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Studies on the Manganese Cycle

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1. Manganese

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Studies on the Manganese Cycle

The first studies on the manganese cycle in impoundments were concerned with the manganese concentrations in and removal from bottom waters of deep impoundments. But as work progressed, the emphasis was more on the investigation of the mechanism by which manganese is dissolved in impounded waters.

Attention has been given to the problem of high manganese concentrations in bottom waters. The problem of a continual manganese concentration can cause discoloration and lead to deposits in pipe lines and filter plants. Also, the reaction of manganese and orthotolidine gives a false chlorine residual that may interfere with maintenance of safe water throughout a distribution system.

Experimentation done on manganese mechanism of dissolvement indicates that a considerable quantity of manganous ion adsorbed to manganic or ferric oxide particles is carried into the hypolimnion. This means that all of the manganese is not oxidized and that bacterial activity is involved in manganese cycle.[1]

Recent studies have shown that manganese entering impounded water will undergo a cyclic transformation. In coming water into a lake contains mostly soluble manganese in the bivalent state. Soluble manganese ions on the top layers will be oxidized in the presence of dissolved oxygen and precipitate to the bottom in the form of Mn^{+4}. A chemical stratification will occur whereby higher concentrations of manganese are found in bottom layers with little or none in the top layers.

Bottom waters receiving no reaeration are deprived of dissolved oxygen and anaerobic conditions prevail. Biological activity takes place due to the organic matter present. Manganese transformation by biological activity will render manganese soluble by both intracellular as well as extracellular activity.

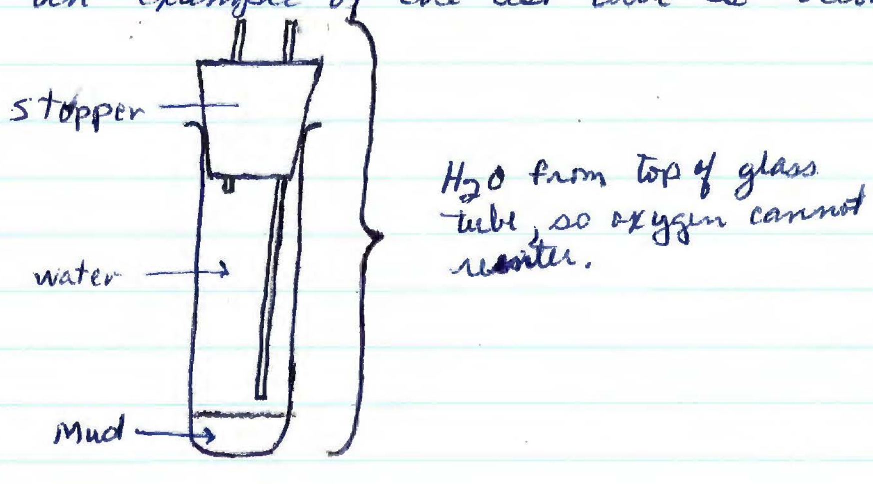
Possible influences of biological activity are: the presence of carbon dioxide that increases the solubility of bivalent manganese to a large extent; metabolic intermediate products that lower the pH of the water; organic acids that form organometallic complexes with manganese; and bilogical reduction that changes Mn^{+4} to Mn^{+2} as an intracellular activity. Dissolved manganese may be brought to the top layers during the lake overturn. This is another influence that is to be considered.

The lake overturn is important because it brings about a deterioration in the quality of the waters. The problem of controlling the quality of impounded water is now under experimentation.[2]

A recent study at Lake Mendota, Wisconsin, provides more data about manganese in lakes. Some of the results showed that the increase in total manganese in the bottom waters closely paralleled the development of thermal stratification in early summer. The initial release of manganese from lake sediments occured prior to the depletion of dissolved oxygen. Most of the total manganese in the lake was soluble and present as some form of Mn^{+2}.[3]

The process and rate of solubility of manganese are important factors in finding out more about the manganese effect on the quality of water in our impoundments. The purpose of this paper is to find out about the rate of solubility.

Samples of mud taken from the bottom of a nearby lake were put in the bottoms of test tubes (twenty). Lake water was poured in the tubes so as not to disturb the mud and a stopper placed on each. The stopper had two glass tubes: one that reached down to about one cm. from the mud and one that was even with the stopper; they were both the same height above the stopper so that oxygen could not be released back into the test tube. An example of the test tube is below:



The tubes were then tested on different dates to determine the rates.

