Oxygen Depletion in the Hypolimnion of Lake Mendota, WI – Relationship to the Demise of the Cisco

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ABSTRACT

Large-scale die-off of cisco, a cold-water fish, occurred in Lake Mendota, WI in the 1930's and 1940's. This die-off was attributed to increased eutrophication of this lake. The increased fertility of the lake was proposed to cause an increased rate of deoxygenation of the hypolimnion. The hypolimnion of this lake has become anoxic since the turn of the century, therefore the cisco must have been inhabiting a layer of water just below the thermocline that was sufficiently cold and oxygenated to meet their physiological requirements. A study was conducted to determine the rate of deoxygenation of various parts of the hypolimnion of this lake in the early 1970's. The results of this study were compared to previous studies made on this lake since 1906.

Marked year-to-year variations were found in the rate of deoxygenation of the hypolimnion. There was a general trend of increasing rates of deoxygenation of the water just below the thermocline. However, the rate of deoxygenation of water just above the sediment in the deep hole of the lake

has not changed during this time. A two component model of the rate of deoxygenation was formulated in which the rate that occurs just below the thermocline fits zero order kinetics with respect to oxygen concentration and is controlled primarily by the biochemical oxygen demand of the algae raining down from the epilimnion. A first order rate expression with respect to oxygen was found for the deoxygenation that occurs just above the sediments. This rate was controlled primarily by abiotic reactions of reduced iron and sulfur compounds diffusing out of the sediments and oxygen diffusion into the sediments.

Using the US OECD phosphorus load hypolimnetic oxygen depletion rate model it was found that in general the oxygen depletion rates just below the thermocline have on the average increased in response to an increased phosphorus load to the waterbody. It is estimated that since 1910 the phosphorus load to this lake has increased from approximately 23×10^6 to 50×10^6 kg P/yr. This change in phosphorus load is supported by the decrease in Secchi depth that has occurred in this lake over that period of time.

It is concluded that the large scale die-off of cisco that occurred in this lake could have been the result of increased phosphorus loads to the lake arising from more intensified agriculture and urbanization of the lake's watershed. This phosphorus caused increase in phytoplankton biomass which increased the rate of deoxygenation of waters just below the thermocline, thereby in some years making the niche the cisco were inhabiting an unsuitable habitat.

INTRODUCTION

Large scale die-offs of cisco occurred in Lake Mendota, Wisconsin in the 1930's and 1940's. Various explanations have been offered to explain these die-offs ranging from disease, introduction of toxic chemicals and increased eutrophication of the lake resulting in the increased deoxygenation of the hypolimnion. This paper presents the results of a study devoted to examining the data available on the rate of deoxygenation of the hypolimnion of the hypolimnion of Lake Mendota for the period from the early 1900's to the early 1970's. It provides additional information on increased eutrophication on the demise of cisco in this lake.

LITERATURE REVIEW

Characteristics of Cisco

Cisco, <u>Leucichthys artedi</u>, are characterized as being pelagic, cold stenotherms, plankton eaters, as having terminal mouths, traveling in schools of one age group only, and exhibiting a need for high dissolved oxygen in the water (Frey, 1955; Cahn, 1927). According to Pritchard (1930), these fish spawn in late November or early December, depending upon the water temperature of the lake. The spawning ground is generally located on a sand or rock bottom in about three meters of water. The young cisco hatch in the spring, March to early May. The fry will

remain in the shallow water, as a school, until about June when they are forced to migrate to the hypolimnion due to the warming of the epilimnion. John (1954) and McCormick et al. (1971) indicate that adult cisco move into the hypolimnion earlier than the younger fish, because the older fish cannot survive at warm temperatures as well as the younger fish. Cisco remain in the hypolimnion until overturn if sufficient dissolved oxygen is present.

McCormick et al. (1971) reports cisco are the most temperature tolerant of the Coregonids, but the least temperature tolerant of the fish in the inland lakes. The ultimate lethal temperature (when all fish die) for all ages of cisco is 26°C, which is the lowest for any North American fish (Edsall and Colby, 1970; Colby and Brooke, 1969). When the dissolved oxygen is depleted in the hypolimnion, the cisco are forced to move up into the warmer water. Older fish will resist the upward movement as long as possible and are the last to make this forced migration (Frey, 1955; Fry, 1937). Cahn (1927) attributes some observed die-offs of cisco to the forced migration into the thermocline where warmer water and insufficient oxygen exist.

Frey (1955) studied thirty-seven lakes with cisco and fifty-three non-cisco lakes. The non-cisco lakes had a variety of oxygen profiles. The deeper lakes with cisco had large amounts of dissolved oxygen in the hypolimnion,

and the shallower lakes with cisco had an oxygen maximum at the thermocline. This plus-heterograde (oxygen maximum at or near the thermocline) oxygen profile in the shallower cisco lakes could explain how the cisco survive in the shallow lakes.

Frey (1955) divides the lakes he studied into three layers:

supra-cisco layer--epilimnion, with oxygen greater than three mg/l, but temperature over 20°C

infra-cisco layer--temperature under 20°C, but oxygen less than three mg/l

cisco layer--oxygen greater than three mg/l, and temperature under 20°C

The non-cisco lakes had little or no cisco layer, while cisco lakes had a large cisco layer and a larger "margin of safety" against oxygen depletion and extreme conditions. The lakes had variations in oxygen from year to year and month to month so the thickness of the cisco layer is important to their survival.

One factor affecting the existence of cisco in a lake could be eutrophication. Eutrophication may cause oxygen depletion in the hypolimnion, and decrease the volume of the lake available for total fish production (Smith, 1969). If eutrophication continues the fisheries change from cold water fish, like cisco, to what are generally considered to be the less desirable warm water fish. Lee and Jones (1979) have recently completed an

extensive discussion of eutrophication fisheries relationships in waterbodies where they have shown that the fish yield in a waterbody can be correlated with a normalized phosphorus load to the waterbody.

Some lakes with oxygen depletion do contain cisco populations. The cisco in lakes with clinograde oxygen profiles, usually considered eutrophic, may be able to survive by remaining at the thermocline-hypolimnion boundary in cooler temperatures and at a point where oxygen is present. Oxygen diffuses slowly across the thermocline, and if a large oxygen demand is not present, the water just below the thermocline should have some oxygen. This area could be exhausted of oxygen as eutrophication increases and causes oxygen depletion at the boundary.

Cisco in Lake Mendota

Lake Mendota, Madison, Wisconsin, once supported a large population of cisco. Many fishermen would catch these fish during their spawning season (John, 1954).

Large die-offs of cisco occurred in Lake Mendota and the population is now essentially extinct. On July 30, 1932 about 1,400,000 dead cisco were found floating on the surface (Telford, 1954). These die-offs amounted to about one-hundred tons of cisco, and was the largest reported die-off of Lake Mendota cisco. Other recorded die-offs occurred in the summers of 1940, 1941, 1953, and 1955 (John, 1954).

In an article in the Wisconsin State Journal, Pyre (1932) quotes Ralph Hile (U.S. Bureau of Fisheries) as saying that the cisco are intolerant of eutrophication. He also quotes A. D. Hasler as saying that the cisco dieoffs were due to oxygen depletion forcing the cisco into warmer waters of the thermocline. Hasler stated, "Their position is precarious at best, and with increased eutrophication there is a greater likelihood that many individuals, not being able to acclimatize, will succumb." Another article in the same paper quotes Dr. Bowman, a Madison City Health Officer, as saying that the cisco deaths were due to oxygen depletion, not any disease. Pearse (1934) also reports few cisco in Lake Mendota due to low oxygen. Cooper (1956) attributes the cisco decline in Mendota to increasing fertility and less oxygen. Birge and Juday (1914) reported that the hypolimnion of Lake Mendota was anoxic in 1909 during late summer. situation would force the cisco to inhabit a narrow band of cold water that exists just below the thermocline where there is sufficient oxygen input from the epilimnion as a result of the diffusion through the thermocline.

The relatively short period of years during which the cisco die-offs occurred would suggest that oxygen depletion played a large role in their demise in Lake Mendota. If the only reason for the decline of the cisco was year class failure, it would be expected that the cisco

population would not become extinct in such a short period of time as had occurred. The rapid demise of the cisco may also suggest that accelerated eutrophication in Lake Mendota effected the hypolimnion just below the thermocline and caused oxygen depletion to an extent to force the cisco into the thermocline, where increased temperature and/or insufficient oxygen caused their deaths.

Oxygen Depletion in Lakes

Dissolved oxygen is depleted both in the water column and at the mud-water interface by animal, plant, bacterial respiration, and by chemical oxidation. The vertical distribution of oxygen after stratification or ice cover will be a result of the oxidation processes at various sites and the mixing processes which distribute the deficit throughout the lake. The significance of respiration in the water column and of respiration and chemical oxidation near the sediment-water interface at any point in the lake, is influenced by physical mixing arising from the vertical mixing, horizontal translations, and density currents.

