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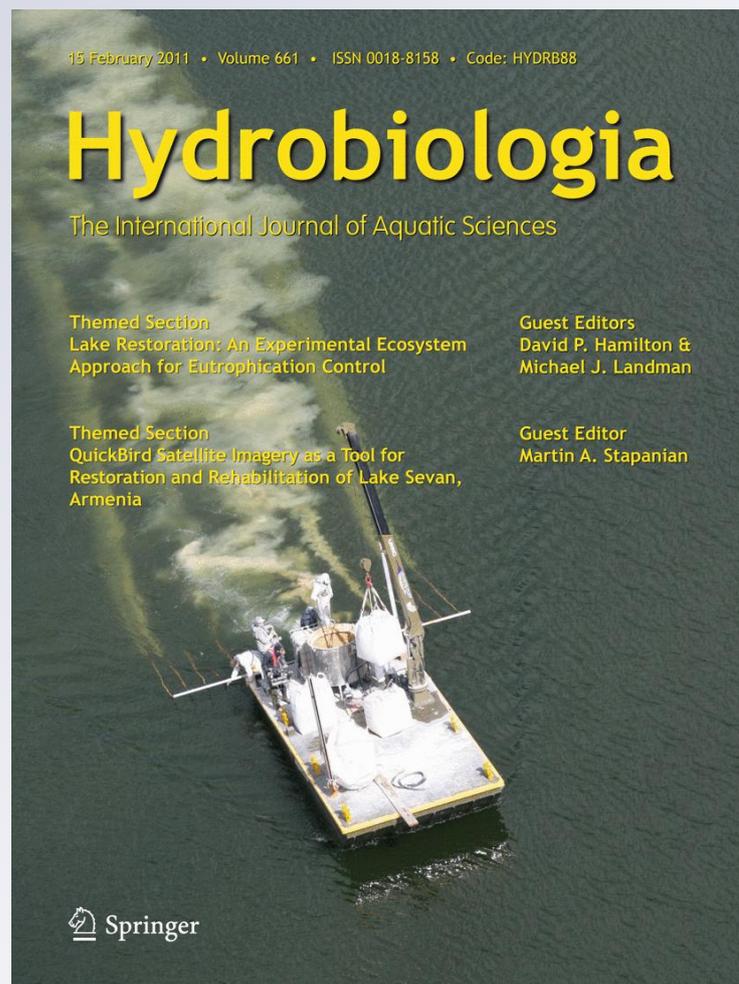
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Nuisance cyanobacteria in an urbanized impoundment: interacting internal phosphorus loading, nitrogen metabolism, and polymixis

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Abstract Severe nuisance blooms of cyanobacteria, mainly *Aphanizomenon* and *Microcystis*, historically have plagued polymictic Ford Lake, one of the most productive warm-water sport fishing lakes in Michigan, U.S.A. Biomass development in the lake is known to be limited by phosphorus. Alternative theories ascribed nuisance conditions either to allochthonous inputs or to internal loading of phosphorus from anoxic sediments. From 2003 to 2009, there was a strong linear relationship between allochthonous total phosphorus income and phosphorus retained within the basin. The relationship had a negative intercept, implying negative retention, or positive export, of phosphorus from the lake from May to September. Mass balance calculations at lake inlet and outlet were consistent with rates of sedimentary phosphorus accumulation measured from sediment cores. Release rates of soluble reactive phosphorus from anoxic sediments were half that of allochthonous inputs. However, severe declines in nitrogen to phosphorus ratio developed in the anoxic, nitrate-poor hypolimnion because accumulation of ammonium was only tenfold that of phosphate. The result

was a steep decline in ratio of total nitrogen to total phosphorus during July and August throughout the lake after episodic mixing events, followed by and coinciding with development of heterocystous *Aphanizomenon* populations. Lake sediment composition determined by X-ray fluorescence in addition to results of sediment core experiments indicates that phosphorus release is governed by an iron trap mechanism such that phosphate and iron are released only when both oxygen and nitrate are depleted.

Keywords Cyanobacteria · Eutrophication · Lake management · Phosphorus budget · X-ray fluorescence

Like many rivers transecting the historical industrial heartland of North America, the Huron River of southeastern Michigan inherits a legacy of rural agriculture, then urbanization, and fragmented management efforts. The river was developed for hydroelectric power generation during the early twentieth century and many of the dams still produce electricity. Impoundment sediments are repositories not only for industrial metals, but also for plant nutrients such as phosphorus that contribute to cultural eutrophication. To the extent that pollutants are trapped within impoundment sediments, they are prevented from entering coastal or Great Lake ecosystems. Given their close proximity to human population centers,

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these impoundments are sites of intense recreational activity, mainly boating and fishing. However, the cultural eutrophication caused by those same human populations can plague the lakes with nuisance blooms of cyanobacteria during summer months, thus degrading their esthetic and recreational value.

