Recent Sedimentary History of Lake Mendota, Wis.

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■ The chemical composition of several sediment cores taken from Lake Mendota, Madison, Wis., has been investigated to determine changes in the flux of various chemicals to this lake. The uppermost sediments consist of approximately 1/2 meter of black gyttja. The chemical stratigraphy of a 9.9 meter-long core indicates that stable conditions existed in Lake Mendota and its watershed prior to the settlement of the area surrounding the lake by white man in the mid to late 1800s. Since that time, there has been an appreciable increase in the amounts of phosphorus, iron, manganese, aluminum, and potassium in the uppermost sediments. The organic carbon content of the sediments has fluctuated several times in the past with the most recent sediments showing slightly higher values than the older sediments. This study has demonstrated the feasibility of using the chemical composition of lake cores to estimate the influence of cultural activities of man on the rate of eutrophication of a lake.

Various human activities contribute to accelerated enrichment (cultural eutrophication) of waters. Among the symptoms of cultural eutrophication are nuisance blooms of algae, increased nutrient levels, depletion of hypolimnetic oxygen, increased turbidity, and changes in the species-composition of phytoplankton, invertebrates, and fishes. In most instances cultural eutrophiccation is an accomplished fact because there are few data to document changes that have occurred in precultural times. The information needed to trace changing limnological and watershed conditions must come from a record preserved in lake sediments. Although several chemical studies have been performed on postglacial sediments and interpreted on the basis of long-term historical trends (Brown, 1969; Gorham, 1961; Horie, 1966; Hutchinson and Wollack, 1940; Kendall, 1969; Livingstone and Boykin, 1962; Mackereth, 1966; Pennak, 1963), few investigators (Stockner and Benson, 1967; Shapiro et al., 1971) have examined the recent historical changes of lakes through the interpretation of chemical profiles of lake sediment cores.

Lake Mendota sediment cores were examined in this study. This lake is a hard-water eutrophic lake formed by morainic damming of the preglacial Yahara River Valley near Madison,

Wis. (Twenhofel, 1933). The lake currently receives domestic drainage from agricultural lands, urban runoff, and some municipal and industrial waste effluents contained in entering streams. For a survey of limnological information on the lake the reader should see Frey (1963).

Experimental Procedures

In October 1966, cores WC-84 and WC-89 were taken from Lake Mendota in 11.2, 18.3, and 23.2 meters of water, respectively, in line from University Bay bottom to the lake to the Yahara River inlet. The only surface outlet from the lake is located on the eastern shoreline. The outlet is actually a continuation of the Yahara River, which flows from Lake Mendota into Lake Monona and subsequently into two other lakes located toward the southeast. University Bay has two inlets; one coming from a pumping station of lowland drainage, and a small creek, University Creek, which serves as a storm sewer for urban Madison.

The sample drive through 1 meter of sediment was accomplished by a coring device consisting of a circular cutting head on the lower end, a clear acrylic plastic core barrel (3.5 in. in diam), a piston assembly, and a set of weights at the upper end. The design and operation of the piston corer was described in detail by Wentz (1967) and Bortleson (1968). A sampling platform and a winch were provided by a converted Army amphibious Dukw to facilitate raising the corer. The sample material after inspection for laminations was extruded and fractionated in the field into 5-cm intervals.
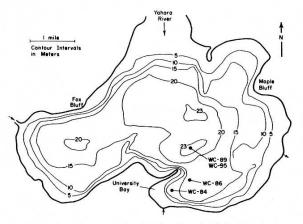

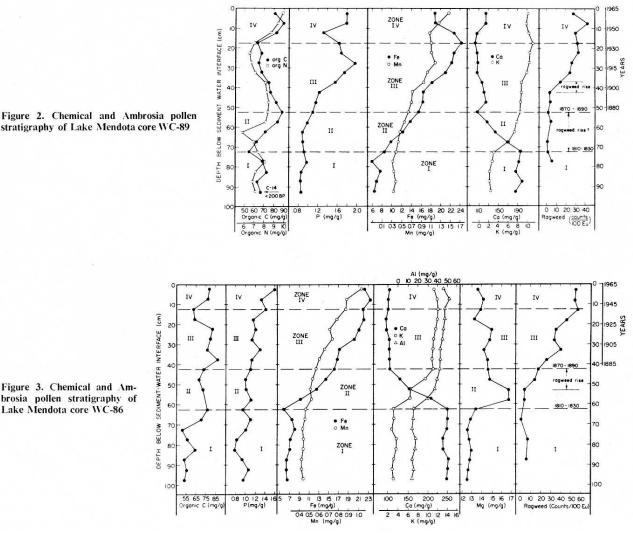**Figure 1. Bathmetry and coring locations for Lake Mendota**

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Table I. Precision of Analytical Methods

Element	No. of replicates, N	Av value of N replicates, mg/g	Std dev, mg/g
Iron	7	23.6	0.6
Phosphorus	5	1.37	0.02
Manganese	5	0.622	0.012
Magnesium	5	13.1	0.4
Potassium	5	12.6	0.1
Calcium	5	110.0	2.0
Aluminum	5	31.3	0.28
Organic nitrogen	5	7.08	0.36
Total carbon	5	128.0	7.0

The samples brought to the laboratory were stored frozen at -20°C until commencement of analysis.

After thawing, 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 0.500-gram sample in a 50-ml polypropylene beaker. The sample was heated to about 100°C for 8 to 12 hr, 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 cooled, passed through a prerinsed Whatman No. 2 filter, and drained directly into a 100-ml volumetric flask. This solution, or an appropriate aliquot thereof, was used for total P, Fe, Mg, K, Ca, and Al determinations.

Iron was determined by the orthophenanthroline method (Olson, 1965) and P by the vanadomolybdophosphoric (vm) yellow colorimetric procedure (Jackson, 1958). Wentz and Lee (1969a) have discussed the sensitivity, minimum detectable concentration, precision, and working range for the VIA yellow color procedure. Analyses for Mn, Al, Mg, K, and Ca were made by direct aspiration of the digestion solution, or diluted aliquots, into a Perkin-Elmer Model 303 atomic absorption spectrophotometer. Organic nitrogen was determined by semimicro Kjeldahl technique outlined by Bremner (1965). Total carbon was determined by a dry combustion technique using a LECO (Laboratory Equipment Corp.) low-carbon analyzer (Model 589-400) and LECO induction furnace. The CO_2 released by combustion of carbon compounds and decomposition of carbonate was measured by a thermal conductivity cell. With calcareous

Figure 2. Chemical and Ambrosia pollen stratigraphy of Lake Mendota core WC-89

Figure 3. Chemical and Ambrosia pollen stratigraphy of Lake Mendota core WC-86

sediments, the choice is between determining organic C on the sample after removal of carbonate C or computing organic C by subtracting carbonate C from total C. In this study the Ca dissolved by $HF-HNO_3-HClO_4$ acid system was converted to carbonate C equivalents; this value was subtracted from total C to obtain organic C. Studies by Bortleson (1970) have shown a good correlation between measured and calculated inorganic C in Lake Mendota sediments.

