorus sedimentation calculated by mass-balance for calendar years 1997-98 (8.83 t·yr<sup>-1</sup>) is about one-third the rate estimated from the sediment core data, and in-lake retention, according to the mass-balance, declined (from 1988-89 levels) to about 30% (Fig. 9). The sediment-core results imply a P retention rate in excess of 80%, a value that is difficult to reconcile with measured P inflows, lake-water P concentrations, and SPWU withdrawals (outflow). A difference of this magnitude is also difficult to explain by errors of estimation or measurement, especially as mass-balance and core data from the two earlier time periods match so well.

Because the increase in sedimentary P concentrations between 1990 and 1998 is so clear-cut, an additional P source (other than inflows) seems highly probable. That source is most likely redox dissolution of Fe-P complexes in sub-surface sediments and upward diffusion along a concentration gradient generated by precipitation at the oxidized surface (Carignan & Flett 1981). In Vadnais Lake, such diagenetic enrichment was likely enhanced by hypolimnetic aeration and FeCl<sub>3</sub> additions, which today inhibit diffusion of P across the sediment-water interface. It also appears that P enrichment has been building gradually since the onset of aeration, as it was not yet detectable in 1985 or 1990 sediment samples above that expected from external sources alone. Similar enrichment of surface sediments has been reported from other lakes subject to long-term hypolimnetic aeration, but in these cases much of the P was not permanently buried, but seasonally released back to the water column (Gächter & Wehrli 1998). Thus the recent build-up of high levels of labile P in Vadnais surface sediments (along with declining Fe/P ratios), imply that internal P-loading could become quite severe if aeration were ever interrupted.

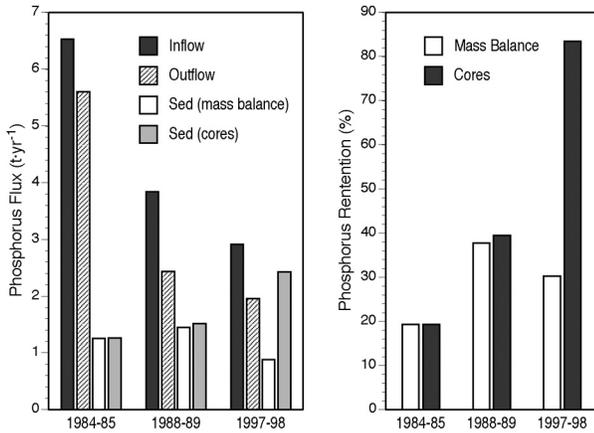
Manganese, which shows an almost identical pattern of increase to that of total-P (Fig. 9), may also be diagenetically enriched. Although there are no mass-balance data for Mn from which to confirm this possibility, Mn is readily mobilized at low redox potentials and is commonly enriched in the surface sediments of lakes. Iron sedimentation, on the other hand, shows only a modest 7% increase (1.6 t·yr<sup>-1</sup>)



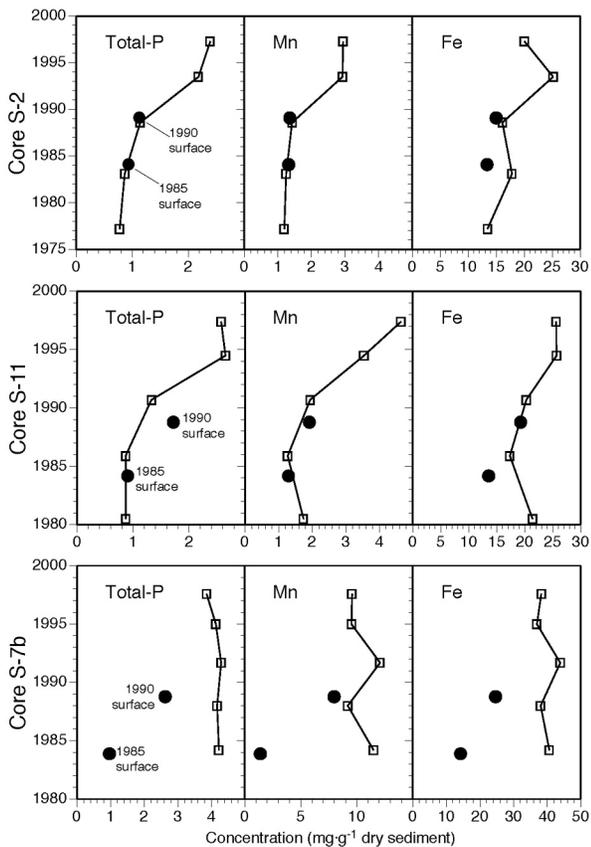
**Figure 7.** Whole-basin sedimentary fluxes of P, Fe, and Mn in Vadnais Lake.