In order to determine this, an atomic

Absorption Spectrophotometer (AAS) was used. The test tube was hooked up to the AAS by a plastic tube that was placed inside the longest tube to its base. The AAS then read the contents of the test tube for manganese. In order to find the results, the AAS was connected to a recorder.

A standard was made and used before each test. There were ten tests. The readings were set against the standard and plotted on a graph. The graphs are on pages five through fourteen. Another graph, on page fifteen, was set up to find the relationship between Manganese and the time.

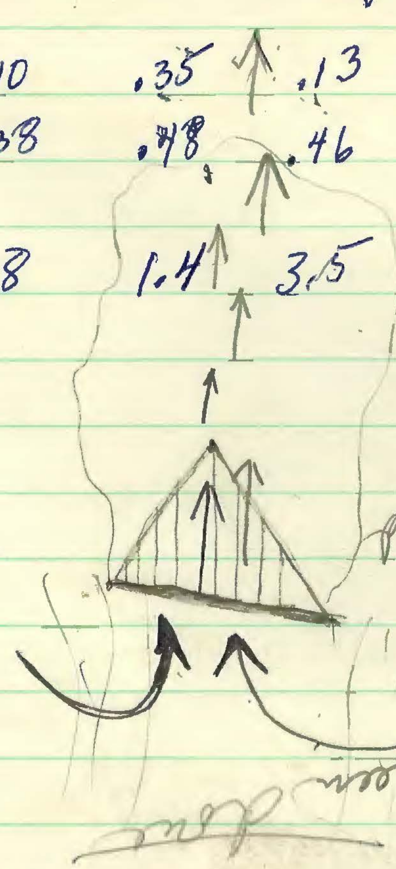
The results showed that there was an increase in the amount of manganese that was soluble, if the absence of oxygen is included. Even though there was an encrease, it was not contant. The increase was not contant in individual (in a small degree) tests and the test as a whole. This is shown on the last graph on page fifteen. The manganese should have a constant increase as the test progressed, but it did not. The could be due to the fact that there were unequal amounts of mud in each test tube. There could also be some unknown factors that have not been considered.

The experiment was a success in that it showed that manganese does become soluble under certain conditions. But it left in doubt the uniform rate at which the manganese does become soluble.

Manganese (ppm)

Depth (cm)	12/15/68	12/16/68	12/17/68	12/21/68	12/22/68	12/27/68	12/27/68	12/31/68	1/2/69	1/3/69
0.7	0.10 (~~0.40~~)	0.39	0.12	0.35 (~~0.66~~)	0.48	1.03	0.92	1.40	.81	.81
1.4	0.09 (~~0.36~~)	0.32	0.14	0.36	0.50	0.96	0.90	1.34	.80	.79
2.1	0.08	0.29	0.14	0.36	0.50	0.97	0.82	1.29	.79	.74
2.8	0.08	0.23	0.14	0.42	0.53	1.00	0.79	1.30	.80	.80
3.5	0.12	0.23	0.14	0.50	0.56	1.03	0.79	1.40	.80	.81
4.2	0.18	0.20	0.15	0.55	0.60	1.11	0.82	1.53	.89	.82
4.9	0.24	0.23	0.19	0.55	0.62	1.28	0.88	1.65	.96	.83 (~~1.02~~)
5.6	0.30	0.23	0.29	0.58	0.61	1.50	1.00	1.79	1.00	1.03 (~~1.10~~)
6.3	0.36	0.30	0.42	0.65	0.63	1.75	1.17	2.10	1.14	1.40
7.0	0.40	0.67	0.51	0.66	0.63	1.80	1.21	2.35	1.23	1.57
Average	0.19 (~~0.105~~)	0.31	0.22	0.50	0.57	1.24	0.93	1.62	.912	.965

.10	.35	.13	.35	.49	1.00	.91	1.37
.38	.78	.46	.66	.63	1.77	1.19	2.21
3.8	1.4	3.5	1.9	1.3	1.8	1.3	1.6



