

Distribution of Mn, Fe, P, Mg, K, Na, and Ca in the Surface Sediments of Lake Mendota, Wisconsin

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Analysis of 32 surface sediment samples from different areas of Lake Mendota, Wisc., indicated a high positive statistical correlation between Mn, Fe, and P concentration in the sample and the depth of water overlying the point of sample recovery. An inverse correlation was found for Mg and K. No statistical correlation between concentration and depth of sample recovery was found for Ca and Na.

Surface sediment samples were collected from Lake Mendota, Wis., during the summer and early fall of 1967. The purpose of the sampling was to assess the chemical composition of the sediments with respect to water depth and location in the lake. Studies conducted during the early 1950's reported by Rohlich (1963) indicate that N, P, and Fe concentrations become greater with increasing depth of water. Later work by Nriagu (1968) showed a correlation between the concentration of total- and sulfide-S and depth of overlying water for seven sediment samples collected from the central area of Lake Mendota, with depths ranging from approximately 11 to 25 meters. Gravity core sediment samples from different areas of Lake Mendota were collected by Murray (1956). The sediments in the deeper areas of the lake were typically black sludge or gyttja, resting on top of buff-colored marl deposits. The average CaCO_3 content of the black sludge is 32% (dry weight basis). The sludge in the deeper area of the lake generally showed a higher carbonate content than sludge in shallower areas.

Lee (1962) summarized previous studies that found shifting of the bottom muds in University Bay, located in the south-central part of the lake. This was determined by plotting concentration contours for the summer and winter seasons. The variations in the element distribution contours were attributed to the effects of bottom currents induced by strong winds which prevail during fall and winter. An extensive survey of the circulation of Lake Mendota was conducted by Bryson and Suomi (1952). They found that wind-driven epilimnetic waters resulted in a depression of the thermocline in the down-wind portion of the lake. A resultant upward release of this depression created measurable hypolimnetic currents. These hypolimnetic currents would be sufficient to disturb the extremely flocculent surface sediments. Gardner and Lee (1965) reported that scuba divers operating in the waters above the surface sediments created sufficient water currents to agitate the sediments, resulting in highly turbid bottom water conditions. Thus, continuous wind-driven circulation of the epilimnion, followed by hypolimnetic circulation, would account for the displacement and partial alteration of sedimentary element distribution patterns.

The study reported here extends the available information

about the distribution of certain elements in the surface sediments of Lake Mendota. The results show the effect of depth and possibly bottom morphology on the concentration of elements in surface sediments, and thus can be used as a guideline for future sampling programs where such information is needed for nutrient or mineral budget computations.

Experimental Procedures

Surface sediment samples were collected with an Ekman dredge from 32 stations at various depths in Lake Mendota; maximum depth is approximately 24 meters. The wet sediments were homogenized in a blender and air-dried. Prior to acid digestion, sediment sample aliquots were ground, passed through a 100-mesh screen, and heated to constant weight at 105°C.

Acid digestion consisted of adding 5 ml. of 48% HF to a 0.50-gram sample in a 50-ml. polypropylene beaker. The sample was heated to about 100°C. for 8 to 12 hours, after which only a dry residue remained. The solid residue was removed from the beaker, transferred to a 100-ml. Kjeldahl flask, and further digested for two hours to decompose the organic matter in the presence of 5 ml. of concentrated HNO_3 and 60% HClO_4 . After this digestion, the sample was heated in the presence of 5 ml. of concentrated HCl for approximately one hour, cooled, diluted to 30 ml., passed through a pre-rinsed Whatman No. 2 filter, and drained directly into a 100-ml. volumetric flask. This solution, or an appropriate aliquot thereof, was used for all analytical determinations. Iron was determined by the orthophenanthroline method (Olson, 1965) and P by the vanadomolybdo-phosphoric yellow colorimetric procedure (Jackson, 1958). Analyses for Mn, Mg, K, Na, and Ca were made by direct aspiration of the digestion solution, or diluted aliquots, into a Perkin-Elmer Model 303 atomic absorption spectrophotometer. Data for the precision of the analyses are given in Table I.