Ford Lake is one such impoundment of the Huron River. It was constructed by Henry Ford from 1929 to 1932 for the purpose of supplying electricity to the Ford Motor Company. The dam and powerhouse (Fig. 1) continue to generate electricity. Ford Lake has exhibited nuisance blooms of cyanobacteria during summer months ever since its construction (Donar et al., 1996). Dense populations of *Aphanizomenon flos aquae* (L.) Ralfs ex Bornet & Flahault typically appear in July and are succeeded by blooms of *Microcystis aeruginosa* (Kützing) Kützing, with elevated levels of microcystin (Lehman, 2007; Lehman et al., 2009). During these times, the lake becomes a virtual monoculture of cyanobacteria that ultimately carpet the lake surface as floating mats. The working hypothesis that has guided management efforts is that nuisance conditions are caused by

excessive phosphate released from wastewater treatment facilities upstream and from non-point sources along the river. It focuses management effort on upstream controls of lake condition. An alternative hypothesis takes note of the fact that nuisance blooms tend to develop immediately after episodic mixing events, which inject nutrient-rich hypolimnetic water into the epilimnion. This suggests that the cyanobacteria blooms result mainly from internal loading of P from lake sediments under conditions of hypolimnetic anoxia. Distinguishing between these two hypotheses is of practical importance. If the alternative hypothesis were to prove credible, management focus should include mechanisms to alleviate seasonal anoxia. For example, the dam was constructed to permit hypolimnetic discharge, but that option is rarely used during the summer so as to maximize water flow through the turbines, which draw from the epilimnion. Hypolimnetic discharge could potentially prevent anoxia, but at the expense of hydroelectric power and downstream water quality (e.g., Steinman et al., 2002; Nürnberg, 2007) if discharge is conducted after hypolimnetic water has become anoxic and nutrient rich.

This article reports the results of a 7-year study of mass balance, sediment chemistry, nutrient flux measurements, and hypolimnetic stoichiometry at Ford Lake in an effort to understand the relative importance of internal versus external nutrient loading to lake water quality and cyanobacterial blooms.

Methods

Study site

Ford Lake (42.21°N, 83.56°W) has a surface area of 4.039 km² and mean depth of 4.3 m; its maximum depth is 11 m at the outlet dam. The local catchment is urbanized, and the City of Ann Arbor maintains the outfall from its municipal wastewater treatment facility with tertiary treatment phosphorus removal 9.5 km upstream from the lake inlet. The lake becomes thermally stratified in early May, and temperature differences across the thermocline are usually only 3 or 4°C throughout the summer. Nonetheless, the lake develops seasonal anoxia with hypolimnetic temperatures of 23–24°C. The hydroelectric turbines draw water from the epilimnion,

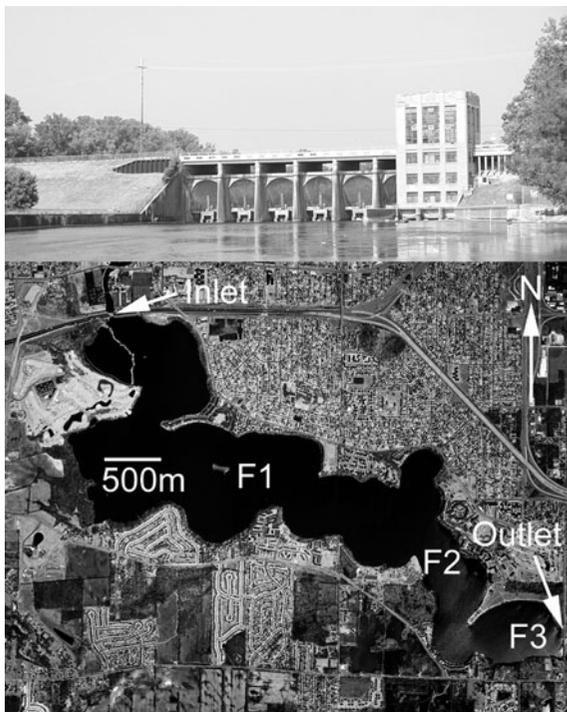


Fig. 1 Upper Ford Lake dam with bottom flood gates and powerhouse at right viewed from downstream. Lower Aerial photograph of Ford Lake with core sites indicated

mainly from the upper 4 m. The surface mixed layer is typically 5 m in depth and seasonal anoxia develops below 6 m. The impoundment is regulated as “run of the river,” meaning that outflow is matched to inflow to maintain constant stage height. Flood gates at the base of the dam are usually closed during the summer, when river flow is slack, to permit maximum power generation. Episodically, cold weather fronts and storms can temporarily destabilize the lake and mix nutrient-rich hypolimnetic water throughout the lake.

The city of Ypsilanti, MI, historically maintained an outfall from its wastewater treatment plant on the north shore of Ford Lake, but the facility was dismantled in 1982. Previous reports (Ferris & Lehman, 2007; Lehman, 2007; Lehman et al., 2007, 2009) have characterized the recent lake as eutrophic, with a variable spring diatom bloom sometimes followed by a clear water phase and then by dense mid-summer blooms of cyanobacteria dominated by *Aphanizomenon*. Mid-summer Secchi depth ranges mainly from 1 to 2 m. Epilimnetic TP averages about 1 μM , and Chl *a* can exceed 50 $\mu\text{g l}^{-1}$ during cyanobacteria blooms. Influent water is nitrate-rich, but nitrate becomes depleted in the lake during summer. Calcium and bicarbonate concentrations exceed 4 mEq during summer at pH exceeding 8.5, and authigenic precipitation of carbonate is observed.

Water samples

Water was collected at weekly intervals from both the inlet and the outlet of Ford Lake from June 2003 to September 2005 and from May to October of 2006 to 2009. Daily hydrologic inflow of water to the lake was calculated according to Ferris & Lehman (2007), and daily discharge from the dam was obtained from the operator's logs. Nutrient concentrations in the inflow and outflow were interpolated linearly between sampling dates. The net difference between inflow and outflow mass of Total P from 2003 to 2005 was used as one estimate of net accumulation or retention of P by Ford Lake during that time interval for the purpose of calculating a sediment phosphorus budget.

