Engineering Experiment Station
Reprint No. 1185

http://www.gfredlee.com/SurfaceWQ/
DelfinoChemistryMn.pdf

Chemistry of Manganese in Lake Mendota, Wisconsin

Joseph J. Delfino and G. Fred Lee*
Water Chemistry Laboratory, University of Wisconsin, Madison, Wis. 53706

The environmental water chemistry of manganese was studied under field and laboratory conditions. Mn(II) was the principal form of Mn measured in Lake Mendota, Wisconsin, throughout an entire seasonal cycle. Only Mn(II) was detected in anoxic waters, whereas both Mn(II) and Mn oxides were present in oxygenated waters. Rates of oxidation of Mn(II) appeared to be slow in the environment and the effect of pH seemed important. Sorption reactions of Mn(II) with Mn and Fe oxides occurred during oxygenation processes and were probably part of the mechanism involved in the removal of Mn from the water column. The presence of Mn(II) in reducing environments yielded rare computed supersaturated conditions with respect to $MnCO_3$, and MnS. These compounds may have limited Mn(II) solubility on those occasions.

Information has become available in recent years regarding the behavior of Mn in well-defined systems. Studies of Mn in aqueous laboratory solutions were conducted by Morgan and Stumm (1963, 1964, 1965a) and Hem (1963, 1964, 1965), in which various parameters were controlled to allow accurate descriptions of the chemical reactions which occurred.

Theoretical descriptions of aqueous Mn behavior, such as those given by Morgan and Stumm (1965a) and Morgan (1967a,b), have evolved from these studies.The descriptions are chemical models which utilize fundamental principles of thermodynamics, redox equilibria, kinetics, and solute interactions in the computation of stability and solubility fields of Mn species predominance.

This paper presents the results of a study of the chemistry of Mn in Lake Mendota and discusses the observed data in terms of previously published theoretical models. Lake Mendota is a hard-water, eutrophic lake of glacial origin in south central Wisconsin.

Theoretical Model

A theoretical model for aqueous Mn can be considered to contain separate sections based on thermodynamic redox equilibria, chemical kinetics, solubility relationships, and sorption and complexation phenomena. The model is abiotic in the sense that direct biological influences on Mn are not considered. The indirect effects of organisms on lake chemistry are inherent in the discussions—e.g., alteration of pH through photosynthesis and respiration.

The first section is a thermodynamic redox equilibrium model, based on free energy and standard potential data given by Latimer (1952) and Morgan (1967a). Redox stability field diagrams have been constructed and presented by Garrels and Christ (1965), Hem (1963), and Morgan (1967a). The Mn species predominance fields in the redox diagrams are based on computed equilibria under various oxidation-reduction conditions. The ordinate *Eh* values are computed from Nernst equation relationships and do not imply correspondence with environmental *Eh* measurements. The redox diagrams demonstrate that some form of oxidized Mn will be in equilibrium with Mn(II) under oxidizing conditions (high *Eh* and pH) and that some form of Mn(II) may be in equilibrium with $MnCO_3$ under reducing conditions (low *Eh* and pH). These assumptions are subject to modification, depending on the presence of other equilibria which might be influencing the Mn system. In most natural waters, oxidizing conditions are generally characterized by high dissolved oxygen and pH values, whereas reducing conditions typically involve oxygen-poor or anoxic waters and low pH.

Attainment of thermodynamic redox equilibrium states can be affected by reaction rates. The kinetics of oxygenation of Mn(II) have been studied in detail by Morgan (1967a). The oxygenation reaction followed an autocatalytic rate expression wherein Mn oxides, initially formed in the reaction sequence, participate in subsequent Mn(II) oxygenation steps. Oxygenation rates are pH-dependent. At pH about 8.5 and above, an intermediate cation-oxide complex is reportedly formed which involves the sorption of Mn(II) onto Mn oxides (Morgan and Stumm, 1965a). The sorption reaction is relatively fast compared to the initial Mn(II) oxidation. Subsequent oxidation of Mn(II) in the sorbed complex, as outlined by Morgan and Stumm (1965a), may take place, but at a different rate than the initial oxidation. As a result, thermodynamically predicted redox equilibrium states are attained only after reaction times of hours or days have elapsed.

When thermodynamic redox and kinetic rate conditions allow a significant amount of Mn(II) to exist as a stable species in equilibrium with MnO_2 or other Mn oxides in the aqueous environment, precipitation reactions between Mn(II) and certain anions may occur. Solubility relationships based on laboratory studies include the equilibria between Mn(II) and $MnCO_3$, MnS, and $Mn(OH)_2$ (Morgan, 1967a). Compounds of the Mn(III) and Mn(IV) oxidation states are not considered in the solubility model. Mn(III) is thermodynamically unstable in aqueous solutions under normal conditions (Cotton and Wilkinson, 1962) and Mn(IV) compounds are generally insoluble at typical environmental pH values (Morgan and Stumm, 1965a).

