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VARIATION OF MANGANESE, DISSOLVED OXYGEN AND RELATED CHEMICAL PARAMETERS IN THE BOTTOM WATERS OF LAKE MENDOTA, WISCONSIN

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Abstract—The increase of Mn concentration and the simultaneous depletion of dissolved oxygen in the bottom waters (hypolimnion) of Lake Mendota, Wisconsin were studied *in situ.* Considerably higher Mn concentrations were found in the hypolimnion compared to Fe, despite a sedimentary Fe/Mn weight ratio of 19:1. Laboratory equilibration studies under anoxic conditions indicated that pH was an important parameter involved in the release of Mn from the sediments. This was also implied by the Mn and pH data measured *in situ.* Possible mechanisms involved in the release of Mn from the sediments including desorption of Mn from oxide substrates, reduction of Mn oxides and dissolution of carbonates and sulfides are discussed.

INTRODUCTION

THE SEASONAL behavior of Mn in dimictic lakes (two annual circulation periods) follows certain reasonably known patterns (HUTCHINSON, 1957). During thermal stratification, Mn concentrations exhibit marked hypolimnetic increases. Otherwise, low concentrations exist throughout lake water columns during times of free circulation, except for short periods immediately following the spring and fall turnovers. At those times, Mn from the bottom water is mixed and transported throughout the water column, creating temporary, relatively high Mn levels in the upper waters. The seasonal pattern of Mn in Lake Mendota has been discussed in detail by DELFINO and LEE (1968).

Manganese enters a lake water system through surface and ground water transport and from biological systems (e.g. through release of Mn from decaying algae and vegetable debris). Also, Mn is released from the bottom sediments during thermal stratification. Mn is originally incorporated into lake sediments through precipitation and deposition from upper waters (via oxidation, sorption and/or solubility reactions) and also from particulate terrestrial material carried by runoff waters from the surrounding drainage basin. Once in lake water, Mn can undergo numerous physical and chemical transformations which are discussed elsewhere (MORGAN and STUMM, 1965; DELFINO and LEE, 1968).

The surface sediments of Lake Mendota consist mainly of a calcareous black ooze or sludge composed of about 32 per cent calcium carbonate (WENTZ and LEE, 1969) as well as 2.5 per cent Fe and 0.13 per cent Mn on an oven dry weight basis (DELFINO *et al.,* 1969). The oxygen demand of the sediments results in the water of the hypolimnion becoming devoid of oxygen in the summer (GARDNER and LEE, 1965). Winter anoxia in the bottom waters can occur when the ice cover duration is relatively long (usually in excess of 4 months). A large bacterial population, generally in excess of 10^6 organisms cm^{-3} of wet sediment, exists in the upper layers of the bottom sediments (HENRICI and McCOY, 1938).

At the onset of thermal stratification, the chemical environment of the bottom waters changes. As the hypolimnion gradually becomes distinct, its waters are removed from contact with the upper waters (epilimnion) and the atmosphere. Generally, there is no oxygen source below the thermocline since solar radiation does not penetrate below about 12 m to support photosynthesis. Bacterial respiration depletes the available hypolimnetic dissolved oxygen (DO) and releases CO_2, decreasing the pH. The hypolimnion is thus transformed from an oxidizing to a reducing environment. Chemical ions migrate from the sediments to the overlying bottom water as seen by increased concentrations of various elements, including dissolved Mn, Fe and titratable carbonate alkalinity. A gradual appearance of hydrogen sulfide is noted, due to the reduction or dissolution of sulfur compounds.

Sediment-water interface reactions have often been discussed in the literature in terms of changes in redox potential, utilizing data from electrode potential measurements (MORTIMER, 1941, 1942). The redox potential, which is useful in a general sense, does not relate to specific half cell reactions, e.g. the reduction of Mn(IV) to Mn(II). STUMM (1963) presented a lucid argument against indiscriminate use of the redox potential concept while HAYES *et al.* (1958) discussed experimental difficulties encountered during redox potential measurements. Thus, it is more realistic to discuss reactions at the sediment-water interface in terms of oxidizing (high DO and pH) or reducing conditions (little or no DO, low pH and H_2S) present. This is especially meaningful since accurate DO, pH and chemical analyses can be related to specific chemical forms whereas environmental electrode potential data cannot be correlated directly with any ion, compound or reaction.