**Figure 8.** Monthly phosphorus budget for Vadnais Lake from data compiled by the St. Paul Water Utility.



**Figure 9.**-Annual phosphorus sedimentation and retention for Vadnais Lake 1984-1998 calculated by mass-balance (difference between inflow and outflow) and directly from sediment-core data; retention is P-sedimentation (by mass-balance or sediment cores) as a percentage of P inflow.



**Figure 10.**-Comparison of P, Fe, and Mn concentrations in 1998 short cores (open squares) with concentrations in surface samples collected from the same sites in 1985 and 1990. Dates for 1998 cores determined by <sup>210</sup>Pb.

between 1990 and 1998, and thus may more closely correspond to actual changes in external Fe loading to the lake. The total increase in Fe sedimentation between 1985 and 1998 (6.3 t·yr<sup>-1</sup>) is only slightly greater than the average rate of hypolimnetic Fe injection between 1988 and 1998 (4.9 t·yr<sup>-1</sup>, Fig. 2), and if the Fe injections at the mouth of Lambert Creek are factored in, the intentional increase in external Fe loads is more than enough to account for the changes in Fe sedimentation in Vadnais Lake.

### Historical Trends from Cores

Three of the surface cores collected in 1998 were sectioned at 3-cm increments to a depth of 15 cm to obtain older sediments corresponding to the 1985 and 1990 surface samples. Results from these 15-cm cores can be used to evaluate the extent to which upward diffusion may have altered P, Fe, and Mn concentrations in the surface sediments. Sediment ages in the core slices are extrapolated from <sup>210</sup>Pb sedimentation rates in the 0-3 cm slice and plotted together with the 1985 and 1990 samples (Fig. 10). For cores S-2 and S-11, elemental concentrations in strata from 1985 and 1990 are generally similar to concentrations measured in the surface samples collected in those years. Such results imply that the core profiles have not been appreciably altered by diffusional processes. In contrast, core S-7b from near one of the two aerators shows P, Fe, and Mn concentrations at depth elevated well above that measured when those sediments were at the surface in 1985 and 1990. These data suggest that the entire 15-cm sediment column may have become enriched by upward diffusion. The difference among these test cores is likely related to proximity to the aeration source which could drive oxygen deep into the sediments at S-7b but much less so at S-2 or S-11. Although somewhat contradictory, these results imply that if near-surface sediments (at sites more distant from the aerators than S-7b) are enriched by post-depositional diffusion, it was not yet evident in 1990, at least at the coarse stratigraphic resolution at which these cores were sampled.

A single meter-long core was collected from site S-11 in 1990 to reconstruct conditions existing in Vadnais Lake prior to hydrologic and land-use alterations in the watershed. Lead-210 dating results indicate that the core extends back to about 1860 and that sedimentation rates, though uncertain early on, have more than doubled since 1900 (Fig. 11). This increase in sediment flux corresponds to a 15-20% rise in inorganic and carbonate content and likely represents increased erosion coupled with a rise in algal productivity which drove calcite precipitation through greater uptake of CO<sub>2</sub> (Hodell *et al.* 1998).

Phosphorus and iron concentrations also decrease markedly up-core (until the mid-1900s), largely as the result of dilution from inputs of inorganic (clastic) materials and carbonates.