The major factor in depletion of oxygen in the water column away from the sediments appears to be bacterial respiration which has been found to have a zero order depletion rate with respect to oxygen. ZoBell and Stradler (1940), using Lake Mendota bacteria, showed that respiration of bacteria is independent of oxygen concentration

in the range of 0.2 to 36.5 mg/l. ZoBell (1940a) incubated bacteria at various temperatures (8, 18, 25, and 37°C), and in all cases, the rate of oxygen use by bacteria was independent of the concentration of oxygen. The same kinetic relationship has been found by other investigators. Burns and Ross (1972), working with Lake Erie; Fruh and Davis (1972), studying Texas impoundments; and Amberson (1928), investigating Arbacia eggs and Paramecium, support the finding of a zero order depletion caused by microbial respiration. Marine bacteria show the same independence of oxygen concentration in their respiration in the range of 0.3 to 12.74 cc/l of oxygen (ZoBell, 1940b).

The zero order rate constant has been found to occur in lakes even though bacterial respiration is dependent upon factors such as the population of bacteria, the amount of organic matter present, the ease of oxidation of the organic matter, the type of cell membrane, and the temperature of the water (ZoBell and Stradler, 1940; ZoBell, 1940a; Waksman and Renn, 1936; ZoBell, 1940b, Hutchinson, 1957; Varma and DiGrano, 1968; Fitzgerald, 1961). It appears that even though these factors are important, the rate of respiration of bacteria is none-theless independent of oxygen, and is zero order with respect to oxygen concentration.

The oxygen deficit resulting from the sediments is more difficult to evaluate than the biochemical oxygen

demand (BOD) of the water column due to the larger number of possible mechanisms involved. McDonnell and Hall (1967) have shown that invertebrates in the sediments exert a zero order oxygen demand with respect to oxygen (Martin and Bella, 1971; Rolley and Owens, 1967). The oxygen depletion may also be catalyzed by the sulfate ion as proposed by Burns and Ross (1972) where <u>Desulfovibrio</u> bacteria are present.

If the diffusion of oxygen into the sediment is the rate-limiting step, the oxygen demand may appear to be first order with respect to oxygen (Mortimer, 1971; Howeler and Bouldin, 1971; Bouldin, 1969). In contrast, if the diffusion of reduced species such as sulfide or Fe(II) from the sediment is greater than the reaction rates with respect to oxygen and/or rates of oxygen supply through mixing, the sediments' oxygen demand may be expected to be zero order with respect to oxygen, and dependent upon the concentration gradient of reduced species in the sediment interstitial water and the overlying water.

The data obtained from river sediments by Rolley and Owens (1967) or from the well mixed laboratory systems of Mortimer (1942) which suggest diffusion controls the depletion of oxygen cannot be applied to stratified, poorly mixed lakes with gyttja sediments. If an anoxic microzone forms above the sediment (Hutchison, 1957), no oxygen gradient exists across the sediment-water interface, and

oxygen diffusion is likely insignificant. In these instances, the oxygen depletion is controlled by the transport of oxygen demand substances from the sediment. The transport of solutes from the sediment is likely controlled by molecular diffusion from the muds and turbulent diffusion from the interface into the water column (Mortimer, 1971).

Martin and Bella (1971), working with estuary sediments found that when the circulation of water above the sediment was stopped, the rate of oxygen uptake decreased gradually rather than sharply. A sharp decrease would be expected if diffusion of oxygen into the sediments controls the rate. Instead, mixing appears to be most important. Sullivan (1967) proposed that the release of dissolved solutes from the sediments into the water and the subsequent dispersion of these into the overlying water are most important in a lake. When the sediments are reduced, iron, manganese, phosphate and sulfide will be released into the interstitial water and be dispersed by turbulent mixing (Mortimer, 1971).

In lakes with a large sediment oxygen demand, it is commonly observed that the vertical oxygen profile during the winter and early summer has some exponential character, with a smaller concentration of oxygen at the sediment—water interface and larger concentrations farther away from the sediment (Hutchinson, 1957). Since the deficit

in the upper portions of the water column is zero order and fairly uniform, the exponential profile above the sediment may be a result of the sediment demand distributed by vertical mixing.

Some of the material released at the anoxic microzone by the sediments may have greater concentration at the surface of the muds than deeper in the sediment. The compounds deeper in the sediment are reduced, even in oligotrophic lakes (Gorham and Swaine, 1965). At overturn, all compounds become oxidized in the upper sediment, except when these sediments become anoxic after stratification in eutrophic lakes the compounds are reduced (McMahon, 1969).

The oxygen demand of sediments is composed of an abiotic and biotic component. The biotic component is made up of the oxygen demand arising from the respiration of benthic organisms utilizing the organic matter present in the sediments. The abiotic component is primarily related to the oxidation of reduced sulfur species, principally sulfide and ferrous iron. Stumm and Lee (1961) found that the oxidation of ferrous iron by dissolved oxygen obeyed the first order rate expression with respect to oxygen

$$\frac{-d \text{ FE (II)}}{d+} = k \text{ FE (II) PO}_2 \text{ (OH)}^2.$$

Mortimer (1941) observed the difference in iron concentration between the aerated and anaerobic sediment. He found no release of iron above aerated sediment, but an increase in iron was noted above anaerobic sediments. The increase in iron concentration and other reduced substances is due to greater solubility of the reduced form over the oxidized form (the oxidized form in some cases forms a precipitate). Mortimer also observed at initially high oxygen concentrations the initial depletion was rapid for lake sediments, but the rate of oxygen depletion decreased as the concentration gradient decreased.

Another major element causing oxygen depletion is oxidizable sulfur compounds. When the sediment or water becomes anoxic, sulfate acts as a hydrogen acceptor to form hydrogen sulfide (H₂S) (Symons, 1969). Burns and Ross (1972) state that bacteria can oxidize hydrogen sulfide to sulfate, which in turn, in anoxic water, could be reduced to hydrogen sulfide. In their study, the reduction occurred in an algae mat covering the sediments and the oxidation occurred in the overlying water. Burns and Ross (1972) concluded that Desulfovibrio and Thiobacillus act as an intermediate, but necessary step in the cyclic process of sulfate catalyzing oxygen depletion.

Some of the hydrogen sulfide produced from sulfate reduction reacts to form iron sulfide and manganese sulfide, and when these are released into the oxygenated

water, the iron is oxidized to ferric which precipitates as a hydroxide and the sulfide is oxidized to sulfate.

Chen and Morris (1972) investigated the kinetics of the oxidation of sulfide, and found the order was fractional for both oxygen and sulfur which indicates that competing pathways and/or diffusion processes are significant.

Manganese (II) is also released from the sediments at oxygen concentrations of five mg/l or less in the overlying water (Delfino, 1968). Manganese is oxidized at a slower rate than iron in the neutral to slightly alkaline range by dissolved oxygen and some reduced manganese can be present in oxygenated natural water. Delfino (1968) and Delfino and Lee (1968; 1971) found a first order depletion reaction with respect to oxygen for manganese, similar to the reaction for iron. The pH is too low in most natural waters, though, to have much manganese oxidized since a pH of 8.5 or greater is necessary before appreciable oxidation occurs (Stumm and Morgan, 1970).

Mixing of the Oxygen Demand

The above discussion takes into account only vertical mixing and would produce isopleths of oxygen parallel to the sediment. Thus, it would be expected that the upper hypolimnion nearest the shore be depleted in oxygen more quickly than the hypolimnion above the deeper areas. This theory assumes that the sediments are of the same type

and oxygen demand, which is not always the case. The sediments near the shore often have less oxygen demand than the deeper sediments and therefore, the deeper areas would be depleted faster.

Vertical turbulence was proposed by Hutchinson (1957) to explain distribution of dissolved solids and reduced substances in the water column of lakes. As the amount of mixing increases, so does the rate of oxygen depletion and the height in the water column that is affected. This vertical mixing affects oxygen status to approximately ten meters above the sediment within one-hundred days of stratification in Lake Mendota. A well-mixed hypolimnion such as Lake Erie (large vertical turbulence) may appear to be depleted uniformly. The hypolimnion currents may also mix the sediments down five to fifteen centimeters in the sediment, though in Lake Mendota, only the top two centimeters are well mixed, with partial mixing to about fifteen centimeters.

In contrast to the vertical turbulence, it has been suggested that the distribution of dissolved oxygen could be modeled by assuming lateral translations to be the overwhelmingly important factor in mixing the lake (Mortimer, 1942). Thus, the zone of oxygen depletion near the sediment would be spread horizontally throughout the hypolimnion, and the deficit at any depth in the center of the lake would become a function of the rate of

depletion at the sediment, the volume of water at that depth, and the magnitude of horizontal currents. Such a model would likely result in the same type of profile as the vertical turbulence model in that the deeper areas of the lake would be depleted less rapidly than the upper hypolimnion due to the closer proximity of the sediments and the smaller volume of water involved. It can be expected that both mixing processes occur in lakes, and that the relative importance of the two is determined by lake morphology.