The gradual increase of Mn at the sediment-water interface was studied closely during the development of thermal stratification in Lake Mendota in 1967. Estimates of the rate of appearance of Mn and the simultaneous disappearance of DO were made. The results of this *in situ* study are presented here. Data from laboratory equilibration experiments involving aqueous suspensions of Lake Mendota sediments are also given since they complement the results of the *in situ* study.

METHODS

A Van Dorn lucite sampler was used to collect water samples. Chemical analyses were completed within 24 h after collection. Analyses for Mn, Fe, sulfide, alkalinity and dissolved oxygen were made according to *Standard Methods* (1965) and DELFINO and LEE (1969). Temperature was recorded in *situ* with a Whitney thermometer. All other analyses were conducted after the samples were returned to the laboratory. The pH readings were taken with a Beckman Model GS pH meter using a combination electrode probe. Standard deviations for the analytical procedures listed above, based on at least five replicate analyses of natural water and dosed samples were: Mn, 0.01 mg l^{-1}; Fe, 0.02 mg l^{-1}; sulfide, 0.19 mg l^{-1} ; alkalinity, 0.03 m-equiv. l^{-1}; dissolved oxygen, 0.08 mg l^{-1} .

In situ water samples were collected from 21 to 23 m depths, 1 m above the sediment-water interface, in the deepest area of Lake Mendota at stations marked by anchored buoys. These samples were collected from three to four times weekly during the period of June 20–July 30, 1967. Complete vertical profile samples were taken on selected dates to demonstrate chemical variations with depths. Some characteristics of Lake Mendota and its water column, not included here, have been reported previously (LEE and HARLIN, 1965; BREZONIK and LEE, 1968; DELFINO and LEE, 1968; NRIAGU and BOWSER, 1969).

RESULTS

Typical depths vs. concentration profiles for Mn, DO, temperature and pH in the deep area of Lake Mendota are shown in FIGS. 1 and 2. FIGURES 3-6 give depth vs.

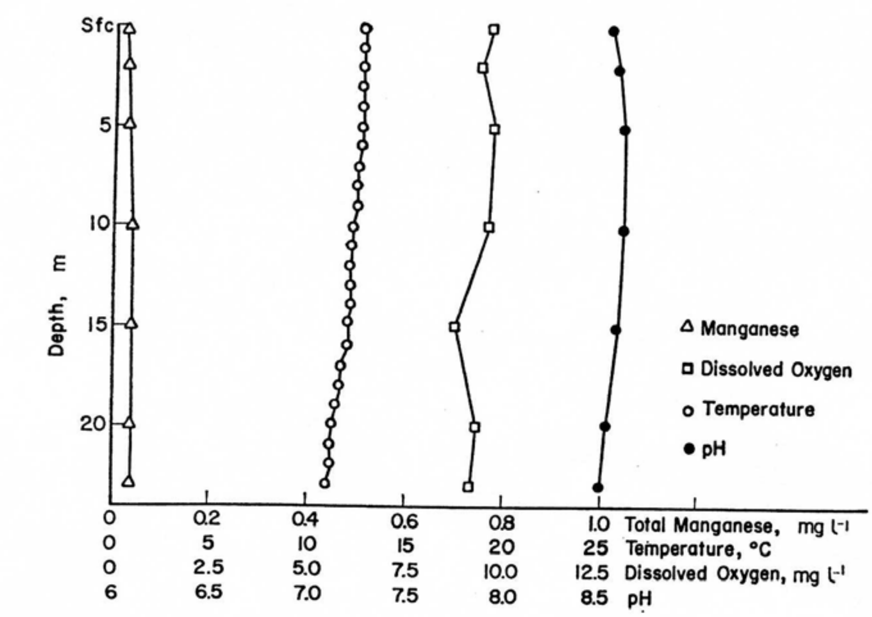

FIG. 1. Sampling profile in Lake Mendota on May 30, 1967.