From May to September of 2003 to 2008, weekly samples were collected at site F3 to monitor changes in hypolimnetic chemistry. Temperature and dissolved oxygen were measured in situ using a Hach

model HQ30 meter with LDO luminescent sensor. Raw water gathered in the field was filtered on site for nutrient analysis using Millipore™ disposable filter capsules of nominal 0.45 μm pore size. Water was pumped from depth using a 12 VDC electric pump and was filtered before exposure to atmospheric air to avoid potential interferences described by Nürnberg (1984). Subsamples for ammonium analysis were collected and stored in glass-stoppered bottles. Soluble reactive P (SRP) was measured from filtrate according to Strickland & Parsons (1972). Total phosphorus (TP) was measured as SRP after unfiltered water samples were oxidized with 1% potassium persulfate at 105°C for 1 h. Dissolved Fe was measured from filtrate by the TPTZ method (Hach Company, Loveland, CO, USA). Dissolved inorganic N (DIN), mainly NH_4^+ and NO_3^- , was measured according to Ferris & Lehman (2007) by OPA fluorescence assay and second derivative UV spectroscopy, respectively. Total dissolved N (DN) and particulate N (PN) were measured as nitrate after alkaline persulfate oxidation. DN was measured from filtrate samples collected in the field, and PN was measured from particulates collected on 25-mm GF/C filters. Some redox potential (ORP) measurements were made in 2003 using a platinum electrode and were corrected to pH 7 (E_7) using Nerst slopes computed from quinhydrone solutions at pH 7 and 10 and referenced to a commercial ORP standard.

Sediment analysis

Eight cores for sediment chemical analysis were collected with a Kajak-Brinkhurst (K B) gravity corer (Brinkhurst et al., 1969) during June 2005. Three cores were taken at a 5.2-m site (F1: 42.219°N, 83.593°W), 3 at an 8-m site (F2: 42.214°N, 83.574°W), and 2 from a 10-m site (F3: 42.206°N, 83.559°W). Core liners were acrylic plastic 5 cm in diameter and 50 cm in length. All cores were complete, with intact sediment water interface and about 10 cm headspace. Cores were extruded at 1-cm intervals to a depth of 8 cm below the sediment water interface. Based on the sediment accumulation rate of 0.5 cm year^{-1} reported by Donar et al. (1996), this depth range represented a time period of about 16 years, or roughly 1990–2005, and excluded earlier sediments likely influenced by wastewater effluent discontinued in 1982. Fresh mass of each section was

recorded, the samples were dried to constant mass at 55°C, and then pulverized in a grinding mill. Subsamples from 35 samples representing all three sites and all depths were subjected to X-ray fluorescence spectroscopy (XRF) for elemental determination (GeoAnalytical Laboratory, Washington State University, Pullman, WA, USA). In addition, 5-mg subsamples from 19 core sections representing all sites and the full range of depths were added to 1% Na₂CO₃ and heated at 85°C for 6 h (Ferris & Lehman, 2007). The digests were cooled, neutralized with 1 N HCl, filtered to remove particulates, and the filtrate was analyzed for soluble molybdate-reactive Si (SRSi). The solubilized Si was deemed to be biogenic Si.

Organic matter (OM) content was assessed from loss of sample mass upon heating in a muffle furnace at 550°C for 4 h. Carbonate content was deduced from loss of carbonate-derived CO₂ demonstrated by additional loss of sample mass upon subsequent ignition (LOI) at 1,000°C for 2 h.

Inspection of the chemistry data revealed (Table 1) that they were symmetrically distributed and suitable for application of parametric statistics without transformation. Compositional differences among sites and by depth were examined by one-way or two-way analysis of variance (AOV) and post-hoc Bonferroni-adjusted probability contrasts using SYSTAT 10. Stepwise linear regression was used to develop statistical models of interrelationships among elements.

Experiments

In 2005 and 2006, additional K B gravity cores were collected at sites F1, F2, and F3 for experimental assessment of nutrient fluxes at the sediment water interface. The cores were obtained with intact sediment water interface and with ca. 10-cm headspaces of overlying water. In the laboratory, headspace water was gently drawn off by slow peristaltic pump and was replaced with filtrate from Ford Lake with measured oxygen and nutrient content. Preliminary experiments with enclosed hypolimnetic water had already demonstrated that oxygen consumption associated with particulate matter in the water was insignificant compared with oxygen consumption at the sediment water interface. The cores were incubated in the dark for 24 h at 23 ± 1°C, at

Table 1 Elemental composition of Ford Lake sediments reported as mean and range of concentration from three sites and depths from 0 to 8 cm below mud water interface (*n* = 35 samples)

Element	MW	Mean	Median	SE	Min	Max
Ca	40.1	156,700	156,900	980	143,600	166,100
Si	28.1	152,300	151,500	570	146,600	161,500
Al	27.0	42,000	42,000	190	39,600	44,300
Fe	55.9	31,300	32,200	300	27,500	33,400
Mg	24.3	14,300	14,500	76	13,400	14,800
K	39.1	9,510	9,570	52	8,780	10,000
Ti	47.9	2,400	2,430	13	2,240	2,510
Na	23.0	1,670	1,630	15	1,570	1,880
P	31.0	1,190	1,250	31	863	1,500
Mn	54.9	1,000	1,000	7.5	939	1,190
Ba	137.3	413	415	1.8	389	430
Zn	65.4	249	255	3.9	208	282
Sr	87.6	221	220	0.7	210	258
Cr	52.0	97	101	1.6	80	109
Zr	91.2	90	88	0.7	85	99
V	50.9	77	78	0.4	71	81
Rb	85.5	73	73	0.4	67	77
Pb	207.2	57	57	1.2	41	75
Cu	63.5	44	45	0.8	36	52
Ce	132.9	43	43	0.5	37	49
Ni	58.7	29	30	0.4	24	33

Values are given as mg of element per kg of dry sediment, or ppm

which time the final oxygen content of the headspace water was measured by inserting an LDO probe 2 cm above the sediment water interface. In some experiments, the water was then drawn off for chemical analyses.