A solubility diagram for Mn(II) under conditions similar to those present in Lake Mendota was given by Morgan (1967a). $MnCO_3$, might be the dominant precipitation product of Mn(II) in Lake Mendota under the conditions of approximately 10^{-3} *M* total dissolved carbonate and 10^{-4} *M* total dissolved sulfide. However, the MnS field closely parallels that of $MnCO_3$ at pH less than about 9.0, so that slightly higher sulfide-carbonate ratios in the hypolimnion might allow the MnS field to predominate. The $Mn(OH)_2$ field appears only at very high pH and should not be important in waters containing the carbonate and sulfide concentrations represented by the model.

Sorption and complexation reactions are not easily quantified in diagrammatic form. The reactions are related to the models presented above and are best described in conjunc-

---

* Present affiliation:
G. Fred Lee & Associates, El Macero, CA 95618
gfredlee33@gmail.com www.gfredlee.com

tion with them. Sorption of Mn(II) by MnO_2 and $Fe(OH)_3$ has been observed and measured in laboratory systems. The pH-dependent nature of the reactions was demonstrated by Morgan and Stumm (1965a), who found significant sorption of Mn(II) by hydrous Mn and Fe oxides above pH 8.5. The high sorptive capacity of the oxides could control Mn(II) reactions in natural waters when pH conditions are favorable. The occurrence of Mn(II) in the presence of hydrous Mn and Fe oxides above pH 8.5 would result in sorption and subsequent removal of Mn(II) from solution.

If the removal is complete, and the sorbed cation-oxide complex settles out of the water column, Mn(II) will remain in a metastable complexed state. It is possible for further oxidation to occur if the sorbed complex comes in contact with oxidizing conditions or, perhaps, combined reduction and desorption reactions will take place if reducing conditions are encountered, as in an anoxic hypolimnion.

Inorganic complexes stabilize Mn(II) and can retard the oxidation rate. Complexing ligands, such as HCO_3^-, have been found to reduce the oxidation rate of Mn(II) in synthetic bicarbonate solutions (Morgan, 1967a). Organic molecules could form stable complexes with Mn(II) if the organic concentrations are high. However, the existence of Mn(II)-organic complexes has not been clearly demonstrated in environmental waters, although Rona, Hood, *et al.* (1962) postulated that a small amount of Mn in sea water may be present as an organic complex.

Experimental Procedures

Water samples were collected from Lake Mendota with a Van Dorn sampler or a generator-powered pumping system described by Lee and Harlin (1965). Total Mn was determined by the persulfate method (American Public Health Association, 1965), with a standard deviation of ±0.01 mg. per liter. Mn forms were measured by passing selected aliquot volumes through prerinsed (100 ml. of distilled water) membrane filters of various pore sizes. The filtrates were analyzed by the persulfate method. The filtrates were also tested with *o*-tolidine reagent (Morgan and Stumm, 1965b) and crystal violet reagent (Presley, Brooks, *et al.,* 1967) for the existence of oxidized Mn. Negative color reactions were observed at all times. Thus, for purposes of differentiation, the total Mn which passed through 0.45-, 0.22-, or 0.10-micron membrane filters (Millipore Filter Co, Redford, Mass), was assumed to be some form of Mn(II)—i.e., the free ion or a complex compound. Oxidized Mn particles were qualitatively identified by the procedure of Ormerod (1966). All of the detectable particulate Mn oxides in Lake Mendota were held by 0.45-micron membrane filters. Approximate detection limits of the Mn oxide procedure were of the order of 1 to 5 μg. per liter.

Dissolved oxygen was measured by the Winkler-azide procedure; alkalinity was titrated with 0.02 *N* H_2SO_4 to the methyl purple end point; and total sulfide was determined by the methylene blue method, all given by the American Public Health Association (1965). *In situ* temperatures were measured with a Whitney underwater thermometer and pH values were obtained by use of Beckman pH meters (Models GS and N). All chemical analyses were completed within 24 hours after sample collection.

Activity coefficients (γ_i) used for ion activity product (IAP) computations were calculated by the Debye-Hückel expression:

$$\log \gamma_i = -\frac{Az_i^2\sqrt{\mu}}{1 + Ba\sqrt{\mu}}$$

The ionic strength of Lake Mendota (μ) was computed to be 0.006. The values for constants *A, B,* and *a* were taken from Klotz (1950).

Results

The seasonal variation of total Mn in Lake Mendota for 1966 and 1967 is shown in Figures 1 and 2, respectively. The observed Mn data followed general discussions given by Hutchinson (1957). The increase in total Mn in the bottom waters closely paralleled the development of thermal stratification in early summer. The initial release of Mn from the lake sediments occurred prior to the depletion of dissolved oxygen. Analytically significant increases of Mn in bottom waters were found in the presence of 5 mg. per liter of dissolved oxygen at pH 8.0 or less. The details of the seasonal Mn isopleths were different for 1966 and 1967. The differences were most likely the result of climatological factors which included thermal structure variations and mixing patterns related to seasonal wind stress on the lake.

The typical forms of Mn measured during the sampling period are summarized in Table I. Mn which passed 0.45-micron or smaller membrane filters was taken to be Mn(II). Mn oxides (unidentified structure and composition) held on 0.45-micron filters are identified as detectable (+) or non-detectable (—) in Table I.

