A CHEMICAL INVESTIGATION OF THE WATER OF DEVILS LAKE, NORTH DAKOTA.

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This study of the composition of the water of Devils Lake, North Dakota, should prove interesting to the members of the Indiana Academy of Science, not only from the scientific point of view, but also because a former active member of the Indiana Academy was instrumental in establishing the State Biological Laboratory on the shores of this lake, where for a number of years many investigators were engaged in studying the unique biological conditions found in its waters.

The State Biological Laboratory was established in 1909 through the efforts of Dr. M. A. Brannon, then Professor of Biology and Dean of the School of Medicine at the University of North Dakota. It was maintained by the state, partly in the hope that through the researches carried on under the supervision of the University, it might be found possible to re-stock the lake with game fish. When Dr. Brannon left the state, the directorship passed to Dr. R. A. Young, the Assistant Director, who succeeded Professor Brannon as Head of the Department of Biology at the University. The laboratory was actively maintained until the session of the legislature in 1923 when the appropriations were discontinued and the property was transferred to the State Fish Commission.

The Devils Lake complex, comprising Main, or Devils Lake proper, Stump Lake, and a number of minor saline lakes, is the remnant of the old glacial Lake Minnewaukan. It lies in a region designated by Simpson[1] as the "Drift Prairie Plain" extending from the old glacial Lake Agassiz floor of the Red River Valley on the east to the Great Plains Plateau on the west, and occupies the southern portion of a drainage basin extending from the Turtle Mountains near the Canadian boundary to the ridge of high morainic hills which form its southern boundary.

The geological history of these lakes indicates plainly that the levels of the water in the past have been both higher and lower than the present level. A few decades ago the waters reached the limits of Devils Lake City which is now five miles from the nearest shores of Creel Bay. At that time Devils Lake received a considerable volume of relatively fresh water from the Mauvaise Coulee, the main stream of this drainage basin, which connected a number of minor lakes with the main lake and at certain seasons was a stream of considerable magnitude. In recent years it has become practically dry except during spring freshets. In 1911 Chandler[2] estimated the combined areas of the lakes of this complex to be 9,000 square kilometers. The steady recession of the lake is due to the fact that evaporation is exceeding the inflow of ground and

[1] H. E. Simpson, Physiography of the Devils-Stump Lake Region of North Dakota. N. D. Geological Survey, 6th Bien. Report, pp. 105-57, 1912.

[2] E. F. Chandler, The Red River of the North. Quart. Journal of the Univ. of North Dakota, Vol. I, pp. 227-55.

"Proc. Ind. Acad. Sci., vol. 34, 1924 (1925)."

surface waters. Doubtless the chief factor in reducing the flow of water into the lake has been the cultivation of the lands of the drainage basin.

The Indian name Minnewaukan, signified "Spirit Water", but this was corrupted by the white man into "Devils Lake". The region is romantic with Indian legends and traditions and rich in historical associations. On the high morainic hills forming the southern shore of the lake, General Sully fought his decisive battle with the Sioux. This site has recently been made a National Park. Nearby is the old Fort Totten Indian Reservation.

During the rapid recession of the lake, there has been a corresponding concentration of the salts in the water. Chemical analyses have been made at intervals since 1907. In 1907 the U. S. Geological Survey reported the total solids of Devils Lake water as 9,448.4 p. p. m. Seven years later Heath found 12,092 p. p. m. In 1918, King reported 14,452 p. p. m., and in 1923 Young reported 15,210 p. p. m.

In 1920, Paul T. Nerhus, then a graduate student in chemistry, made a detailed study of the solubility relations of the salts of Devils Lake water, under the personal supervision of the writer. His analyses showed the following percentage composition of the salts obtained by evaporation.

ANALYSIS OF SALTS FROM DEVILS LAKE.

Potassium	K	2.74	per cent
Sodium	Na	22.60	
Calcium	Ca	0.24	
Magnesium	Mg	4.87	
Iron and Aluminum	Fe and Al	0.05	
Silica	SiO_2	0.15	
Chloride	Cl	9.28	
Sulphate	SO_4	51.23	
Carbonate	CO_3	5.50	
Water of composition, organic matter, and undetermined		3.34	
		100.00	

The sample was collected under the ice after the long period of solar evaporation during the summer months, which accounts for the higher value of total solids found, 15,889 p. p. m.

It is apparent that the chief salts are sodium sulphate, (Glauber's salt), sodium chloride, (common salt) and magnesium sulphate, (Epsom salt). It thus differs strikingly from the composition of such western lake waters as those of Searles Lakes, California; Owens Lake, California; Dixie Salt Marsh, Nevada; and Jesse Lake, Nebraska, all of which are rich in chlorides rather than sulphates.

Mr. Nerhus and the writer studied the solubility relations of these salts from the point of view of the Phase Rule equilibria and found that the relationships were much simpler than those of sea water and other chloride waters. We were able to devise a procedure for the separation of the following salts in a state of purity: Mirabilite, Na_2SO_4, 10 H_2O, Astrakanite, $MgSO_4$. Na_2SO_4. 4 H_2O, Halite, NaCl, and Sylvite, KCl.