Figure 1 is a bottom contour map of Lake Mendota. The main tributary to the lake, the Yahara River, enters from the north. The only surface outlet from the lake is located on the eastern shoreline, and is indicated by an arrow pointing in a southeasterly direction. The outlet is actually a continuation of the Yahara River, which flows from Lake Mendota into

Table I. Precision of Analytical Methods

Element	Number of replicates, <i>N</i>	Average value of <i>N</i> replicates, mg./g.	Standard deviation, σ , mg./g.
Manganese	10	1.32	0.02
Iron	7	23.6	0.6
Phosphorus	5	1.37	0.02
Magnesium	5	13.1	0.4
Potassium	5	12.6	0.1
Calcium	5	110.0	2.0
Sodium	5	14.6	0.3

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Table II. Lake Mendota Surface Sediment Data

Sample number ^a	Depth of recovery, meters	Date of recovery, 1967	Mg./G. ^b						
			Manganese	Total iron	Total phosphorus	Total magnesium	Total potassium	Total sodium	Total calcium
1	22	June 12	1.34	22.4	1.35	12.5	12.5	14.2	108
1	22	June 19	1.33	22.8	1.35	13.2	12.5	14.6	111
1	22	June 21	1.32	22.8	1.38	13.5	12.7	14.9	111
1	22	June 22	1.32	23.6	1.38	13.4	12.5	14.7	111
2	19	June 12	1.19	21.2	1.29	17.0	13.0	15.5	112
3	15	June 12	0.90	19.1	0.85	17.8	12.5	15.6	114
4	12	June 14	1.22	23.0	1.30	14.9	15.0	16.5	114
5	9	June 14	0.76	20.8	0.92	15.3	14.3	16.7	100
6	18	June 14	1.19	24.2	1.45	13.2	13.0	15.1	105
7	9	June 15	0.64	21.2	0.89	15.7	14.7	16.4	80
8	17	June 15	1.22	21.4	1.29	14.0	12.0	14.8	114
9	22	June 19	1.26	24.4	1.45	11.6	12.3	15.0	112
10	15	June 19	1.11	22.3	1.01	15.9	10.5	16.4	108
11	9	June 19	0.76	20.8	0.89	16.4	12.3	16.6	125
12	10	June 19	0.90	16.0	0.84	26.0	26.0	13.6	80
13	23	June 21	1.40	25.6	1.35	13.0	12.5	14.6	103
14	10	June 21	1.04	19.5	1.17	15.2	11.5	14.6	117
15	12	June 21	1.11	20.8	1.02	12.7	12.2	14.4	90
16	21	June 21	1.12	24.8	1.42	12.3	12.2	14.3	97
17	21	June 22	1.34	25.2	1.38	11.8	12.2	...	90
18	19	June 22	1.17	24.4	1.42	12.8	13.5	...	89
19	23	June 26	1.30	23.4	1.47	13.0	12.2	15.1	99
20	23	June 28	1.34	23.4	1.53	16.0	12.0	14.7	100
21	22	June 28	1.20	23.2	1.37	12.1	12.0	18.4	98
22	21	July 5	1.18	25.0	1.62	11.1	13.1	14.2	78
23	20	July 5	1.34	25.0	1.52	12.6	13.8	15.0	88
24	21	July 5	1.04	24.8	1.22	10.9	12.3	15.2	97
25	18	July 6	1.14	21.2	1.20
26	18	July 6	1.15	21.4	1.25	13.7	11.8	15.1	113
27	18	July 6	1.15	22.3	1.26	12.9	12.5	16.4	120
28	23	July 12	1.32	24.0	1.50	11.4	12.3	16.8	109
29	18	July 12	1.00	21.2	1.09	14.6	12.3	15.5	109
30	19	July 12	1.00	23.0	1.15	11.8	12.0	15.8	106
31	23	Oct. 11	1.43	22.8	1.41	13.0	11.8	15.0	124
32	24	Nov. 6	1.50	26.7	1.82	12.2	12.2	15.0	112

^a Samples 1-30 were collected during summer thermal stratification. Samples 31 and 32 were collected during the fall circulation period.

