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ESTIMATION OF TOTAL MERCURY IN LAKE ST. CLAIR WALLEYES

by

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Introduction

Mercury contamination of biological systems has recently joined the fast-growing list of environmental problems of public concern. In March 1970, commercial fishing was banned in Ontario waters of Lake St. Clair because mercury residues in walleyes, *Stizostedion vitreum vitreum* (Mitchill), and certain other species exceeded the 0.5 ppm government "action level." Also, sport fishing was limited to a catch-and-release basis in both Ontario and Michigan waters of the lake. Subsequent actions by the governments have curtailed mercury discharges into Lake St. Clair, but a substantial period may be required for natural degradative processes to reduce contamination of fish to a tolerable (i.e., less than 0.5 ppm) level.

Efforts to detect any significant reduction of mercury residues in Lake St. Clair fishes will require the systematic collection of samples at regular intervals. Since mercury analyses are expensive and often time-consuming, it is desirable to limit the samples to the minimum number required to detect real changes in residue levels. We examine here the question of sample size required for analyses of mercury in walleyes.

Methods

Walleyes were collected by personnel of the Michigan Department of Natural Resources (DNR) at station 1 in Anchor Bay, Lake St. Clair (Figure 1). The station is one of a series established by DNR to monitor mercury in the environment and biota of Lake St. Clair. Of 56 walleyes captured, 49 were taken in a gill net on August 14, and 7 in a trap net on August 10-11. The fish (21 males, 35 females) ranged from 18.4 to 23.2 inches in total length (average 20.3 inches), and 2 lb. 1 oz. to 4 lb. 1 oz. in weight (average 2 lb. 11 oz.). Cursory examination of scale samples suggested that most of the walleyes were age V (1965 year class), and all were ages IV-VI.

The fish were iced and sent to the Great Lakes Fishery Laboratory (GLFL), Ann Arbor, soon after capture. There the right fillet was removed from each fish, then skinned and homogenized. Two subsamples of each of the homogenized fillets were frozen separately. One set of subsamples was retained at the GLFL for possible later comparison studies. The second set was delivered to Environmental Health Laboratories, Inc. (EHL), Farmington, Michigan, where four determinations (replicates) for total mercury on each subsample were made by an atomic absorption method (Hermann et al., 1968). Two additional subsamples from each of five fillets, selected randomly, were sent coded as routine subsamples to provide an unbiased evaluation of sample repeatability by EHL. Length, weight, sex, and results of mercury determinations are listed for each fish in the Appendix.