Most experiments were commenced with starting oxygen concentrations at saturation to measure the rate of oxygen consumption. In one experimental series, however, the lake water filtrate was bubbled with nitrogen gas before addition to the core headspace to reduce oxygen concentration to 1.1 mg l⁻¹, and NaNO₃ was added to raise the starting level to 107.8 μM NO₃. The cores were then incubated for 41 h at 23 ± 1°C to measure rates of nitrate depletion as well as release of ammonium, dissolved organic N, SRP, and SRSi under anaerobic conditions.

In 2006, an experiment was conducted with four K B cores collected at site F2 and incubated for 72 h

to deplete both oxygen and nitrate. The final chemistry of the headspace water was analyzed to determine the stoichiometry of SRP and Fe released.

Sediment phosphorus budget

The sediment phosphorus budget was calculated by two independent methods. The first method was to multiply the mean mass of P in lake sediments by the linear sediment accumulation rate reported by Donar et al. (1996). This also required a determination of the subsurface area in which sediment accumulates. The second method simply calculated the difference between Total P mass entering the lake at its inlet and discharging at its outlet. There are no inlet streams other than the Huron River, and local runoff was ignored as a first approximation.

Results

Sediment accumulation rate

Water content of the sediments averaged 74.7% (SE = 0.5%, $n = 62$) and ranged from 83.3% (SE = 1.3%) at the surface to 71.5% (SE = 0.4%) at 8 cm. Water content did not decrease significantly below 4 cm (linear regression, $P = 0.08$). Dry mass within the topmost 8 cm of the eight cores collected in this study averaged $3,140 \text{ g m}^{-2}$ (SE = 120, $n = 62$) per cm of sediment depth. At 0.5 cm year^{-1} (Donar et al., 1996), the dry mass accumulation rate is $1,570 \text{ g m}^{-2} \text{ year}^{-1}$ (SE = 60). The rate reported by Donar et al. is an average rate over approximately 60 years measured near site F1 and does not account for any spatial or interannual variations that may exist.

XRF analysis

Bulk elemental composition of Ford Lake sediments by XRF (Table 1) revealed that the sediments were dominated by Ca, Si, Al, and Fe. Two-way AOV with site and depth as factors could detect no significant differences in percent organic matter (OM) with depth in the 0–8 cm sampling zone, but there were differences among sites ($P = 0.012$). Organic matter averaged 10.3% (SE = 0.2%, $n = 41$) of dry mass overall. Pairwise Bonferroni-adjusted contrasts identified differences between F1 and F2 ($P = 0.015$). F1 had

11.1% (SE = 0.4, $n = 12$) OM versus 9.6% (SE = 0.4, $n = 19$) at F2. F3 (mean = 10.7%, SE = 0.3%, $n = 10$) was indistinguishable from both other sites.

Total loss of mass upon heating at $1,000^\circ\text{C}$ (loss on ignition = LOI) was indistinguishable among sites (AOV $P = 0.32$) and averaged 27.77% (SE = 0.15%, $n = 34$). LOI per unit dry mass did not vary significantly with depth ($P = 0.87$). The sum of both organic matter and carbonate content thus varied little, but the two components varied in reciprocal proportions, likely because spatial variations in authigenic carbonate precipitation diluted the organic matter.

Analytical mass balance was assessed by summing the mean total LOI at $1,000^\circ\text{C}$ (including OM) with the sum of XRF-determined elemental composition, assuming all elements were present as oxides during analysis. Mean mass recovery thus calculated was 99.72% (SD = 0.31%, $n = 35$).

Mean Ca content by XRF was 15.67% (SE = 0.10, $n = 35$) of dry mass. If all Ca were originally present as carbonate, the expected amount of CO_2 evolved at $1,000^\circ\text{C}$ would be $15.67 \times 44/40.08 = 17.20\%$. Mean empirical loss of CO_2 as LOI was 17.48% (SE = 0.26, $n = 34$), a value indistinguishable from the expected value. The strongest positive correlation with Ca was $R = 0.44$ for K. However, 18 elements correlated negatively with Ca, some strongly so (Table 2), suggesting that carbonate precipitated from the lake water was acting as a diluent of other minerals in the sediment. Elemental composition of the sediment was consequently examined on the basis of its CaCO_3 -free ash content, thereby eliminating the diluting influences of both organic matter and authigenic carbonate. Total CaCO_3 -free ash content was calculated as the total mass of all XRF elements, except Ca, assuming all

Table 2 Correlation coefficients (R) with Ca for elements in Ford Lake sediments ($n = 35$)

Element	R
P	0.884
Zn	0.875
Si	0.874
Fe	0.754
Cu	0.748
Ba	0.747

Table 3 Elemental composition of CaCO₃ free ash from Ford Lake mud

Element	Units	Mean	SD	Site effect
Si	mmol kg ⁻¹	10,836	129	*
Al	mmol kg ⁻¹	3,116	93	*
Mg	mmol kg ⁻¹	1,172	27	*
Fe	mmol kg ⁻¹	1,121	51	*
K	mmol kg ⁻¹	486	19	*
Na	mmol kg ⁻¹	145	8	*
Ti	mmol kg ⁻¹	100	2	*
P	mmol kg ⁻¹	76	11	*
Mn	mmol kg ⁻¹	36	1	ns
Zn	μmol kg ⁻¹	7,614	593	*
Ba	μmol kg ⁻¹	6,005	100	*
Sr	μmol kg ⁻¹	5,051	212	*
Cr	μmol kg ⁻¹	3,726	334	*
V	μmol kg ⁻¹	3,030	110	*
Zr	μmol kg ⁻¹	1,970	82	*
Rb	μmol kg ⁻¹	1,698	64	*
Cu	μmol kg ⁻¹	1,380	126	*
Ni	μmol kg ⁻¹	996	73	*
Pb	μmol kg ⁻¹	552	69	*

n = 35; asterisk (*) denotes statistically significant effect of core site at $\alpha < 0.002$

ns Not significant

elements were present as oxides during XRF analysis. Elemental composition was expressed as mmol or μmol per kg of CaCO₃-free ash (Table 3).

