The Use of Alkalinity and Conductivity Measurements to Estimate Concentrations of 3-Trifluormethyl-4-Nitrophenol Required for Treating Lamprey Streams.

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THE USE OF ALKALINITY AND CONDUCTIVITY MEASUREMENTS TO ESTIMATE CONCENTRATIONS OF 3-TRIFLUORMETHYL-4-NITROPHENOL REQUIRED FOR TREATING LAMPREY STREAMS.

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‘THE USE OF ALKALINITY AND CONDUCTIVITY MEASUREMENTS TO ESTIMATE CONCENTRATIONS OF 3-TRIFLUORMETHYL-4-NITROPHENOL REQUIRED FOR TREATING LAMPREY STREAMS.

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ABSTRACT

A method has been devised to estimate the minimum concentration of TFM that will kill sea lampreys and the maximum that will not kill fish. It is based on the relation of these concentrations to the alkalinity and conductivity of various waters. Pretreatment bioassays will continue to be required for precise determination of treatment concentrations, but the estimates made possible by the method will permit a great reduction in the number of bioassays on a single stream.

Introduction

The selective sea lamprey larvicide, 3-trifluormethyl-4-nitrophenol (TFM) , has been used extensively by the U.S. Bureau of Commercial Fisheries and the Fisheries Research Board of Canada in the experimental program of sea lamprey control. The toxicity of TFM is influenced strongly by chemical and physical properties of water. As pH, conductivity, and alkalinity increase, the amount of TFM required to kill larval lampreys and rainbow trout increases (Applegate, Howell, Moffett, Johnson, and Smith, 1961). Consequently, the amount of toxicant required and the degree of selectivity of TFM between lamprey larvae and stream fishes vary from stream to stream and also with season and location within the same stream system (Howell and Marquette, 1962). This variability in toxicity necessitates the performance of bioassays prior to each larvicide application to determine the minimum concentration of TFM required to kill all lamprey larvae and the maximum concentration that can be used without causing significant fishmortality.

‘This report describes a method for the preliminary estimation of minimum lethal and maximum allowable concentrations of TFM. It is based on records of the relation of these treatment concentrations to the alkalinity and conductivity of the water. The estimation of biological activity of TFM by its relation to properties of water will not supplant the bioassays prior to treatments but will reduce the total number required.

The term "minimum lethal concentration" refers to the lowest concentration of TFM that kills 100 percent of the lamprey larvae in 9 hours or less, and the term "maximum allowable concentration" refers to the highest concentration of TFM that does not kill more than 25 percent of the fish in 18 to 24 hours. These two concentrations may be termed the limiting concentrations of TFM.

Materials and Methods

Data for this report were obtained from bioassays made in conjunction with chemical treatments of streams tributary to the U.S. shore of Lake Superior and the north and west shores of Lake Michigan in 1960-62.

The methods of bioassay, all carried out in mobile laboratories, were described by Howell and Marquette (1962). Phenolphthalein alkalinity and total alkalinity by the methyl-purple indicator method were determined for all bioassay test waters according to the procedures in the 11th edition of "Standard Methods for the Examination of Water and Wastewater" (1960). The results were recorded as parts per million (mg./1.) $CaCO_3$. Conductance was measured at 20° C. (68° F.) with a manually operated, A.C. conductivity bridge[1]; results were recorded in micromhos.

Relation of Water Properties to the Limiting Concentrations of TFM

Alkalinity

Alkalinity values ranged from 13 to 122 ppm $CaCO_3$ for Lake Superior and from 16 to 196 ppm $CaCO_3$ for Lake Michigan tributaries. Records for the two groups of tributaries were combined since no difference could be found between them in the relation between alkalinity and the limiting values of TFM. Only alkalinities up to 165 ppm are considered in this report due to the scarcity of data between 165 and 196 ppm. Alkalinity values were grouped by intervals of 10 ppm (10-19, 20-29, 30-39, . . .) and the means of the minimum lethal and maximum allowable TFM concentrations computed for each group (Table 1). The plot of the regression of the limiting

1 Industrial Instruments, Model RC-16B2, conductivity bridge.

Table 1. - Relation between alkalinity and limiting concentrations of TFM in tributaries of Lakes Superior and Michigan

[Computed values obtained from equations given in text; data shown graphically in Figure 1.]

