

Chemical Composition of the Recent Sediments of Ford Lake, Michigan, by X-ray Fluorescence Spectroscopy

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This report summarizes the results of an investigation of the inorganic components present in the surface mud of Ford Lake, to a depth of 8 cm. Ford Lake historically exhibits large nuisance blooms of cyanobacteria during summer months. This investigation was part of an effort to understand the potential role of the lake sediments in bloom dynamics.

METHODS

Eight cores 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), 3 at an 8 m site (F2), and 2 from a 10 m site (F3). All cores were extruded at 1-cm intervals to a depth of 8 cm below the mud-water interface. Based on a sediment accumulation rate of 0.5 cm yr⁻¹ reported by Donar *et al.* (1996), this depth range represented a time period of about 16 yr, or roughly 1990 to 2005. 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 stations 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 and Lehman in ms.). The digests were cooled, neutralized with 1 N HCl, filtered to remove particulates, and the filtrate was analyzed for SRSi. The solubilized Si was regarded as 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 CO₂ demonstrated by additional loss of sample mass upon subsequent ignition (LOI) at 1000 °C for 2 h.

Compositional differences among sites were examined by one-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.

RESULTS

Bulk elemental composition of Ford Lake sediments by XRF is shown in Table 1. AOV could detect no significant differences with depth in the 0 to 8 cm sampling zone. Organic matter averaged 10.3% (SE= 0.2%, n= 41) overall, although AOV detected differences among sites (P= 0.012). Pairwise Bonferroni-adjusted contrasts identified differences only 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 1000 °C was indistinguishable among sites (AOV $P=0.32$) and averaged 27.77% (SE= 0.15%, $n=34$). The sum of both organic matter and carbonate content thus varied little, but the two components varied in reciprocal proportions.

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

Element	MW	Mean	Min	Max
Ca	40.1	156740	143608	166131
Si	28.1	152253	146642	161528
Al	27.0	42047	39638	44343
Fe	55.9	31325	27525	33406
Mg	24.3	14252	13433	14837
K	39.1	9510	8776	10039
Ti	47.9	2397	2239	2512
Na	23.0	1671	1571	1880
P	31.0	1186	863	1500
Mn	54.9	1002	939	1190
Ba	137.3	413	389	430
Zn	65.4	249	208	282
Sr	87.6	221	210	258
Cr	52.0	97	80	109
Zr	91.2	90	85	99
V	50.9	77	71	81
Rb	85.5	73	67	77
Pb	207.2	57	41	75
Cu	63.5	44	36	52
Ce	132.9	43	37	49
Ni	58.7	29	24	33
La	138.9	23	18	27
Nd	144.2	19	16	22
Y	88.9	18	17	19
Sc	45.0	13	12	15
Ga	69.7	10	9	13
Th	232.0	7	6	9
Nb	92.9	7	6	8

Analytical mass balance was assessed by summing the mean total LOI at 1000 °C (including OM) with the sum of XRF-determined elemental composition, assuming all elements were present as oxides. 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 CO₂ evolved at 1000 °C would be 15.67×44/40.08= 17.20%. Mean empirical loss of CO₂ as LOI was 17.48% (SE= 0.26, n= 34), a value indistinguishable from the expected value. No elements were correlated strongly positively with Ca; the highest correlation coefficient was R= 0.44 for K. However, 18 elements correlated negatively with Ca, some strongly so (Table 2). Elemental composition of the sediment was consequently examined on the basis of its CaCO₃-free ash content, thereby eliminating the diluting influences of both organic matter and carbonate. Total CaCO₃-free ash content was calculated as the total mass of all XRF elements, except Ca, assuming all elements were present as oxides during XRF analysis. Elemental composition was expressed as mmol or μmol per kg of CaCO₃-free ash (Table 3).

Table 2. Correlation coefficients (R) with Ca for elements in Ford Lake sediments.

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

Owing to the large number of independent elements (27) being subjected to analysis, a conservative $\alpha = 0.002$ was chosen as the threshold probability for ascribing statistical significance. One way AOV detected statistically significant effect of Site at $\alpha = 0.002$ for all but 8 elements, all of which, except for Mn, were minor trace metals (Table 3). Those 8 elements were consequently excluded from further analysis.

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 (9644 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 most limiting to algal biomass in the lake (Ferris and Lehman in ms.). P was strongly correlated with Fe (R= 0.88). Stepwise linear regression was used to predict sediment concentrations of P from 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:

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

where all elements are expressed as mmol kg⁻¹ CaCO₃-free dry mass.

Table 3. Elemental composition of CaCO₃-free ash from Ford Lake mud. n= 35. (*) denotes statistically significant effect of core site at $\alpha < 0.002$; ns= not significant.

