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PULP-MILL POLLUTION OF THE RAINY RIVER NEAR INTERNATIONAL FALLS, MINNESOTA

By

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Introduction

The effects of pulp and paper-mill effluents on river waters in the immediate vicinity of inlets carrying such wastes and in those portions of the stream where these wastes are still in high concentrations, that is, before extensive dilutions have been effected by the stream, are known to be definitely detrimental to fish and other aquatic life (Ellis, 1937, 1938). Studies of regions well downstream where these wastes are diluted and where fish may be present are of particular importance in determining the cumulative effects of diluted wastes. In the investigations of the Rainy River conducted during September 1938, evidences of gross pollution were for the most part confined to the sector immediately below the pulp mills at International Falls, Minnesota. Since the local citizens were of the opinion that the pulp mills killed few fish except in the portion of the river immediately below the mills, but persisted in the belief that the flavor of the fish caught from Rainy River was so changed by pollution that few of the fish taken from the stream below the mills were suitable for human consumption, particular attention was given to Rainy River between International Falls and Baudette, Minnesota.

After working in the vicinity of International Falls both above and below the two large pulp mills operated by the Ontario and Minnesota Paper Mills Company, the work was continued downstream westward along the south bank of the Rainy River. A base station was established at Baudette, Minnesota, and subsequently another base station was located on the shore of the west arm of Lake of the Woods to the north of Warroad, Minnesota.

Large numbers of logs are floated along Rainy River between Rainy Lake and the paper mills at International Falls. This use of the river constitutes a potential hazard to aquatic life since the flow of Rainy River is slowed near the international bridge at International Falls and thousands of logs accumulate in the back waters thus impounded. The color of the water of Rainy River just above the mills resembled weak coffee and was very similar in appearance to waters of streams that drain dense cypress swamps. Immediately below the mills the river water had a dull brownish color with an opaque cast due to the mixture of various wastes from the two pulp mills. Large quantities of foam floated on the surface of the river and a huge load of suspended fibrous material (wood pulp) was being carried by the lower water layers of the stream. At Baudette, 75 miles downstream from the mills the color and general appearance of the water of Rainy River was about the same as that of the water above the mills at International Falls, near the outlet of Rainy Lake.

For the field investigations a truck equipped with apparatus and reagents for the collection of water and biological samples and for water analyses was employed. Samples of various types were collected and returned to the Columbia (Mo.) laboratory for detailed assays and analyses.

Physical and Chemical Conditions

At the time of the survey in September 1938, the water temperatures ranged between 16° and 17° C. from Rainy River to Lake of the Woods, inclusive, and as no peculiar temperature differentials were noted at any of the stations the water temperatures may be dismissed with the above statement.

Similarly, with certain exceptions noted specifically, the dissolved oxygen values which were above 5 p.p.m. (parts per million) and therefore suitable for fish life (Ellis, 1937) throughout the stretch of river and lake between Rainy Lake and Lake of the Woods, inclusive, may be grouped in general as presenting no significant deviations from conditions favorable for fish life.

The determinations of hydrogen-ion concentration, specific conductance and carbon dioxide complexes, however, were more significant (table 1). In Rainy River, one half mile upstream from the mills at International Falls, the hydrogen-ion concentration (pH) was definitely on the acid side of neutrality, at pH 6.0 (± 0.2). This determination characterizes the waters in the impoundment of Rainy River above the dam at International Falls, therefore, as more acid than average unpolluted streams supporting good, fresh-water fish fauna (pH 6.7-8.5) as was shown by Ellis (1937). However, since many mountain streams and bog waters containing little in the way of soluble salts have hydrogen-ion concentrations of approximately pH 6.0 and still maintain an abundant stock of certain types of fresh-water fishes, the slightly acid condition of the waters of Rainy River above the mills is not significant in itself. The specific conductance of the waters from Rainy River above the mills was only 58.7×10^{-6} mho at 25°C. and indicates that this river was carrying a very small load of ionizable material above the mills. This same water contained 1.12 c.c. of free carbon dioxide per liter which is an average value for acidic streams supporting good fish populations. The fixed carbonates computed as carbon dioxide were even lower than was expected, approximately 4.08 c.c. per liter, and a calcium-carbonate hardness of 15 p.p.m. determined by the soap method which corroborated the other carbonate figures just given, marks this water as definitely "soft".

