REVIEW OF RELATIONSHIP OF WILD RICE TO SULFATE CONCENTRATION OF WATERS

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INTRODUCTION

The question has been asked: Is it reasonable for the State of Minnesota to set an upper limit of 10 mg/l (ppm) sulfate ion for waters having natural stands of wild rice and receiving an industrial effluent containing sulfates. The limit referred to is in Section (d) (4) (A) of "Criteria for Classifications of Interstate Waters etc.". The specific situation is discharge of wastewater containing sulfates from the Clay Boswell Steam Electric Station at Cohasset, Minnesota. This station is operated by the Minnesota Power and Light Company. The Company considers the 10 ppm limit "unreasonable" and retained Dr. J.M. Stewart of the University of Manitoba, who has prepared a report on the situation.[10]

As a matter of background, the 10 ppm limit was placed in the Critera following a telephone call to me from someone (I do not remember whom) in the P.C.A. inquiring about water quality and wild rice. I said that there were no large and important natural and self-perpetuating wild rice stands in Minnesota where the sulfate ion content exceeded 10 ppm.

This is true, but it does not mean that there are <u>no</u> stands in which sulfates, at least at times, are higher. The upper limit for self-perpetuating stands in Minnesota appears to be about 40 ppm, with most of them usually below 10 ppm. The attached bar diagram (Figure 15 from a 1965 manuscript report by Mr. Roy Nelson of Minnesota D.N.R.) illustrates this. It is based upon field surveys by D.N.R. personnel of 283 lakes in which wild rice was found. It will be noted that about 90 percent of the areas with wild rice (mostly lakes) had waters in which the sulfate ion concentration was 10 ppm or less and that no "heavy yield" stands were found above 50 ppm.

An earlier compilation of data by myself (Moyle 1956) showed that the southern and western limits of the wild rice range in Minnesota coincided with the isoline (based on county averages) of 10 ppm sulphate[6] and, still earlier (Moyle 1945), data compliled as part of a Ph.D. study at the University of Minnesota showed a sulfate range of 2 to 36 ppm with a median of 4.2 ppm for northern wild rice (Zizania aquatica var. angustifolia) and 3.0 to 282.0 with a median of 21.2 ppm for giant wild rice (Z. aquatica)[5]. The 282 ppm site was a small stand in Marsh Lake near Montevideo that had probably been planted.

NATURE OF THE RELATIONSHIP

In Minnesota, because of geology, soils and climate, the concentration of dissolved salts in surface waters increases from northeast to southwest; there are soft carbonate waters in the northeast, hard carbonate waters in much of northern, central and southern Minnesota, and sulfate or "alkali" waters in the southwest and extreme west - see attached maps.[6] Each water type has an associated aquatic flora. Wild Rice is a typical hard carbonate water plant of northern and central Minnesota. It also grows in the soft carbonate water area, but usually not in very soft waters (those with a total alkalinity below 20 ppm.). Westward and southward it becomes increasingly scarce as sulfate concentrations increase. It is usually absent from waters with sulfates higher than 40 ppm. It is absent, and probably always has been, from the Minnesota River, which usually has about 200 ppm sulfates, and from the Red River, which usually is around 80 ppm.[11] The Pelican River, which flows through Becker County near the western edge of the natural wild rice range, has a sulfate ion concentration of about 16 ppm (range 10- 25). It has wild rice in it.[9]

Because of its value to waterfowl, wild rice has been planted in many lakes where it did not grow naturally. Plantings in waters higher than 40 ppm sulfates have had the usual history of producing some plants the first year, a few plants the second year, and none the third year. Conditions other than water chemistry may also be involved, such as a abundance of carp and competition from other water plants (such as cattails) and algae. As a general rule of thumb, used for many years, the D.N.R. has not recommended planting of wild rice in waters where the sulfates exceed 10 ppm.