The dominant constituents of the carbonate-free ash were Si and Al. Total Si content of Ford Lake sediments determined by XRF spectroscopy was 15.2 (SD = 0.3, *n* = 35) percent of dry mass. Biogenic Si (presumptively diatom Si) was 1.7 (SD = 0.3, *n* = 19) percent of dry mass or 11% of total Si. The other 89% of the sedimentary Si (9,644 mmol kg⁻¹) is presumptively mineral Si, mainly clays, in a ratio approximately 3:1 with Al.

Particular attention was given to the distribution of P because of evidence that P is the element regulating algal biomass in the lake (Ferris & Lehman, 2007). Sediment P was strongly correlated with Fe ($R = 0.88$) and was equally strongly negatively correlated with Ca ($R = -0.88$). The negative correlation with Ca owed to a strong effect of sample site. P content of Ford Lake sediment decreased from F1 to F2 to F3 (Fig. 1), according to increasing distance from the

lake inlet, whereas Ca content increased with distance from the lake inlet. One explanatory theory for this pattern is that much sedimentary P is delivered to the lake in particulate form by the Huron River, whereas much of the CaCO₃ is precipitated within the lake authigenically. Consequently, stepwise linear regression was used to predict sediment concentrations of P associated with the largely terrigenous elements Si, Al, Ti, and Fe. The resulting model required only Fe and Al to predict 96.1% of the variation in P among samples:

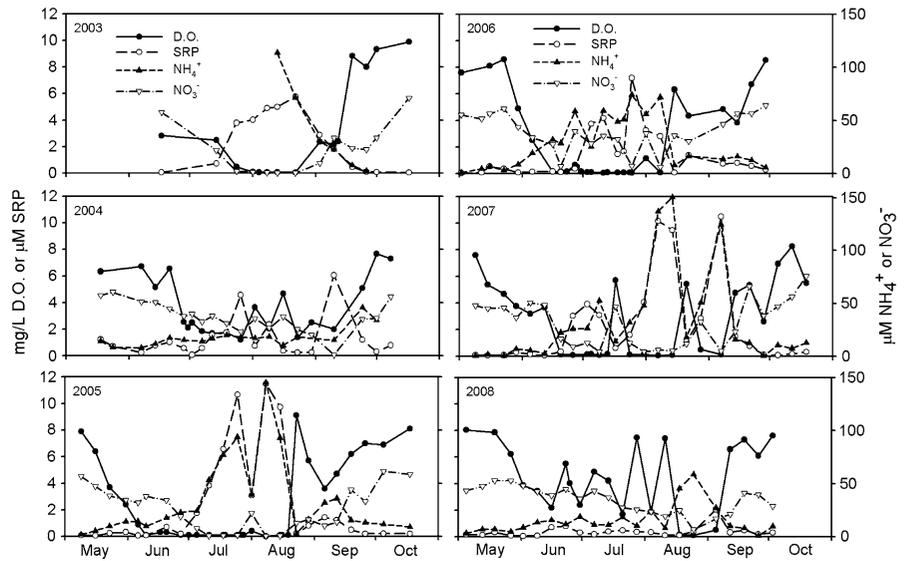
$$P = 0.190(\text{SE} = 0.007)\text{Fe} - 0.0045(\text{SE} = 0.0009)\text{Al} + 22.5(\text{SE} = 15.0), \quad (1)$$

where all elements are expressed as mmol kg⁻¹ CaCO₃-free ash dry mass. Note that P was positively associated with Fe and negatively associated with Al. Moreover, the magnitude of the association with Fe was 42 times greater than that with Al even though Al is represented at threefold greater mole fraction than Fe in the sediments (Table 3).

Field observations

Prolonged periods of hypolimnetic anoxia developed in 2003, 2005, 2006, and 2007 (Fig. 2). SRP typically did not begin to accumulate until both dissolved oxygen and nitrate were largely depleted. These conditions are consistent with low redox potentials measured in 2003. Hypolimnetic E_h values as low as +51 mv were recorded with DO > 0.1 mg l⁻¹ and nitrate < 2 μM. In Fig. 2, whenever SRP exceeds 2 μM (*n* = 30), mean DO = 0.42 mg l⁻¹ (SE = 0.10) and mean nitrate = 10.0 μM (SE = 2.1). Across the 6 years of data depicted in Fig. 2, DO and nitrate correlated positively with each other ($R = 0.64$, *n* = 128), as did SRP and ammonium ($R = 0.87$, *n* = 116). Oxygen correlated negatively with SRP ($R = -0.54$, *n* = 129) and ammonium ($R = -0.61$, *n* = 116), as did nitrate ($R = -0.63$ with SRP, $R = -0.64$ with ammonium). The slope of the inverse linear relationship between nitrate and ammonium was statistically indistinguishable from one to one by moles (slope = -1.05, SE = 0.12, *n* = 114). In spite of this, there was net accumulation of DIN as ammonium during anoxia, after nitrate became depleted. For all cases depicted in Fig. 2 for which DO was less than

Fig. 2 Concentrations of dissolved oxygen, SRP, nitrate, and ammonium in Ford Lake hypolimnion, site F3, $z = 10$ m during summer, 2003–2008



0.2 mg l⁻¹ and nitrate was less than 10 μM ($n = 21$), about 9.5 mol of N (as ammonium) accompanied each mole of SRP ($r^2 = 0.70$):

$$\text{NH}_4 = 9.5(\text{SE} = 1.5)\text{SRP} + 22.7(\text{SE} = 10.0), \quad (2)$$

where concentrations are expressed in micromolar units.