The above picture is definitely changed one-quarter mile downstream from the point of entrance of the pulp-mill effluents into Rainy River at International Falls, Minnesota (Station 1754.). The hydrogen-ion concentration increased from pH 6.0 to pH 4.75, a degree of acidity which is lethal to most fish, or if survived by them is detrimental to the gills and gastro-intestinal tract. The free carbon dioxide rose from 1.12 c.c, per liter to 13.9 c.c. per liter, a level definitely higher than that found in waters normally frequented by fish in good condition, and a quantity sufficient to produce impairment of several vital functions (including

TABLE 1. - Summarized average values for certain physico-chemical characteristics of waters at five of the major base stations, September 1938.

Locality number	Locality	Temperature degrees Centigrade: Air	Temperature degrees Centigrade: Water	pH	Specific conductance mho x 10^{-6} at 25°C.	Free carbon dioxide c.c. per liter	Fixed carbon dioxide c.c. per liter	Hardness parts per million $CaCO_3$	Tannic acid compound parts per million
1753	Rainy River, International Falls, off ferry landing one-half mile above mills.	23.0	16.4	6.0	59.7	1.12	4.08	15.0	±4.0
1754	Rainy River, International Falls, 100 yards below mill	23.0	16.7	4.8	112.1	13.90	4.08	43.0	±2.0
1755	Rainy River, International Falls, 1¼ miles below mill.	23.0	16.6	5.6	93.0	10.20	4.88	22.5	±2.0
1752	Rainy River, 1½ miles east of Baudette.	23.0	16.4	6.5	67.6	1.60	4.98	24.0	±3.0
1751	Lake of Woods, Warroad, 3 miles from shore.	21.8	17.0	6.9	131.8	0.67	10.75	72.5	0.0

respiration and heart action) of fishes surviving in such waters. The specific conductance was approximately doubled changing from 59.7 to 112.1 x 10^{-6} mho at 25° C. and the calcium carbonate hardness increased practically threefold, that is, from 15 to 43 p.p.m. These changes are of the type expected to result from the introduction of pulp-mill wastes and are particularly interesting in that they show the magnitude of the pollution which was produced at a time when the volume of the pulp-mill effluent was minimum.

About 1-1/4 miles downstream from the mills (Station 1755) the specific conductance fell to 93 x 10^{-6} mho at 25° C., the fixed carbonates to 4.88 c.c. of carbon dioxide per liter and the calcium carbonate hardness to 22.5 p.p.m., as the dilution of these effluents proceeded. The free carbon dioxide of these waters, however, remained high at a level of 10.2 c.c. of free carbon dioxide per liter with a pH of 5.6. These last two items indicate definitely extensive organic pollution in that portion of the stream.

The data just presented for Stations 1754 and 1755, that is, the sector of Rainy River just below the pulp mills at International Falls, Minnesota, were collected at a time when, according to the local mill people, the pulp mills were discharging the minimal amount of waste effluents. These samples were taken at that time for the specific purpose of obtaining a measure of the modifications in the physico-chemical complexes of the river water by the minimal effluent discharge. These data show an abrupt rise in the load of dissolved ionizable material, in the acidity and in the total free carbon dioxide of the waters of Rainy River after passing the outlets of the pulp mills at the time of minimal flow of effluents.

These changes in physico-chemical complexes constituted conditions unfavorable to lethal for fishes in a sector extending over 2 miles downstream from the openings of the effluent flumes. The waters of Rainy River, however, had readjusted as regards total acidity and free carbon dioxide at Baudette, Minnesota, some 75 miles downstream from the mills (table 1) at the time of these minimal flows.

When the outflow of the wastes from pulp mills increased the disturbances were observable further downstream in proportion to the increased volume of effluent outflow. At no time during this survey were marked disturbances of the physico-chemical complexes observed at Baudette, although the senior author was informed that occasionally changes in the color and odor of the river, presumably correlated with the sudden introduction of large amounts of pulp-mill wastes at International Falls, were noted at Baudette.

The physico-chemical measurements discussed in the foregoing paragraphs give little information concerning the organic load carried by the waters of Rainy River. The several wastes and wash waters from pulp mills contribute numerous organic constituents such as tannic acid, terpenes, pentosans, and furfural together with various organic and inorganic unsaturated compounds. Special tests for tannic acid and phenols were made and the oxidation-reduction curves plotted for the reducing substances collectively found in these waters.