The data showed that a significant fraction of the total Mn in Lake Mendota throughout the study period passed specified membrane filters and gave negative color reactions with the reagents mentioned earlier. This means that most of the total Mn in Lake Mendota was soluble and present as some form of Mn(II). The analytical procedures did not detect colloidal Mn oxides in the membrane filtrate fractions, but such forms may have been present in very small concentrations.

Mn oxides were present in all oxygenated waters, independent of depth and season. No Mn oxides were detected in anoxic waters which contained dissolved sulfide. On occasion, small concentrations of Mn oxides were found in

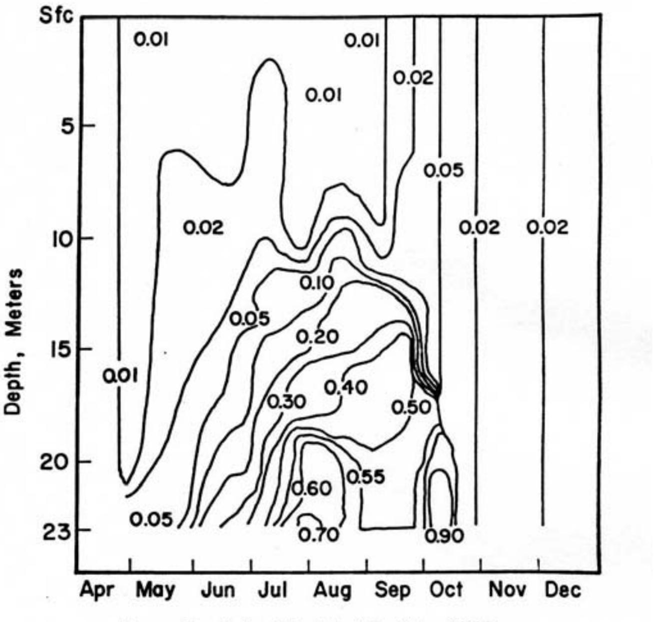

Figure 1. Lake Mendota Mn data, 1966

Seasonal variation of total Mn at the deep hole station, total depth 23 meters. Data in mg. per liter

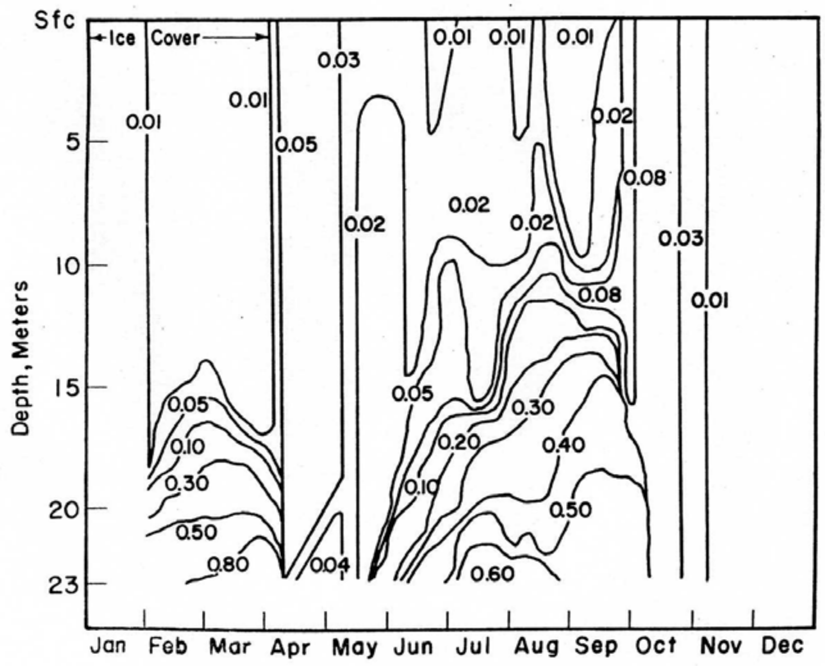

Figure 2. Lake Mendota Mn data, 1967

Seasonal variation of total Mn at the deep hole station, total depth 23 meters. Data in mg. per liter

waters which had just become anoxic but did not have any detectable sulfide concentration. These small amounts are denoted as (±) in Table I. There was at time lag of about one week between the beginning of anoxia in the bottom waters and the disappearance of detectable Mn oxides, and approximately the same time interval elapsed before sulfide initially was detected. Attempts to determine the nature of the particulate Mn oxides failed because of the completely amorphous characteristics found by x-ray analytical techniques.