^b Oven-dry weight (105° C.) basis.

Lake Monona and subsequently into two other lakes located toward the southeast.

The Ekman dredge sediment samples were collected at the 32 stations plotted in Figure 2. Sample numbers given in Table II relate the appropriate analytical data to the station numbers plotted in Figure 2, including the station depths and dates of recovery. Station 1, represented in the lake by a securely anchored buoy, was sampled four times during June, 1967. This was done to determine whether samples from the same location would give replicate analytical data from one sampling date to another during a short period of time.

Results and Discussion

The analytical data for Mn, Fe, P, Mg, K, Na, and Ca are listed in Table II. Close replicate analyses among the four samples from Station 1 taken on different dates were noted.

As an aid in the interpretation of the analytical data, statistical analyses were applied, comparing the elemental concentration (mg. per gram, dry weight basis) with the depth of sample recovery. The results of these calculations are given in Table III. Manganese, Fe, and P showed a positive

statistical correlation between concentration and sample depth. The Mg and K data also showed a correlation, although the *p* values were slightly less at the 0.025 level, compared with *p* = 0.001 for the three elements listed above. An inverse trend of decreasing Mg and K concentration with increasing sample depth was observed. On the other hand, Na and Ca showed no statistical correlation between concentration and sample depth. Statistical correlation does not necessarily imply causation, so that sample depth and morphology need not be the primary controlling factors bearing on element concentration in the sediments. Other unmeasured or unidentified variables could be in operation, and these might just as easily be the factors responsible for the findings reported.

The difference between the significance levels of correlation for Mn, Fe, and P (*p* = 0.001) and Mg and K (*p* = 0.025) are not sufficient to warrant discussion. One possible reason for the slight dissimilarity is the fact that the standard deviations of the analytical procedures were not incorporated into the correlation computations. The slightly lower correlation coefficients for Mg and K, *r* = -0.59 and -0.40, respectively, still indicate a significant level of correlation between depth and concentration.

Table III. Statistical Correlation Data

Relationship Between Depth of Sample Recovery and Element Concentration				
Element	r^a	p^b	s^c	n^d
Manganese	0.81	0.001	0.13	30
Iron	0.74	0.001	0.98	30
Phosphorus	0.82	0.001	0.22	30
Magnesium	-0.59	0.025	2.29	29
Potassium	-0.40	0.025	2.34	29
Sodium	-0.15	<i>e</i>	<i>f</i>	27
Calcium	0.04	<i>e</i>	<i>f</i>	29

^a Linear correlation coefficient from the equation $r = \frac{N\sum XY - \sum X\sum Y}{\sqrt{N\sum X^2 - (\sum X)^2} \sqrt{N\sum Y^2 - (\sum Y)^2}}$; X = element concentration, Y = depth of sample recovery.
^b Significance level of correlation based on "t" tables from the equation $t = \frac{r\sqrt{N-2}}{\sqrt{1-r^2}}$
^c Standard error of estimate of r from the equation $s = \frac{\sqrt{\sum Y^2 - (a\sum Y + b\sum XY)}}{N}$; i.e., the standard deviation of points from a least squares fitted line drawn on a plot of element concentration vs. depth of sample recovery.
^d Degrees of freedom, $n = N - 2$.
^e Not significant.
^f Not computed.