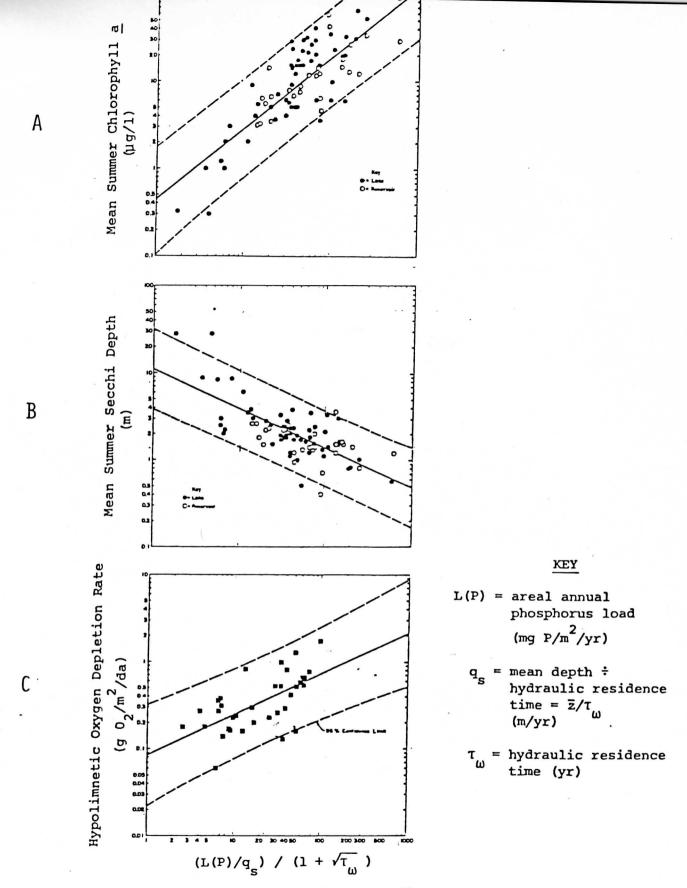
Mortimer (1942) feels that most water flow in the hypolimnion is horizontal and that the turbulence from it is the mechanism of heat and chemical exchange in large lakes. Hypolimnetic currents have been observed in Lake Mendota at a depth of 15 meters of 20 m/min. (Bryson and Suomi, 1952; Frey, 1966).

Both models (vertical and horizontal mixing) have neglected profile-bound density currents, which can be regarded as the seepage of a thin layer of water down the slope of the sediments due to increased density from either the temperature differences or solutes derived from the sediments after they become anoxic (Mortimer and Mackereth, 1958). Although these currents may be neglected in large lakes in the summer where wind generated currents are large and the slope of the basin is small, it is unlikely that these currents can be neglected on small, deep lakes,

especially with ice cover. This process is quite different from the considerations of vertical and horizontal mixing in lakes in the summer, in that it can be envisioned as "filling" the deep hole area of the lake with anaerobic water. However, as discussed by Lee (1970), the release of benthic gases from anaerobic conditions can cause mixing of this water with overlying water and also contribute to oxygen depletion through methane oxidation and contribute to oxygen depletion in lakes. For further information on the oxygen demand of aquatic sediments consult the reviews by Burdick (1976), Bowman and Delfino (1978) and Conway (1972).

US OECD Eutrophication Studies on Oxygen Depletion

Rast and Lee (1978) and Lee et al. (1978a) have found a reasonably good correlation between a normalized phosphorus load to a waterbody and the waterbody's summer mean planktonic algal chlorophyll, Secchi depth, and hypolimnetic oxygen depletion rate. The original Rast and Lee relationship is based on about 40 US waterbodies. Recently, Jones and Lee (1981) have expanded the number of waterbodies covered by these relationships to about 90 lakes and impoundments located throughout the US. The Jones and Lee relationships are shown in Figure 1. As shown in part C of this figure there is remarkably good agreement considering the multitude of factors involved



Normalized Annual Areal Phosphorus Loading $(mg P/m^3)$

Figure 1. Updated P load - eutrophication-related water quality response relationships for U.S. waterbodies. (After Jones and Lee, 1981).

between the normalized phosphorus loads and the hypolimnetic oxygen depletion rate.

Subsequently, Cornett and Rigler (1979) have developed a similar relationship to that of Rast and Lee between the phosphorus retention coefficient of lakes and their hypolimnetic oxygen depletion rates. It is clear from the US OECD eutrophication studies that the oxygen depletion of the hypolimnion of many lakes and impoundments is tied to the phosphorus load to the waterbody and the planktonic algal chlorophyll that results from this load. This would account for the so-called BOD oxygen depletion rates in lakes. The sediment oxygen demand, while originally for waterbodies, was controlled by phosphorus load through productional BOD (algae) in the surface waters, once the waterbody sediments begin to build up a significant reservoir of reduced iron and sulphur species the sediment demand becomes dominated by abiotic processes through the oxidation of these species.

Newbry et al. (1979; 1980) have applied the US OECD eutrophication modeling results to TVA Cherokee Reservoir which is part of the Tennessee River system and found that the phosphorus load derived planktonic algal chlorophyll accounted for about one-third of the total oxygen demand of the hypolimnion of this waterbody. The remainder could be accounted for by the nitrification of ammonia (bacterial

oxidation to nitrite and nitrate) that was present in the hypolimnion at the onset of thermal stratification.

MODEL FOR OXYGEN DEPLETION IN THE HYPOLIMNION Oxygen Demand of the Water

As previously discussed, the depletion of oxygen in the water, far removed from the sediments, can be modeled by the zero order expression:

$$\frac{dO_2}{dt} = -k_0.$$

This expression can be written as:

$$D_{BOD} = k_o t$$

where $k_{\rm O}$ may be expected to vary with temperature, primary production in the euphotic zone, and the relative volumes of the euphotic zone and the hypolimnion, and $D_{\rm BOD}$ is the deficit caused by BOD.

Oxygen Demand of the Sediments

The sediment system contains a variety of different possible mechanisms of oxygen depletion occurring simultaneously. It appears that mixing processes control the sediment-water interface oxygen demand. Generally, mixing processes are formulated as first order processes (Lerman, 1979). Lakes with large sediment oxygen demand have been observed to have oxygen profiles that approach

exponential character with rapid oxygen depletion at the sediment-water interface and less oxygen change with depth at depths more than a few meters above the sediment-water interface. The exponential shape of the oxygen profiles can be explained by the sediment oxygen demand being distributed into the overlying water by vertical mixing.

Hutchinson (1957) has discussed these oxygen profiles and proposes that they can be approximated by:

$$D_{\text{sed}} = D_{\text{Z}} = Z_{\text{m}} e^{-\left[\frac{Z_{\text{m}} - Z}{2\sqrt{At}}\right]}$$

where $D_{\rm sed}$ is the deficit due to the sediment demand and mixing, Z is the depth, t is the time, $Z_{\rm m}$ is the depth of the mud-water interface, and A is the turbulent mixing coefficient for the lake in cm²/sec.

The value for A in Lake Mendota has been estimated by Hutchinson (1957) to be above 2 x 10⁻²cm²/sec and therefore is a lake with about medium mixing characteristics. In Lake Mendota the sediment affects the dissolved oxygen to about ten meters above the interface. Lake Erie has a much larger A value and the hypolimnion appears to be depleted uniformly (Hutchinson, 1957; Burns and Ross, 1972).

To determine the effect of the sediment and the BOD on any point in the hypolimnion the two deficits must

be added:

The concentration of dissolved oxygen at any point in the lake can be obtained from the above. This simple model was described by Hutchinson (1957).

$$C_{Z,t}$$
 $\begin{bmatrix} z_h \\ z_m \end{bmatrix}$ = $C_o - k_o t - C_o e^{-\left[\frac{Z_m - A}{2\sqrt{At}}\right]}$

where $C_{\rm o}$ is the initial concentration of oxygen at stratification, $k_{\rm o}$ is the zero order rate constant (mg/l/day), t is the time since stratification in days, $Z_{\rm m}-Z_{\rm h}$ is the depth of the boundary of the hypolimnion and the thermocline, $Z_{\rm h}$ is the thickness of the hypolimnion and $Z_{\rm m}$ is the depth of the sediment-water interface in meters. In order to evaluate the applicability of Hutchinson's (1957) model to Lake Mendota, a study was conducted of the oxygen depletion rates at several depths in this lake. The results of this study are presented below.

MATERIALS AND METHODS

Lake Mendota is a hard water eutrophic lake located in Madison, Wisconsin. The lake has a surface area of 15.2 square miles (39.4 x 10^6 meters²), a maximum depth of about twenty-three meters, an average depth of thirteen

meters, and a total volume of 487 x 10⁶ meters³ (Delfino, 1968; Torrey, 1972). The temperature and oxygen profiles during the summer are of the clinograde type. As previously mentioned, the lake experienced large cisco dieoff in the period 1930 to the 1950's.