Solar evaporation is practicable in this climate and it possesses the advantage that it reduces the hydrolysis of the magnesium salts. For the final separation of the sodium and potassium chlorides artificial heat is required. The low cost of the process ought to make possible the economic recovery of the small amounts of potassium salts in this and similar saline waters under the condition of war-time prices.

But the chief interest in the chemical composition of the water lies in its relation to the flora and fauna of the lake. In the eighties Devils Lake is said to have abounded with fish, which have now disappeared except a single species of stickel back (*Eucalia inconstans*). Pickerel were caught in great abundance and ruthlessly destroyed by the fishermen. Young[3] has published a detailed report of the studies of the flora and fauna of the lake, covering a period of 14 years. In this report he states: "The reasons for the disappearance of fish from Devils Lake are probably primarily the increase in concentration of the lake water, and secondarily the loss of suitable breeding grounds for the pickerel, through the cutting off of the coulee which formerly flowed into Minnewaukan Bay, but which in recent years has only done so exceptionally. The ruthless destruction of the pickerel by the fishermen was probably a contributing cause, and there is some evidence (but very uncertain), from the accounts of early observers, of an epidemic among the fish."

"Since 1908 numerous experiments have been made in the introduction of various species of fish (chiefly yellow perch, (*Perca flavescens*) into Devils Lake, but without any permanent success, and on the tolerance of fish for several different salts in varying concentrations."

Concerning the stickel back, Young states further: "The stickel back occurs in both Main and Stump Lakes and probably in other lakes of the complex, as well as in the fresh waters. It was formerly common in Main Lake, but appears to be much less so at present. In the summer of 1914 several were found dying in the lake, *for a reason which could not be ascertained.* (The italics are the writer's). The temperature of the water at the time was not higher than probably occurs frequently in lakes where the stickel back abounds, and bacteriological examinations made a few hours after death gave no evidence of pathogenic bacteria in the fish."

"In 1912 also the stickel backs were found dead in large numbers on shore *in spring about the time of the opening of the lake. The cause of this fatality is also obscure.* It is possible, although it seems unlikely, that the fish may have been trapped in the ice and frozen to death. Lack of oxygen will hardly account for it, since it always appears to be ample through the greater part, at least, of the water stratum."

"In recent years their death has not been noted, although they appear to be present in considerably diminished numbers."

In his reports from time to time, Young describes experiments in which fish were placed in gradually increasing concentrations of Devils Lake water added to fresh water in the hope of acclimatizing them to tolerate the undiluted water of the lake, but these experiments were

[3] R. A. Young, Bulletin of the North Dakota Biological Station, 1924.

uniformly unsuccessful. Two theories apparently guided these investigations: (1) the theory that the death of the fish might be due to the higher osmotic pressure of the lake water, and (2) that some of the salts might exert a toxic action. He also placed fish in solutions of the individual salts occurring in Devils Lake with the highly remarkable results that in some cases the fish continued to live at *concentrations higher than the concentration of that specific salt in the lake, and in some instances at concentrations of the salt higher than the total salt concentration in the lake.* He concluded that although the individual salts when used separately were not fatal to the fish at such concentration the effect was probably to be ascribed to their combined action.

From the chemical point of view the conclusion reached from these experiments seemed very doubtful. It also seems improbable that fish could not be bred to tolerate the osmotic pressure prevailing in the lake which is much less than that of sea water. All of the facts noted above when considered together point clearly to the possibility that we may be dealing with a problem in chemical toxicology, and this suggestion was made. Although the station had been discontinued, and active biological work abandoned, the interest in this problem was such as to impel us to satisfy our chemical curiosity. Accordingly samples were collected in scrupulously clean glass vessels and were subjected to more minute chemical investigation, with the interesting result that about 15 parts per million of *zinc* were detected in the samples. The zinc was obtained both as sulphide and colorimetrically. The first sample was collected in May and an independent sample in September. Both samples gave practically the same results.

A few experiments were then made with small fish by placing a number of them in a solution of zinc chloride containing a concentration of zinc equal to that found in the lake. Some of them died in one hour and all of them were dead in less than 8 hours. Some of the same varieties of fish were placed in Devils Lake water and all of them died in a few hours. All of the control fishes lived many months after the conclusion of these experiments.

This search for zinc was suggested by the knowledge that a transcontinental railway which runs for many miles through the drainage basin uses railway ties which are treated with zinc chloride solution to delay decay. I am informed that this use of treated ties has continued for a number of years during which time many replacements have been made, and it is the practice of the company to burn the old ties on the right-of-way. The conclusion seems justified that some of this zinc chloride has found its way into the lake through the inflow of surface and ground waters.

Without presuming to minimize other factors which may be involved, we believe we have found the "Devil" in Devils Lake. This observation obviously opens up a field of interesting study for the biologist and biochemist in the investigation of the specific toleration of various species of flora and fauna toward dilute zinc solutions.