A pertinent question is: Is the relationship between sulfate concentrations and wild rice cause-and-effect or coincidental, with both related to one or more other conditions? This is not easily answered for it probably entails both concentrations of sulfates with associated ions, such as calcium and magnesium, are not themselves toxic in the sense that they kill aquatic plants directly. At higher concentrations (several hundred ppm) sulfates probably have an adverse osmotic effect, upsetting absorptive and water-regulating systems of the plant. For example, it has been found that along the Atlantic coast, wild rice does not grow in brackish waters where the salinity exceeds 400 ppm.[12] Also it does not grow in North Dakota waters that have a high concentration of dissolved salts (carbonates, sulfates, and chlorides).[11]

Sulfate salts, however, differ from carbonates and chlorides in that the sulfate ion can be reduced by bacteria to hydrogen sulfide. This occurs under anaerobic conditions, either in water or in bottom soils. Hydrogen sulfide is a toxic gas and in water has long been known to be toxic to fish at low concentrations (under 1 ppm). There is a general rule among fisheries workers that if you can smell it in a water supply, there is too much.

In recent years careful analytical work at the University of Minnesota by Dr. Lloyd L. Smith and his graduate students has shown it to be toxic to fish eggs (walleye and northern pike) and to small crustacean or "scud" (Gammarus) in concentrations of less than 0.3 ppm.[1,2,7] A level of less than 1/10 of this (about 0.02 ppm) is considered to be "safe".

Similarly, hydrogen sulfide has recently been found to be toxic for domestic rice (*Oryza sativa*) in paddies of southern United States when concentrations are about 0.1 ppm in paddy soils.[8] Here an interesting and important relationship has been found. Hydrogen sulfide can be and often is, utilized by the anaerobic bacterium (Beggiatoa) and thereby removed from the soil, benefitting the rice. In turn the rice roots give off a substance that benefits the bacteria.

It has also been found by Smith and his students that little or no hydrogen sulfide is given off by submerged inorganic soils (such as sand and gravel) and that it is removed and dispersed by flowing water.

As related to wild rice, it seems likely that hydrogen sulfide may well inhibit the germinating of the seed or growth of young plants, but this remains to be investigated. It is known that the germination and growth is best in larger areas where there is wave action or in smaller areas where there is inflow of water. Planting is often done at such sites.

Finally, it should be emphasized that a small amount of sulfur is necessary for all life, it being an essential component of protein.

RECOMMENDATIONS

In view of the foregoing considerations and the fact that the wastewater from the Clay Boswell Station will be discharged into flowing water, it seems safe to set an upper limit on sulfates in the river water after mixing, of 20 mg/l. The concentration of sulfate ion from other sources in this stretch of the Mississippi River is usually between 7 and 12 ppm. Twenty ppm is within the range of sulfate known in Minnesota to be associated with self perpetuating stands, such as the rice in the Pelican River, Becker County.

It is my opinion that the upper limit of "at least 200 ppm" recommended by Dr. Stewart in his report is too high under Minnesota Conditions and may be injurious to wild rice stands downstream, especially in backwaters or where the water is pumped from the river for use in paddies.