Sediment sample aliquots (0.200-gram sample, 100-mesh, dried 105°C) for Ambrosia pollen analysis consisted of removal of carbonates with HCl, silicates with HF, solubilization of humic material with KOH, and removal of cellulose with acetolysis solution (Faegri and Iversen, 1950; Andersen, 1960; and Maher, 1969). Since a total pollen assemblage was not counted and identified—e.g., oak, pine, hickory, grass pollen—to obtain a percentage of ragweed pollen, it was necessary to add an internal standard. A suspension volume of 0.20 ml of internal standard (1 gram of pure Eucalyptus pollen in 500 ml of tertiary butyl alcohol) was pipetted while well-stirred and at constant temperature (27.5-0.5°C) and transferred to the sediment aliquot. The Eucalyptus pollens, which are exotic pollens, were easily identifiable triangular-shaped grains. Identification of Ambrosia-type pollen was made with high power magnification using a Bausch & Lomb microscope. No reference was given to a particular species of ragweed. Continuous sweeps were made across the entire width of the preparation; in each sample, 100 to 200 grains were counted. The abundance of ragweed found in the sediment cores was based on the average ragweed-to-Eucalyptus pollen ratio of duplicate or triplicate samples.

The results presented for the chemical analyses of each core are mean values of two or five replicate determinations. Data for the precision of the analysis are given in Table I. The relative standard error was less than 5% for 73% of the analyses performed in replicates of five. Duplicate pollen counts were made from each processed sample. In the transition zone (high or low ragweed) triplicate counts were made.

Results and Discussion

The sediments laid down from the precultural period to the present day can be subdivided into four zones according to changes in ragweed pollen and chemical distribution patterns as shown in Figures 2-4. The main physical and historical features of the Lake Mendota cores are shown in Table II, and the mean

concentrations of organic C, carbonate C, P, Fe, K, and % solids are shown in Table III for each of the sediment zones.

No evidence of laminations or lenses, which could be used for dating purposes, was observed for any of the cores. To identify pre- and postcultural periods of deposition in the sedimentary column, Ambrosia pollen counts were performed; the appearance of these pollen grains provided a stratigraphic horizon which could be dated from historical records showing when man moved into southern Wisconsin and began modifying the environment. Ragweed pollen occurs in relatively high percentages (5-40%) in surface sediment samples from the deciduous forest region of the northeastern and north-central USA; the plant seems to have increased as a result of disturbance and creation of open habitats through forest clearance by European settlers (Ogden, 1967; Davis, 1967; Wright, 1968). For instance, a short core (50 cm) was taken from Frains Lake in Michigan by Davis (1968). The ragweed pollen increased from less than 1% to about 30% of the total from below to above 25 cm of sediment, respectively. According to Davis, the time of land settlement and forest clearance around Frains Lake occurred in 1830.

The lowermost sediments in Zone I consist of a buff marl containing 45-60% $CaCO_3$ or 190-255 mg/g Ca. The sedimentary concentrations of Fe, Mn, Al, K, Mg, P, and organic C show little or no change with depth in the buff marl. Minimum ragweed pollen counts were observed in Zone I. Presumably, the buff marl was laid down prior to any major disturbance by white settlers in the Lake Mendota drainage basin. Although most of the Lake Mendota cores observed by Murray (1956) showed a simple sequence of black gyttja (called sludge by Murray) over buff marl, other sequences were found in parts of the Lake Mendota basin, usually in the shallower regions. Among the sequences found with sediment depth by Murray (1956) were a sludge-marl-blue plastic marl, sandy sludge-blue plastic marl-pink clay with sand and pebbles, and a sludge-blue plastic marl-blue plastic clay.

The sediments in Zone II consist of gray-colored gyttja-marl which represents the transition zone between the buff marl and black gyttja. The reported (Murray, 1956) knife-sharp nature of the contact between gyttja and marl was not observed in any of the cores used in this study. In all the core sections examined, the buff marl passed gradually upward into a gyttja marked by a gradual darkening of color. Apparently, the false impression of a knife-sharp contact was created by either compression of the core sec-
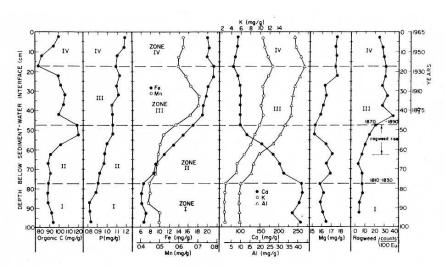

Figure 4. Chemical and Ambrosia pollen stratigraphy of Lake Mendota core WC-84

Table II. Main Features of the Lake Mendota Cores and Corresponding Historical Events

Core No.	Sediment depth and thickness of zones, cm	Chemical zone	Type of deposit	Period	Relevant historical events
WC-89	0–15	IV	Black	Late cultural	Accelerated urbanization in Madison (pop.
WC-86	0–10		gyttja	1940 to present	67,000–158,000, 1940–1965)
WC-84	0–15				"Detergent era"
					Decline in cisco (*Coregonus artedii*) after 1940 (Frey, 1963)
					Large decline in wetland from 1938 to 1950's
					Sewage diversion around lake December 1971
WC-89	15–50	III	Black		Rapid urbanization of Madison (pop. 12,000–
WC-86	10–40		gyttja	Midcultural	67,000, 1884–1940)
WC-84	15–45			1880 to 1940	Rapid settlement in L. Mendota basin
					L. Mendota received sewage effluent from Madison, 1884–1899
WC-89	50–70	II	Gray-	Early cultural	Early urbanization in Madison (pop. 2500–
WC-86	40–60		colored	1820 to 1880	12,000, 1850–1884)
WC-84	40–75		gyttja-marl		Raised lake level 5 ft by outlet dam in 1847
					Early settlement in southern Wisconsin
					Privies, cesspools, and direct drains to lake to dispose sewage
WC-89	70–95	I	Buff marl		Presettlement in southern Wisconsin
WC-86	60–100			Precultural	
WC-84	75–100			before 1820	

C-14 date, <200 yr B.P.
at 90–95 cm level of
WC-89 (Bender, 1969).

tions during sampling or the manner of fractionating the core column. The increase in ragweed pollen begins in the middle of Zone II and increases upward throughout Zone III in cores WC-84 and WC-86. The ragweed pollen rise probably corresponds to the period of active settlement of southern Wisconsin and the Madison area in the decades following 1820. The population of Madison increased from 2000 in 1850 to 12,000 in 1884 and to 30,000 by 1918; the acreage devoted to crop production in southern Wisconsin increased from about 400,000 to 2,900,000 to 15,300,000 in 1830, 1850, and 1880, respectively (Curtis, 1959; Smith, 1929; Sarles, 1961). Thus, the time period for the early postcultural interval (Zone II) is estimated to have taken place from 1820-1880. During this period, concentrations of organic C, Fe, Mn, K, Al, and P show an initial upward rise, and Ca mostly in the form of $CaCO_3$ shows a rapid decrease in concentration. Selenium was found by Wiersma and Lee (1971) to increase from a background concentration of 0.8-1.4 mg/g in Zone I to 2.2 mg/g in Zone II.