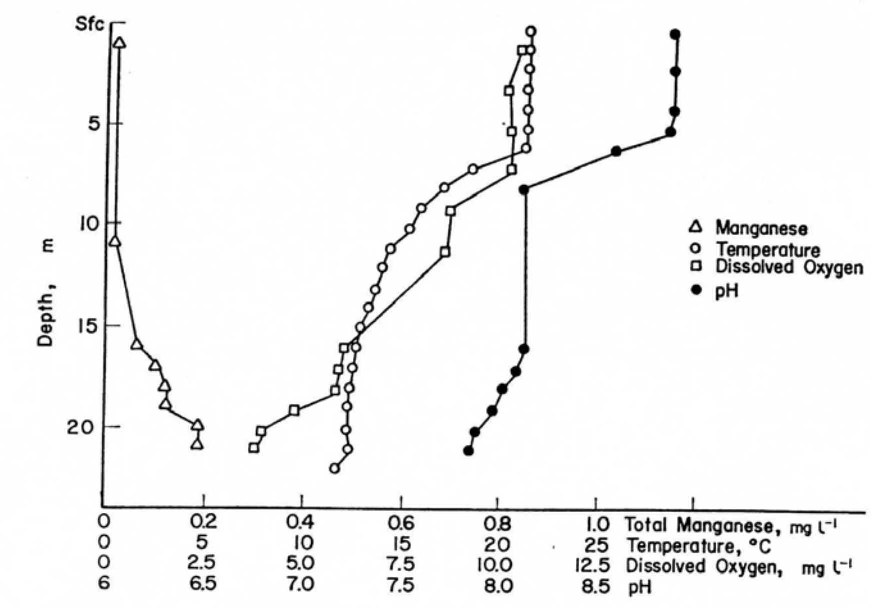

FIG. 2. Sampling profile in Lake Mendota on June 19, 1967.

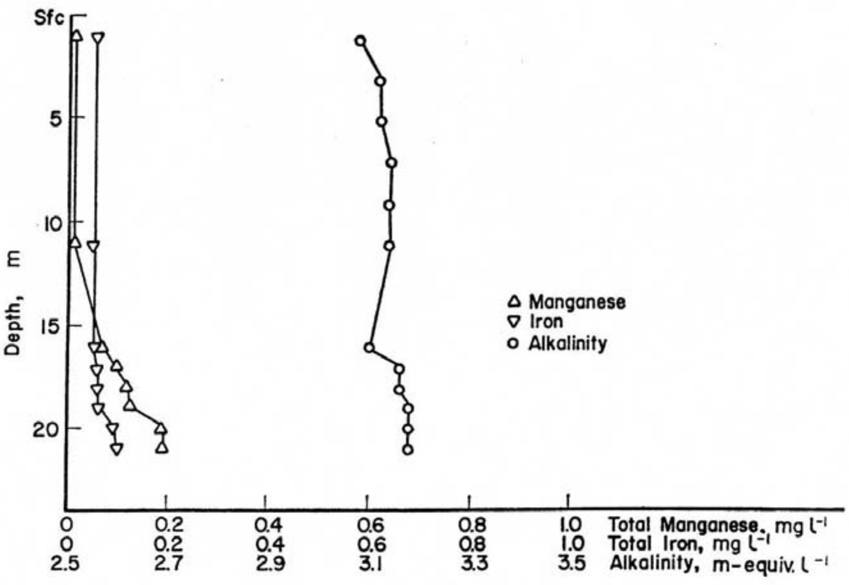

FIG. 3. Sampling profile in Lake Mendota on June 19, 1967.

concentration profiles for Mn, Fe, alkalinity and sulfide. The vertical distribution of Mn was generally related to the thermal structure and redox environment of the lake. Iso-chemical and iso-thermal conditions prevailed on May 30 (FIG. 1) as the lake was in the spring circulation period and essentially equilibriated with the atmosphere. Three weeks later on June 19, distinct physical and chemical changes were observed. FIGURE 2 depicts a well developed thermal stratification with initial evidence of chemical stratification. Mn concentration had increased in the bottom waters while DO and pH decreased. FIGURE 3, for the same date, shows relatively slight increases in Fe and alkalinity in the bottom waters. Chemical stratification was well advanced by August 2 (FIG. 4). The thermal structure was similar to that given in FIG. 2 but the thermocline had