During this study, the dissolved oxygen and temperature data were collected by a YSI (Yellow Springs Instrument Company) oxygen membrane electrode, as were the data from Torrey (1972) and Sonzogni (1974). All other data collected by Birge and Juday (archives data), Stewart (1965), and Delfino (1968), were done by the Winkler procedure. Birge and Juday, however, used an unmodified Winkler procedure which would be subject to interferences by nitrite.

RESULTS

Oxygen Demand of the Water

To determine the zero order rate constant for oxygen depletion in a lake, it is necessary to physically separate the various sites for oxygen demand. A depth of fifteen meters (in a deep hole of twenty-three meters) should be sufficiently high in the water column when the A value is 2×10^{-2} cm²/sec as in Lake Mendota, to minimize the effect of mixing above the thermocline.

The depletion rate constants at fifteen meters for

1906, 1907 and 1909 are respectively, 0.15, 0.18 and 0.10 mg/l/day. These rate constants are obtained from the slope of a plot of dissolved oxygen concentration obtained by Birge and Juday (archives data) versus time (Figure 2). The oxygen depletion rate constants for the years 1961 to 1963 at fifteen meters can be obtained from the data of Stewart and are respectively, 0.20, 0.17 and 0.20 mg/l/day (Figure 3). In 1966 and 1967, the depletion rate constants were 0.20 and 0.23 at fifteen meters based on the data of Delfino (1968) (Figure 4). Data obtained in this study from 1970 and 1971 was measured at sixteen meters (Figure 5) where the values were 0.20 and 0.24 mg/l/day. In 1972, at fifteen meters, the rate constant was 0.15 mg/l/day (Figure 5).

Figure 6 presents the observed rate constants for oxygen depletion for Lake Mendota at a fifteen to sixteen meter depth for the period 1906-1972. It is evident upon examination of this figure that there are marked year to year differences in oxygen demand within any short time interval. The data of Sonzogni (1974) and Conway (1972) for 1972 shows that the rate of oxygen depletion that year was approximately the same as what Birge and Juday observed in 1906 and 1907. However, all of the other 1960-1970 data show an apparent increase in the rate of oxygen depletion at the fifteen to sixteen meter depth compared to 1906-1907. Examination of the data for the

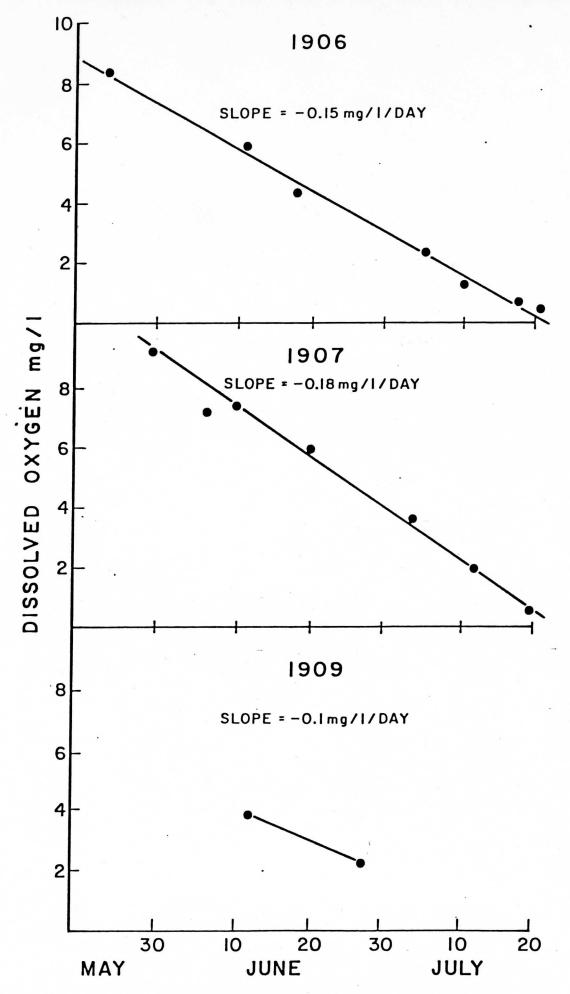


Figure 2. Oxygen depletion in Lake Mendota at 15 m depth for the period 1906-1909. Data from Birge and Juday (archives).

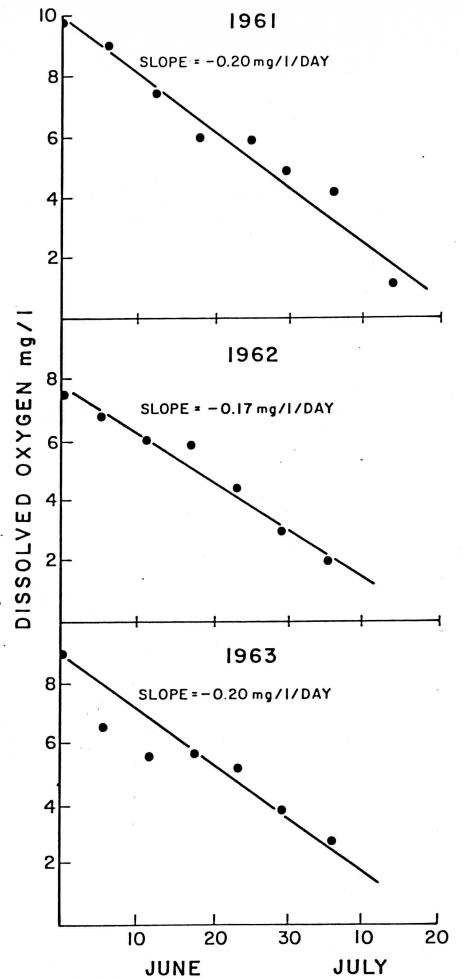


Figure 3. Oxygen depletion in Lake Mendota at 15m depth for the period 1961-1963. Data from Stewart (1965).

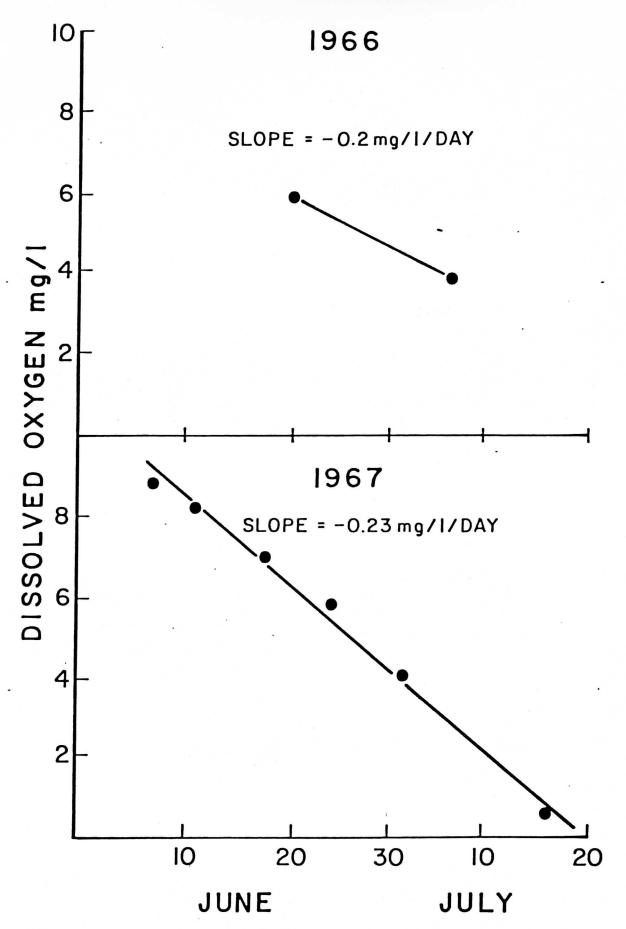


Figure 4. Oxygen depletion in Lake Mendota at 15 m depth for the period 1966-1967. Data from Delfino (1968).