The lower column of black gyttja is shown in Zone III; the interval thickness ranges from 40-50 to 10-15 cm depending on the core locations. During the midpostcultural interval, estimated to span the period 1880-1940, concentrations of P, Fe, Mn, Al, and K show a rapid upward increase. At the same time, Fe, Al, and K reach maximum concentrations in Zone III. Goldberg (1971), who used ^{210}Pb with a half-life of 22.4 years, has determined the sedimentation rate for core WC-89 for the past 100 years to be 5.8 mm/yr. This is in agreement with a mean sedimentation rate of 6.2 mm/yr and the time scale given for core WC-89. The mean sedimentation rates of cores WC-86 and WC-84 are 5.0 mm/yr and 5.6 mm/yr, respectively.

High counts of Ambrosia pollen are observed in all three cores in Zone III, but the distribution pattern of ragweed pollen in each of the cores is different. In core WC-89 the first increase in abundant ragweed pollen occurs at the 35-40 cm level in Zone III while in the other Lake Mendota cores, ragweed pollen first appears in abundance in Zone II and increases upward to reach a peak in Zone III. It seems, based on the chemical and ragweed pollen evidence from cores WC-84 and WC-86, that the ragweed horizon shown in Zone III for WC-89 is an anomaly.

Additional evidence supporting the above contention is given by sediment studies of Nriagu and Bowser (1970). They observed the presence of magnetic iron spherules beginning at the 35-40 cm horizon and continuing to the sediment-water interface in a deepwater Lake Mendota core. Nriagu and Bowser (1970) suggested the iron spherules are flue products derived from industrial and domestic activities supplied to the lake through the action of washing the atmosphere or as a detrital load from urban runoff. The depth of appearance in the magnetic iron spherules (Zone III) and ragweed pollen grains (Zone II) is in approximate agreement if it is assumed that extensive fossil fuel burning occurred approximately 50-80 years after the commencement of initial land clearance in the Mendota basin. No clear explanation for the late rise in ragweed pollen in profile WC-89 can be given. It is observed, however, that the relative counts of ragweed pollen against the Eucalyptus standard throughout the entire core for WC-89 are less than in WC-86, but in core WC-84 the relative ragweed count is about the same as WC-89.

These differences suggest that the final deposition of ragweed pollen may vary locally within the lake depending on sedimentation rate of the pollen grains and whole sediment at dif-

ferent water depths or locations within the lake. Davis (1968) noted at Frains Lake, Mich., the pollen grains are deposited an average of two to four times before being buried deeply enough to escape further disturbance. Davis 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."

The black gyttja in Zone IV (upper 10-15 cm) is characterized by high ragweed counts. Iron, Al, and K concentrations level off or decrease slightly from maximum concentrations in Zone III while P, Ca, organic C, and organic N concentrations increase upward to the sediment-water interface. This interval is estimated to cover the period 1940 to the present. Among the domestic changes taking place in the Lake Mendota basin during this time were the rapid urbanization of Madison, rapid growth of towns in the northern part of the drainage basin which contribute effluent to Lake Mendota tributaries, drainage of large acreages of wetlands in the Lake Mendota basin, and emergence of the "detergent era" as an additional P source. Since 1940, a decline in the cisco fish population has been noted (Frey, 1963). The changes in the catchment basin that have been responsible for the decline of this species are not known, but increasing quantities of domestic sewage and severe siltation are suspected offenders (Frey, 1963).

Distribution of Carbon. Several investigators have examined the distribution of organic C with sediment depth to measure trends in historical aquatic productivity (Mackereth, 1966; Gorham, 1961; Hutchinson and Wollack, 1940; Horie, 1966). Often the organic C profile has been used to explain lake succession from oligotrophic to eutrophic conditions.

The deepwater core and University Bay cores show similarities as well as differences in the organic C profiles. The fact that the three cores show such a degree of similarity indicates that they are reflecting general conditions of the lake, not just local conditions. Especially notable are the similarities in the organic C profile of cores WC-89 and WC-84 and the similarities of the organic C and organic N profiles in WC-89. In the case of organic C and organic N almost every irregularity of the former is reflected in the latter. However, sedimentary profiles of organic matter varied for three cores taken in Lake Washington at different locations (Shapiro et al., 1971). The authors concluded that the different rates of deposition of eroded inorganic material in various parts of the lake caused the observed changes in organic matter in the three cores. In soils and lake sediments organic N is the dominant N form usually ranging from 95 to 98% of the total N (Bremner, 1965; Keeney et al., 1970) and is a function of the amount of particulate organic matter deposited. The deposition of organic C is rather uniform during the precultural period, but in the early postcultural period the organic C concentration increases upward to a maximum near the junction of Zones II and III for cores WC-84 and WC-89. In all three cores there is a subsequent upward decline in organic C throughout Zone III which is followed by an increase in organic C in Zone IV.

To discuss the factors believed to be controlling the deposition of organic C, a review of various possible methods of organic C deposition in lakes is necessary. The primary factors controlling the abundance of organic C in the sediments are: (1) production of organic C of autochthonous origin, (2) sedimentation of allochthonous organic matter, (3) destruction of organic material

by organisms or nonbiological processes, and (4) variation in deposition rate of the whole sediment.

The trends in the organic C deposition may be due to variations in any of the four factors mentioned in controlling the organic C deposition. Belcher and .Fogg (as quoted by Brown, 1969) reported that eutrophy and the associated hypolimnetic deoxygenation were considered as major factors in favoring the preservation of pigments in cores from Windermere and Ennerdale Water. A rapid rate of sedimentation would also favor the preservation of organic C, since the period of time during which the organic substance is in contact with the oxygen-bearing bottom water is reduced before being buried. Thus, a portion of the increase in organic matter in the Lake Mendota postcultural sediments may be the result of anaerobiosis favoring preservation of organic molecules and a more rapid rate of sediment accumulation.