Alkalinity (ppm CaCO3)		Number of	Minimum lethal TFM (ppm)			Maximum allowable TFM (ppm)		
Interval	Mean	bioassays	Computed	Actual	Difference	Computed	Actual	Difference
10- 19	16.3	10	1.2	1.0	-0.2	2.4	2.3	-0.1
20- 29	24.7	10	1.5	1.2	-0.3	3.2	3.1	-0.1
30- 39	34.4	14	1.8	1.7	-0.1	4.1	4.5	0.4
40- 49	45.4	26	2.2	2.1	-0.1	5.1	5.5	0.4
50- 59	55.1	18	2.5	2.5	0.0	6.0	6.0	0.0
60- 69	64.8	18	2.9	2.8	-0.1	6.9	5.9	-1.0
70- 79	74.8	25	3.2	3.4	0.2	7.8	7.8	0.0
80- 89	83.2	12	3.5	4.0	0.5	8.6	8.2	-0.4
90- 99	94.5	13	3.9	4.0	0.1	9.6	8.9	-0.7
100-109	105.0	19	4.3	4.7	0.4	10.6	10.9	0.3
110-119	115.3	6	4.6	4.3	-0.3	11.6	12.8	1.2
120- 129	122.2	5	4.9	5.5	0.6	12.2	12.6	0.4
130- 139	134.9	7	5.3	5.3	0.0	13.4	13.4	0.0
140-149	148.0	2	5.8	6.0	0.2	14.6	14.0	-0.6
150-159	157.0	3	6.1	4.7	-1.4	15.5	14.3	-1.2
160-169	163.0	5	6.3	6.7	0.4	16.0	17.0	1.0

concentrations of ‘TFM on alkalinity indicated a straight-line relation (Fig. 1). The fitting of lines by least squares gave the equation C_l = 0 0.035A + 0.6 for the minimum lethal concentration and the equation C_h = 0.093A + *0.856* for the maximum allowable concentration. In these equations C_l and C_h refer to the lower and higher limiting concentrations (ppm) of TFM and *A* to alkalinity. Each equation fitted the original data satisfactorily.

Conductivity

Conductivity values ranged from 42.5 to 265.0 micromhos (at 20° C.) for Lake Superior tributaries and from 60.6 to 413.0 micromhos for Lake Michigan tributaries. Only Conductivities up to 278 micromhos are considered in this report since few waters had higher values. Conductivity values were divided into 20-micromho groupings (40-59, 60-79, 80-99, . . .) and the means of minimum and maximum TFM concentrations obtained from corresponding bioassays were determined for each group. With conductivity as with alkalinity, it was possible to combine the data for the Lake Superior and Lake Michigan tributaries (Table 2) . The plot of the data again indicated a straight-line relation (Fig. 2). Equations fitted by least squares were C_l = 0.022M - 0.12 for the minimum lethal and C_h = 0.053M - 0.379 for the maximum allowable concentrations; C_l and C_h are the same as in the previous equations and M refers to conductivity. As was true for alkalinity, the equations fitted the data most satisfactorily.

Dependability of Estimates of Limiting Concentrations

The data presented on the regression of TFM and alkalinity and conductivity clearly indicated possible usefulness of the estimates in the planning of bioassays, but judgment of the dependability of estimates could not be based on deviation of means from the regression. Dependability is better indicated by the distribution of the deviations of individual estimates from the true limiting concentrations obtained from bioassay. The distributions of errors of estimate are tabulated for the minimum lethal concentration (Table 3) and the maximum allowable concentration (Table 4) by selected intervals of TFM concentrations.

For minimum lethal concentration (Table 3), tests within the range of + 3 ppm of the estimate seem almost certain to include the true minimum. If a lower probability averaging 97-98 percent is acceptable, testing within the range of + 2 ppm will suffice. At the lower estimated concentrations of TFM even smaller testing ranges can be accepted.