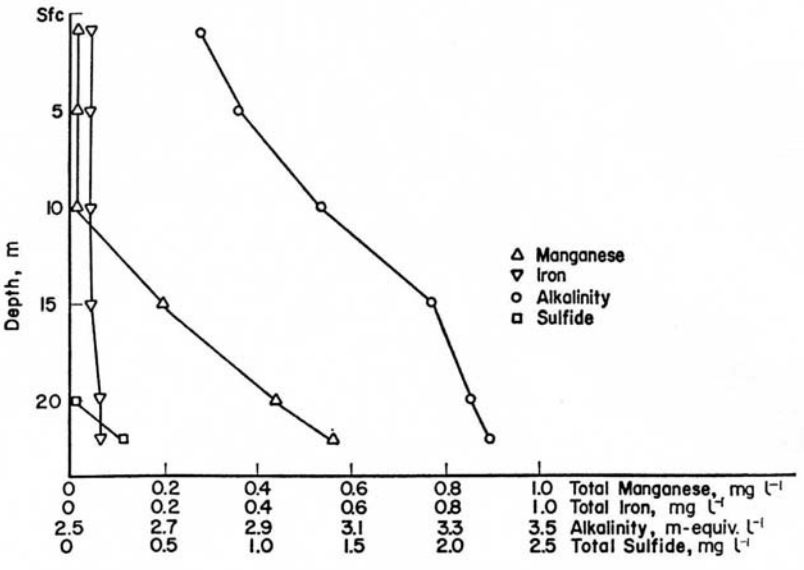

FIG. 4. Sampling profile in Lake Mendota on August 2, 1967.

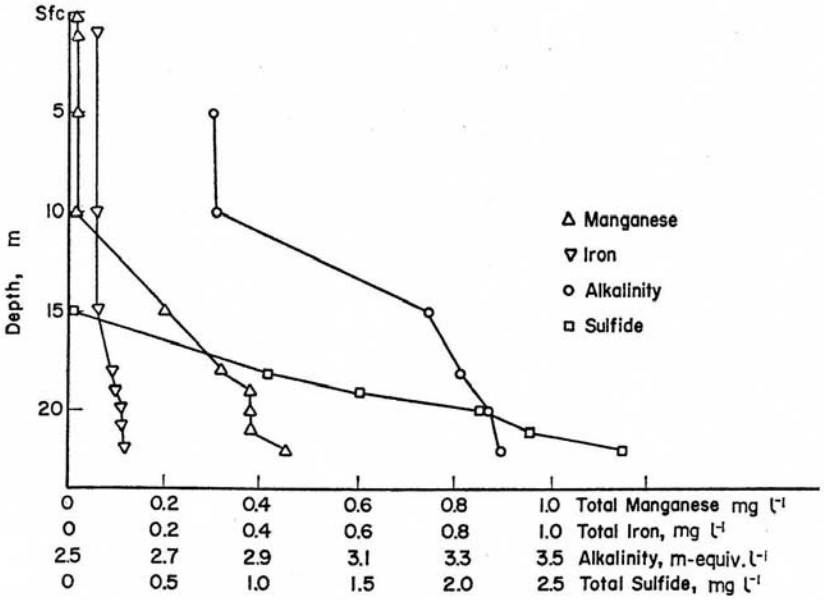

FIG. 5. Sampling profile in Lake Mendota on August 24, 1967.

moved downward to about 10 m. Mn increased to almost 0.60 mg l^{-1} and alkalinity to about 3.4 m-equiv. l^{-1}. Fe, in contrast, remained at a relatively low concentration throughout the water column. The initial appearance of H_2S was noted. Significant increases in hypolimnetic sulfide concentrations were observed on August 24 (FIG. 5) as the values approached 3.0 mg l^{-1}. Mn concentration had decreased slightly probably due to dilution and mixing with upper hypolimnetic waters. Conditions favorable for MnS precipitation were present as the observed ion activity product slightly exceeded the known K_{sp} (solubility product) value for MnS (DELFINO and LEE, 1968). Fe did not show significant increases in the bottom waters whereas a definite