The average tannic acid findings are listed in table 1, namely, about 4 p.p.m. of tannic acid (total tannic acid and tannates) were recovered from the impounded waters of Rainy River just above the mills. The tannic acid fell to ±2.0 p.p.m. after the river received the pulp-mill effluents; and rose again to ±3.0 p.p.m. at Baudette. Waters from Lake of the Woods, as tested, were free from tannic acid. As the tannic acid and tannates found in these waters are primarily derived from the bark of the logs and from certain of the wash waters leaving the pulp mills, the distribution of tannic acid and tennates was as expected. The actual amount of tannic acid found, although sufficient to contribute to the "woody" taste and odor of these waters, was insignificant as a lethal agent for fishes, since most fish can survive a concentration of 10 p.p.m. or more of tannic acid.

Phenol was not detectable, that is, was less than 0.001 p.p.m. in the water of the Rainy River above the dam at International Falls, before the introduction of pulp wastes. The waters of Lake of the Woods 3 miles offshore from Warroad, Minnesota, were also free from phenols. At International Falls, however, in the waters just below the mills approximately 0.1 p.p.m. was found at Station 1755, 1-1/4 miles below the mills, but only traces were detected in the waters at Baudette, 75 miles downstream. These quantities of phenolic compounds are trivial as affecting life of fish in this stream for at least 0.4 p.p.m. of phenol is required to affect most fish and some species can survive in waters carrying 10 p.p.m. or more. However, Demyanenko (1931) has shown that the flesh of fish living in waters containing small quantities of phenol develops a phenolic and tarry flavor which makes them undesirable for human food. We have confirmed the observations of Demyanenko in the U. S. Bureau of Fisheries Laboratory at Columbia, Missouri, using very small quantities of phenol. Consequently, even traces of phenol in the water may have significance in affecting the flavor of fish living in such waters.

The findings from the oxidation-reduction curves obtained in the studies of the waters are summarized below. Oxidizable material (both organic and inorganic reducing substances) was practically negligible in the water of Lake of the Woods, that is, the oxidation-reduction curves from the potassium permanganate studies of these waters were almost the same as those for distilled water. The waters of Rainy River above the dam, that is, in the impoundment carrying the floating log booms, showed a reducing action equal to 2.0 p.p.m. of dissolved oxygen. This oxygen demand was due largely to the organic extractives released from floating logs. Such an oxygen demand did not effect the oxygen supply of this river water to any noticeable extent.

Just below the entrance of pulp-mill effluents during the period of minimal effluent flow from the mills the amount of reducing substances rose abruptly to levels equivalent to more than 32 p.p.m. of dissolved oxygen. It is not surprising, therefore, to find the dissolved oxygen in portions of the stream just below the effluent outlets reduced to zero or seriously lowered whenever these effluents enter the stream in quantity. This condition of low dissolved oxygen following the action of the reducing

substances contained in the pulp-mill effluents may be effective for some distances downstream. As pointed out previously, the extent of the zone of low dissolved oxygen depends upon the interrelation of two major factors, namely, the stream flow from Rainy Lake and volume of effluents from the mills. Consequently the figures for samples collected at time of minimal effluent flow are particularly significant in pointing out the minimum size of the zone affected under average stream flow conditions.

At a time of minimum flow of the effluent the reducing substances in the Rainy River two miles downstream from pulp mills, although these effluents had been diluted in that distance, were still equivalent to 20 p.p.m. of dissolved oxygen which is a sufficient oxygen demand to produce a serious drain on the dissolved oxygen of the river for some distance farther downstream.

Bottom and Banks

Above the mills at International Falls the banks of Rainy River were clean and grassy and the bottom sandy with some mud. Just below the mills at the Itasca boat landing there was a fibrous mass of waste pulp 4 to 6 feet deep on the banks and the high water marks on the trees and bushes in this vicinity were conspicuously indicated by the large amounts of pulp fibers attached to them. The bottom of Rainy River at this station was composed of soft dark, foul-smelling mud covered with a furry mass of fibers which were aggregated on every available stick or stone. Bubbles of gas rose continuously from the bottom and a very disagreeable odor of decaying material permeated the air. At Station 1755, about 1-1/4 miles below the mills, practically the same bottom and bank conditions existed although conditions were not so extreme.