Total Mn which passed the 0.45-micron membrane filters was defined as Mn(II) and the concentrations were substituted into solubility computations. The activity coefficients used for the IAP expressions were, respectively, Mn^{2+}, 0.73; S^{2-}, 0.73; HCO_3^{-}, 0.92; and CO_3^{2-}, 0.72. Table II presents the results of such computations for oxygenated and anoxic waters. The data in Table II show that on two occasions $MnCO_3$ might have limited Mn(II) solubility in oxygenated Lake Mendota waters. The IAP/K_{sp} ratio exceeded 1.0 at those times with both samples from deep water beneath the winter ice cover. No sulfide was detected on those sampling dates. The ratios were not large enough, however, to indicate significant supersaturation, since small analytical differences would alter the exact values. Despite this uncertainty, the data pointed to the possibility that saturation equilibrium between Mn(II) and $MnCO_3$ might occur in bottom waters in contact with carbonate-rich sediments. Temperature corrections were not made for the calculations of the IAP/K_{sp} ratios. This may have affected the outcome of the winter data computations.

For purposes of interpretation, IAP/K_{sp} ratios which equal 1.0 indicate that the ion activity product of (Mn^{2+}) times (CO_3^{2-}) is equal to the solubility product of $MnCO_3$. If the ratio is significantly less than 1.0, the system is undersaturated with respect to $MnCO_3$, while ratios in excess of 1.0 indicate supersaturation. Small variations above and below 1.0 are not considered very significant, since variations in analytical procedures could account for the small differences. However, large variances of the IAP/K_{sp} ratio from 1.0 would be considered significant.

Under anoxic conditions in the summer hypolimnion, the solubility of MnS might limit Mn(II) concentrations, although only one IAP/K_{sp} ratio in Table II exceeded 1.0. That value did not necessarily indicate saturation equilibrium or supersaturation, because of possible analytical variations, but showed that equilibrium between Mn(II) and MnS might be important when high sulfide-carbonate ratios exist in the bottom waters.

A laboratory aeration experiment was conducted to estimate the relative rate of oxidation and removal of Mn(II) in Lake Mendota waters. Approximately 20 liters of anoxic Lake Mendota bottom water were collected and placed in a borosilicate glass vessel. The system was oxygenated with water-scrubbed laboratory compressed air. Dissolved oxygen reached near saturation levels at room temperature (22° ± 1° C.) within 1 to 2 hours and remained at or near saturation for the duration of the experiment. The pH increased rapidly during the first few hours because of stripping of CO_2. A pH of about 8.5 was reached after 3 days of aeration and remained constant (±0.05 pH unit) thereafter. Results of the aeration experiment are depicted in Figure 3.

No Mn oxides were detected on 0.45-micron membrane filter pads until at least 30 hours had elapsed. This showed that oxidation of Mn(II) occurred relatively slowly under the conditions employed. The analytical differences between total Mn and Mn which passed 0.45-micron filters were not significant. The gradual decrease of total Mn in the system was due to the formation of a reddish brown flocculent material composed of Mn, Fe, and algal cell debris. This material gradually adhered to the sides of the reaction vessel and a rough film was observed on most of the interior surface in contact with the water column. Present in the flocculent material were amorphous Mn and Fe oxides and probably a cation-oxide complex composed of Mn(II) bound to Mn and Fe hydrous oxides.

Table I. Forms of Mn Measured in Lake Mendota in Deep Hole Area

Total depth = 23 to 24 meters

			Mg./L.				
			Dissolved oxygen	Total Mn	Mn Passing		
Depth, M.	Temp., °C.	pH			0.45 μ	0.22 μ	MnO_x
April 25, 1966							
8	6.5	8.85	13.2	0.04	0.02	. . .	[a]
22	6.2	8.70	12.8	0.03	0.01	. . .	[a]
June 22, 1966							
1	22.0	8.95	[a]	0.01	0.01	. . .	+
17	10.6	8.00	5.66	0.05	0.02	. . .	+
23	10.1	7.72	1.84	0.40	0.27	. . .	+
August 17, 1966							
2	24.0	8.68	9.34	0.01	0.01	. . .	+
14	13.8	7.50	0.00	0.25	0.18	. . .	±[b]
21	11.5	7.38	0.00	0.60	0.57	. . .	−
September 24, 1966							
2	18.2	8.30	8.70	0.02	0.01	. . .	+
17	12.0	6.95	0.00	0.52	0.47	. . .	−
22	11.3	6.80	0.00	0.55	0.53	. . .	−
October 26, 1966							
1	11.7	7.90	9.25	0.02	0.01	. . .	+
22	11.3	7.80	8.80	0.02	0.01	. . .	+
December 3, 1966							
Sfc.	2.5	8.20	13.90	0.02	0.01	. . .	+
22	3.1	8.20	12.40	0.02	0.01	. . .	+
February 4, 1967							
10	1.0	8.05	12.40	0.01	0.01	0.01[c]	+
20	1.9	7.80	8.89	0.16	0.16	0.16[c]	+
23	2.6	7.45	1.63	0.66	0.66	0.65[c]	+
March 29, 1967							
10	2.0	8.00	10.35	0.01	0.01	0.01[c]	+
18	2.2	7.80	7.30	0.12	0.11	0.10	+
22	3.3	7.50	0.50	0.79	0.79	0.79[c]	+
May 6, 1967							
9	8.3	8.60	12.00	0.03	0.03	[a]	+
21	7.6	8.53	11.40	0.04	0.03	[a]	+
June 12, 1967							
5	18.7	8.45	10.65	0.02	0.01	0.01	+
15	13.0	7.98	8.30	0.04	0.02	0.02	+
21	12.1	7.80	6.27	0.13	0.10	0.10	+
August 24, 1967							
1	21.7	8.87	10.17	0.01	0.01	0.01	+
15	13.8	7.72	0.00	0.20	0.17	0.17	±[b]
22	12.3	7.38	0.00	0.45	0.44	0.43	−
September 30, 1967							
5	16.4	8.40	9.62	0.08	0.05	[a]	+
15	16.4	8.28	9.42	0.07	0.05	[a]	+
22	12.6	6.98	0.00	0.57	0.56	[a]	−
October 23, 1967							
5	12.4	8.10	9.09	0.03	0.01	[a]	+
15	12.3	8.10	9.08	0.03	0.01	[a]	+