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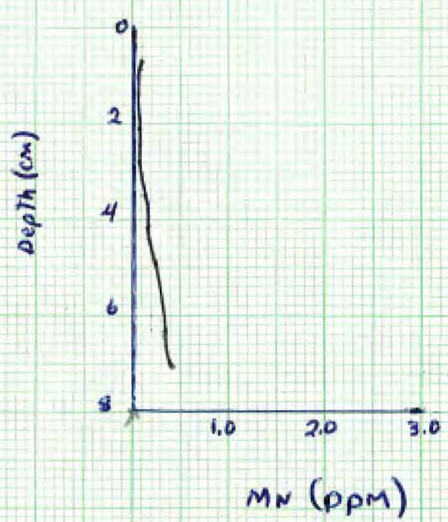

Date: 12/16/68

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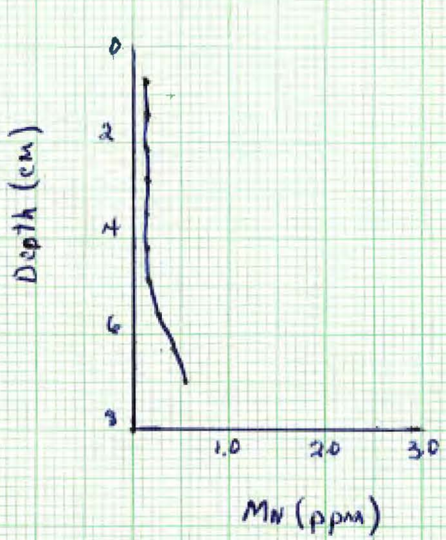

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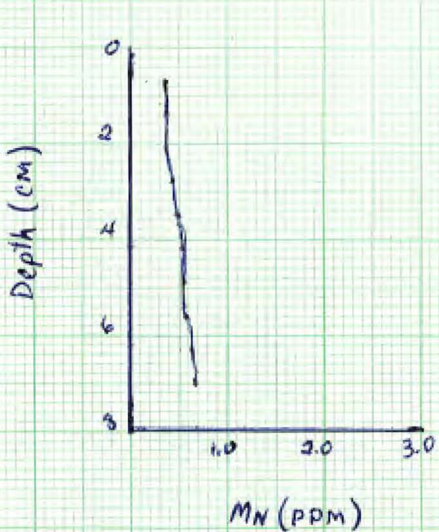

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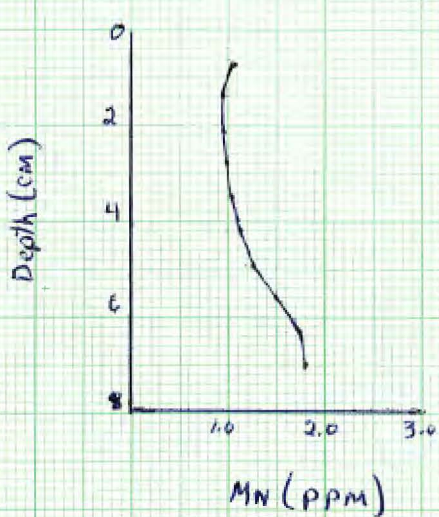

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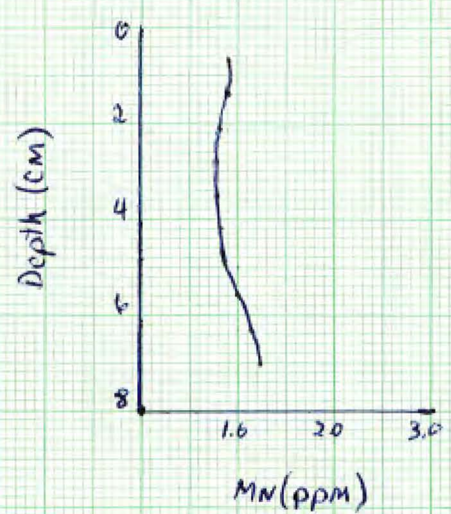