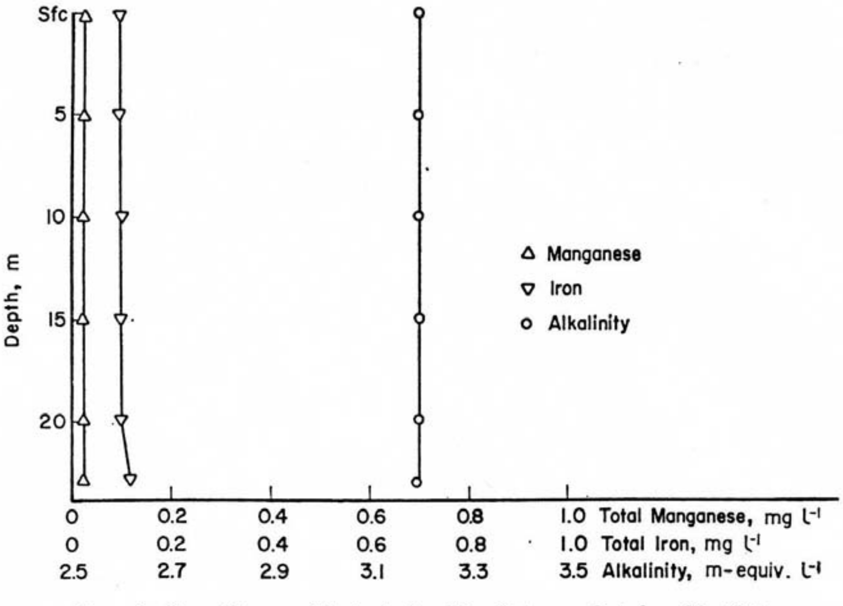

FIG. 6. Sampling profile in Lake Mendota on October 23, 1967.

alkalinity stratification was observed. The alkalinity value for the prevailing pH and temperature conditions indicated that the bottom water was undersaturated with respect to $CaCO_3$ solubility (LEE and DELFINO, 1968). Chemical stratification continued through late September until the fall turnover was initiated. Fall turnover was apparently complete by mid-October as a vertical sampling profile taken on October 23 (FIG. 6) showed iso-chemical profiles very similar to those found in May and early June. The water column was completely oxygenated and the Mn concentration in the column had decreased to a typically low value of about 0.02 mg l^{-1}.

Appearance of Mn

The environmental data show that the increase of Mn concentration in the bottom waters is linear with time. FIGURE 7 is a plot of the observed Mn concentrations vs. time. The samples were taken at the 21 m depth, one meter above the sediment-water interface in the deepest area of the lake. The linear correlation coefficient was computed to verify the observed linear relationship and this was statistically significant at the p = 0.001 probability level. The standard error of estimate, s, was calculated to show the standard deviation of the data from the least squares fitted line drawn in FIG. 7. The slope of the least squares line shows that the Mn concentration in the bottom water increased at the rate of 0.015 mg l^{-1} day^{-1}. This value actually represents the net increase of Mn at the 21 m depth as Mn is also removed from the bottom water by currents and mixing processes and is distributed in upper hypolimnetic waters.

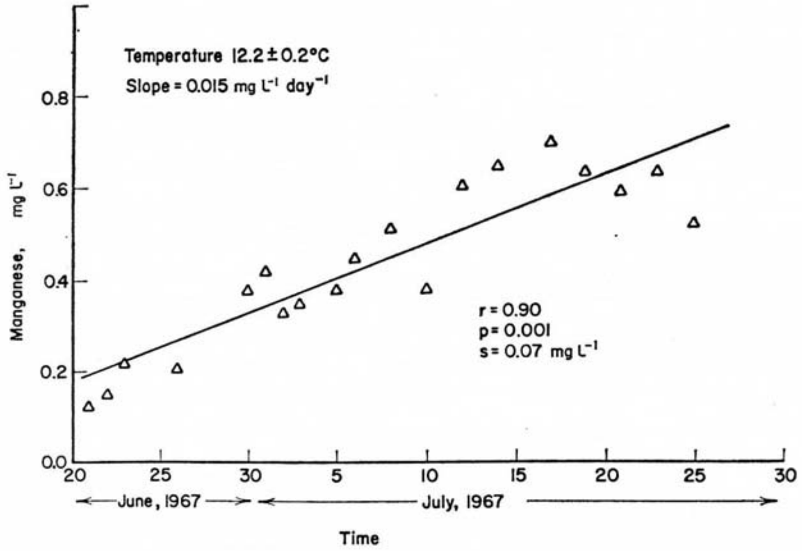

FIG. 7. Observed Mn concentrations at 21 m in Lake Mendota. r = linear correlation coefficient, p = significance level of correlation and s = standard error of estimate.

Depletion of dissolved oxygen

The depletion of dissolved oxygen (DO) as a function of time during this study is shown in FIG. 8. The rate of depletion of DO in the bottom water level was approximately 0.17 mg l^{-1} day^{-1} during the period June 20-July 21 (bottom water was anoxic after July 21). The temperature of the bottom water was constant at 12.2 ± 0.2 °C.