Field sampling during 2006 documented the onset of hypolimnetic anoxia at 10 m depth in June, and its end in August (Fig. 3) with the advent of a hypolimnetic discharge experiment that completely destabilized the lake. Dissolved Fe became elevated in late June, followed quickly by elevated SRP. The mean ratio of Fe to SRP from 5 July to 8 August was 0.5 (SE = 0.1) by moles, a stoichiometry substantially

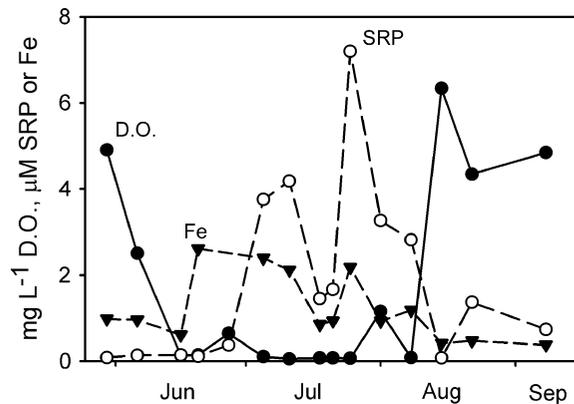


Fig. 3 Concentrations of dissolved oxygen, SRP, and dissolved Fe in Ford Lake hypolimnion, site F3, $z = 10$ m during summer, 2006

lower than was observed from laboratory experiments with sediment cores (see below).

Experiments

The mean rate of oxygen consumption in sediment core incubation experiments was 20.9 (SE = 1.9, $n = 28$) mmol O₂ m⁻² day⁻¹ at 23°C (=0.67 g O₂ m⁻² day⁻¹). Nitrate concentrations declined in the absence of oxygen, but at only about one-third the aerobic rate of oxygen consumption by moles (6.00 mmol m⁻² day⁻¹, SE = 0.55, $n = 8$). In contrast to stoichiometries observed in the lake hypolimnion, nitrate disappeared at over three times the rate that ammonium was produced (1.79 mmol NH₄⁺ m⁻² day⁻¹, SE = 0.42, $n = 8$). Even by accounting for accumulation of dissolved organic N (DON = DN – DIN) in the core headspace, total dissolved N (DN) declined by 44.3% (SE = 5.5%, $n = 8$), putatively by denitrification. In the 72-h incubation experiment performed in 2006, the molar ratio of Fe to SRP accumulation was 4.3 (SE = 1.2, $n = 4$). The molar ratio of ammonium to SRP release was 8.4 (SE = 1.9, $n = 8$), not significantly different ($\alpha = 0.05$) from that observed in the anoxic hypolimnion.

Sediment phosphorus budget

Based on the reported linear rate of sediment accumulation (0.5 cm year⁻¹) and mean dry mass of sediments in the 0 to 8 cm stratum, mean dry mass

accumulation was $1.570 \text{ kg m}^{-2} \text{ year}^{-1}$ ($\text{SE} = 0.060$) per cm of sediment depth (see Sediment Accumulation Rate). Mean P content of the dry lake sediments was $38.4 \text{ mmol kg}^{-1}$ ($1,190 \text{ mg kg}^{-1}$; Table 1), with SE less than 3% of the mean. Using these numbers, the average accumulation rate of P in actively accruing Ford Lake sediments is about $60 \text{ mmol m}^{-2} \text{ year}^{-1}$ ($\approx 0.165 \text{ mmol m}^{-2} \text{ day}^{-1} = 5.1 \text{ mg m}^{-2} \text{ day}^{-1}$). The only unknown uncertainty in the calculation is linear sediment accumulation rate for which no uncertainty estimate was available; otherwise, the estimate has less than 10% uncertainty.

Daily water income (Q_{in} , $\text{m}^3 \text{ day}^{-1}$) from May 2003 to September 2009 correlated very well ($r^2 = 0.93$) with discharge at the Ford Lake dam (Q_{out}), such that

$$Q_{\text{out}} = 1.052(\text{SE} = 0.009)Q_{\text{in}} - 53000(\text{SE} = 13000). \quad (3)$$

The 5% excess of Q_{out} compared to Q_{in} amounts to 1.6 mm day^{-1} across the surface area of Ford Lake. Typical rainfall in southeastern Michigan during May to September is 2.7 mm day^{-1} . Thus, the disparity is less than the magnitude of direct interception of precipitation by the lake surface. During the continuous 27-month period from May 2003 to September 2005, Ford Lake had a net income of 450,600 mol of P based on fluxes measured at both inlet and outlet. If this mass of P had been deposited uniformly under the entire lake surface area (4.039 km^2), the accumulation would have been $50 \text{ mmol m}^{-2} \text{ year}^{-1}$. However, field observations reveal that sediment accumulation is only evident at water depths greater than 1 m, because shallow sediments are mainly coarse material unyielding to the K B coring device, unlike the deeper lake sediments. Using the area below 1 m (3.648 km^2), accumulation was $55 \text{ mmol P m}^{-2} \text{ year}^{-1}$ ($\approx 0.15 \text{ mmol m}^{-2} \text{ day}^{-1} = 4.7 \text{ mg m}^{-2} \text{ day}^{-1}$), which agrees within 10% with the P accumulation rate measured from sediment cores. This independent calculation supports the assumption that non-point source additions of P from lakeshore areas are relatively modest.