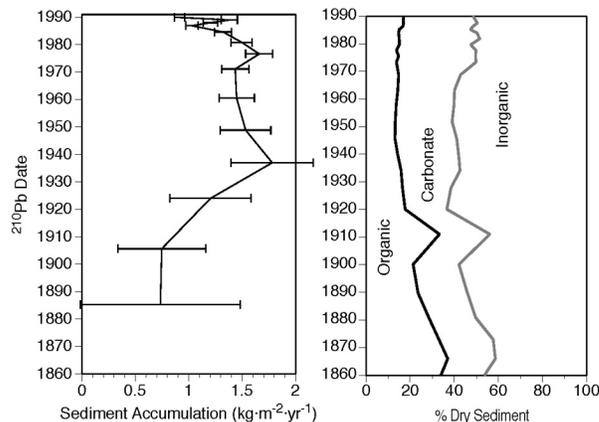
## Long-term Changes in Iron and Phosphorus Sedimentation in Vadnais Lake, Minnesota, Resulting from Ferric Chloride Addition and Hypolimnetic Aeration

Total-P concentrations decline from 1.2 mg·g<sup>-1</sup> in 1860 to 0.7 mg·g<sup>-1</sup> in 1940 while Fe content decreases from 36 to 14 mg·g<sup>-1</sup> over this same time period (Fig. 12). Accumulation rates (which correct for dilution) indicate that the flux of Fe and total-P have not changed systematically over time. Total-P accumulation rates average around 1.1 g·m<sup>-2</sup>·yr<sup>-1</sup> and Fe about 22 g·m<sup>-2</sup>·yr<sup>-1</sup> for the period of record. Only in the uppermost 2 cm of core do elemental concentrations and fluxes increase appreciably.

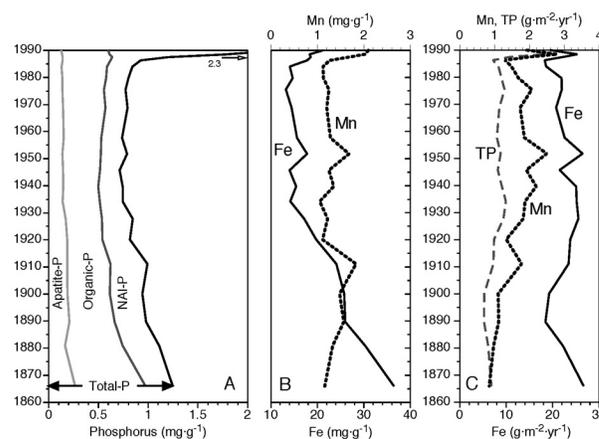
Viewed in the context of these long-term data, the recent FeCl<sub>3</sub> injections to Vadnais Lake and Lambert Creek have had measurable though modest effects on sedimentary P and Fe concentrations and fluxes. Mean lake-wide Fe concentrations in surface sediments (23 mg·g<sup>-1</sup>) are still well below historical baseline (36 mg·g<sup>-1</sup>), and only in the vicinity of the hypolimnetic aerators (S-4 and S-7) do present-day concentrations approach these 1860 values. Present-day Fe accumulation rates are about 24 t·yr<sup>-1</sup> as compared to a baseline (1860) flux of 21 t·yr<sup>-1</sup>, or an average 18 t·yr<sup>-1</sup> for the entire period of record. These historic whole-basin fluxes are obtained by scaling Fe accumulation rates at S-11 to the present-day lake-wide average. Thus the recent iron injections represent at most 25% of the modern Fe flux to Vadnais Lake and as little as 14% of the pre-settlement Fe accumulation rate. Because hypolimnetic aeration may have increased Fe retention to something approaching pre-settlement conditions, 14% is probably a better estimate of actual changes in Fe loading brought about by FeCl<sub>3</sub> additions.