[a] Not determined.
[b] Indicates slightly positive reaction.
[c] 0.10-micron pore size used instead of 0.22.

Table II. Lake Mendota Mn Solubilily Data, 1967

Date	Depth M.	$(Mn^{2+})^a$	$(CO_3^{2-})^a$	$(S^{2-})^a$	$(H^+)^a$	IAP/K_{sp} MnCO$_3$	IAP/K_{sp} MnS
			Oxygenated Waters				
Feb. 1[b]	1	1.35E–07[c]	1.52E–05	[d]	7.94E–09	0.05	[e]
	21	6.49E–06	1.38E–05	[d]	1.26E–08	1.6	[e]
March 29[b]	5	1.35E–07	1.26E–05	[d]	1.26E–08	0.3	[e]
	22	1.07E–05	4.00E–06	[d]	3.16E–08	1.1	[e]
April 5	1	5.41E–07	8.13E–06	[d]	1.35E–08	0.1	[e]
	23	6.75E–07	1.10E–06	[d]	9.76E–09	0.01	[e]
May 30	3	2.70E–07	4.12E–05	[d]	2.69E–09	0.3	[e]
	23	5.41E–07	3.52E–05	[d]	3.16E–09	0.5	[e]
June 19	1	1.35E–07	8.10E–05	[d]	1.32E–09	0.3	[e]
	21	2.57E–06	7.86E–06	[d]	1.41E–08	0.5	[e]
July 3	5	2.70E–07	7.48E–05	[d]	1.48E–09	0.5	[e]
	21	4.73E–06	4.23E–06	[d]	2.63E–08	0.5	[e]
Aug. 2	1	1.35E–07	1.06E–04	[d]	8.91E–10	0.4	[e]
Sept. 6	5	1.32E–07	5.45E–05	[d]	1.91E–09	0.2	[e]
Sept. 30	5	1.08E–06	2.76E–05	[d]	3.98E–09	0.7	[e]
Oct. 23	5	4.05E–07	1.41E–05	[d]	7.94E–09	0.1	[e]
	23	2.66E–07	1.32E–05	[d]	8.50E–09	0.1	[e]
Nov. 6	5	1.35E–07	1.13E–04	[d]	5.01E–09	0.4	[e]
			Anoxic Hypolimnetic Waters				
Aug. 2	22	7.19E–06	3.08E–06	1.72E–11	3.08E–08	0.5	0.2
Aug. 9	20	5.86E–06	3.04E–06	2.37E–11	3.70E–11	0.4	0.2
	22	7.96E–06	2.53E–06	3.02E–11	4.50E–08	0.6	0.5
Aug. 16	20	5.18E–06	1.43E–06	2.92E–11	7.60E–11	0.2	0.2
	21	5.99E–06	1.63E–06	4.46E–11	6.90E–08	0.2	0.4
Aug. 24	18	3.86E–06	2.92E–06	5.40E–11	3.80E–08	0.2	0.3
	20	4.78E–06	2.66E–06	9.80E–11	4.20E–08	0.4	0.7
	22	5.85E–06	2.69E–06	1.32E–10	4.20E–08	0.4	1.1
Sept. 6	20	6.92E–06	2.33E–06	7.96E–11	5.00E–08	0.4	0.8
	22	7.19E–06	2.48E–06	8.30E–11	5.00E–08	0.6	0.8
Sept. 11	22	7.45E–06	9.04E–07	[f]	1.20E–07	0.2	[f]
Sept. 19	21	7.45E–06	1.21E–06	4.00E–11	8.90E–08	0.2	0.4
Sept. 30	20	7.45E–06	1.68E–06	6.25E–11	6.80E–08	0.2	0.7
	22	7.45E–06	9.67E–07	4.45E–11	1.05E–07	0.2	0.5

[a] Activity, mole/liter.
[b] Winter ice cover was present.
[c] ~~1.35 × 10~~ == 1.35E-07 (Correction published in Environ. Sci. Technol. 3(9):835, September (1969))
[d] Not present.
[e] Not calculated.
[f] Not determined.

Discussion

The published theoretical models for aqueous Mn can be evaluated by comparing the predicted equilibrium reactions with analytical data obtained from the environment.