During the most biologically productive months of May to September, from 2003 to 2009 retention of TP was $0.13 \text{ mmol m}^{-2} \text{ day}^{-1}$ ($\text{SE} = 0.045$, $n = 7$ years). SRP represented about one-third (mean = 0.355 , $\text{SE} = 0.010$, $n = 156$) of the TP supplied by the river; particulate P accounted for 0.403

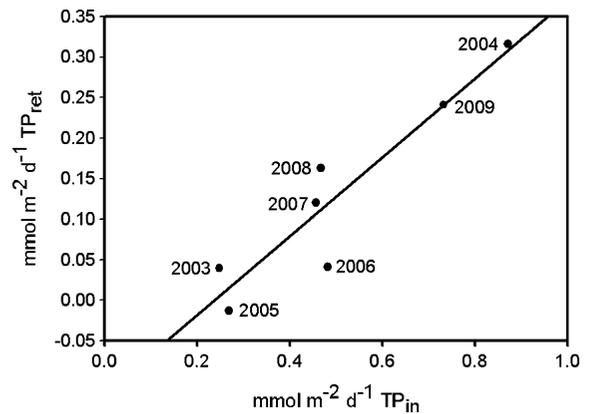


Fig. 4 Mean daily retention of TP influent to Ford Lake from the Huron River (TP_{in}) from May to September of 2003 to 2009

($\text{SE} = 0.012$, $n = 155$) of the TP. Interannual variation in mass retention of TP in Ford Lake was a strong linear function ($r^2 = 0.87$) of external load (Fig. 4):

$$\text{TP}_{\text{ret}} = 0.486(\text{SE} = 0.084)\text{TP}_{\text{in}} - 0.116(\text{SE} = 0.046), \quad (4)$$

where TP_{ret} and TP_{in} are in units of $\text{mmol m}^{-2} \text{ day}^{-1}$. The relationship implies that essentially 50% of the TP income is retained within the lake, and that even if income was zero, the lake could be expected to export $0.116 \text{ mmol m}^{-2} \text{ day}^{-1}$.

Input of SRP measured at the Ford Lake inlet during those months was $0.16 \text{ mmol m}^{-2} \text{ day}^{-1}$ ($\text{SE} = 0.03$, $n = 7$). This compares with a release rate of $0.28 \text{ mmol SRP m}^{-2} \text{ day}^{-1}$ from anoxic sediments (Table 3). The region of seasonal anoxia, however, is confined to depths greater than 6 m, representing 1.155 km^2 , or 28.6% of lake surface area. Thus, internal P loading normalized to total lake surface area is $0.08 \text{ mmol m}^{-2} \text{ day}^{-1}$, not statistically different from the intercept in Eq. 4, or half of the allochthonous loading. The estimate based on release rates from anoxic sediments may be regarded as a lower estimate of internal P loading because littoral sediments can also contribute to internal P loading via bioturbation and wind-induced shear stress.

Nitrogen to phosphorus ratio

From May 2003 to September 2008, the ratio of TN to TP in the Huron River entering Ford Lake was 73.6 ($\text{SE} = 2.0$, $n = 129$) by moles, with nitrate

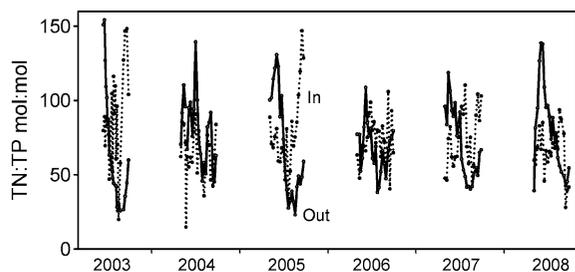


Fig. 5 TN:TP ratio by moles at inlet and outlet of Ford Lake weekly from May 2003 to September 2008

representing 0.690 (SE = 0.008, $n = 129$) of the TN. From June to August, nitrate was progressively depleted within the lake each year, a trend repeated for TN, as well. In contrast, both SRP and TP at the outlet typically increase from June to August. The result is a steep decline in the TN:TP ratio of lake water during July and August (Fig. 5).

Discussion

The surface sediments of Ford Lake consist of about 10% organic matter, 40% calcium carbonate, and 40% aluminum-silicates. Only about 10% of the silicon in the sediments appears to come from settling diatoms; the remainder most likely represents clay discharged to the lake by the Huron River.

Internal phosphorus loading

Both Owen (1991) and Quets (1991) constructed nutrient budgets for Ford Lake which indicated that the lake sometimes exports more P than enters it, indicating sources of P at or in the lake itself (see also the year 2005 in Fig. 4). These internal sources include release of P from lake sediments (e.g., Søndergaard et al., 2003). The P release rates measured from Ford Lake sediment cores ($0.28 \text{ mmol m}^{-2} \text{ day}^{-1} = 8.7 \text{ mg P m}^{-2} \text{ day}^{-1}$) were about threefold higher than Steinman et al. (2006) reported for another eutrophic riverine lake in western Michigan. Mass balance at both inlet and outlet of Ford Lake indicate that allochthonous P loading exceeds internal loading by a factor of two during the period when nuisance blooms arise. Nonetheless, hypolimnetic metabolism and nutrient fluxes at the sediment surface appear to play a pivotal role in bloom generation.