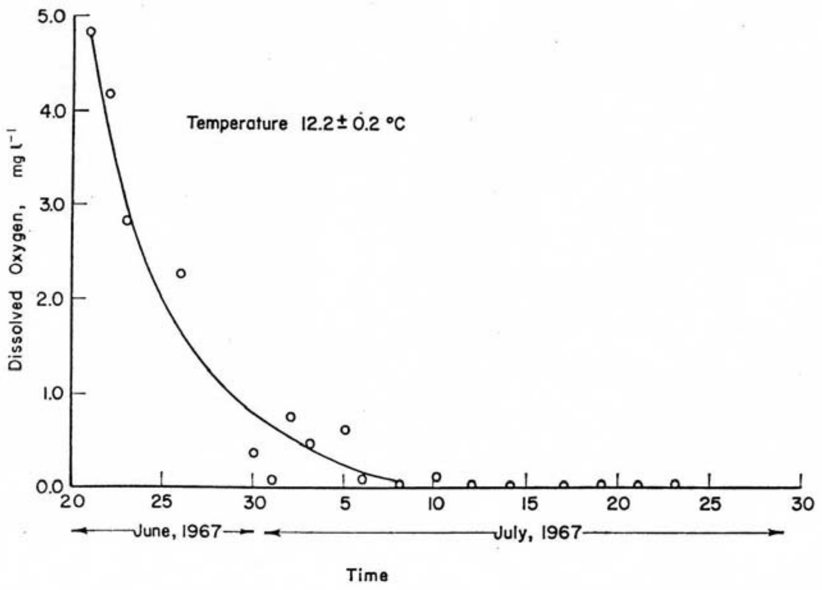

FIG. 8. Depletion of dissolved oxygen at 21 m in Lake Mendota.

This value can be compared with a hypolimnetic DO depletion rate of 0.007 mg l^{-1} day^{-1} reported by DOBSON (1967) during a study of Lake Ontario. The oxygen demand exerted in the hypolimnion is responsible for the relatively rapid rate of DO depletion.

Role of pH

The H^+ concentration of a natural water is usually discussed and measured as pH (the - log of the H^+ concentration). Changes in pH affect the distribution of chemical forms by influencing solubility, sorption and redox processes. The pH variations are primarily related to biological activity (LEE and HOADLEY, 1967). The biota apparently exert considerable indirect influence through their metabolic activities. The uptake of DO during the bacterial respiration process at the sediment-water interface results in the production of CO_2. Hydrolysis of CO_2 follows, depressing the pH and allowing the chemical transformations to occur. During the *in situ* study, the variation of Mn concentration with DO and pH at 1 m above the sediment-water interface was recorded. This is illustrated in FIGS. 9-A and 9-B. The data plotted represent simultaneous observations of Mn with DO (FIG. 9-A) and Mn with pH (FIG. 9-B). FIGURE 9-A shows that up to 0.2 mg l^{-1} Mn existed in the presence of 3 mg l^{-1} DO (this was a ten fold increase over Mn concentrations under non-stratified conditions) and occurred when pH was in the 7.5-7.9 range. If the pH had been near 8.5, the increase in Mn would not have been observed—as illustrated by data from the spring and fall circulation periods. Thus, DO depletion, of itself, is not the only agent limiting the concentration of Mn in Lake Mendota bottom waters. A pH depression must also occur. During thermal stratification periods in the lake, DO depletion in the bottom waters is always accompanied by (1) a decrease in pH and (2) an increase in Mn concentration. FIGURE 9-B illustrates that a pH of 7.5, with simultaneous low DO concentration of anoxic conditions, is sufficient to allow a considerable increase in the bottom water Mn concentration.

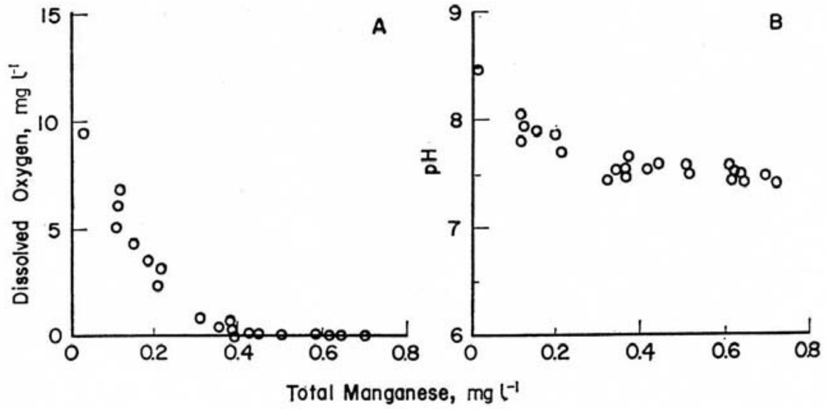

FIG. 9. Variation of Mn with dissolved oxygen (A) and with pH (B) in the bottom waters during the *in situ* study.