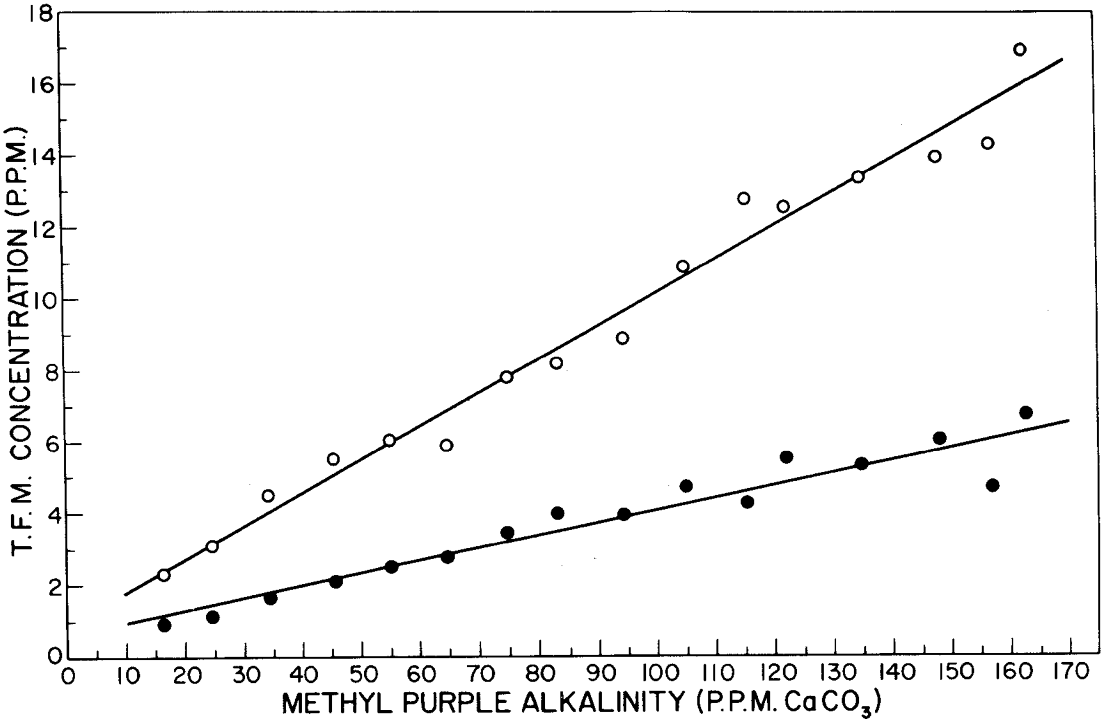

Figure 1. Relation between alkalinity and the minimum lethal (lower regression line) and maximum allowable (upper regression line) concentrations of TFM. The plotted points represent averages for groupings by intervals of alkalinity measurements (solid circles for minimum and open circles for maximum).