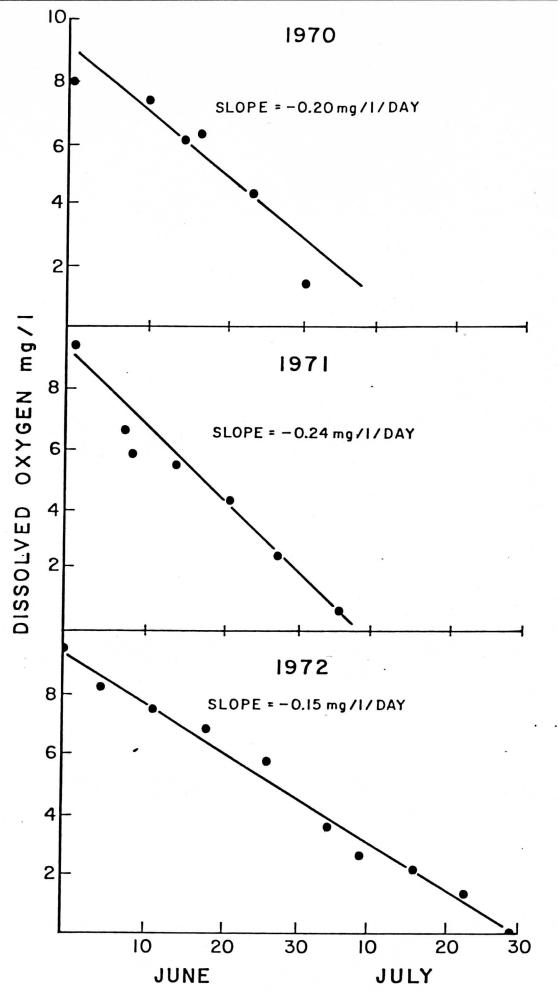
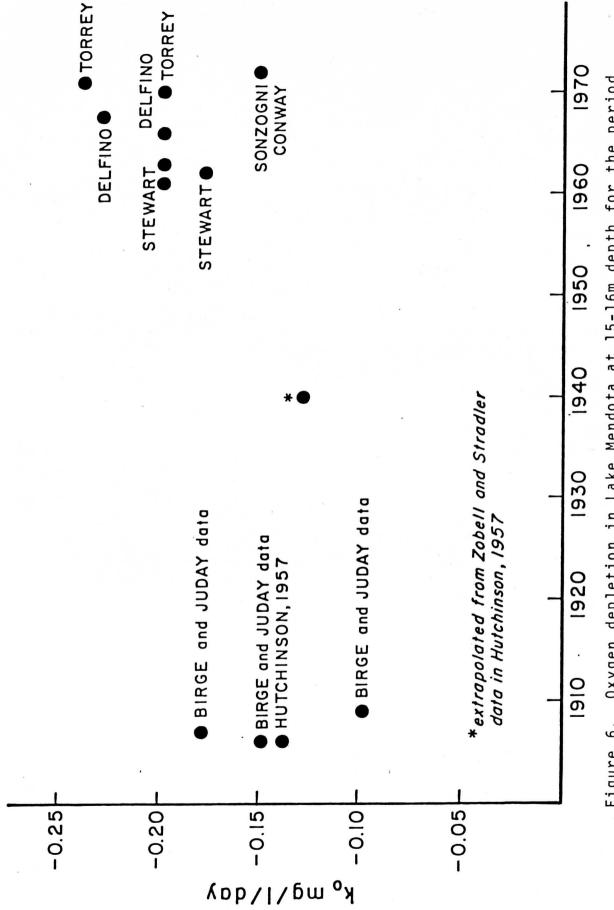


Figure 5. Oxygen depletion in Lake Mendota at 16m depth (1970-1971) and 15m depth (1972). Based on data from Torrey (1972), Sonzogni (1972) and Conway (1972).



Oxygen depletion in Lake Mendota at 15-16m depth for the period 1906-1972. Figure 6.

various periods shows that 1972 was an atypical year for Lake Mendota both in terms of hypolimnetic temperatures and algal productivity. The hypolimnion of Lake Mendota in 1972 was four to five degrees colder than normal due to early onset of thermal stratification in the spring. Also, the frequency and severity of algal blooms during late spring and early summer was less than normally experienced during the past ten years on this lake. Both of these factors would tend to reduce the rate of dissolved oxygen depletion just below the thermocline and thereby contribute to the low rate constants observed in this year. If the 1972 data is judged to be atypical it is apparent that the rate of oxygen depletion just below the thermocline has increased from 0.15 to 0.2 mg/l/day in the period 1906-1910 to 1960-1970. This rate of increase can be attributed to increased influx of algae available phosphorus since phosphorus has been found to be limiting algal growth in this lake. This point is discussed further below.

In order to determine the sensitivity of the estimate of oxygen depletion rate constants on depths, the rates were evaluated for depths of ten, eleven and twelve meters. This data is presented in Figure 7. The oxygen depletion rate constants for ten and twelve meters in 1906 are respectively 0.11 and 0.13 mg/l/day; for 1971, they are 0.17, 0.17 and 0.18 (10, 11 and 12 meters); and

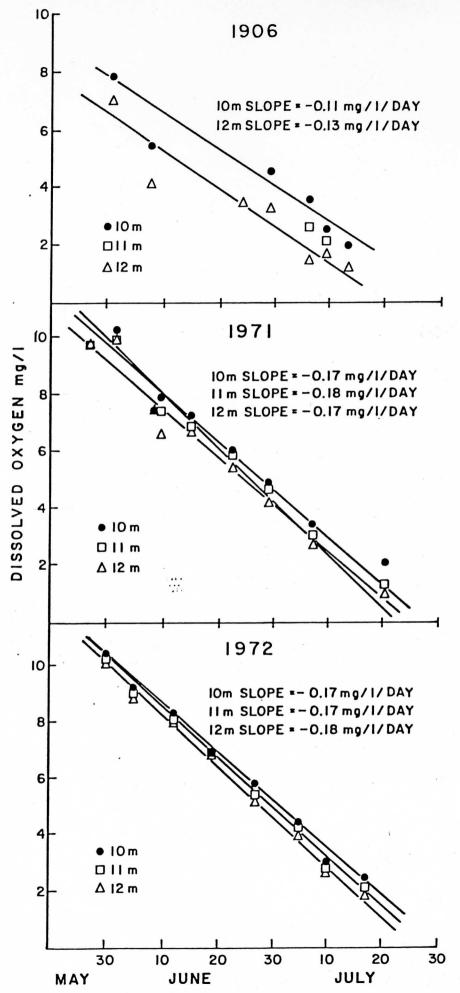


Figure 7. Oxygen depletion in Lake Mendota at 10, 11 and 12m depth, for the period 1906-1972. Based on data from Birge and Juday (archives) for 1906, Torrey (1972) for 1971, Sonzogni (1974) and Conway (1972) for 1972.

for 1972, the rate constants are 0.17, 0.18 and 0.17 mg/l/day. The rate constants at fifteen meters are slightly greater than at ten, eleven and twelve meters, though the difference is small.

Oxygen Demand of the Sediments

To evaluate the sediment impact on oxygen demand, a depth of twenty-one meters (in the deep hole of twentythree meters) was chosen. This depth should reflect mostly the sediment oxygen demand. The oxygen depletion at the sediment has been observed to be exponential with time (Figures 8, 9 and 10) (See Conway (1972) for complete data). A first order plot can be obtained from a log of oxygen concentration versus time. The slope of this plot is the apparent first order rate constant. This rate constant should include the diffusion of dissolved substances, oxygen diffusion into the sediment, and the controlling factor of mixing. The rate constants for oxygen depletion from 1906 to 1972 are in Figure 11 and no apparent increase in the rate constants is observed. diagram appears to be scattered, with no definite increase in rate with time. The scatter could be partially due to different depths being sampled, but as can be seen in Figure 10, there is not much difference in rates between twenty and twenty-one meters of 0.041 and 0.044 day-1.

An increase in rate constants would not be expected

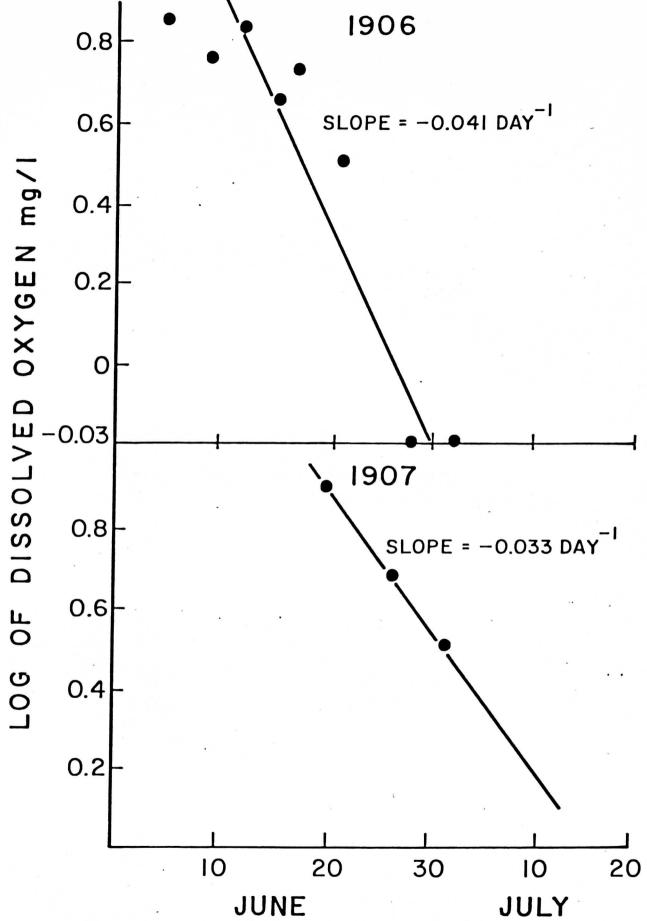


Figure 8. Oxygen depletion in Lake Mendota at 22m depth for 1906 and 1907. Data from Birge and Juday (archives).