### Littoral Sediments

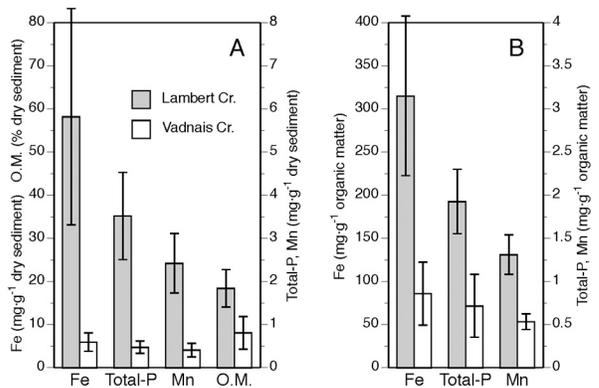
Over the past decade a total of 54 metric tons of iron have been added to Lambert Creek just above its outfall to Vadnais Lake (Fig. 2). Most of this Fe is presumably transported to the lake where it sediments as a floc in the deeper, quiescent parts of the basin. However, a portion of the Fe load may also be deposited in shallow-water areas (at least temporarily until transported offshore by wave action), thereby raising Fe concentrations in littoral sediments, especially those near the mouth of Lambert Creek (Fig. 1). Concentrations of extractable Fe, as well as Mn and total-P, were measured from six sampling stations near Lambert mouth and a control region near the outfall of Vadnais Creek. Results show that Fe levels in sediments near the Lambert outfall are about ten times those from the Vadnais outfall (58 ± 25 mg·g<sup>-1</sup> vs. 6 ± 2 mg·g<sup>-1</sup>), and Mn and total-P concentrations at Lambert are 6-7 times higher (Fig. 13). However, the littoral shelf at the Lambert outfall is broader and more protected than that at Vadnais Creek, which results in a finer grain-size and higher organic content in the Lambert samples. Because amorphous iron (and associated Mn and P) is also preferentially deposited with fine-grained sediments, the higher Fe content in the Lambert outfall may represent, at least partially, differences in sediment lithology and ultimately the depositional



**Figure 11.**—Lead-210 chronology and accumulation rates and loss-on-ignition of a meter-long sediment core collected from site S-11 in 1990.



**Figure 12.**—Chemical stratigraphy of a <sup>210</sup>Pb-dated sediment core from site S-11; (A) Phosphorus concentrations (P-fractions are stacked to equal total-P), (B) Fe and Mn concentrations, (C) P, Fe, and Mn accumulation rates.



**Figure 13.**—Chemical composition of littoral sediments from near the outfalls of Lambert and Vadnais creeks; (A) normalized to total sediment mass, (B) normalized to organic matter.

environment of the two littoral regions. To correct for such lithological difference, Fe (Mn and P) concentrations have been normalized to organic content. These results show that Fe levels near the Lambert outfall are still about 4 times those at Vadnais Creek, while Mn and P concentrations are about 2.5 times higher.

Pre-treatment sediment collections from 1985 provide additional evidence that  $\text{FeCl}_3$  injections have enriched littoral sediments near the Lambert Creek outfall. A single sediment sample collected near the mouth of Lambert Creek in 1985 contained  $7.6 \text{ mg Fe}\cdot\text{g}^{-1}$  dry sediment (or  $81.9 \text{ mg Fe}\cdot\text{g}^{-1}$  organic matter), virtually the same as that measured in 1998 collections from the Vadnais Creek outfall. In turn, the 1998 Vadnais Creek collections were virtually unchanged from those measured in 1985 (two samples). Taken as a whole, these data provide strong evidence that iron injections to Lambert Creek have locally altered littoral sediment chemistry in Vadnais Lake; whether biotic changes might have accompanied such impacts is currently unknown.