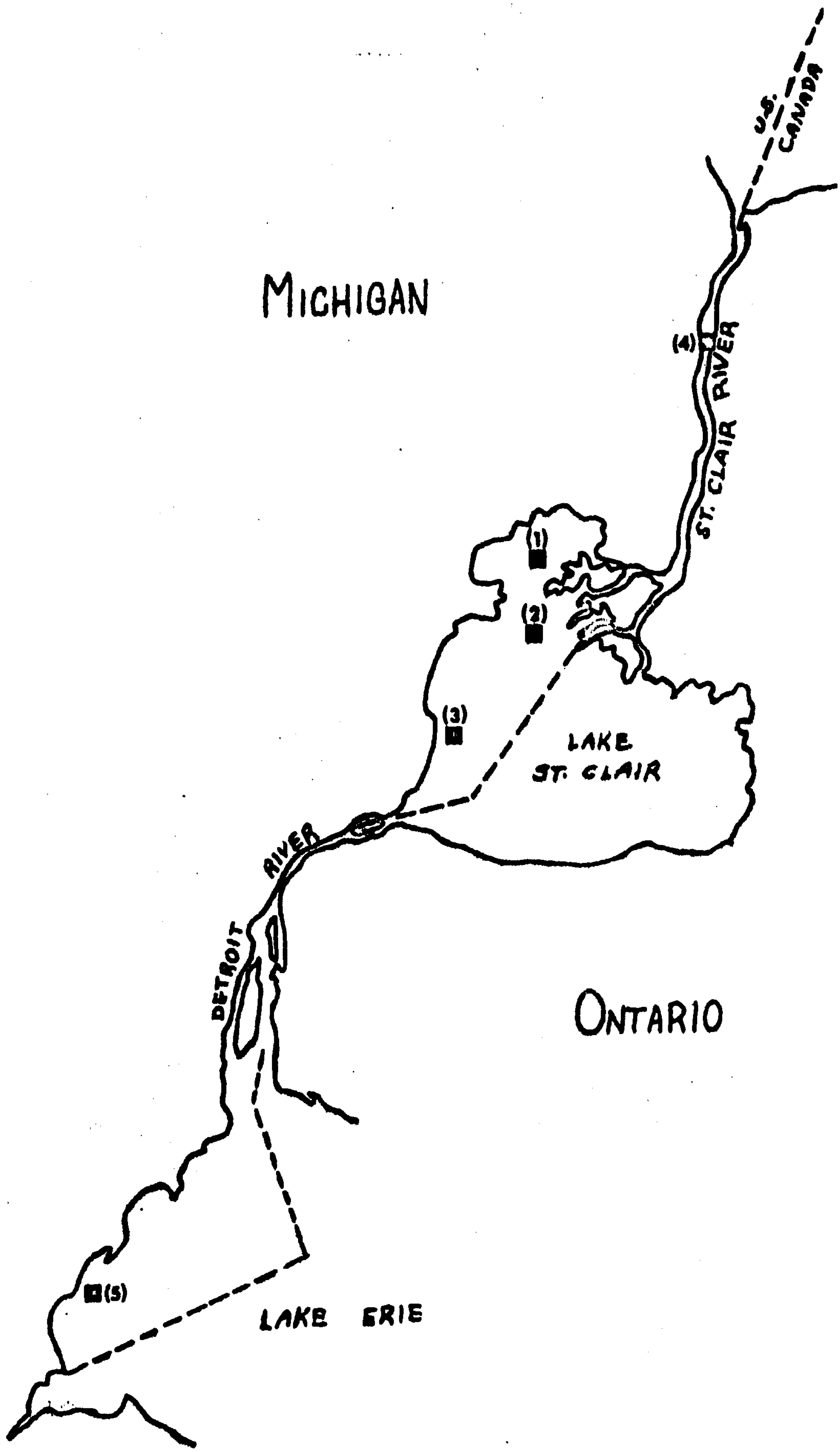

Figure 1.--Locations of DNR sampling stations in Lake St. Clair

Analysis of Mercury Contamination

General statistics

Considering all determinations, total mercury ranged from 0.24 to 5.80 ppm (average, 1.4 ppm; standard deviation about 1.0) in the 56 walleyes examined (Table 1). Coefficient of variation was generally 70-80 percent; this statistic would probably be useful to detect changes in variation and average of future samples. Each of the statistics was similar in all sets of determinations.

Distribution of values

A frequency distribution for each set of determinations showed that mercury concentrations were not normally distributed in relation to their mean value (Figure 2). About two-thirds of the fish contained 0.5-1.5 ppm total mercury; 10 percent or less had mercury residues less than 0.5 ppm, and the remainder were rather evenly spread out between 1.5 and 5.8 ppm. About 90 percent of the walleyes sampled contained mercury at or above the 0.5 ppm "action level." Logarithmic transformation did not change the distribution from skewed to normal.

Sex differences

A frequency distribution by sex (Figure 2) suggested that mercury concentration may have been slightly higher in females than males (Table 2). When the fish were divided among four categories of contamination, males were relatively more numerous than females in the 0.00-0.49 ppm and 1.00-1.49 ppm groups, and females were definitely the more numerous in the group with levels above 1.49 ppm. Although distribution of mercury contaminations appeared to be less skewed among males than among females,

Table 1.--Mercury content of fillets of walleyes collected in Lake St. Clair, August 1970

Determination number	Number of fish	Total mercury (ppm) Average	Range	Standard deviation	Coefficient of variation (100 x s/$\bar{x}$)
1	56	1.39	0.26-4.85	1.01	72.7
2	56	1.44	0.24-5.70	1.14	79.2
3	56	1.43	0.25-5.80	1.16	81.1
4	54[1/]	1.36	0.32-4.70	1.00	73.5

