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POLLUTION STUDIES RELATED TO WAR INDUSTRIES

By

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Industrial trade wastes have long been a menace to our public waters. Today more than ever before, our lakes and streams are in danger of being polluted by these wastes. New types and larger quantities of pollutants are being produced by the expanding war industries. Since June of 1942 the Institute for Fisheries Research in cooperation with the Stream Control Commission and certain other industries has been engaged in the investigation of several types of trade pollutants. A series of experiments have been undertaken primarily to determine the toxicity of these wastes to fish life, so that by appropriate methods or regulations, serious pollution may be avoided or prevented. And secondarily, to determine facts that may be useful in working out methods of waste treatment. A contribution has also been made to the standardization of methods for the determination of the effects of pollution on fish life.

The methods and techniques involved in these experiments consisted in the selection of suitable test fish and the testing of these fish in various concentrations of each waste until the consistent toleration limit was determined. Consistent toleration limit is a term used to designate a maximum concentration at which all of the test fish will tolerate.

These fish toleration experiments involved the products of 3 industries. The first dealt with treated cyanide products; the second involved wastes from the styrene process for the manufacture of synthetic rubber, and the last pertained to Michigan oil well brines.

Large quantities of cyanide compounds are being used by war industries and the disposal of these cyanide wastes present a

serious pollution menace. Minute quantities of cyanide (less than 1 p.p.m.) are lethal to aquatic life. An economical and safe method of disposal or treatment of these wastes has long been sought. Several types of treatment designated to reduce the toxicity of these wastes have been proposed. The latest proposal comes from the I. E. du Pont de Nemours Company of Niagara Falls. Chemists of the du Pont Company have developed a process of treating various cyanide compounds with an excess of calcium polysulfide, which changes the cyanide to thiocyanide. Our problem was to determine the relative toxicity of cyanide and thiocyanide, and to test the toxicity of cyanide wastes and industrial effluents resultory from treatment with polysulfide.

With the supervision and help of Dr. Carl L. Hubbs and the advice and planning of Dr. Albert S. Hazzard, the toxicity experiments were undertaken. Two species of fish were used in these tests - the pumpkinseed and the creek chub. The basis for computing the toxicity of the treated cyanide wastes was in terms of the amount of NaCNS present in each. After establishing the toxicity thresholds for the two species of fish with pure NaCNS, it was a simple matter to compute the percentage of toxicity of each waste in terms of NaCNS content.

Three treated cyanide products were tested for relative toxicity. In terms of the NaCNS content, the consistent toleration limit for the pumpkinseed and the chub were 400 and 600 ppm. Eighty per cent of the toxicity of a treated cyanide waste could be accounted for in terms of NaCNS, only 11.9% of the toxicity of a treated carburizing salts solution and only 1.4% of a treated copper plating solution. Other toxic substances were obviously present.

It was noted during the course of the tests that a whitish precipitate was brought down, which proved to be monclinic sulfur. Apparently a break down of the excess polysulfide had been effected by aeration of the test solutions. This observation led to a modification of the treatment method and new additional tests. The treated wastes were first pre-aerated for 24 hours to remove all of the excess polysulfide, then filtered and tested for toxicity. After this treatment we could ascribe to the NaCNS 100% of the toxicity of sodium cyanide solution; 80% of the toxicity of the treated carburizing salts solution and 12.5% of the toxicity of the copper plating solution. It was suspected that the high toxicity of the copper plating solution was due to the presence of copper. The chemists had not considered the possibility that copper was present in this treated waste, but after our tests were concluded, they found copper was present in sufficient quantities to explain the residual toxicity which we had found.

These toxicity tests revealed that the polysulfide treatment of cyanide wastes very greatly reduce the toxicity, the resulting

thiocyanide radical is indicated to be approximately 1,000 times less toxic to fish than is the cyanide radical (as previously determined). It was also shown that any residual calcium polysulfide is toxic, but easily removed.

I would like to add that additional toxicity tests are to be run in the near future to determine the effect of these treated wastes on activated sludge in sewage disposal plants. Dr. Carl L. Hubbs and Mr. John Greenbank will conduct this project in cooperation with the I. E. du Pont de Nemours Company.

The second type of industrial waste to be tested were those derived from the manufacture of synthetic rubber. The Dow Chemical Company of Midland, Michigan is planning large scale operations of a synthetic rubber plant. As a prelude to a safe disposal program for the wastes involved in this type of manufacture, fish toleration tests were necessary. We were supplied by the company a set of samples, representative of the wastes to be encountered in this type of manufacture. These samples consisted of 5 different types of wastes, namely: 1. Mixed waste waters; 2. Ethylene waste; 3. Styrene still condensate; 4. Ethyl Benzene HCl Scrubber; and 5. Ethyl Benzene Composit wash.