Element	Units	Mean	SD	Site Effect
Si	mmol kg ⁻¹	10836	129	*
Al	mmol kg ⁻¹	3116	93	*
Mg	mmol kg ⁻¹	1172	27	*
Fe	mmol kg ⁻¹	1121	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	7614	593	*
Ba	μmol kg ⁻¹	6005	100	*
Sr	μmol kg ⁻¹	5051	212	*
Cr	μmol kg ⁻¹	3726	334	*
V	μmol kg ⁻¹	3030	110	*
Zr	μmol kg ⁻¹	1970	82	*
Rb	μmol kg ⁻¹	1698	64	*
Cu	μmol kg ⁻¹	1380	126	*
Ni	μmol kg ⁻¹	996	73	*
Ce	μmol kg ⁻¹	646	41	ns
Sc	μmol kg ⁻¹	582	29	ns
Pb	μmol kg ⁻¹	552	69	*
Y	μmol kg ⁻¹	396	11	*
La	μmol kg ⁻¹	326	29	ns
Ga	μmol kg ⁻¹	299	24	ns
Nd	μmol kg ⁻¹	259	19	ns
Nb	μmol kg ⁻¹	151	8	ns
Th	μmol kg ⁻¹	63	6	ns

The remaining elements were subjected to stepwise linear regression using Si, Al, and Ti as independent variables in order to ascertain whether they were positively or negatively associated with terrigenous materials, particularly the dominant clays. Fe was negatively associated in stepwise linear regression with both Si and Al (Table 4), suggesting a dilution effect by Fe-poor aluminosilicates. The same was true of Mg, Cr, and even Ti, but not K, V, or Zr.

High correlations were found among some trace metals of presumptive industrial origin: Cu-Cr (R= 0.755), Zn-Cr (R= 0.800), Cu-Zn (R= 0.819), and Rb-V (R= 0.916).

Table 4. Model coefficients (and SE) generated by stepwise linear regression seeking to explain intersample variation in elemental composition of 14 elements from linear combinations of Si, Ti, and Al, all as mmol kg⁻¹ CaCO₃-free ash. All cases in which r² > 0.8 are shown.

Dependent	Si	Al	Ti	Constant	r ²
Fe, mmol kg ⁻¹	-0.626 (0.014)	-0.686 (0.019)	ns	1005 (199)	0.984
K, mmol kg ⁻¹	0.039 (0.004)	0.243 (0.006)	ns	-688 (62)	0.989
Rb, μmol kg ⁻¹	ns	0.750 (0.055)	6.19 (2.84)	-2582 (1191)	0.975
Cr, μmol kg ⁻¹	-4.03 (0.15)	-3.75 (0.21)	ns	5906 (2151)	0.957
Ti, mmol kg ⁻¹	-0.023 (0.001)	-0.016 (0.002)	.	406 (19)	0.915
Mg, mmol kg ⁻¹	-0.282 (0.019)	-0.179 (0.026)	ns	4782 (271)	0.894
V, μmol kg ⁻¹	ns	1.07 (0.08)	ns	ns	0.826
Zr, μmol kg ⁻¹	0.736 (0.077)	0.323 (0.106)	ns	-7010 (1110)	0.818

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 mud appears to come from settling diatoms produced within the lake itself; the remainder most likely represents sand and clay discharged to the lake by the Huron River.

Internal Phosphorus Loading- Both Owen (1991) and Quets (1991) constructed nutrient budgets for Ford Lake that indicated that the lake sometimes exports more P than enters it, indicating major sources of P at or in the lake itself. These internal sources may include release of P from lake mud under anoxic conditions.

Ever since Mortimer's (1941) classic experiment with enclosed lake mud, limnologists have recognized that so long as oxygen remains at the sediment surface and redox potential remains high, ferric iron works as an insoluble "trap" for phosphate in the mud (Edmondson 1991). When oxygen is absent, ferric iron becomes reduced to the ferrous form, the "iron trap" for P is defeated, and both Fe²⁺ and P enter the lake water in large quantities. 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. 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.

These principles have been the basis for numerous remediation efforts through hypolimnetic aeration (reviewed extensively by Pastorok et al. 1980, McQueen and Lean 1984, Prepas and 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 technique. Prepas et al. (1997) summarized results from Amisk Lake, Alberta, a lake of ca. 5 km² 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, it must be acknowledged that 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.

Anoxic conditions regularly occur during summer near the bottom of both Ford Lake, and phosphate concentrations become enriched as phosphate leaves the sediment. Significantly, anoxia does not affect Barton Pond, upstream of Ford Lake. The City of Ann Arbor draws about 70,000 m³ d⁻¹ for drinking water from the bottom of the lake. This results in a detention time of only 6 days for hypolimnion water in that basin.

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 during daytime (Hecky et al. 1994). P that leaks from the sediments into bottom waters during daytime stratification may become entrained by convection into upper lake waters during the night, or during cold and windy weather events.

In combination with adequate P concentrations, important bloom-generating factors are (1) ratio of TN to TP, (2) water column stability, or incomplete vertical mixing, and (3) optical depth, the ratio of light penetration depth to mixing depth of the lakes. Cyanobacteria prosper at low ratios of N to P because many species can fix nitrogen from dissolved gas (Carpenter et al. 1998), and because other species seem to outcompete eukaryotes for ammonium in the absence of nitrate (Edmondson et al., 2003). In order to protect lakes from nuisance blooms of cyanobacteria, it is necessary to keep the ratio of TN to TP at about 30:1 or greater by mass (66 by moles). 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 to 100 mg m⁻³ (3.6 to 7.1 μM; Horne and 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 changes in phosphate, anaerobic respiration produces reactions that eliminate nitrate, and also create or release ammonium into the water. The net result is internal loading of TN to TP at particular ratios. The ratio of these fluxes in Ford Lake is roughly 10:1 by moles, a ratio that strongly favors cyanobacteria.

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