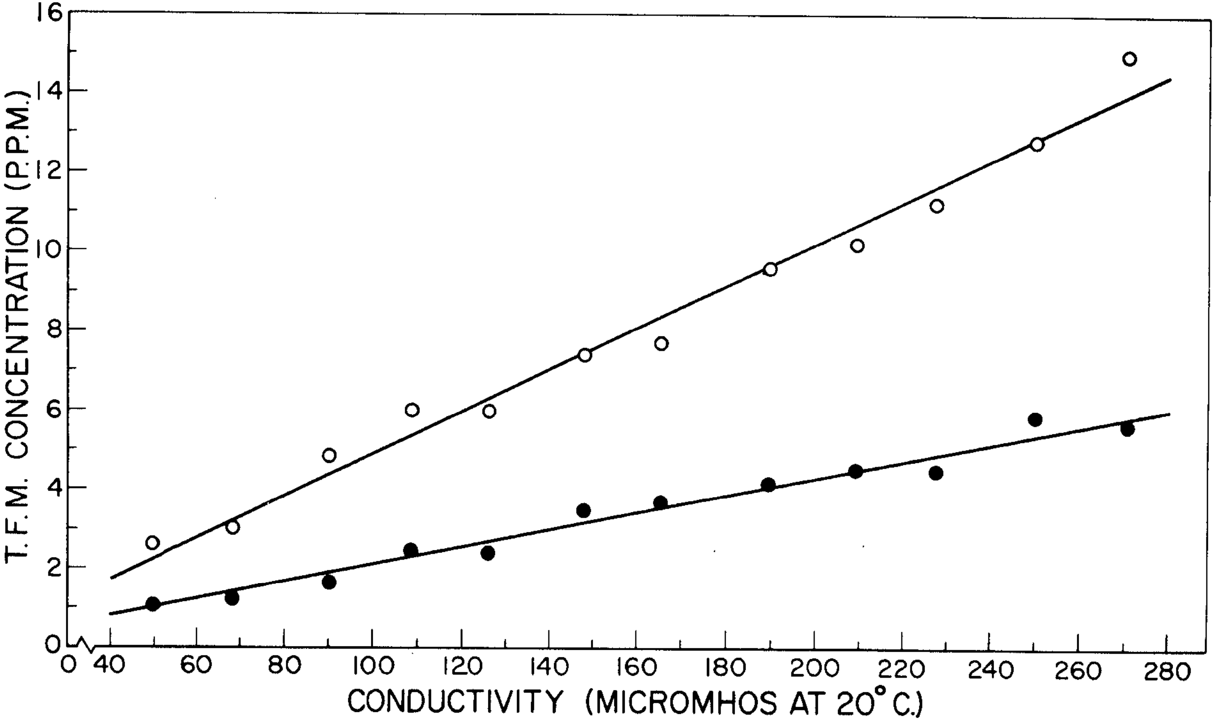

Figure 2. Relation between conductivity and the minimum lethal (lower regression line) and maximum allowable (upper regression line) concentrations of TFM. The plotted points represent averages for groupings by intervals of conductivity measurements (solid circles for minimum and open circles for maximum).

Table 2. - Relation between conductivity and limiting concentrations of TFM in tributaries of Lakes Superior and Michigan

[Computed values obtained from equations given in text; data shown graphically in Figure 2.]

Conductivity (micromhos)		Number of bioassays	Minimum lethal TFM (ppm)			Maximum allowable TFM (ppm)		
Interval	Mean		Computed	Actual	Difference	Computed	Actual	Difference
40- 59	49.9	10	1.0	1.0	0.0	2.3	2.6	0.3
60- 79	68.5	15	1.4	1.3	-0.1	3.3	3.1	-0.2
80- 99	90.2	21	1.9	1.7	-0.2	4.4	4.8	0.4
100-119	108.8	16	2.3	2.4	0.1	5.4	6.0	0.6
120- 139	126.3	22	2.7	2.5	-0.2	6.3	6.0	-0.3
140-159	148.1	22	3.1	3.4	0.3	7.5	7.4	-0.1
160-179	165.4	20	3.5	3.6	0.1	8.4	7.7	-0.7
180- 199	189.7	14	4.1	4.1	0.0	9.7	9.6	-0.1
200-219	209.4	20	4.5	4.5	0.0	10.7	10.2	-0.5
220-239	227.4	12	4.9	4.5	-0.4	11.7	11.2	-0.5
240-259	250.2	4	5.4	5.8	0.4	12.9	12.8	-0.1
260-279	270.8	8	5.8	5.7	-0.1	14.0	15.0	1.0

Table 3. - Relation between minimum lethal concentrations of TFM as estimated from regression and as determined by bioassay

Method of estimation and range of TFM values (ppm)	umber of bioassays	Percentage in which bioassay result differe[1] fro estimate by less than				
		0.5 ppm	1.0 ppm	1.5 ppm	[illegible].O ppm	3.0 ppm
Alkalinity						
0.5 - 1.4	15	87	100	...	...	...
1.5 - 1.9	21	76	95	100	...	...
2.0 - 2.4	30	57	87	93	100	...
2.5 - 2.9	27	63	85	100	...	...
3.0 - 3.4	33	45	76	91	100	...
3.5 - 3.9	17	47	65	88	94	100
4.0 - 4.4	23	39	61	74	96	100
4.5 - 5.4	17	35	65	82	94	100
5.5 - 6.4	10	20	40	70	80	100
Mean	...	53	77	90	97	100
Conductivity						
0.5 - 1.4	22	91	100	...	...	...
1.5 - 1.9	22	77	95	100	...	...
2.0 - 2.4	18	56	94	94	100	...
2.5 - 2.9	27	52	96	100	...	...
3.0 - 3.4	29	48	83	97	100	...
3.5 - 3.9	14	43	64	93	100	...
4.0 - 4.4	16	19	56	75	94	100
4.5 - 5.4	27	30	74	96	100	...
5.5 - 6.4	9	33	67	78	78	100
Mean	...	52	84	95	98	100
Alkalinity and conductivity'2						
0.5 - 1.4	18	83	too	...	...	...
1.5 - 1.9	17	88	100	...	...	...
2.0 - 2.4	30	67	97	97	100	...
2.5 - 2.9	22	64	91	100	...	...
3.0 - 3.4	30	47	83	100	...	...
3.5 - 3.9	18	39	61	94	100	...
4.0 - 4.4	20	30	65	75	95	100
4.5 - 5.4	22	45	82	91	95	100
5.5 - 6.4	7	14	57	71	86	100
Mean	...	55	84	94	98	100