The thermodynamic redox model predicted Mn(II) to be in equilibrium with $Mn0_2$ (or, in general, hydrous Mn oxides) under oxidizing conditions. Mn oxides were observed in the presence of dissolved oxygen and high pH. Mn(II) was also present under oxidizing conditions, as well as in reducing environments, generally as the major fraction under both conditions.

The presence of Mn(II) as a dominant Mn form was apparently due to reaction kinetics. The rate of Mn(II) oxidation in environmental waters and subsequent equilibration with Mn oxides was slow compared with results from laboratory solution studies, such as those reported by Morgan (1967a). The high pH required in laboratory systems for rapid oxidation (pH 9.0 or above) was not often encountered in Lake Mendota except during midsummer algal blooms. At lower pH values, generally 8.0 to 8.5, oxidation proceeded slowly and longer reaction times were needed to attain equilibrium between Mn(II) and Mn oxides. Reaction kinetics seemed to influence the rate at which thermodynamic redox equilibrium between Mn(II) and Mn oxides was attained in Lake Mendota waters.

The solubility model suggested that $MnCO_3$ might be a stable precipitated form in equilibrium with Mn(II) in the presence of sufficient carbonate alkalinity. MnS was predicted to be the important form in equilibrium with Mn(II) only if the sulfide-carbonate ratio increased sufficiently. The model was only infrequently valid in Lake Mendota based on computed IAP/K_{sp} ratios. The ratios showed that either $MnCO_3$ or MnS could have limited Mn(II) solubility on rare occasions, if proper conditions prevailed. As noted earlier, temperature corrections were not taken into account. Attempts to identify the solid forms of Mn in the Lake Mendota sediments by x-ray methods were not successful. Thus, it appears that the forms of particulate Mn oxides in the water column, as well as the solid Mn forms in the sediments, are amorphous.

The roles of sorption and complexation were interrelated with the other reaction systems. The sorption of Mn(II) onto Mn and Fe oxides appeared to occur in Lake Mendota and was best demonstrated by the findings of the laboratory aeration experiment. The amorphous nature of the oxidation products of Mn(II) supported the incomplete oxidation theory and this implied sorptive uptake of Mn(II) by Mn and Fe oxides (cation sorption onto Mn oxides is favored by higher pH where negative oxide charges prevail). Complexation, particularly involving HCO_3^-, likely played a role in reducing the rate of Mn(II) oxidation, although this was not determined experimentally. Laboratory studies reported in the literature discussed the stabilizing effect of HCO_3^- solutions on Mn(II) oxidation compared to distilled water solutions with little or no HCO_3^- present. Lake Mendota generally has a HCO_3^- concentration of 2.5 to 3.5 mmoles per liter. This is equivalent to between 125 and 175 mg. per liter as $CaCO_3$.

Based on the field and laboratory observations, a Mn system can be postulated to account for the presence of Mn in different forms in stratified lakes, as represented by Lake Mendota. Figure 4 summarizes experimental results and certain necessary hypotheses based upon those results.

The thermal structure used as a framework in Figure 4 is a typical midsummer Lake Mendota profile. It could represent any moderately deep lake (maximum depth of Lake Mendota is about 24 meters) in the temperate zone. The chemical reactions shown in Figure 4 could take place if the required compounds and ions are present under the specified conditions in each of the strata.

The conditions in the epilimnion are considered to be oxidizing. Dissolved oxygen values are near saturation and pH is elevated to near pH 9 because of photosynthetic activity. The epilimnion is in constant circulation due to wind action and is generally in equilibrium with the atmosphere.

Manganese is present as Mn(II) and Mn oxides. Also present are uncharacterized Fe oxides. A number of reactions are possible under the oxidizing conditions. Mn(II) may be slowly oxidized to Mn oxides in the presence of dissolved oxygen. The rate is slow without sufficient or suitable catalytic surface sites. Mn(II) may sorb onto the Mn and Fe oxides, since the high pH favors sorption reactions. The Mn(II) sorbed onto the Mn and Fe oxides may be catalytically oxidized to form more Mn oxides. The oxides may initially be colloidal with small particle dimensions but in time may develop into particle sizes larger than 0.45 micron. Eventually, some of the oxide particles and sorbed cation-oxide complexes will sink and enter the thermocline region.

The thermocline zone has intermediate properties between the two surrounding zones. The upper part has dissolved oxygen but at lower levels than in the circulating epilimnion. Exchange of materials across the boundary with the epilimnion no doubt occurs but because of density differences, a time lapse probably exists. Essentially the same species in the epilimnion are present in the thermocline. These were present prior to the development of stratification or entered after the three stable zones were formed.

The thermocline is a transition zone and as such it is difficult to estimate the extent of the chemical reactions which occur within its limits. It is most likely that some of the epilimnetic reactions occur in the upper thermocline zone and similarly some hypolimnetic reactions occur at the lower levels of the zone. The waters nearest the two boundary edges of the thermocline would least be in equilibrium due to constant exchange with the other zones. A metastable state may exist within the thermocline, depending on the duration of its existence and the intensity of physical factors (currents, internal waves) which would tend to destabilize the zone.