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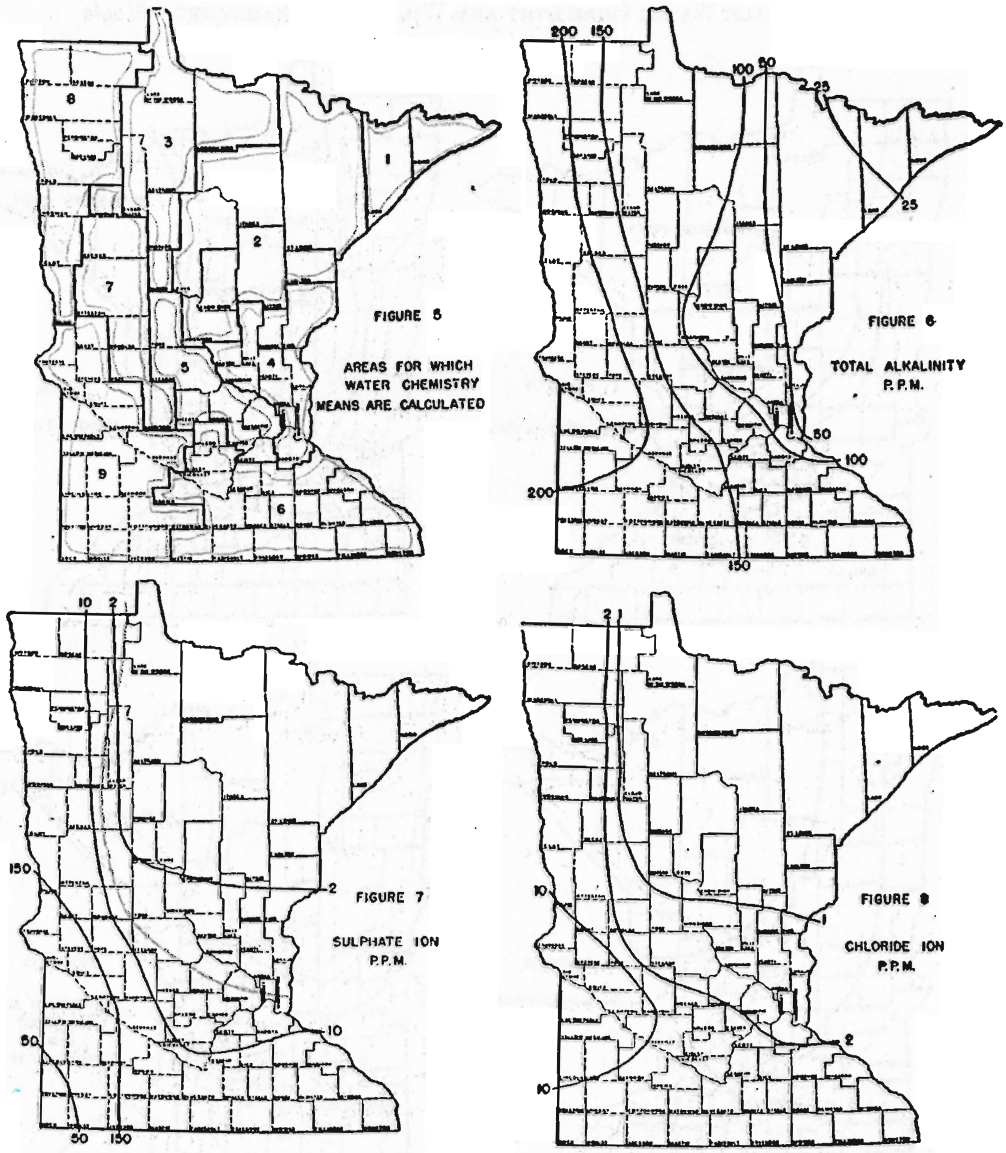

FIG. 5. Areas of similar water quality arranged in order of increasing salinity. FIGS. 6 to 8. Isolines of some chemical components of surface waters. See text for explanation.

sidered on a regional basis and means and medians of fairly large series used. Of these two kinds of averages, the median appears to be most representative of usual conditions in lakes of the series. The mean tends to be influenced by analyses from a few bodies of water in which salt concentrations are usually high or low. Except for analyses for total alkalinity, the means of series are usually somewhat larger than the medians.