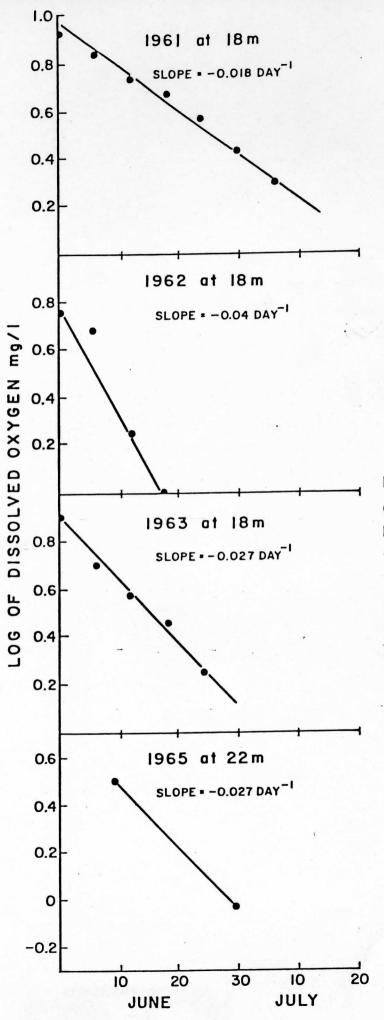


Figure 9. Oxygen depletion in Lake Mendota at 18m dept for 1961, 1962 and 1963 after Stewart (1965). Data for 1965 is for 22m depth after Delfino (1968).

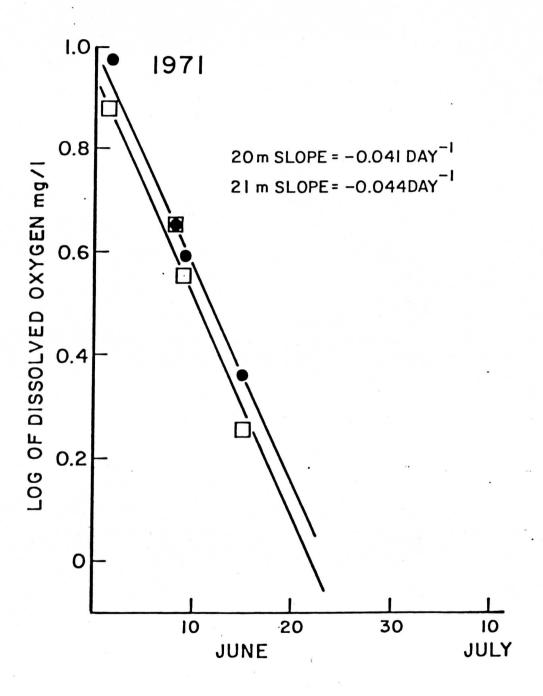
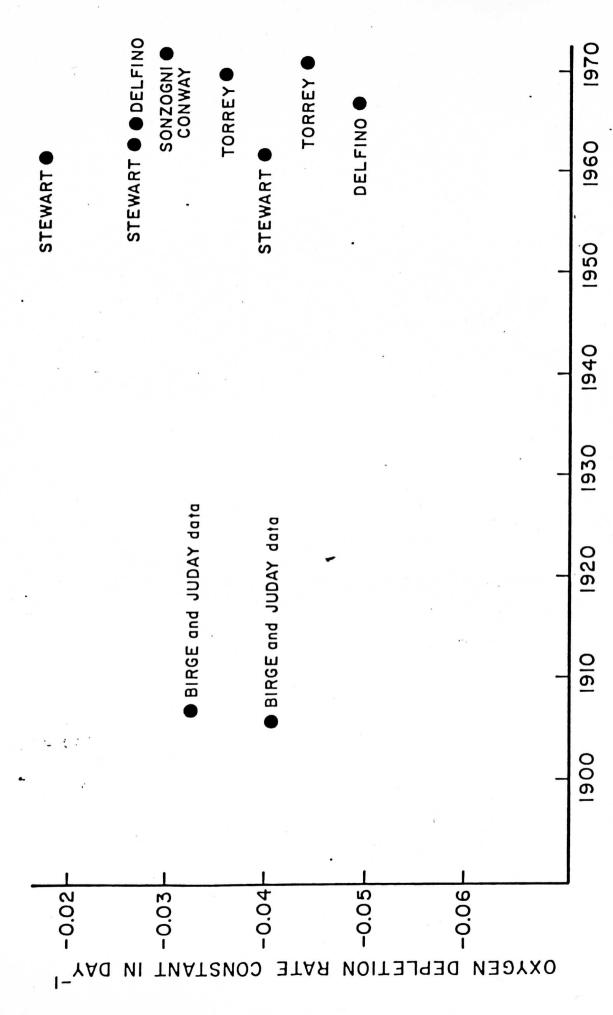


Figure 10. Oxygen depletion in Lake Mendota at 20 and 21m in 1971 after Torrey (1972).



Oxygen depletion rate constants at 21m in Lake Mendota for the period 1906-1972. Figure 11.

above the sediment, if the rate is dependent upon mixing and release of inorganic substances. If the anoxic microzone, as described by Hutchinson (1957), is assumed to form, mixing is the most important factor in the dispersal of reduced substances, and the rate would not be expected to change with time. The anoxic microzone develops as a result of chemical oxidation and bacterial respiration at the mud-water interface in relatively stagnant (quiescent) water (Hutchinson, 1957). The effect of this microzone on the rest of the hypolimnion is a result of turbulent diffusion, not molecular diffusion. The molecular diffusion is too slow to explain macrostratification in the hypolimnion when compared to the turbulent diffusion. Gorham (1958), on the other hand, suggested that when an oxidized microzone develops during reaeration of the bottom waters, that it is due to the mixing of the sediments into the overlying water. Gorham feels that this zone is not a barrier to diffusion as Mortimer (1941) and Hutchinson (1957) describe it. authors are in agreement with Gorham on this point.

The reduced substances in the sediment that become oxidized and cause oxygen depletion are mostly sulfur, iron and possibly manganese. Lee (1962), Bortleson (1970), and Bortleson and Lee (1972; 1974) found that Lake Mendota sediments contain large amounts of these chemicals.

Gardner and Lee (1965) have shown that Lake Mendota

sediments have a high oxygen demand that is exerted almost instantaneously, i.e. within a couple of minutes, followed by a much slower demand of at least equal or possibly greater magnitude which is exerted at a steady rate over a period of months or more.

DISCUSSION

From the data obtained in this study it is evident that a combined zero order first order model discussed above adequately describes the oxygen demand of the Lake Mendota hypolimnion. This model, when coupled with Hutchinson's (1957) mixing coefficient expression described above, can be used to formulate oxygen concentration depth profiles in the hypolimnion. The rate constant for any particular waterbody for the water column depletion rate (zero order k_o) can be estimated from the relationships developed by Rast and Lee (1978) and Lee et al. (1978a) based on either the planktonic algal chlorophyll in the waterbody or for phosphorus limited phytoplankton biomass, the phosphorus load to the waterbody normalized by the waterbody's mean depth and hydraulic residence time as shown in Figure 1. Further k may be estimated from the Secchi depth (see Figure 1) for those waterbodies in which the water clarity is primarily determined by phytoplankton. Rast and Lee (1978) and Jones and Lee (1981) have discussed the appropriate application of the US OECD

eutrophication modeling results which relates phosphorus loads to various eutrophication related response parameters. As they discuss, these relationships cannot be used blindly. Much of the criticism about the so-called lack of applicability to a particular waterbody relates to the fact that the individual suggesting the lack of applicability has not taken the time to follow the directions provided by Rast and Lee (1978), Lee et al. (1978a) and Jones and Lee (1981). If used properly these relationships provide water quality managers with extremely powerful tools by which they can judge the impact of altering phosphorus loads to waterbodies on the waterbody's eutrophication related water quality.

ment oxygen demand cannot be estimated based on the results of the US OECD eutrophication study since this rate is <u>not</u> determined by the current trophic status of the waterbody but as described above is determined primarily by the abiotic processes involving the oxidation of iron and sulfur compounds present in the sediments by dissolved oxygen. These rates are primarily controlled by mixing processes rather than chemical kinetics. Lee (1970) has presented an extensive discussion of the factors influencing the transfer of materials between sediments and overlying water. He reports that transfer is primarily controlled by abiotic and biotic mixing processes. While

it is relatively easy to measure the kinetics of oxygen demand of sediments under completely mixed conditions using procedures similar to those used by Gardner and Lee (1965) and Lee et al. (1978b), it appears that the greatest problem in modeling oxygen depletion in the hypolimnion is the appropriate characterization of the mixing processes associated with the sediments and the overlying waters. Until a much better understanding in this area is achieved, it is going to be difficult to predict the oxygen profiles in the hypolimnion of the lake based on the characteristics of the sediments and the normalized phosphorus load to the waterbody. It is important to emphasize however that while the shape of the oxygen concentration depth curve in the hypolimnion cannot be reliably predicted at this time, the extent of deoxygenation of the hypolimnion can be predicted through the use of the results of the US OECD eutrophication study program as described by Rast and Lee (1978) and Lee et al. (1978 a).