However, there are some compounds, such as DDT, which only break down more rapidly under anaerobic conditions (Stalling, 1970); therefore, the overall effects of anaerobic conditions on the breakdown of organic compounds are not known. It is important to remember that the concentration and the rate of deposition of organic constituents in sediments are the result of differences between rates of formation and decomposition. Sediment trap studies by Kleerekoper (1953) show at least 70-90% of the organic matter synthesized in a column of lake water is decomposed prior to incorporation in surface sediments. Nevertheless, Mackereth (1966) and Hutchinson and Wollack (1940) believed that the organic matter which becomes incorporated below the biologically surface-active layers of the English Lakes and Linsley Pond reaches a state of considerable stability toward further oxidation shortly after burial.

The lignin content of the gyttja from several cores in Trout Lake was determined by Twenhofel et al. (1945). They had anticipated that bacterial decomposition would have led to a decrease in the nonligneous materials, and thus an increase in ligneous materials with depth. Twenhofel et al. (1945) concluded that the fact that such a decrease was not observed suggested that bacterial activity ceased in the organic sediments of Trout Lake shortly after burial. However, Shapiro et al. (1971) found organic matter, as measured by loss on ignition, increased in the upper 15 cm of sediment in a core taken from Lake Washington in 1958. Another core taken in the same location in 1970 revealed that the high values for organic matter found in 1958 had decayed. The authors concluded that diagenetic changes caused the decrease in organic matter after burial with newer sediments. Thus, the final concentration of organic C in the sediments will probably depend on all factors (1)–(4) mentioned above.

In all the Lake Mendota cores examined, the mean concentration of organic C was lowest in Zone I as shown in Table III. The observed increases in the mean concentrations of organic C in the postcultural muds may represent an increase in both an auto- and allochthonous organic C. Thus, an increase in a lake's own total production of organic C becomes mixed with and is indistinguishable from that of external origin. However, organic production of either internal or external origin may increase since the cultural period may result in increasing the hypolimnetic oxygen uptake rate. In Lake Mendota the oxygen is allowed to deplete without replenishment during stagnation, but the rate of change in hypolimnetic oxygen deficiency is not known since the cultural period began about 140 years ago. The increase in the organic C deposition in the recent sediments could be attributed in part to

increased biological productivity since the advent of domestic drainage. The observed variation in the organic C content in the cores from Lake Mendota may best be attributed to the combined influence in the rates of carbonate C, organic C, and inorganic sedimentation since the onset of extensive agricultural and urban activities in the Lake Mendota watershed.

Further insight into the relative importance of the variation in the sedimentation rates of carbonates and inorganic materials in controlling organic C deposition may be gained from Murray's (1956) studies on Lake Mendota. The relationship of gyttja to marl as suggested by Murray (1956) may be considered from the three possibilities: the gyttja is a diagenetic precursor of the marl, the gyttja is developed by leaching of the marl, and the gyttja and marl are separate sedimentary units developed under different limnologic conditions. Twenhofel (1933) postulated that the black gyttja was a diagenetic precursor of the marl and that the process of change was one of removal of organic matter by bacteria and precipitation of $CaCO_3$ at depth in the gyttja, thereby the gyttja was converted to marl. Twenhofel based his conclusion that the gyttja was a preliminary product in the production of marl on the assumption that the color of the gyttja resulted from the disappearance of organic matter with depth to produce the light marl. Murray (1956) maintained the black color in the gyttja results from the presence of ferrous sulfides deposited under conditions of oxygen deficiency and not from the organic content. Berner (1964) found that recent sediments containing fine-grained black FeS, even in small concentrations, tend to be colored gray and black. Furthermore, Murray (1956) argues that it is doubtful the gyttja might have resulted from alteration of the marl by removal of carbonate since the deeper stagnated waters would be expected to develop leaching conditions first and thus to a greater degree retain a lower carbonate content. But in fact, the greater the carbonate content, the deeper the water. Murray thus concluded that the gyttja is simply the most recent sedimentary unit to be deposited in the lake postdating the buff marl. According to Murray, the fact that the gyttja is a universal deepwater sediment resting not only on marl but on other varied sediment types suggests that it is a unit in itself. The change in sedimentation from marl to gyttja was explained as being the result of increasing rates of clastic and organic matter sedimentation superimposed on a constant carbonate deposition pattern.

The variations in organic C shown for Zones II-IV can be explained by variations in the superimposed inorganic sedimentation rates. A pronounced increase in either auto- or allochthonous organic C early in Zone II is attributed to the simultaneous increase in inorganic and organic sedimentation. The net effect of the early cultural activities in the Lake Mendota basin appears to have been to produce an increase in organic C and inorganic materials in somewhat the same proportion. If the organic sedimentation rates were not high, it would be reflected as a decrease in the concentration depth diagram the same as $CaCO_3$. In Zone III, the inorganic sedimentation rate is probably occurring faster than the organic production rate which produces a decrease in the organic C profiles. In Zone IV, the organic C profiles show an increase toward the sediment-water interface indicating perhaps an accelerated rate of organic C production of either internal or external origin in the last 20-25 years.

The carbonate profiles of the Lake Mendota cores indicate uniform deposition has occurred in the precultural period. The constant deposition is interrupted during the cultural period

to depress the carbonate C concentration. Calcium carbonate precipitation initiated by planktonic photosynthesis or physiochemical precipitation has probably not decreased in recent times as inferred directly by the concentration profile of Ca. If photosynthetic uptake of carbon dioxide is the dominant mechanism for carbonate precipitation, then an increase in $CaCO_3$ precipitation in recent times might be slightly favored with increased productivity. However, increased biological respiration, bacterial activity, and chemical oxidation serve to decrease $CaCO_3$ precipitation. Furthermore, Megard (1969) noted that it is unlikely the productivity during the history of lakes can be inferred from the concentration of carbonate in the sediment because a large proportion of the carbonate formed in the epilimnion of productive lakes is dissolved in deep water during periods of stratification. It appears that the most likely explanation for the postcultural decrease in carbonate C concentration is the masking of a somewhat constant (or increasing) carbonate deposition by the increased inorganic sedimentation. The distribution of carbonate C in the marl increases with decreasing water depth. The distribution of carbonate C in the gyttja shows the opposite relationship. The content of carbonate C decreases with decreasing water depth. The same phenomenon was observed by Murray (1956). The basic change in carbonate C deposition may be the result of a relative increase in dilution of carbonate C by inorganic materials closer to the shore regions or to a relative increase in planktonic photosynthesis in the deeper water vs. the shallower water of Lake Mendota since the cultural period. However, Wetzel (1970) noted that the present-day deposition rates of littoral carbonate were much higher than those of the central portion of the allochthonous carbonates associated with warm, wet climatic conditions precipitating before entering the major volume of the lake.