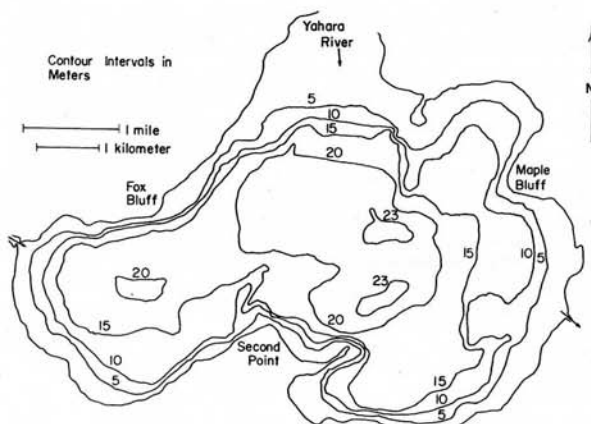


Figure 1. Bottom contour map of Lake Mendota, Wis.

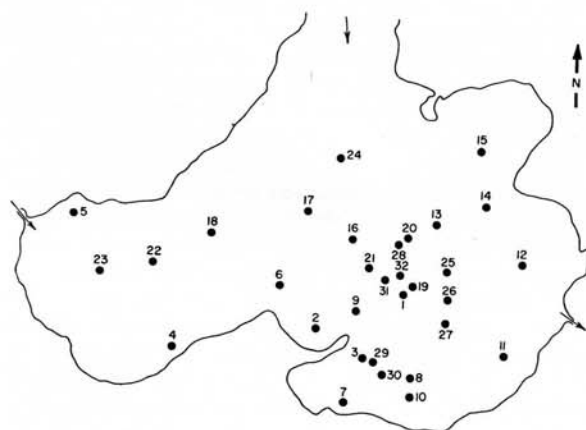


Figure 2. Location of surface sediment samples taken from Lake Mendota, Wis. Numbers indicate location of samples listed in Table II

Twenhofel (1961) discussed the nature of sedimentary environments. Since fresh waters generally permit slower settling of finely-grained sediments, in contrast to marine waters, he envisioned that portions of fine suspended sediments would be carried to the middle or central area of a lake and then deposited in some type of laminar formations. These laminations may or may not be readily apparent, due to the lake morphology, water circulation patterns, and bottom currents. The occurrence of fine-particle settling could explain the correlations found in this work. Since higher concentrations of Mn, Fe, and P were found at deeper depths in Lake Mendota, and since these deeper depths are essentially in the middle or central part of the lake, a relatively simple particle fractionation of tributary-borne suspended matter may have occurred. Particle size analyses of the sediment samples were not conducted, so that conclusive evidence is lacking.

Delfino and Lee (1968) reported that essentially all of the Mn in Lake Mendota waters was soluble and passed through either 0.45-, 0.22-, or 0.10-micron pore size membrane filters. Thus, any residual suspended particulate Mn would have to be on the order of less than 0.10-micron diameter. This would require the suspended material and its associated elements to be present in a very small colloidal form. Another possibility is that the elements carried in suspension primarily by the Yahara River tributary may be brought into the lake during the spring run-off period. After the particulate suspended matter had settled out, the element distributions in the water column would be independent of the transport mechanism, but the sedimentary distributions could be related to fractional settling of suspended particulate matter according to size and travel distance from the river mouth into the lake proper. Manganese, for example, as a soluble element in the water column, primarily comes out of the sediments during thermal stratification periods. Mn could be transported into the lake in a suspended form, originating as run-off, carried soil particles and erosion fragments, and then eventually settle out according to the particle sizes with which the element is associated. After deposition, Mn would be released from the sediments during stagnation periods and participate in the chemical sequences outlined previously (Delfino and Lee, 1968). The fates of Fe, P, Mg, and K similarly transported into Lake Mendota have not been extensively followed, but their initial distribution in the sediments may be related to the type and size of particulate matter to which the elements were found in soil, rocks, and other material in the tributary drainage area. If the particle size explanation is extended from Mn to the other elements, then Fe and P would be bound to small or finely-divided particles, while Mg and K would be associated with the more coarsely-grained larger particles. This interpretation is supported by studies of annual pollen deposition per unit area measured in sediment traps at Frains Lake in Michigan by Davis (1968). At Frains, the ratio of deposition, as measured in traps, to net accumulation, as measured in sediment cores, shows the pollen grains are deposited an average of two to four times before being buried deeply enough to escape further disturbance. Davis (1968) explains that the sediments in shallow water are apparently stirred up and resuspended more frequently or more extensively than sediment in deep water. The net result of repeated resuspension, mainly from shallow water sediment, followed by redeposition over the entire basin, is movement of material from shallow to deep water. Nichols *et al.* (1946) noted that copper sulfate applied to the bay areas of Lake Monona (1925-44) was recovered in highest concentrations in the deep portions of the lake. It seems that the natural grading process tended to carry the precipitated copper compounds