## Conclusions

- (1) Surface sediments from the deep-water regions of Vadnais Lake were sampled from a series of fixed stations on three occasions (October 1985, May 1990, and October 1988) to assess the efficacy of hypolimnetic aeration and iron injections in controlling phosphorus loading and sedimentation in the lake. Phosphorus concentrations, particularly the labile NAI-P fraction (non-apatite inorganic phosphorus) increased at almost all sites between the three sampling periods. In 1985, prior to the onset of aeration and Fe injection, total-P concentrations were uniform across the basin, averaging  $0.88 \text{ mg}\cdot\text{g}^{-1}$  dry mass. By 1990 total-P had risen to  $1.21 \text{ mg}\cdot\text{g}^{-1}$  and the NAI-P fraction had increased from 38% to 53%; this change was most apparent at sites nearest the two aerators. By 1998 total-P had increased markedly at all sites below the 12-m depth contour, rising to a lake-wide average of  $2.35 \text{ mg}\cdot\text{g}^{-1}$ , with an excess of 70% in the NAI-P fraction. These changes were accompanied by more gradual increases in extractable Fe from  $12.5 \text{ mg}\cdot\text{g}^{-1}$  in 1985 to  $16.3 \text{ mg}\cdot\text{g}^{-1}$  in 1990 and  $23 \text{ mg}\cdot\text{g}^{-1}$  in 1998.
- (2) Annual whole-basin sedimentation of total-P rose from 1.26 metric tons (t) in 1985 to 1.52 t in 1990 and 2.43 t in 1998, with virtually the entire increase represented in the NAI-P fraction. The sedimentary fluxes for 1985 and 1990 are very similar to those calculated by mass balance (the difference between measured P inflows and outflows), and the change represents a doubling of in-lake retention of external P loads (from 19% to 38%). In contrast, 1998 estimates of P sedimentation from core data were almost three times higher than those derived from mass-balance calculations. These results strongly suggest that upward diffusion of dissolved P from sediments at depth have gradually enriched surface sediments beyond that attributable to external P-loading. This diagenetic enrichment was likely enhanced by hypolimnetic aeration and iron injections, although evidence for this process from dated sediment cores is equivocal.
- (3) The increase in Fe sedimentation over the period of study is consistent with changes in external Fe inputs from iron injections, although enhanced retention from hypolimnetic aeration may also be a factor. The chemical stratigraphy of a  $^{210}\text{Pb}$ -dated, meter-long sediment core indicates that Fe concentrations in Vadnais sediments from the mid 1800s ( $36 \text{ mg}\cdot\text{g}^{-1}$ ) were considerably higher than they are today, even at the most Fe-enriched sample sites. Iron (as well as P and Mn) concentrations decrease progressively up-core, largely as a result of dilution from erosional inputs of clastic materials and increased carbonate sedimentation. Present-day Fe accumulation rates ( $24 \text{ t}\cdot\text{yr}^{-1}$ ) are about 33% greater than the mean Fe flux for the period of record ( $18 \text{ t}\cdot\text{yr}^{-1}$ ) and only 14% greater than the baseline (1860) flux of  $21 \text{ t}\cdot\text{yr}^{-1}$ . The recent increase in Fe accumulation – about  $6 \text{ t}\cdot\text{yr}^{-1}$  between 1985 and 1998 – is roughly equal to the average annual rate of Fe injections directly to Vadnais Lake.
- (4) Littoral sediments in the region of the Lambert Creek outfall appear enriched in Fe relative to a control site near the mouth of Vadnais Creek. Collections of surface sediments from the Lambert outfall have Fe concentrations that are an order of magnitude higher than those from the Vadnais outfall as expressed on a dry-mass basis. When normalized to organic content, which reduces variability caused by differences in grain size and lithology, this difference decreases to a 4x enrichment factor. Sediments from the Lambert outfall are also higher in P and Mn than those at the Vadnais outfall, largely due to the binding of these elements to Fe.
- (5) The results from this study document major changes in elemental cycling and sedimentary mass balance brought about by more than a decade of iron injection and hypolimnetic aeration of Vadnais Lake. Surface sediments have become increasingly enriched in labile phosphorus and iron hydroxides as a consequence of supplemental iron injections, increased scavenging and sedimentation, and suppression of recycling across the sediment-water interface. The resulting reductions in water-column phosphorus and associated algal blooms attest to the long-term success of these engineering solutions to previously severe internal phosphorus loading. However, continued hypolimnetic aeration will be

required to prevent massive phosphorus releases to the water column from the large reservoir of sedimentary P that has been created in the process.

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