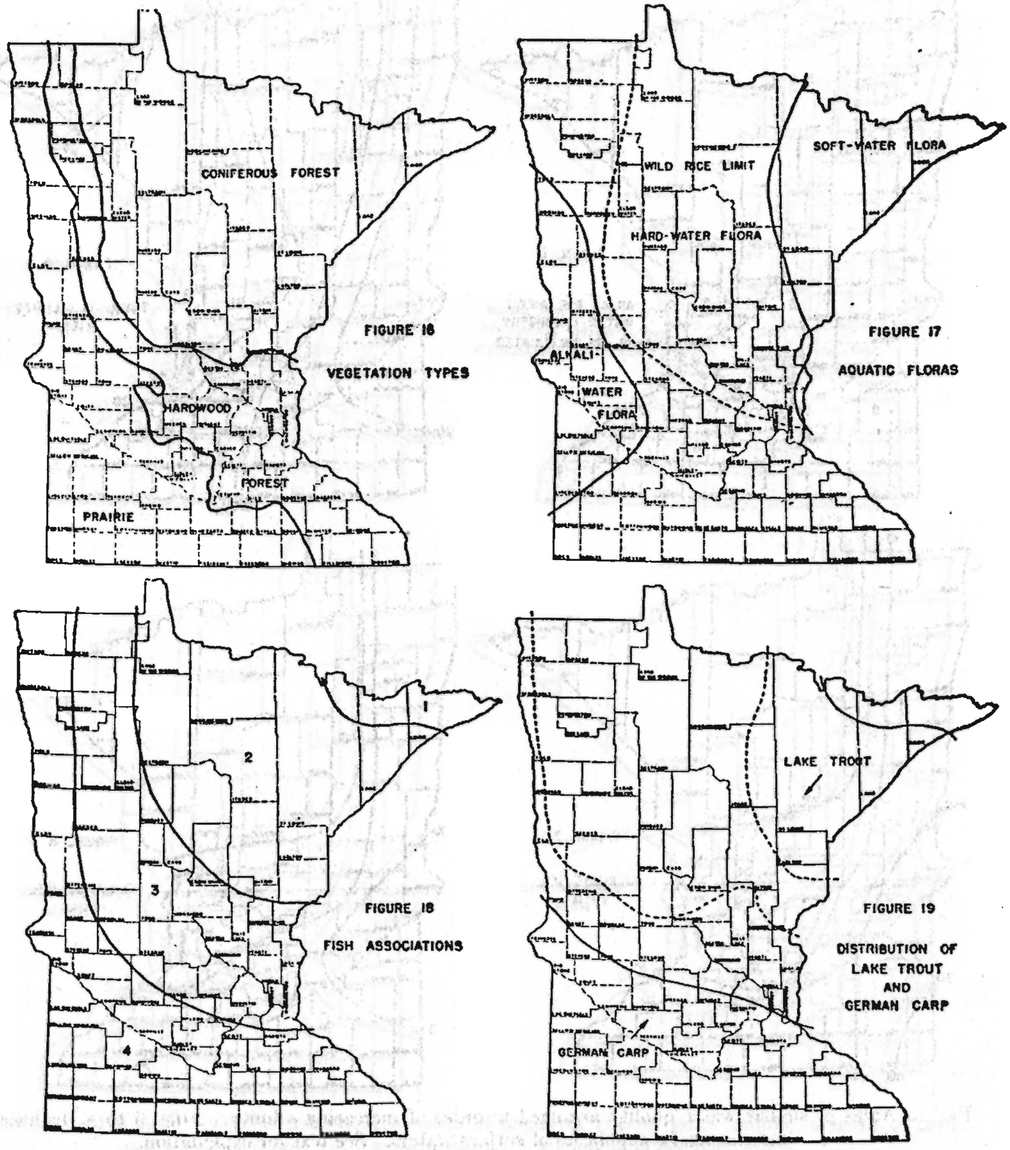

FIG. 16. Generalized plant geography of Minnesota. FIG. 17. Aquatic floras of Minnesota. Data from Moyle (1945). FIG. 18. Generalized original distribution of fish associations. FIG. 19. Ranges of lake trout and German carp. Solid line is principal range; broken line is limit of range.

ever, in most Minnesota waters is slight. Second, it should be remembered that although total alkalinity is expressed as calcium carbonate, a considerable portion of the carbonates may be and often is associated with metallic ions other than calcium; especially with magnesium. Calcium bicarbonate in pure water is soluble to the amount of 385 ppm at 59°F. (Clarke, 1924, p. 131) while calcium monocarbonate is soluble to the extent of 14 ppm at 77°F. (Hodgman, 1937). Sometimes, however, higher analytical results may be obtained because of suspension of limey material.