Distribution of Phosphorus. The migration and precipitation of P into the bottom muds may take place both by P incorporation into plant and animal remains and by sorption or precipitation with inorganic components. The final concentration of P residing in the sediment depends primarily on the rates of supply of P in the form of inorganic and organic P from inflowing waters; the efficiency at which P is precipitated or sorbed with other chemical components such as Ca, Al, Fe, and Mn or sorbed onto particulate matter and carried into the sediment; the retentive capacity of the sediments for P; and the rate of accumulation of the whole sediment.

A period of constant P deposition (0.8-0.94 mg/g) occurs in Zone I of the Lake Mendota cores. During this time, the concentrations of Fe, Mn, Ca, Mg, K, Al, and ragweed pollen are all relatively constant. It probably can be assumed that all factors mentioned in controlling the distribution of P maintain a relatively constant ratio to each other during this period.

During the subsequent interval (Zone II), the P concentration steadily increases upward. There is a concomitant increase in Fe, Mn, and K concentrations in all the cores. The additional source of P provided to the lake during the early postcultural period may most likely be associated with increased erosional products, presumably, owing to man's first appearance in the watershed. An increased influx of Fe and Mn hydrous oxides, clay minerals, and oxides and hydroxides of Al from domestic drainage of urban and rural areas may have provided for increased efficiency for P precipitation. Phosphorus may be taken from solution by precipitated ferric and aluminum hydroxides or clay minerals (Carritt and Goodgal, 1954; Hsu, 1965); however, the mode of P deposi-

tion which is favored in the calcareous lake system is sorption or precipitation with $CaCO_3$ (Frink, 1969; Wentz and Lee, 1969b). An eroded colloidal soil, low in P, might remove considerable amounts of P from the water before final deposition. Wang and Brabec (1969) have shown that the turbidity in Illinois River water was related to particulate P, particulate Si, and particulate Fe(III). With the increase in runoff waters since the advent of agricultural practices in the Lake Mendota watershed, a particulate P-Fe-Si complex associated with clay minerals similar to that proposed by Wang and Brabec may have contributed to an increased depositional efficiency of P since the cultural period.

High concentrations of P are maintained in Zone III representing the period 1880-1940. Any of the observed increases in the concentration of sorbed or precipitated P in the sediment could be attributed to an increase in the supply of P to the waters as well as the increase in efficiency of P deposition. For example, from 1884 to 1899, Lake Mendota received the effluent from Madison's sewage treatment plant (Sawyer, 1947). In core WC-89 a reversal in P concentration is shown to occur in about 1920; however, no reversal in the trend of P concentration is shown for WC-86 and WC-84 in University Bay. Thus, it appears that a different interpretation for explaining the P profiles may be given for the two locations within the lake. An explanation for the minimum P value in the late postcultural interval may be due either to a decrease in P supply and/or P depositional efficiency or to an increase in inorganic or organic sedimentation diluting the P fraction. The latter alternative seems the most plausible considering all the additional sources of P which usually accompany urbanization of a watershed.

Maximum concentrations of P are found in Zone IV for WC-84 and WC-86, but in the deepwater core a maximum peak for P occurs in both Zones IV and III. Increases in P concentration in the recent sediment of Zone IV are only modest—i.e., 1.3-1.8 mg/g for WC-89—compared to the P increase in Zone III from 1.0-2.0 mg/g. If substantial P has been added to the lake waters from storm sewer runoff and domestic waste since the detergent era, then either the additional source of P is masked by increased sedimentation rate of the whole sediment throughout Zone IV or the P associated with agricultural runoff (Zones III and IV) overwhelms the P added from new sources since the detergent era (Zone IV).

The final concentration of P that resides in the sediment is also dependent on the P sorptive and retentive capacity of the sediment. If the chemical composition of the sediments has changed historically, presumably, the P sorptive and desorptive capacity of the sediment will also be influenced. Bortleson (1970) conducted a laboratory study to assess the P sorptive characteristics on selected strata representing pre and postcultural sediments in WC-89. The sorption and desorption of added increments of P to the sediments indicated that the postcultural gyttja is a more favorable sorptive and less favorable desorptive environment for P than the precultural marl. In other words, the postcultural sediment which sorbed the most P during the sorption step released the least P during the subsequent desorption. The higher concentrations of Fe, Mn, Al, and K in the gyttja probably account for the greater P binding capacity. Thus, it appears during the precultural period the marl sediment was less capable of sorbing and retaining P, but in recent lake history the muds are capable of sorbing and retaining P which may be added to the lake. Livingstone and Boykin (1962) noted that the productivity in a lake could be inversely proportional to the sorptive capacity of the mud. They found the P con-

tent was highest in the deeper-lying samples of the sedimentary column of Linsley Pond, which formed during the oligotrophic stage in the lake's history. In such a case, the P that had not been released from the mud during the early history of the lake would still be trapped in the sediment. Acid-soluble P concentration, as determined and reported by Wentz and Lee (1969a,b), provides additional evidence for a greater P binding capacity in the gyItja. The acid-soluble P concentration follows a similar trend to total P in core WC-89. The P released with 0.075N $HCl-H_2SO_4$ extractant is an operationally defined fraction of the total which is desorbed at 20°C at pH 1-2 (Wentz and Lee, 1969a). Presumably, the acid extractant would remove Ca-bound forms of P plus an undefined fraction of Fe-P and Al-P. The ratio of acid-soluble P to total P decreases above the 55-60-cm level indicating that the more recent sediments contain a greater fraction of P which is not acid extractable. Acid treatment probably would not extract organic P or occluded forms of Fe-P and Al-P (Shah et al., 1968). Williams et al. (1970) reported values indicating that 26% of the total P is organic P in Lake Mendota surface muds.

The mean P concentration in the precultural marl is about the same in cores WC-84, WC-86, and WC-89, but, for the same cores, the P concentration increases more in the post-cultural sediment the deeper the water. It appears that the P concentration in the marl sediment was more uniform over the lake, but since the advent of domestic drainage, the influent materials have allowed fractionation of sediment particles with water depth which has complicated the sedimentation regime of the postcultural sediments. Based on surface sampling of 32 stations in Lake Mendota, P, Fe, and Mn concentrations show a positive statistical correlation with sample depth (Delfino et al., 1969); a linear correlation coefficient of 0.82, 0.74, and 0.81 was found for P, Fe, and Mn, respectively. Since higher concentrations of P, Fe, and Mn 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-born suspended matter may have occurred (Delfino et al., 1969). Apparently, the P in the center of the lake is associated with the finer sediment fraction (see Table III). The differences in the thickness of the sedimentary Zones for cores WC-84, 86, and 89 can also be partially attributed to changes in percent solids in a given interval which is a function of the particle fractionation in the lake and consolidation after burial. Frink (1969) found in eutrophic Bantam Lake, Conn., that the center of the lake was enriched in clay, organic matter, and P when compared with the sediments around the lake edge. The Fe-P and Al-P fractions were always highest in the finer fractions toward the center of the lake, but Ca-P decreased with increasing water depth in Bantam Lake and was associated with the coarser fraction (Frink, 1969).