Stewart (1976) attempted to utilize oxygen depletion and Secchi depth data collected on Lake Mendota over a 70-year period to examine the eutrophication of this lake. He indicated that he could see little if any trend in the data. With respect to hypolimnetic oxygen depletion Stewart attempted to examine trends based on a weighted mean oxygen concentration in the hypolimnion of the lake.

However, Conway (1972) pointed out that the oxygen demand of the lower waters of Lake Mendota has not changed in the 70-year period of record and therefore Stewart's weighted mean oxygen concentration is influenced by the oxygen demand of the sediments which is independent within the time period examined of the eutrophication of this lake.

With respect to Secchi depth, the data Stewart presented show that between 1916 and the mid 1960's there was an apparent change in average summer Secchi depth from about 3 m in 1916 to slightly less than 2 m in the 1960's, i.e. a little over a 1 meter change in 50 years. Rast and Lee (1978) pointed out that significant changes in chlorophyll could take place in a eutrophic waterbody and have little impact on the water clarity of the waterbody as measured by Secchi depth. Secchi depth is only sensitive to chlorophyll changes at chlorophyll levels of a few µg/l. At chlorophylls of above 10 µg/l which are typical for Lake Mendota during the summer, large changes in the planktonic algal chlorophyll can occur . and have little or no impact on the waterbody's Secchi depth. As discussed below, the changes in Secchi depth as reported by Stewart for Lake Mendota for the period from 1916 to the 1960's are the two changes that would be predicted based on the US OECD eutrophication study results as reported by Rast and Lee (1978). For some

unexplained reason the Rast and Lee (1978) phosphorus load hypolimnetic oxygen depletion rate relationship shown in Figure 1 part C did not include Lake Mendota data. It is of interest therefore to see how well this lake fits the line of best fit for this relationship. The 1971 and 1972 points for Lake Mendota are shown as LM 1 and 2, respectively, on Figure 1. It is evident that Lake Mendota also fits the same relationship in which its normalized phosphorus load can be used to predict its hypolimnetic oxygen depletion rate. Further and most importantly, it is apparent that the year to year variations that occur in a lake's phosphorus load in hypolimnetic oxygen depletion rates can readily account for an appreciable part of the scatter of the data about the line of best fit for the relationship shown in part C.of Figure 1.

From the Birge and Juday (archives data) oxygen depletion rates, and the US OECD phosphorus load eutrophication response relationships shown in Figure 1, it is concluded that about a 0.75 meter change in Secchi depth should have occurred between 1910 and 1970. This is very close to that estimated by Stewart to have occurred during this period.

Using the phosphorus load oxygen depletion rate relationship shown in Figure 1, it is estimated that the 1910 phosphorus load to Lake Mendota was in the order of

23 x 10⁶ kg/year. This computes to over a 200 percent increase in phosphorus load occurring to this lake in the 60-year period of record. This estimate is based on an average of the three rates found by Birge and Juday (archives data). Examination of the phosphorus loads to Lake Mendota as reported by Sonzogni (1974) in which he estimated that the early 1970 loads to this lake were a little less than 50×10^6 kgP/year, that the urbanization of the Lake Mendota watershed in the 60-year period could readily account for the increased fertility of Lake Mendota that has occurred. No single factor seems to stand out as the primary cause of the increased phosphorus loads. It appears to be due to a combination of domestic wastewater input from several small communities located within the watershed, increased urban area within the watershed and increased or at least more intensive . agricultural practices with the latter probably the most important of the three. It is also of interest to estimate the change in planktonic algal chlorophyll in Lake Mendota during this 60-year period. The 1972 summer average planktonic algal chlorophyll was 20 µg/l which fits well the normalized phosphorus load chlorophyll relationships shown in Figure 1A. Using this relationship, based on the changes in hypolimnetic oxygen depletion rates and Secchi depth, it is estimated that the average planktonic algal chlorophyll in 1910 would

be on the order of 10 μ g/l. Using the relationships developed by Jones <u>et al</u>. (1979) to relate mean summer to maximum summer chlorophyll where the maximum is estimated at being 1.7 times the mean, in 1910 the maximum algal bloom should have produced a concentration of about 17 μ g/l while in the early 1970's a concentration of 34 μ g/l of peak chlorophyll would have been expected.

While the data upon which these estimates are made are quite limited, they are felt to have considerable reliability based on the fact that Lake Mendota's normalized phosphorus load fits well the US OECD eutrophication study program results for planktonic algal chlorophyll, Secchi depth, and hypolimnetic oxygen depletion rate.

Rast et al. (1981) have shown that the relationships shown in Figure 1 have considerable reliability in being able to predict new water quality response terms based on altered phosphorus loads to the waterbody.

It is evident from this review that there has in general been appreciable eutrophication of Lake Mendota in the 60-year period from 1910 to 1970. This eutrophication could have readily resulted in the BOD type oxygen demand arising from increased algal production in the surface waters to cause the limited ecological niche, that the cisco were inhabiting in the colder water just below the thermocline, to disappear. While it is impossible at this time to reconstruct the conditions that surrounded the

massive die-offs that occurred in 1932, 1940, 1941, 1953, and 1955 it is highly likely that these were years with a warmer than normal hypolimnion and/or greater than normal phosphorus loads and the associated planktonic algal chlorophyll.

It is interesting to note that the year to year variations in hypolimnetic oxygen depletion rates, measured by Birge and Juday (archives data) as well as those found in this study, are such that even though there has been an estimated 24 x 10⁶ kg/year increase in phosphorus load to the waterbody, some of the depletion rates prior to 1910 are greater than some of those found in the 1970's. This strongly supports the large scale cisco die-off occurring within a particular year, which would be coincident with the factors that control hypolimnetic oxygen depletion rate, combined in such a way as to create worst case conditions for a particular phosphorus load.

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REFERENCES

Amberson, W. R. 1928. The influence of oxygen tension upon the respiration of unicellular organisms. Biol. Bull. 55:79-91.

Birge, E. A. and Juday, C. 1914. Wisconsin Geological Survey, bull. no. 27.

Birge, E. A. and Juday, C. Archives data, University of Wisconsin-Madison, WI.

Bortleson, G. C. and Lee, G. F. 1972. Recent sedimentary history of Lake Mendota, Wisconsin. Environ. Sci. & Technol. 6:799-808.

Bortleson, G. C. and Lee, G. F. 1974. Phosphorus, iron and manganese distribution in sediment cores of six Wisconsin lakes. Limno & Oceano. 19:794-801.

Bouldin, D. R. 1969. Models for describing the diffusion of oxygen and other mobile constituents across the mud-water interface. J Ecol. <u>56</u>:77-88.

Bowman, G. and Delfino, J. J. 1978. Sediment oxygen demand techniques: a review. Technical Report ES78-1 Environmental Sciences Division, State of Wisconsin, Laboratory of Hygiene.

Bryson, R. A. and Suomi, V. E. 1952. The circulation of Lake Mendota. Trans Amer. Goephy Union 33:707-712.

Burdick III, J. C. 1976. Analysis of oxygen demand of sediments. Proceedings of the Specialty Conference on Dredging and its Environmental Effects, American Soc. of Civil Engineers, pp. 319-352.

Burns, N. M. and Ross, C. 1972. Project hypo - an intensive study of the Lake Erie central basin hypolimnion and related surface water phenomena, US Environmental Protection Agency report TS-05-71-208-24.

Cahn, A. R. 1927. An ecological study of southern Wisconsin fishes, Ill. Biol. Monogr. 11:94-115.

Chen, K. Y. and Morris, J. C. 1972. Kinetics of oxidation of aqueous sulfide by oxygen. Environ. Sci. Technol. 6:529-537.

Colby, P. J. and Brooke, L. T. 1969. Cisco (coregonus artedii) mortalities in a southern Michigan lake, July 1969. Limnol. Oceanogr. 14:958-960.

Conway, C. J. 1972. Oxygen depletion in the hypolimnion. University of Wisconsin-Madison, Water Chemistry.

Cooper, E. L. 1956. What's happened to the cisco?, Wis. Cons. Bull. 21:1-4.

Cornett, R. J. and Rigler, F. H. 1979. Hypolimnetic oxygen deficits: their prediction and interpretation. Sci. 205:580-581.

Delfino, J. J. 1968. Aqueous environmental chemistry of manganese, Ph.D. thesis (Water Chemistry), University of Wisconsin.

Delfino, J. J. and Lee, G. F. 1968. Chemistry of manganese in Lake Mendota, Wisconsin. Environ. Sci. & Technol. 2:1094-1100.