The smallmouth bass and the black bullhead were used as test fish. As before, the toxicity was expressed in terms of consistent toleration limit. Four of the five wastes proved lethal to the bass and three of the five for the bullhead. Of the five wastes, Ethyl benzene HCl scrubber and the ethly benzene composite wash were found to be the most toxic, requiring dilutions of 1 to1100 and 1 to 1000. Both of these wastes were the only wastes which were acid in reaction, Ethyl benzene HCl scrubber containing approximately 15% HCl. Chemists of the Dow Chemical Company suggested that these wastes be neutralized before testing. Their suggestions were followed and additional toxicity tests run. The results with the neutralized Ethyl Benzene HCl scrubber were most gratifying. Instead of a 1 to 1100 dilution to render it non-toxic, a 1 to 15 was used, which represented a reduction in toxicity of 90 times. Complications were presented by the neutralization of the last waste. This waste contained a high concentration of $Al\,Cl_3$ and upon the addition of NaOH, a heavy precipitate of $Al(OH)_3$ resulted. This required the filtering and separate testing of the supernatant and the precipitate. However, the results indicate that treatment by neutralization is practical. The toxicity was reduced about 60 times. Formerly a 1 to 1000 dilution was required, after treatment only a 1 to 16. The consistent toleration limit was based on the average of the toleration limits separately determined for the supernatant and the precipitate. The bullheads were approximately twice as resistant to the toxic substances in these wastes as were the bass. By neutralizing the last two wastes, all 5 wastes can be rendered tolerable by a 1 to 20 dilution. It should be emphasized however, that this dilution does not include

a margin of safety. Other fish may be more susceptible than those tested.

The last series of tests concern Michigan oil-well brines. Many oil fields in Michigan are associated with brine areas and during exploration and oil pumping operations, large quantities of brine are allowed to escape into public waters, which constitutes a serious pollution menace. It is hoped that the results of these toleration tests conducted with Michigan oil-well brines will help to solve this problem of safe brine disposal. The samples used in these tests were obtained from a brine well in the east central part of the state. Chemical analyses reveal this to be concentrated brine containing over 300,000 p.p.m. of salts of which roughly 92% were chlorides.

Seven species of fish were used in these toleration tests. Four are warm water species: bullheads, smallmouth bass, pumpkinseed and brook stickleback. Three are cold water ones: brook trout, brown and rainbow trout. The warm water forms were tested at a termperature range comparable to summer conditions; the trout were tested under cooler conditions - 50°F.

The three species of trout were found to be capable of tolerating two to four times as strong a concentration of brine as the four warm water fishes could stand. They were about twice as resistant as the bullheads and four times as tolerant as the bass, the pumpkinseeds and sticklebacks falling in between this range. At first thought this was a most unexpected result for trout are always regarded as among the most susceptible of all fishes to pollution. There is, however, a biological reason for the high tolerance of the trout to chlorides. All or almost all Salmonidae are euryhaline fishes, for those which live near the coast migrate back and forth between salt and fresh waters and possess some mechanism which enables them to become adjusted to difference in salinity. The warm water species studied are strictly fresh water fishes and for this reason presumably lack the ability of the Salmonidae fish to tolerate salt water.

The Consistent Toleration Limit Expressed in P.P.M. of Chlorides for the 7 Species of Fishes Are:

Brook trout	23,000 to 24,000
Brown and rainbow trout	20,000 to 21,000
Bullhead	11,000 to 12,000
Stickleback	8,000 to 9,000
Pumpkinseed	8,000 to 9,000
Smallmouth bass	5,000 to 6,000

An alternative explanation for the greater tolerance of the trout to brine would be that they were tested at 50° F. whereas the warm water species were run at 80° F. It is a physiological principle that fishes become more susceptible to pollutants at higher temperatures for the metabolic rate rises with the increase of temperature.

To check the possibility that the relative greater resistance of trout to brine was due to the fact that they were tested in cold samples, experiments were conducted as to the resistance of the bullheads to brine when kept at 80° F. and at 50° F. The results of these tests indicate that there is no apparent differences in toleration as the consistent toleration limit was the same at both temperatures.

The fact that the creek which receives the brine studied has been ruined as a trout stream, and the fact the smaller yearlings tested, died earlier than the larger ones in each test, have suggested that the critical effect of the brine may be on some early stage in the development of the trout. Preliminary tests indicate that eggs and sac fry are about twice as susceptible as yearling trout.

It is gratifying to receive indications that the results of these researches will help industries in the safe disposal of wastes and will aid the proper authorities in the regulation of pollution.

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