Iron and Manganese Distribution. Total Fe and Mn analyses were performed on all the cores investigated. The distribution of Fe and Mn in the sediments may depend primarily on the supply rate of particulate and dissolved Fe and Mn, the migration of Fe and Mn as influenced by redox conditions and the rate of accumulation of the whole sediment.

The Fe and Mn content increases by two- to fourfold in the postcultural over the precultural interval; the initial upward increase in Fe and Mn occurs in the early cultural period prior to an increase in P in WC-86 and WC-89. The increase in sedimentary Fe is probably associated with an increased Fe supply to the lakes from land runoff. Wang and

Brabec (1969) found the turbidity in Illinois River water to be related to the particulate P, Si, and Fe(III) concentrations. The molar ratio of Si to Fe(III) was 1.0:1.47. Carroll (1958) found that the association of Fe with clay minerals is an important means whereby Fe is transported by rivers to lakes. According to Carroll, Fe is associated with clay minerals as an essential constituent, as a minor constituent within the crystal lattice, and as iron oxide on the surface of mineral platelets. The close relationship between the Fe, K, and Al profiles in the calcareous lakes are further evidence that Fe is mainly associated with the clay mineral fraction. Analyses of the clay fractions of soils show that Fe is mainly associated with the finest fractions (the clay and silt grades), which have extremely large surface areas (Carroll, 1958). This may account for the high concentrations of Fe found in the center of Lake Mendota (Delfino et al., 1969).

Nriagu (1967) proposed from his studies of Fe and S in Lake Mendota cores that the progressive upward enrichment of Fe in the sediments may be due to the increased efficiency of precipitation and retention of ferrous iron in the sediments as sulfides. Nriagu (1967) found a positive relationship between Fe and sulfide in the cores. However, a feature shared by the gyttja and marl is that the Fe content is greater than should be required to hold all the sulfur as FeS. Murray (1956) concluded that the black color of the gyttja resulted from the presence of ferrous sulfides deposited under conditions of oxygen deficiency which occurred contemporaneously with increased clastic deposition as a consequence of farm and domestic drainage. However, Nriagu (1968) suggested prior to the change in sedimentation of Lake Mendota associated with human activity, the lake had developed an oxygen deficiency intense enough to cause reduction of sulfates to sulfides, but the lake was able to maintain its basin free of black muds by the process of self-purification.

Distribution of Aluminum, Potassium, Calcium, and Magnesium. The distribution of Al, K, Mg, and Ca may depend primarily on the rate of supply of dissolved and particulate mineral matter, the biological or chemical precipitation of carbonates, and the variation in the accumulation of the whole sediment. Al, Mg, Ca, and K may occur in a large variety of mineral structures such as feldspars, clay minerals, and amorphous aluminosilicate gels. Mackereth (1966) noted that Na, K, and Mg were associated with the mineral fraction of the sediment of English lakes, but Ca was not so clearly associated with mineral erosion. Calcium was evidently more easily leached from the soil than Mg. According to Mackereth, the Ca is abundantly deposited into the English lake sediments only at times of very intense erosion when the rate of precipitation of clastic material is high enough to prevent removal by leaching of much Ca. In Lake Mendota the Ca concentration is controlled mainly by carbonate deposition (discussed previously), but Mg concentration is influenced by the rate of detrital inorganic sedimentation and Mg carbonate deposition. Processes other than Mg carbonate (or mixtures of Mg with $CaCO_3$) sedimentation are dominant in Zones II-IV because the Mg concentration is not depressed in the recent muds as is CaCO3.

Al and K concentrations increase initially in Zone II and continue to increase throughout Zone HI before leveling off in Zone IV. The K and Al concentration is enriched two to five times in the postcultural over the precultural sediments indicating erosional activity has increased since man moved into the Madison lake region. The construction of a dam at the Yahara outlet in 1847 led to raising the level of the lake 5 ft and has exposed new shoreline to erosion. There should, on the grounds discussed above, exist a direct relationship between Al and K content in the sediments and erosion intensity of the drainage basin.

Lake Mendota Long Core. In November 1968, a 990-cm core was taken from the center of Lake Mendota in 23 meters of water using a 1-1.5-in. piston-operated corer. The 9.9-meter core was fractionated in 20-cm intervals as shown in Figure 5. The zones shown in Figure 5 indicate approximate changes in chemical stratigraphy as described previously for the short cores WC-84, 86, and 89. The purpose of the sample probe was to determine the physical and chemical homogeneity of the precultural sediment during the late postglacial period. The top 62 cm of sediment consisted of a black gyttja containing 98-111 mg/g Ca; below 62 cm to 990 cm (Zone I), the fine-grained, buff-marl deposits contain 183-226 mg/g Ca. There was no variation in appearance from 62 to 990 cm of sediment..

The marked increase in ragweed abundance occurs upward of the 42-62 cm stratum (Zone H). The low ragweed pollen deposited during the period represented by 920 cm of sediment below the recent muds supports the use of Ambrosia pollen as an indicator of the cultural base in a sedimentary sequence. A ragweed maximum in pollen diagrams may not necessarily be related to European-type settlement. At Silver Lake, Ohio, and at Rogers Lake, Conn., high ragweed pollen counts were found in core intervals dated 5000-8000 years B. P. (Ogden, 1966; Davis, 1967).

Organic C concentration varies from 59 to 77 mg/g over the core interval of 62-990 cm. This compares favorably with 55-73 mg/g organic C found in the marl sediment of WC-89, a short deepwater core. The postcultural sediment contains 87-92 mg/g organic C.