The hypolimnion zone during thermal stratification is characterized by little or no dissolved oxygen, low pH values, and reduced temperatures. It is no longer in equilibrium with the atmosphere but rather is involved in exchange reactions with the sediments.

Mn is primarily Mn(II) in the hypolimnetic waters. Reactions may take place in the hypolimnetic water column whereby desorption of Mn(II) from Mn and Fe oxides occurs. The Mn and Fe oxides may be reduced, although these are generally not present in any significant amount. The presence of dissolved sulfide and carbonate may result in the precipitation of MnS and $MnCO_3$, respectively, although evidence for this is still circumstantial. These compounds

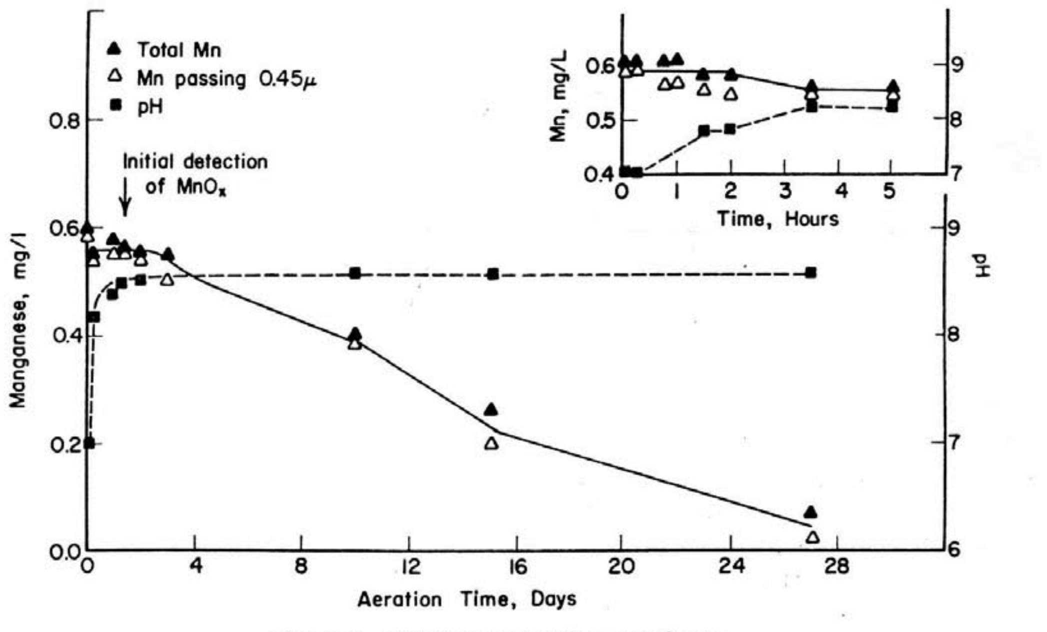

Figure 3. Laboratory aeration experiment.

Anoxic Lake Mendota bottom water taken from 22-meter depth in deep hole region Sept. 30, 1967

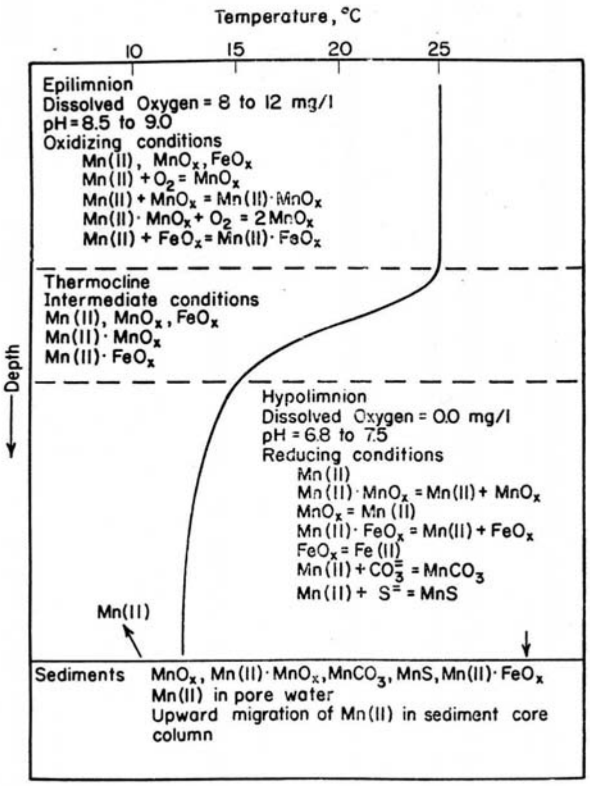

Figure 4. Mn system in Lake Mendota based on experimental results and hypotheses

could exist in a stable colloidal suspension due to slow nucleation and precipitation rates and the absence of precipitation nuclei.