Mortimer (1941) first demonstrated that as long as oxygen remains at the sediment surface and redox potential remains high, ferric iron works as an insoluble “trap” for phosphate in the sediments (Edmondson, 1991). These principles have been well reviewed recently (Nürnberg, 2009). When oxygen and nitrate are absent, ferric iron is reduced, the “iron trap” for P is defeated, and both Fe^{2+} and P enter the lake water. The molar ratio of Fe to P generally needs to be greater than 2 for this mechanism to operate effectively (Manning et al., 1994). At lower ratios, a different mechanism can operate with similar outcomes. For example, Gächter et al. (1988) demonstrated that sediment bacteria release intracellular P into the water under anoxia but that they re-assimilate the P when oxygen is supplied. The strong positive correlation between Fe and P in Ford Lake sediments (Eq. 1) and the high molar Fe:P ratio of almost 15 to 1 (Table 3) suggest that Ford Lake sediments conform to the “iron trap” model (see also Jensen et al., 1992).

The best statistical model describing inter-sample variation in Fe and P contents (Eq. 1) implies that roughly 5 mol of Fe are associated with each mole of P within the sediments. In experiments with Ford Lake sediment cores, the ratio of Fe to SRP released into the water was not significantly different from 5:1 at $\alpha = 0.05$. Levels of dissolved Fe that accumulated in the anoxic hypolimnion, on the other hand, are much less than the 5:1 ratio with respect to P that the sediment stoichiometry and experiments suggest. It seems likely that secondary Fe removal mechanisms (e.g., precipitation of iron sulfides) operate at the longer time scales observed in the lake than were achieved in laboratory experiments. Alternatively, redox potential variations owing to episodic mixing events might permit some ferrous iron to become oxidized and to precipitate as ferric oxide without associated phosphate.

The principles of the “iron trap” have been the basis for numerous remediation efforts through hypolimnetic aeration (reviewed extensively by Pastorok et al., 1980; McQueen & Lean, 1984; Prepas & Burke, 1997). The efforts have yielded inconsistent results, attributed in part to incomplete data, improper experiment design, or inadequate experiment control. Direct injection of oxygen has been another remediation technique. Prepas et al. (1997) summarized results from Amisk Lake, Alberta, a lake of ca. 5 km^2

surface area, similar to Ford Lake. Hypolimnetic anoxia was prevented, TP concentrations in both epilimnion and hypolimnion declined dramatically, chlorophyll levels were halved, and the phytoplankton community became more diverse. Nonetheless, aeration does not always produce the expected outcome. Typically, stratification and temperature regimes are affected, and these can change metabolism and ecological interactions. Even in Amisk Lake, with less physical disturbance owing to use of pure oxygen, hypolimnetic temperatures became elevated and oxygen demand correspondingly increased.

In Ford Lake, the iron trap appears to be maintained by nitrate as well as oxygen. Only when anaerobic respiration depletes nitrate, Fe and SRP are released. Thus, the N and P economy of the lake are tightly interwoven. Denitrification removes N from the water and then under anoxia only 9 mol of ammonium are released with each mole of P. The result is a dramatic decline in TN:TP ratio (Fig. 5).

Conditions that favor internal loading of P also favor blooms of cyanobacteria (Schindler, 1977). These are (1) little vertical mixing—slack winds, strong sunlight and warm temperatures, and (2) low oxygen levels at the sediment surface (Hecky et al., 1994). In combination with adequate P concentrations, important bloom-generating factors are ratio of TN to TP, incomplete vertical mixing, and the ratio of light penetration depth to mixing depth of the lakes. Cyanobacteria flourish at low ratios of N to P because many species can fix nitrogen (Carpenter et al., 1998; Schindler et al., 2008), and because cyanobacteria seem to outcompete eukaryotes for ammonium in the absence of nitrate (Edmondson et al., 2003). Cyanobacteria are considered to be competitively favored over other species at lower TN:TP ratios (Schindler, 1977; Smith, 1983; Barica, 1990). Eukaryotes typically become growth limited by lack of N, and N-fixing cyanobacteria typically appear, when the total of nitrate and ammonium nitrogen drops below $50\text{--}100\text{ mg m}^{-3}$ ($3.6\text{--}7.1\text{ }\mu\text{M}$; Horne & Commins, 1987). The degree to which internal P loading promotes the growth of cyanobacteria rather than other kinds of algae is thus tied to the N dynamics of the sediment water interface (Gophen et al., 1999). Along with redox-related changes in phosphate concentration, anaerobic respiration can eliminate nitrate and also create or release ammonium into the water. The combination of anaerobic respiration of

nitrate plus release of phosphate from anoxic lake sediments produces the dramatic declines in TN:TP ratio (Fig. 4) that strongly favor N-fixing cyanobacteria such as *Aphanizomenon flos aquae*, the species that dominates the lake most summers.

During August 2006, we performed an experimental discharge of hypolimnetic water that interrupted thermal stratification and oxygenated the deep sediments (Lehman et al., 2009). As reported in that article, the *Aphanizomenon* bloom was replaced by a bloom of the diatom *Aulacoseira*. A subsequent bloom of *Microcystis* occurred only after the hypolimnetic discharge experiment was terminated. The results of that experiment and the mechanisms identified here make an argument that management effort focused on internal processes may be an effective way to alleviate the mid-summer nuisance blooms that plague this urban water resource and others like it.

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