The enrichment of P in the postcultural sediments of Lake Mendota is of particular interest because the long core (9.9 meters) provides a background concentration of P that was
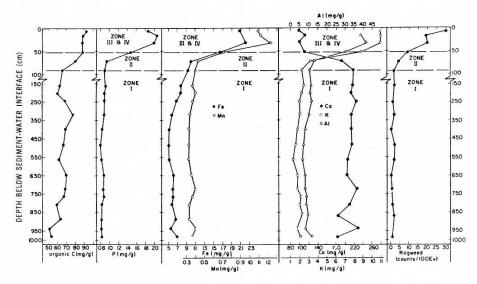

Table III. Mean Concentrations of Phosphorus, Iron, Potassium, Organic Carbon, Carbonate Carbon, and % Solids in the Lake Mendota Cores[a]

Core	Chemical component	Zone			
		Precultural I	Early postcultural II	Midpostcultural III	Late postcultural IV
WC-89	P	0.90	0.96	1.57	1.63
	Fe	7.00	12.9	20.2	20.2
	K	2.43	7.45	9.78	10.2
	Organic C	64.8	76.3	70.5	84.1
	Carbonate C	57.6	41.3	33.6	35.6
	% solids	13.4	12.6	16.3	15.5
WC-86	P	0.96	1.06	1.23	1.46
	Fe	6.90	13.1	19.8	22.9
	K	3.12	8.42	11.5	11.7
	Organic C	59.8	70.0	74.7	77.4
	Carbonate C	74.9	46.1	30.5	30.5
	% solids	18.0	23.2	24.4	17.9
WC-84	P	0.85	0.997	1.09	1.16
	Fe	6.70	12.4	20.2	20.0
	K	2.71	7.34	11.1	11.1
	Organic C	90.5	102	98.6	92.3
	Carbonate C	76.1	48.4	28.4	27.4
	% solids	26.2	27.7	33.3	28.9

[a] All concentrations are mg element/g dry wt of solids.

Figure 5. Chemical and Ambrosia pollen stratigraphy of Lake Mendota core WC-95

deposited for a long period historically. The P concentration remains constant at 0.8-0.94 mg/g throughout Zone I, then in Zones III and IV, the P concentration increases to 1.5-2.1 mg/gin the postcultural sediment.

The depth plot of Fe, Mn, K, and Al concentrations is remarkably uniform below the ragweed horizon to 990 cm, but the postcultural concentrations of these elements increases three-five times that found in the precultural sediment. For all the above elemental concentrations, a slight minimum inflection is observed in the zone of 400-650 cm.

Several species of ostracodes were described by Burrell (1971) for Lake Mendota core WC-95. Ostracodes were present throughout the 990-cm core length, but in the upper 60 cm (Zone III and IV) there was an increase in diversity of species and total ostracod numbers. Species reported as exclusive to the recent upper 60 cm of sediment were *Darwinula aurea, Candona caudata, Candona pose yensis,* and *Candona spinaensis* (Burrell, 1971).

In summary, the chemical stratigraphy of the 9.9-m core indicates that stable conditions existed in Lake Mendota and its watershed for a long historical period before the settlement period in Wisconsin.

Summary and Conclusions

The composition of the sediments with depth and, therefore with time, presents a pattern of change which documents the progressive increment of materials deposited to Lake Mendota. Thus, changes in the chemical stratigraphy can be traced to man's activities in the watershed. If it is assumed that the sedimentation rate throughout the period represented by the concentration-depth diagram is constant, a calculation can be made showing the incremental increase or decrease in concentration per unit thickness of sediment (or per year if time is estimated). However, this study has revealed that concentration-depth diagrams do not generally contain sufficient information to estimate an incremental rate change in nutrient concentration which accurately reflects changes in nutrient supply owing to man's activities in the watershed. The deposition rate of the whole sediment imposes a constraint on the system which necessitates an absolute time scale in the pre- and postcultural sediments.

A basic change in sedimentation is recorded in the Lake Mendota cores by a buff marl (Zone I) overlain by a gray-colored gyttja-marl (Zone II) and a black gyttja (Zones III and IV). Initial increases in Fe, Mn, Al, K, and ragweed pollen occur in Zone II corresponding to the first active period of settlement in southern Wisconsin and the Lake Mendota basin (ca. 1820-1880) while carbonate C shows a rapid decrease in concentration during the same interval. The change in sedimentation is attributed to increased deposition of erosional material as a consequence of farm and urban activities in the drainage basin. Further increases in the deposition of Al-, K-, Fe-, and Mn-containing compounds in Zone III (ca. 1800-1940) are correlated to the increased runoff and leaching of the soils in the Lake Mendota basin. The overall trend in Lake Mendota has been to increase in the rate of deposition of the whole sediment from about 1820-1940. The core profiles indicate that the runoff of erosional products reached a peak and leveled off approximately 20-30 years ago. The enrichment of Fe appears to be caused by an increase in the rate of sedimentation of a detrital mineral or group of minerals that contain the element as a firmly bound major component or sorbed constituent. The marked ability of the postcultural sediments to retain inorganic P compared to the precultural marl is probably due to the higher Fe content in the black gyttja.

Analysis of past rates of change must be taken together with the detection and measurement of recent man-induced changes. Therefore, the chemical stratigraphy of lake sediment cores provides the understanding which is needed to detect a change as an acceleration; only by detecting accelerations is it possible to distinguish between normal and cultural processes. In the Lake Mendota cores, the normal rate of P change (before man's influence) with sediment depth is nearly zero. The chemical stratigraphy of precultural interval of the Lake Mendota long core indicates that stable limnological and watershed conditions existed in Lake Mendota and its basin prior to man's influence for a long period historically. The concentrations of P, organic C, Fe, Mn, Al, K, Ca, as well as ragweed pollen are all relatively constant in Zone I. In the midcultural period (Zone III) an accelerated upward increase in P occurs and reaches a first maximum (ca. 1920) in core WC-89; a second maximum in P concentration occurs in the most recent sediment (Zone IV). The enrichment of P in the postcultural sediments of Lake Mendota is due not only to an increase in supply of P from domestic drainage, but to

an increase in P retentive capacity of the postcultural sediment and to an increase of P depositional efficiency owing to the concomitant increase in Fe-, Mn-, K-, and Al-containing compounds. The P concentration in the marl sediment is more uniform over the lake, but since the advent of domestic drainage, the influent materials have allowed fractionation of sediment particles with water depth to produce higher concentrations of P toward the center of the lake.

Organic C concentrations in the Lake Mendota sediments have increased since the precultural period indicating an increase in biological productivity of the lake; however, it is difficult to determine what part of the increase is attributable to alto- or autochthonous organic production. In Zone IV organic C increases upward to the sediment-water interface perhaps indicating an accelerated increase in level of organic productivity since 1940. The increase in organic C concentration in Zone IV is accompanied by an increase in P and a slight increase in carbonate C.

Literature Cited

Andersen, S. T., "Silicone Oil as a Counting Medium for Pollen Grains: Geological Survey of Denmark," Series IV, pp 5–24, 1960.

Bender, M. M., personal communication, "Radiocarbon Dating," Meteorology Department, University of Wisconsin, 1969.

Berner, R. A., *Mar. Geol.*, **1**, 117–40 (1964).

Bortleson, G. C., "Chemistry of Lake Sediment Cores," MS thesis, Water Chemistry Department, University of Wisconsin, 165 pp, 1968.