Mn(II) is released from the sediments under reducing conditions and pH was one of the most influential factors. The form of Mn in the sediments is probably complex. However, about 40% of the total Mn was easily exchangeable with 1*N* ammonium acetate, buffered at pH 7. This means that Mn(II) may be sorbed onto amorphous Mn and Fe oxides in the sediments. Mn may also be released by dissolution of compounds which are moderately soluble at pH about 7.0. Mn(II) released through the sedimentary pore waters may contribute a small amount to the total concentration. Mn can be supplied to the surface sediments from above and possibly from below. Mn may precipitate in upper waters and be deposited as the oxide, carbonate, or sulfide, or as a sorbed cation-oxide complex. There is evidence that Mn may migrate upward through the sedimentary column and become enriched in the upper sediment layers. Definite proof of this is lacking, but data of Lynn and Bonatti (1965) and Presley, Brooks, *et al*. (1967) from marine sediment cores showed that phenomenon might exist. However, data presented by Mackereth (1966) indicated that changes to the basin surrounding a lake, as well as variations in the redox conditions within a lake, could yield sedimentary Mn patterns suggesting migration. This particular process is still poorly understood and further work, possibly utilizing radioisotope tracers, is indicated.

If Mn(II) did in fact migrate upward in the core column, the enrichment of Mn in the upper sediment layers might occur during periods of circulation when oxidizing conditions prevail at the sediment-water interface. When Mn(II) ions were in the process of diffusing upward in the reduced sediment column, they would encounter oxidizing conditions in the uppermost sediment layers, become oxidized, and deposit Mn oxides or sorbed cation-oxide complexes. The data indicate that a number of processes are occurring at the same time, and that the Mn forms in the sediments are no doubt complex, involving different compounds in different oxidation states.

Conclusions

The environmental chemistry of Mn in Lake Mendota is complex. A number of different chemical reactions may occur, independently or simultaneously, at different rates and involving different reaction intermediates. Chemical equilibrium may or may not be attained, depending on the nature of the reactions.

The principal form of Mn in Lake Mendota is Mn(II). Small amounts of Mn oxides are present under oxidizing conditions but absent in reducing environments. Mn oxygenation reactions are pH-dependent and sorption and complexation reactions could be interrelated with Mn(II) oxygenation processes. Precipitation reactions involving $MnCO_2$ and MnS might limit Mn(II) solubility under appropriate environmental conditions.

Literature Cited

American Public Health Association. New York, "Standard Methods for the Examination of Water and Waste-Water," APHA, AWWA, WPCF, 12th ed., 1965.

Cotton, F. A., Wilkinson. G., "Advanced Inorganic Chemistry," pp. 694-706, Wiley, New York, 1962.

Garrels, R. M., Christ, C. L., "Solutions, Minerals and Equilibria," Harper and Row, New York, 1965.

Hem, J. D., U. S. Geol. Survey Water-Supply Paper **1667**-A (1963).

Hem, J. D., U. S. Geol. Survey Water-Supply Paper **1667**-B (1964).

Hem, J. D., U. S. Geol. Survey Water-Supply Paper **1667**-D (1965).

Hutchinson, G. E., "Treatise on Limnology," Vol. **I**, Wiley, New York, 1957.

Klotz, I. M., "Chemical Thermodynamics," Prentice-Hall, Englewood Cliffs, N. J., 1950.

Latimer, W. M., "Oxidation Potentials," 2nd ed., pp. 234-41, Prentice-Hall, Englewood Cliffs, N. J., 1952.

Lee, G. F., Harlin, C. C., Jr., *Ind. Water Eng.* **2**, 36-40 (1965).

Lynn, D. C., Bonatti, E., *Marine Geol.* **3**,457-74 (1965).

Mackereth, F. J. H., *Phil. Trans. Roy. Soc. London* **250**, No. 765, 165-213 (1966).

Morgan, J. J., "Principles and Applications of Water Chemistry," S. D. Faust, J. V. Hunter, eds., Wiley, New York. 1967a.

Morgan, J. J., *Advan. Chem. Ser.,* No. **67**, 1-29 (1967b).

Morgan, J. J., Stumm, W., Division of Water and Waste Chemistry, 145th Meeting, ACS, New York, September 1963.

Morgan, J. J., Stumm, W., *J. Colloid Sci.* **19**, 347-59 (1964).

Morgan, J. J., Stumm, W., Proceedings of 2nd International Conference on Water Pollution Research, pp. 103-31, Pergamon Press, New York, 1965a.

Morgan, J. J., Stumm, W., *J. Am. Water Works Assoc.* **57**, 107-19 (1965b).

Ormerod, J. G., *Limnol. Oceanog.* **11**, 635 (1966).

Presley, B. J., Brooks, R. R., Kaplan, I. R., *Science* **158**, 906-9 (1967).

Rona, E., Hood, D. W., Muse, L., Buglio, B., *Limnol. Oceanog.* **7**, 201-6 (1962).

Received for review April 26, 1968. Accepted September 30, 1968. Investigation supported by Training Grant 2T1-WP-22 and Research Fellowship No. 1-F1-WP-26, 217-01, Federal Water Pollution Control Administration. In addition, support was given by the University of Wisconsin Engineering Experiment Station and the Department of Civil Engineering and the U. S Office of Naval Research. Part of the results of this investigation were obtained in the University of Wisconsin Laboratory of Limnology and the use of these facilities is greatly appreciated.