Delfino, J. J. and Lee, G. F. 1971. Variation of manganese, dissolved oxygen and related chemical parameters in the bottom waters of Lake Mendota, Wisconsin. Water Research 5:1207-1217.

Edsall, T. A. and Colby, P. J. 1970. Temperature tolerance of young-of-the-year cisco, coregonus artedi. Trans. Amer. Fish Soc. 99:526-531.

Fitzgerald, G. P. 1961. The effect of algae in BOD measurements. Nat. Inst. Health Project, K-17, University of Wisconsin.

Frey, D. G. 1955. Distributional ecology of the cisco in Indiana. Invest. Ind. Lakes Streams 4:177-228.

Frey, D. G. 1966. Limnology in North America, University of Wisconsin Press, Madison.

Fruh, E. G. and Davis, E. M. 1972. Limnological investigations of Texas impoundments for water quality management purposes. OWRR, EHE 72-6, CRWR 87.

Fry, F. E. J. 1937. The summer migration of the cisco 'leucichthys artedi'(le sueur) in Lake Nipissing, Ontario. Pub Ont. Fish Res. Lab. no. 55, Biol. Ser. no. 44:9-91.

Gardner, W. S. and Lee, G. F. 1965. Oxygenation of lake sediments. Air & Water Poll. 9:553-564.

Gorham, E. 1958. Observations and breakdown of the oxidized microzone at the mud surface in lakes. Limnol. Oceanogr. 3:291-298.

Gorham, E. and Swaine, D. J. 1965. Influence of oxidizing and reducing conditions upon the distribution of some elements in lake sediments. Limnol. Oceanogr. 10:269-279.

Howeler, R. H. and Bouldin, D. R. 1971. The diffusion and consumption of oxygen in submerged soils. Soil Sci. Soc. Amer. Proc. 35:202-208.

Hutchinson, G. E. 1957. A treatise on limnology.

Volume I, John Wiley and Sons, New York.

John, K. R. 1954. Ecological study of cisco in Lake Mendota. Ph.D. thesis (Zoology), University of Wisconsin.

Jones, R. A., Rast, W., and Lee, G. F. 1979. Relationship between mean and maximum chlorophyll <u>a</u> concentrations in lakes. Environ. Sci. & Technol. <u>13</u>:869-870.

Jones, R. A. and Lee, G. F. 1982. Recent advances in assessing the impact of phosphorus loads on eutrophication-related water quality. Water Res. 16:503-515. http://www.gfredlee.com/Nutrients/RecentAdvWaterRes.pdf

Lee, G. F. 1962. Studies on the iron, manganese, sulfate, and silica balances and distributions for Lake Mendota, Madison, Wisconsin. Trans. Wisc. Academy Sci., Arts and Letters LI:141-155.

Lee, G. F. 1970. Factors affecting the transfer of materials between water and sediments. Lit. Review no. 1, Eutrophication Information Program, Water Resources Center, University of Wisconsin, Madison.

Lee, G. F., Rast, W., and Jones, R. A. 1978a. Eutrophication of waterbodies: insights for an age-old problem. Environ. Sci. & Technol. 12:900-908.

Lee, G. F., Jones, R. A., Saleh, F. Y., Mariani, G. M., Homer, D. H., Butler, J. S. and Bandyopadhyay, P. 1978b.

Evaluation of the elutriate test as a method of predicting contaminant release during open water disposal of dredged sediment and environmental impact of open water dredged materials disposal, Vol. II: data report. Technical Report D78-45, U.S. Army Corps of Engineers, WES, Vicksburg, MS, 1186 pp.

Lee, G. F. and Jones, R. A. 1991. Effects of eutrophication on fisheries.

Reviews in Aquatic Sciences, 5:287-305, CRC Press, Boca Raton, FL. Also published in condensed form in "Lake Line" 12(4):13-20 (1992).

Lerman, A. 1979. Geochemical processes water and sediment environments. Wiley, New York.

Martin, D. C. and Bella, D. A. 1971. Effect of mixing on oxygen uptake rate of estuarine bottom deposits.

J. Water Pollut. Contr. Fed. 43:1865-1876.

McCormick, J. H., Jones, B. R. and Syrett, R. F. 1971. Temperature requirements for growth and survival of larval cisco (coregonus artedi). J. Fish Res. Bd. Can. 28:924-927.

McDonnell, A. J. and Hall, S. D. 1967. Effect of environmental factors on benthal oxygen uptake. Proc. 22nd Ind. Waste Conf. Purdue U, Ind. 414-427.

McMahon, J. W. 1969. The annual and dirunal variation in the vertical distribution of acid-soluble ferrous and total iron in a small dimictic lake. Limnol. Oceanogr. 14:357-367.

Mortimer, C. H. 1941. 1942. Exchange of dissolved substances between mud and water in lakes. J. Ecol. 29: 280-329 (1941), 30:147 (1942).

Mortimer, C. H. 1971. Chemical exchange between sediment and water in the great lakes - speculations on probable regulatory mechanisms. Limnol. Oceanogr. <u>16</u>: 387-404.

Mortimer, C. H. and Mackereth, F. J. H. 1958. Convection and its consequences in ice-covered lakes. Verh. Internat. Ver. Limnol. <u>13</u>:923-932.

Newbry, B. W., Jones, R. A. and Lee, G. F. 1981. Assessment and analysis of eutrophication of Tennessee River system impoundments. Proc. ISCHIA Symposium on Surface Water Impoundments ISCHIA, NY, pp 413-424.

Newbry, B. W., Jones, R. A. and Lee, G. F. 1980.

Assessment and analysis of eutrophication of Tennessee river system impoundments. To be published in ASCE et al. Proc. Symposium on Impoundments.

Pearse, A. S. 1934. Ecology of lake fishes. Ecol. Monogr. 4:475-480.

Pritchard, A. L. 1930. Spawning habits and fry of the cisco (leucichthys artedi) in Lake Ontario. Can. Biol. Fish Contrib. 6:225-240.

Pyre, R. 1932. Wisconsin State Journal, 140:118.

Rast, W. and Lee, G. F. 1978. Summary analysis of the North American (US portion) OECD eutrophication project: nutrient loading-lake response relationships and trophic state indices. Report EPA-Corvallis. EPA 600/3-78-008.

Rast, W., Jones, R. A. and Lee, G. F. 1983. Predictive capability of US OECD phosphorus loading-eutrophication response models. Journ. Water Pollut. Control Fed. 55:990-1003.

http://www.gfredlee.com/Nutrients/PredictiveCapabilityOECD.pdf

Rolley, H. L. J. and Owens, M. 1967. Oxygen consumption rates and some chemical properties of river muds. Water Res. 1:11-12,759-766.

Smith, T. L. 1969. Effect of eutrophication on fish and related organisms. WRRC University of Minnesota Bull no. 13.

Sonzogni, W. C. 1974. Effect of nutrient input reduction on the eutrophication of the Madison lakes. University of Wisconsin-Madison, Water Chemistry.

Stewart, K. M. 1965. Physical limnology of some Madison lakes. Ph.D. thesis (Zoology), University of Wisconsin.

Stewart, K. M. 1976. Oxygen deficits, clarity, and eutrophication in some Madison lakes. Int. Review Ged. Hydrobiol. Bd. 61, Heft 5 pp 563-579.

Stumm, W. and Lee, G. F. 1961. Oxygenation of ferrous iron. Ind. Eng. Chem. <u>53</u>:143-146.

Stumm, W. and Morgan, J. J. 1970. Aquatic chemistry, John Wiley and Sons, New York.

Sullivan, W. T. 1967. Chemical composition of the mud-water interface zone, with the description of an interface sampling device. 10th Conf. Great Lakes Res. 390-403.

Symons, J. M. 1969. Water quality behavior in reservoirs. US Dept. HEW, Pub no. 1930, Cincinnati, Ohio.

Telford, J. 1954. The life history of the cisco, leucichthys artedi (le sueur) with special reference to the Lake Mendota population. Zoology 125.

Torrey, M. S. 1972. Biological nitrogen fixation, Ph.D. thesis, (Water Chemistry) University of Wisconsin.

Varma, M. M. and DiGrano, F. 1968. Kinetics of oxygen uptake by dead algae. J. Water Pollut. Contr. Fed. 40:613-620.

Waksman, S. H. and Renn, C. E. 1936. Decomposition of organic matter in sea water by bacteria, III, factors influencing the rate of decomposition. Biol. Bull. 70: 472-483.

ZoBell, C. E. 1940a. Some factors which influence oxygen consumption by bacteria in lake water. Biol. Bull. 78:388-402.

ZoBell, C. E. 1940b. The effect of oxygen tension on the rate of oxidation of organic matter in sea water by bacteria. J. Mar. Res. 3:211-223.

ZoBell, C. E. and Stradler, J. 1940. The effect of oxygen tension on the oxygen uptake of lake bacteria. J. Bact. 39:308-322.