1 In terms of absolute values of deviation from regression.
[2]Means of the two estimates.

Table 4.--Relation between maximum allowable concentrations of TFM as estimated from regression and as determined by bioassay

Method of estimation and range of TFM values (ppm)	Number of bioassays	Percentage in which bioassay result differed[1] from estimate by less than				
		1.0 ppm	2.0 ppm	3.0 ppm	4.0 ppm	6.0 ppm
Alkalinity						
1.0 - 2.9	13	100	...	...	...	...
3.0 - 4.9	30	70	90	100	...	...
5.0 - 6.9	46	39	74	91	100	...
7.0 - 8.9	44	48	77	93	98	100
9.0 -10.9	32	38	69	84	94	97
11.0 -16.9	28	18	39	54	79	96
Mean	...	47	73	87	95	99
Conductivity						
1.0 - 2.9	14	93	100	...	...	...
3.0 - 4.9	34	59	91	100	...	...
5.0 - 6.9	36	42	78	94	100	...
7.0 - 8.9	41	44	73	88	98	100
9.0 -10.9	28	36	57	71	86	96
11.0 -16.9	31	13	35	71	84	100
Mean	...	43	71	87	95	99
Alkalinity and conductivity[2]						
1.0 - 2.9	13	92	100	...	...	...
3.0 - 4.9	29	72	93	100	...	...
5.0 - 6.9	41	49	80	95	100	...
7.0 - 8.9	38	45	82	97	97	100
9.0 -10.9	35	43	66	83	95	97
11.0 -16.9	28	18	50	64	86	100
Mean	...	49	77	90	96	99

[1] In terms of absolute values of deviation from regression.
[2] Means of the two estimates.

The situation is similar for estimates of maximum allowable concentrations of TFM except for the greater ranges of error (Table 4) . Here, if probabilities in the range of 96-100 percent and averaging 99 percent are acceptable, it should not be necessary to extend tests beyond + 6 ppm from the estimated concentration. At the lower estimated concentrations the testing ranges may be reduced to ± 2 ppm.

The mean of the estimates from alkalinity and conductivity is recommended as a basis for estimating the limiting concentrations. Neither alkalinity nor conductivity showed a consistent advantage over the other. Although the mean showed no advantage over estimates from conductivity alone for minimum lethal, it appeared superior to estimates from alkalinity, and to either single estimate on maximum allowable. More importantly, the mean is recommended as being the more dependable because each estimate will serve as a check against the other.

The estimates are in no sense substitutes for bioassays, but contribute to efficient planning of bioassays by indicating the limits over which tests need to be made and the concentrations near which close spacing of test concentrations is required.

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The Great Lakes Fishery Commission was established by the Convention on Great Lakes Fisheries, between Canada and the United States, ratified on October 11, 1955. It was organized in April, 1956 and assumed its duties as set forth in the Convention on July 1, 1956. The Commission has two major responsibilities: the first, to develop co-ordinated programs of research in the Great Lakes and, on the basis of the findings, recommend measures which will permit the maximum sustained productivity of stocks of fish of common concern; the second, to formulate *and* implement a program to eradicate *or* minimize sea lamprey populations in the Great Lakes. The Commission is also required to publish or authorize the publication of scientific or other information obtained in the performance of its duties.