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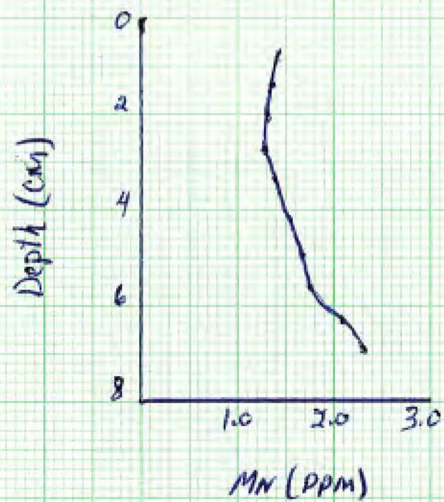

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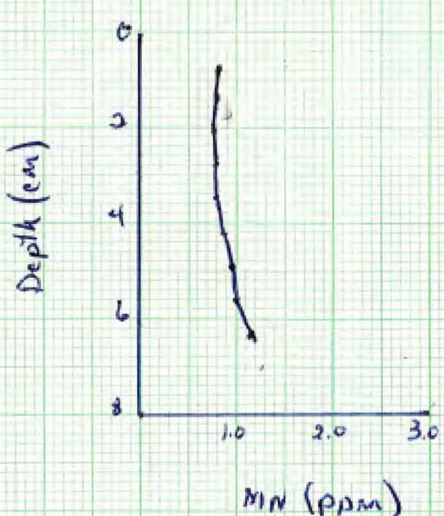

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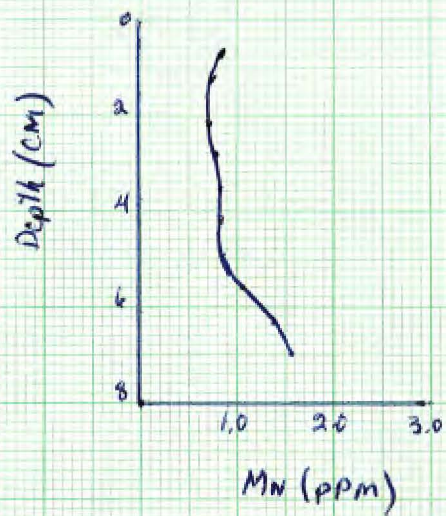
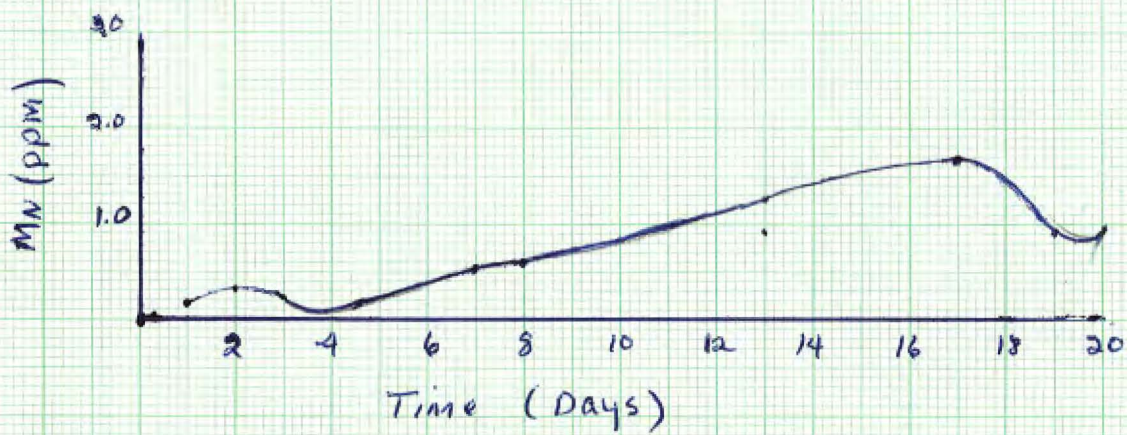


20 Squares to the Inch


3.0
2.0
1.0
Mn (ppm)
2
4
6
8
10
12
14
16
18
20
Time (Days)

1 "Manganese", *Influence of Impoundments on Water Quality*, (October 1964), 30-31.

2 Calvin P.C. Poon and Frank J. DeLuise, "Manganese Cycle in Impoundments Waters," *Water Resources Bulliten*, III (December 1967), 26-34.

3 Joseph J. Delfino and G. Fred Lee, "Chemistry of manganese in Lake Mendota, Wisconsin", *Environmental Science and Technology*, IV (December 1968), 1095.