Laboratory experiments

Two laboratory experiments were conducted to demonstrate the relationship between sedimentary Mn and pH under anoxic conditions. Surface sediment samples were collected at the water sampling station in the deepest part of the lake using an Ekman dredge. The wet sediments were then suspended in deoxygenated, distilled water and stirred continuously. Approximately 500 g of wet sediment (12 per cent solids) were suspended in 18 l. of distilled water in experiment I while 1000 g were suspended in 38 l. of distilled water in experiment II. Various mixtures of CO_2 and N_2 were bubbled through the suspensions in order to maintain or change the pH. Samples were removed with a siphon tube and were then immediately passed through glass fiber filters aided by a water aspirator vacuum. The filtrates were then passed through 0.45μm membrane filters (no Mn was sorbed on the filters as shown by Mn-dosed trial runs). The Mn data therefore represented soluble Mn released from the sediment suspensions and not finely divided particulate Mn.

The Mn and pH data were plotted as a function of contact time and are given in FIGS. 10 (experiment I) and 11 (experiment II). In both experiments, general trends showed that Mn was released as pH was decreased (CO_2 added to the suspensions) and, conversely, Mn was taken up or incorporated into the sediments when the pH was increased (CO_2 purged from the suspensions). Thus, under anoxic conditions, Mn concentrations showed a direct variation with pH changes. It should also be pointed out that in experiment II (FIG. 11), the concentration of Mn increased steadily with time while the pH was held constant at pH 7.35 ±0.10. This is analogous to the observations made during the Lake Mendota *in situ* study. Also, in the laboratory studies, as shown in FIG. 11, when the pH was lowered to slightly below pH 7, the Mn concentration increased very rapidly. A similar rapid response was seen when the pH was increased quickly and the Mn concentration decreased significantly.

DISCUSSION

The data from the *in situ* and laboratory studies pose questions as to the mechanism(s) whereby Mn is released or taken up by Lake Mendota sediments. The vertical profile data demonstrate that considerably more Mn was released into the hypolim-

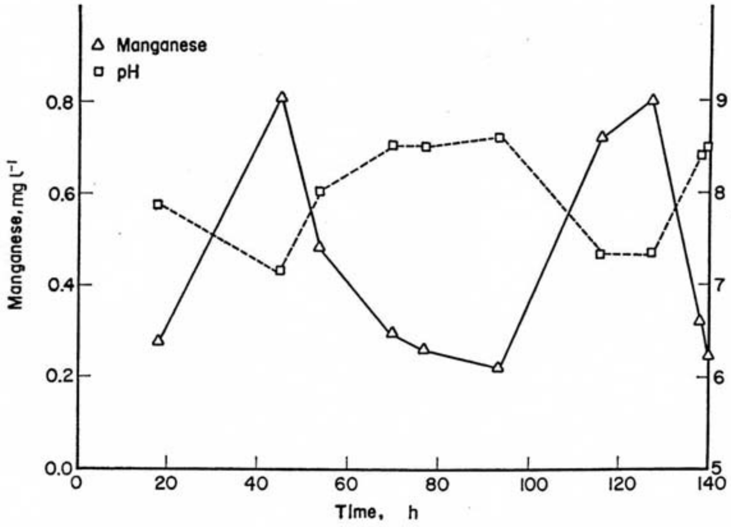

FIG. 10. Laboratory equilibration of Lake Mendota sediment with distilled water, experiment I. Room temperature = 22 ± 2°C.

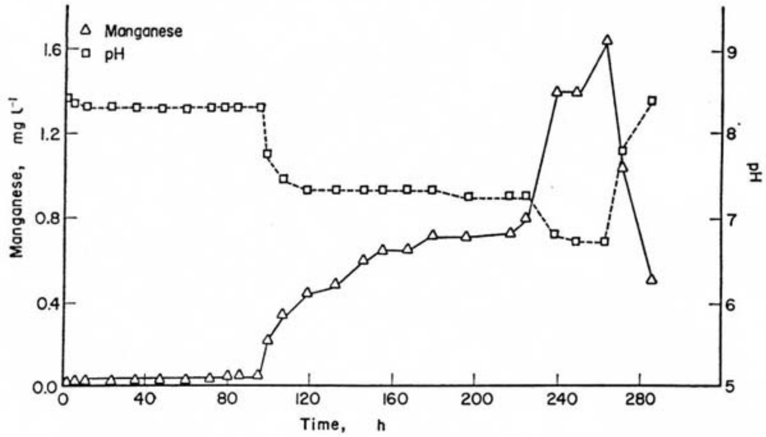

FIG. 11. Laboratory equilibration of Lake Mendota sediment with distilled water, experiment II. Room temperature = 22 ± 2°C.