Bortleson, G. C., "The Chemical Investigation of Recent Lake Sediments from Wisconsin Lakes," PhD thesis, Water Chemistry Department, University of Wisconsin, 278 pp, 1970.

Bremner, J. M., "Inorganic Forms of Nitrogen," in "Methods of Soil Analysis," C. A. Black, Ed., Part 2, Amer. Soc. Agronomy, Madison, Wis., pp 1149–318, 1965.

Brown, S. P., *Mitt. Int. Ver. Limnol.*, **17**, 95–103 (1969).

Burrell, J. A., "Distribution, Ecology and Taxonomy of Recent Freshwater Ostracoda of Lake Mendota, Wisconsin," MS thesis, Geology and Geophysics Department, University of Wisconsin, 124 pp, 1971.

Carritt, D. E., Goodgal, S., *Deep-Sea Res.*, **1**, 224–43 (1954).

Carroll, D., *Geochem. Cosmochim. Acta*, **30**, 1–27 (1958).

Curtis, J. T., "The Vegetation of Wisconsin," University of Wisconsin Press, 657 pp, 1959.

Davis, M. B., *Rev. Palaeobotan. Palynol.*, **2**, 219–30 (1967).

Davis, M. B., *Science*, **162**, 796–9 (1968).

Delfino, J. J., Bortleson, G. C., Lee, G. F., ENVIRON. SCI. TECHNOL. **3**, 1189–92 (1969).

Faegri, K., Iversen, J., "Textbook of Modern Pollen Analysis: Copenhagen, Ejnor Munksgaard, 168 pp, 1950.

Frey, D. C., "Limnology of North America," E. G. Frey, Ed., University of Wisconsin Press, pp 34–54, 1963.

Frink, C. R., *Soil Sci. Soc. Amer. Proc.*, **33**, 369–72 (1969).

Goldberg, E., personal communication, "^{210}Pb Dating," Scripps Institute of Oceanography, University of California, 1971.

Gorham, E., *Can. J. Bot.*, **39**, 333–8 (1961).

Horie, S., *Verh. Int. Ver. Limnol.*, **16**, 274–81 (1966).

Hsu, P. H., *Soil Sci.*, **99**, 398–402 (1965).

Hutchinson, G. E., Wollack A., *Amer. J. Sci.*, **238**, 493–517 (1940).

Jackson, M. L., "Soil Chemical Analysis," 468 pp, Prentice-Hall, Englewood Cliffs, N.J., 1958.

Keeney, D. R., Konrad, J. G., Chester, G., *J. Water Pollut. Contr. Fed.*, **42**, 411–17 (1970).

Kendall, R. L., *Ecol. Monogr.*, **39**, 121–76 (1969).

Kleerekoper, H., *J. Fish Res. Bd. Can.*, **10**, 283–91 (1953).

Livingstone, D. A., Boykin, J. C., *Limnol. Oceanogr.*, **7**, 57–62 (1962).

Mackereth, F. J. H., *Phil. Trans. Royal Soc.* London (B), **250**, 165–213 (1966).

Maher, L., personal communication, University of Wisconsin, 1969.

Megard, R. O., *Mitt. Int. Ver. Limnol.*, **17**, 94 (1969).

Murray, R. C., *Bull. Geol. Soc. Amer.*, **67**, 883–910 (1956).

Nriagu, J. O., "The Distribution of Sulfur and Iron in Lake Mendota Sediments," MS thesis, Geology Department, University of Wisconsin, 102 pp, 1967.

Nriagu, J. O., *Limnol. Oceanogr.*, **13**, 430–9 (1968).

Nriagu, J. O., Bowser, C. J., *Water Res.*, **3**, 833–42 (1970).

Ogden, J. G., III, "Radiocarbon Determinations of Sedimentation Rates from Hard- and Soft-Water Lakes in Northeastern North America," in "Quaternary Paleoecology," E. J. Cushing and H. E. Wright, Eds., Yale Univ. Press, New Haven, Conn., pp 175–83, 1967.

Ogden, J. G., III, *Ohio J. Sci.*, **66**, 387–400 (1966).

Olson, R. V., "Iron," in "Methods of Soil Analysis," C. A. Black, Ed., Part 2, Amer. Soc. Agronomy, Madison, Wis, pp 1179–1237, 1965.

Pennak, R. W., *Ecology*, **44**, 1–15 (1963).

Sarles, W. B., "Madison Lakes: Must Urbanization Destroy their Beauty and Productivity?" in *Trans.* 1960 Seminar on Algae and Metropolitan Wastes, Robt. A. Taft Sanitary Engineering Center, Tech. Rept. W61-3, 1961.

Sawyer, C. N., *J. N. Engl. Water Works Ass.*, **51**, 109–27 (1947).

Shah, R., Syers, J. K. Williams, J. D. H., Walker, T. W., *N. Z. J. Agr. Res.*, **11**, 184–92 (1968).

Shapiro, J., Edmondson, W. T., Allison, D. E., *Limnol. Oceanogr.*, **16**, 437–52 (1971).

Smith, G. H., *Wis. Acad. Arts Sci. Lett.*, **24**, 53–107 (1929).

Stalling, D. L., personal communication, Bureau of Sports, Fisheries & Wildlife, Columbia, Mo., 1970.

Stockner, J. G., Benson, W. W., *Limnol. Oceanogr.*, **12**, 513–32 (1967).

Twenhofel, W. H., *Sediment. Petrology*, **3**, 68–76 (1933).

Twenhofel, W. H., McKelvey, V. E., Nelson, H. F., Feray, D. E., *Bull. Geol. Soc. Amer.*, **56**, 1099–1142 (1945).

Wang, W. C., Brabec, D. J., *J. Amer. Water Works Ass.*, **61**, 460–4 (1969).

Wentz, D. A., "Available Phosphorus in Lake Sediments," MS thesis, Water Chemistry Department, University of Wisconsin, 106 pp, 1967.

Wentz, D. A., Lee, G. F., ENVIRON. SCI. TECHNOL. **3**, 750–4 (1969a).

Wentz, D. A., Lee, G. F., *ibid.*, **1969b**, pp 754–9.

Wetzel, R. G., *Limnol. Oceanogr.*, **15**, 491–503 (1970).

Wiersma, J. H., Lee, G. F., "Selenium in Lake Sediments—Analytical Procedure and Preliminary Results," ENVIRON. SCI. TECHNOL., **5**, 1203–6 (1971).

Williams, J. D. H., Syers, J. K., Harris, R. F., Armstrong, D. E., *ibid.*, **4**, 517–19 (1970).

Wright, H. E., Jr., *Ecology*, **49**, 937–55 (1968).