to the deeper waters. Frink (1967) collected bottom samples from Bantam Lake, Conn., and found that total P and N increased with water depth. The sediments in the deeper water of Bantam Lake contained more P, and an increasing proportion of this P was readily exchangeable (Frink, 1967). At a water depth of 6.4 meters, in the deep part of Bantam Lake, the total P concentration was 2.1 mg. per gram and the inorganic fraction 1.8 mg. per gram. The highest concentration of total P was 1.8 mg. per gram from the deepest part of Lake Mendota, and the concentration of P decreased by about one-half of the above amount in the shallower areas of Lake Mendota.

Magnesium and K concentrations showed a significant inverse correlation with depth of water, indicating that these elements are probably associated with coarsely-grained sediments. Presumably, this fraction may include clastic feldspars, clays, and alumino-silicate minerals. However, Ca and Na did not show any significant correlation with water depth. The Na content showed a fairly uniform distribution over the lake bottom. The total Ca concentration reported here represents Ca both as CaCO₃ and as other calcium-bearing minerals. The lack of analytical discrimination between the different forms of Ca limits the interpretation. However, Murray (1956) found that the sludge in the deeper area of the lake generally showed higher CaCO₃ content than sludge in shallow areas.

Conclusions

The results presented in this paper show a definite relationship between the concentration of certain elements in Lake Mendota sediments and the depth from which the sample is recovered. There is a significant positive correlation between water depth (sample depth recovery) and the concentration of Mn, Fe, and P. Presumably, these elements are carried to the center of the lake by a natural grading process bound to small and finely divided particles. A significant inverse correlation was found for Mg and K, but no significant trend was shown by the Ca and Na distributions.

The high correlation of P, Fe, and Mn concentration with

sample depth shows the need for preliminary surveys of lake sediment elemental compositions before extensive computations of nutrient balances in lake systems can be accurately completed.

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Literature Cited

- Bryson, R. A., Suomi, V. E., *Trans. Am. Geophys. Union* **33**, 707-12 (1952).
Davis, M. B., *Science* **162**, 796-9 (1968).
Delfino, J. J., Lee, G. F., *ENVIRON. SCI. TECHNOL.* **2**, 1094-1100 (1968).
Frink, C. R., *ENVIRON. SCI. TECHNOL.* **2**, 425-8 (1967).
Gardner, W. S., Lee, G. F., *Intern. J. Air Pollution* **9**, 533-64 (1965).
Jackson, M. L., "Soil Chemical Analysis," Prentice-Hall, Englewood Cliffs, N.J., 468 pp., 1958.
Lee, G. F., *Trans. Wisconsin Acad. Sci.* **51**, 141-55 (1962).
Murray, R. C., *Bull. Geol. Soc. Am.* **67**, 883-910 (1956).
Nichols, M. S., Henkel, T., McNall, D., *Trans. Wisconsin Acad. Sci.* **38**, 333-50 (1946).
Nriagu, J. O., *Limnol. Oceanog.* **13**, 430-9 (1968).
Olson, R. V., in "Methods of Soil Analysis," C. A. Black, Ed., Am. Soc. Agronomy, Madison, Wis., 1572 pp., 1965.
Rohlich, G. A., in "Limnology in North America," D. G. Frey, Ed., Univ. of Wisconsin Press, Madison, Wis., 734 pp., 1963.
Twenhofel, W. H., "Treatise on Sedimentation," Vol. 2, Dover Publications, New York, pp. 824, 1961.

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