By the time the river reached Station 1752, near Baudette, the bottom and bank seemed reasonably free of fibrous material or other debris suggestive of pulp-mill pollution. Local residents and fishermen along the Rainy River stated that at various times during the year and apparently without warning large masses of decomposing pulp having the appearance of "coming up from the bottom" moved down the river past Baudette. This is precisely what can be expected in view of the disposition of the pulp-fiber masses on the bottom of Rainy River in the sector below International Falls.

Pulp that escapes from pulp and fiber mills is one of the greatest pollution hazards. Most concerns find it uneconomical to waste pulp because it can be salvaged easily from the waste waters by the use of proper screens. If allowed to escape as it is at the International Falls mills, waste pulp blankets the bottom of the river and kills important food organisms; pulp fouled with mud harbors a variety of noxious bacteria; the slowly decomposing pulp creates a high oxygen demand which depletes the water of oxygen necessary for the proper maintenance of fish and other organisms. The decomposing pulp also liberates large quantities of carbon dioxide and other harmful gases. At times the combined action of these gas bubbles and the river current detaches large masses of the foul material so that the river may be polluted temporarily for many miles below the actual pulp deposits. This type of temporary pollution has been seen repeatedly by the writers in various streams throughout the country particularly in Maine and Wisconsin

where pulp-fiber mills were operating. Therefore, although the deposits of waste pulp in the Rainy River region were found for the most part on the bottom or banks of the sector extending a few miles downstream from International Falls, these same masses of polluted and decomposing pulp as our field studies in this region demonstrate, can become detached at any time and pollute the Rainy River throughout its length below International Falls and may be carried out at times even into the east arm of the Lake of the Woods.

Toxicity of Effluents

The immediate toxicity to fish of the various wastes leaving pulp mills and the oxygen demands of such wastes have been studied repeatedly so that the findings need not be reviewed here (Ellis, 1938). It is important, however, to point out that some pulp-mill wastes may have an oxygen demand of 8,000 p p.m. of dissolved oxygen or greater. Depending upon the kind of wood used, the amount of wash water added and other variable factors in the plant operations, the oxygen demand of wastes from the same plant may be very low at times. The effluents from the mills at International Falls were no exception to these general statements.

Tests in the laboratories of the U. S. Bureau of Fisheries at Columbia, Missouri, have shown that various pulp-mill wastes must be diluted approximately 1:1000 if the toxicity of the wastes is to be reduced so that the major danger of immediate death to fish exposed to these wastes is to be avoided. However, additional tests demonstrate that dilutions as great as 1:100,000 may be harmful. The effluents from the International Falls mills should be diluted therefore not less than 1:1000 if the hazard of immediate lethality is to be avoided. This statement does not mean that all danger would be averted, however, even by that dilution.

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SUMMARY

From the field studies of the pulp-mill pollution in the sector of Rainy River below International Falls and from the supplementary analyses made at the Columbia (Mo.) laboratories of the U. S. Bureau of Fisheries the following statement can be made:

1. The waters of Rainy River upstream from International Falls, Minnesota; that is, above the pulp mills, are very soft, very poorly buffered, slightly acid waters and therefore very susceptible to chemical pollution.

2. At International Falls typical pulp-mill pollution was found in the Rainy River, resulting from the introduction of the effluents from the mills of the Ontario and Minnesota plants.

3. The pollution of the Rainy River was of major proportions; that is, the physico-chemical balances of the stream were definitely disturbed to a point dangerous to fish and other aquatic life in a sector from 2 to 5 miles in extent downstream from the mills at the time of minimal effluent discharge. This sector in which the physico-chemical conditions of the waters were disturbed extended proportionally farther downstream when larger quantities of effluent were being discharged.

4. Pulp-fiber pollution was extensive and severe in a sector of Rainy River extending 2 to 5 miles downstream from International Falls, Minnesota. The decomposing waste pulp in this sector also constituted a serious potential pollution hazard to the entire Rainy River from International Falls to the Lake of the Woods.

5. The undesirable flavor of the flesh of fish living in the lower sectors of the Rainy River below the mills at International Falls is due to a combination of factors. Most important is the absorption of unpleasantly flavored substances both from the liquid effluents of the pulp mills and from the decomposition products of the disintegrating waste pulp fiber. The poor flavor of the fish in this river is therefore directly traceable to the pulp-mill pollution.

Recommendations

1. The effluents of the pulp mills at International Falls should be diluted at least 1:1000 by using larger quantities of flushing water drawn from the impoundment above the plant.

2. Proper screens should be installed to exclude as completely as possible all pulp fiber from the Rainy River.

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