netic waters than Fe, although the sedimentary Fe:Mn ratio was 19:1. The fact that relatively little Fe was released from the sediments compared with Mn indicated that reducing conditions in the anoxic summer hypolimnion were not sufficient to promote the release of Fe. NRIAGU (1968) reported good evidence for the presence of amorphous iron sulfides in the lake sediments. There is an excess of Fe over the amount stoichiometrically predicted for the sulfide compounds. This excess Fe was postulated to be present in mixed carbonates where Fe might be partially substituted for Ca. However, regardless of the sedimentary Fe forms, relatively small Fe concentrations were found in the hypolimnetic waters. HUTCHINSON (1957) stated that a pH near 6.5 was necessary for Fe^{2+} to appear in the hypolimnion of Esthwaite Lake in England and it appears that a similar pH value is required in Lake Mendota.

Also, during the latter part of summer stratification, Fe solubility may have been limited by FeS precipitation equilibrium. The analytical concentrations of both iron and sulfide (after DeBye-Hückel activity corrections were made based on a computed Lake Mendota ionic strength of 0.006) indicated highly supersaturated conditions with respect to FeS (LEE and DELFINO, 1968). The presence of colloidal FeS was suspected as one possible explanation for the apparent supersaturated condition. Another variable in the sedimentary Fe system is the presence of small particulate magnetic iron oxide spherules which entered the lake system as a result of coal burning activities in the area adjacent to the lake (NRIAGU and BOWSER, 1969). The effect of these spherules on the Fe system is as of yet unassessed.

The specific form(s) of Mn in the sediments were not identifiable by X-ray analysis. This might be explained by (1) the preponderance of $CaCO_3$ in the sediments and (2) the possibility that essentially all of the sedimentary Mn is present in the amorphous state. The latter explanation is reasonable since much of the sedimentary Fe is similarly amorphous. Based on this evidence, it is postulated that Mn is present in the sediments as amorphous hydrous Mn oxide. This also follows from the results of DELFINO and LEE (1968) who found Mn^{2+} adsorbed onto Mn and Fe oxides formed during the laboratory aeration of anoxic hypolimnetic Lake Mendota water. The subsequent sinking of these particulate cation-oxide complexes leads to an accumulation of amorphous Fe and Mn oxides in the sediments. Some of the Mn involved in these sedimentary complexes is adsorbed Mn^{2+}. This adsorbed Mn, present at the sediment-water interface, would be easily leached as the H+ concentration increases (pH decreases).

This sorption-desorption explanation is reinforced by the observed relationship between Mn and pH under both *in situ* and laboratory conditions. The theoretical basis for these reactions was given by MORGAN and STUMM (1965). Sorption processes are highly pH dependent. The rapid response of Mn to changes in H^+ concentration indicates that sorption processes control at least part of the Mn exchange reactions at the sediment-water interface.

Among other mechanistic possibilities, the chemical or biochemical reduction of Mn oxides to Mn^{2+} appears to be of considerably less significance since these reduction processes are generally slow in natural water systems devoid of strong reducing agents. The laboratory controlled suspensions, however, showed that Mn responses to pH changes occur within a few hours which is quite fast by most environmental reaction rate standards. This laboratory response rate could be a little misleading since the sediment suspensions were well mixed—something uncommon in most lakes.

The dissolution of $MnCO_3$ or MnS, leading to the appearance of Mn in the hypolimnion, remains to be explained, but this seems unlikely to occur. This is based on the large amount of $CaCO_3$ and amorphous FeS in the sediments and also on the lack of satisfactory proof for the existence of either $MnCO_3$ or MnS, since neither were found upon X-ray analysis. MANHEIM (1961) suggested the presence of Mn as a mixed carbonate in the Baltic Sea sediments on the basis of X-ray evidence but such is not the case in Lake Mendota. Therefore, pending further experimental results, the evidence points to a pH influenced sorption-desorption mechanism controlling the behavior of Mn in the bottom waters of Lake Mendota at the sediment—water interface.

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