1/ Two samples yielded no data

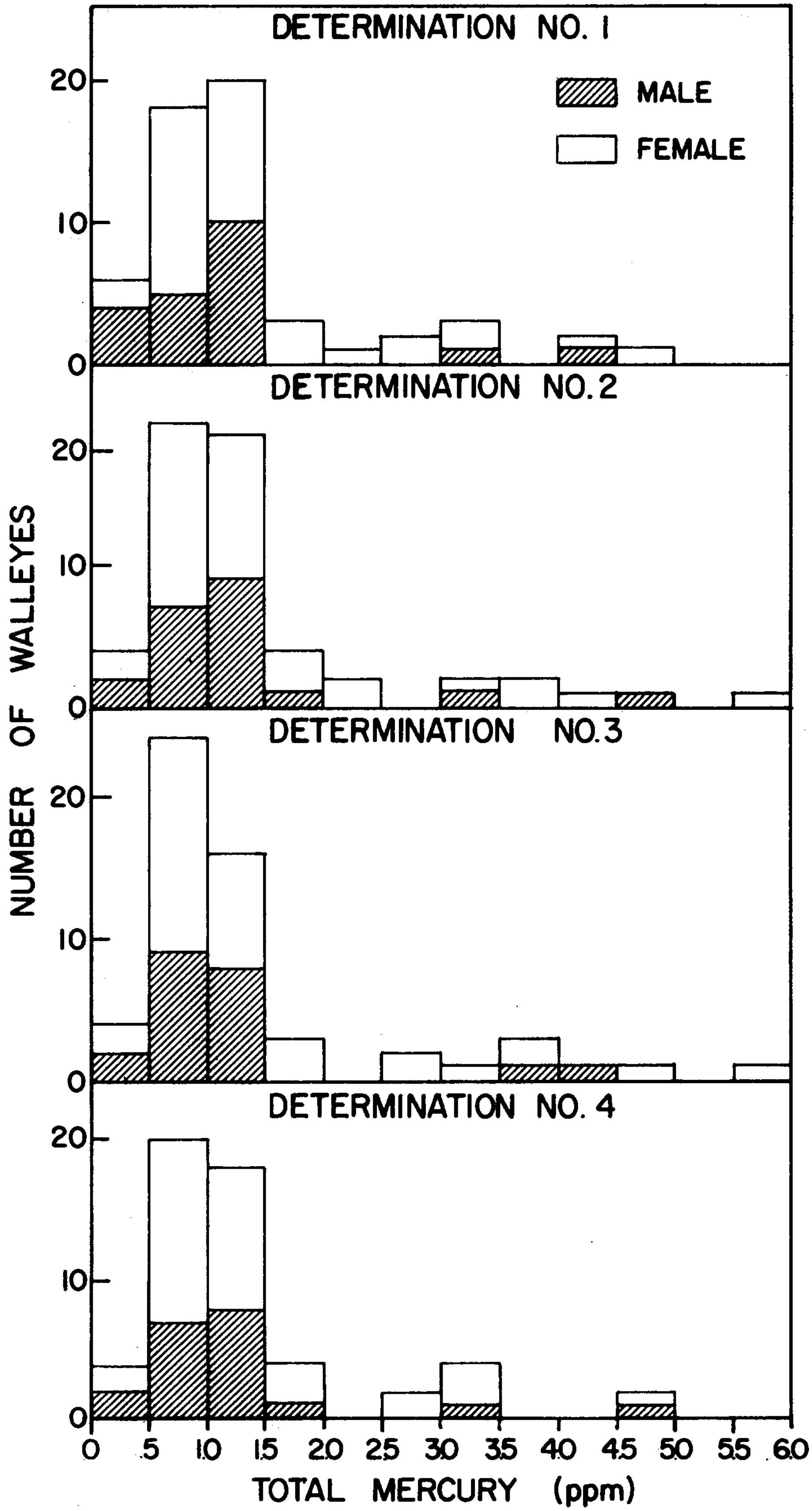

Figure 2.--Frequency distribution of mercury content in 56 walleyes from Lake St. Clair, August 1970

Table 2.--Percentages of male and female walleyes with different concentrations of mercury

Determination number and sex	Number of fish	Total mercury (ppm) 0.00-0.49	0.50-0.99	1.00-1.49	>1.49
1					
Male	21	19	24	48	9
Female	35	6	37	29	28
2					
Male	21	10	33	43	14
Female	35	6	37	29	28
3					
Male	21	9	43	38	10
Female	35	6	43	23	28
4					
Male	20	10	35	40	15
Female	34	6	38	29	27

extensive overlap of values precludes any practical probability statement about a difference between sexes.

Sample repeatability

Two additional subsamples from each of five homogenates (Table 3) made possible a statistical test to determine relative contributions to variation in mercury values from different fillets (samples), and different subsamples from the same fillet. Fillet-to-fillet variation in mercury was highly significant relative to any variation caused by laboratory method (Table 4). The data used are probably not from a normal distribution, and the test (which assumes a normal distribution) cannot be considered exact. However, we do not doubt the validity of the conclusion.

Estimation of sample size

Plotting sample variance versus sample size is an often-used technique to determine the point at which increasing sample size has little influence in reducing variance. The point selected indicates the sample size with "optimally minimum" variance. That is, samples of larger size would provide a lower variance (giving a more precise estimate of the mean), but not sufficiently lower to justify the added cost of increasing sample size.

For each set of determinations, the number of walleyes (sample size) was plotted against variance of mercury values. All four plots yielded similar curves; data from set number 3, which had the highest variance, were used (Figure 3). As sample size increased, variance peaked, then declined rapidly, and began stabilizing near sample size 25. A sample of 25 walleyes would provide an "optimally precise" estimate of average mercury contamination.

Table 3.--Total mercury in five walleye fillets--three subsamples from each fillet and four determinations from each subsample

Fish number	Subsample number	Determinations 1	2	3	4
3005	1	1.44	1.41	1.33	1.42
	2	1.06	1.25	1.04	1.30
	3	1.49	1.22	1.06	1.08
3006	1	1.24	1.08	1.10	1.01
	2	0.95	1.01	1.15	1.10
	3	1.20	1.26	1.19	1.07
3080	1	0.95	0.97	0.96	0.88
	2	0.95	0.84	0.92	0.87
	3	0.92	0.90	1.01	1.11
3079	1	1.37	1.51	1.30	1.37
	2	1.94	1.81	1.75	1.76
	3	1.24	1.26	1.35	1.44
3027	1	0.89	0.88	0.88	0.95
	2	1.08	0.91	1.29	1.12
	3	0.92	0.71	0.78	0.94

Table 4.--Analysis of variance in mercury values from five walleye fillets

Source of variation	Degrees of freedom	Sum of squares	Mean square	F-value
Fillet (sample)	4	3.4766	0.8692	58.73**
Subsamples within a fillet	10	0.1475	0.0148	1.41 (NS)
Determinations within a subsample	45	0.4726	0.0105	

**-Significant at 0.01 level of probability; N.S.-nonsignificant at 0.01 level

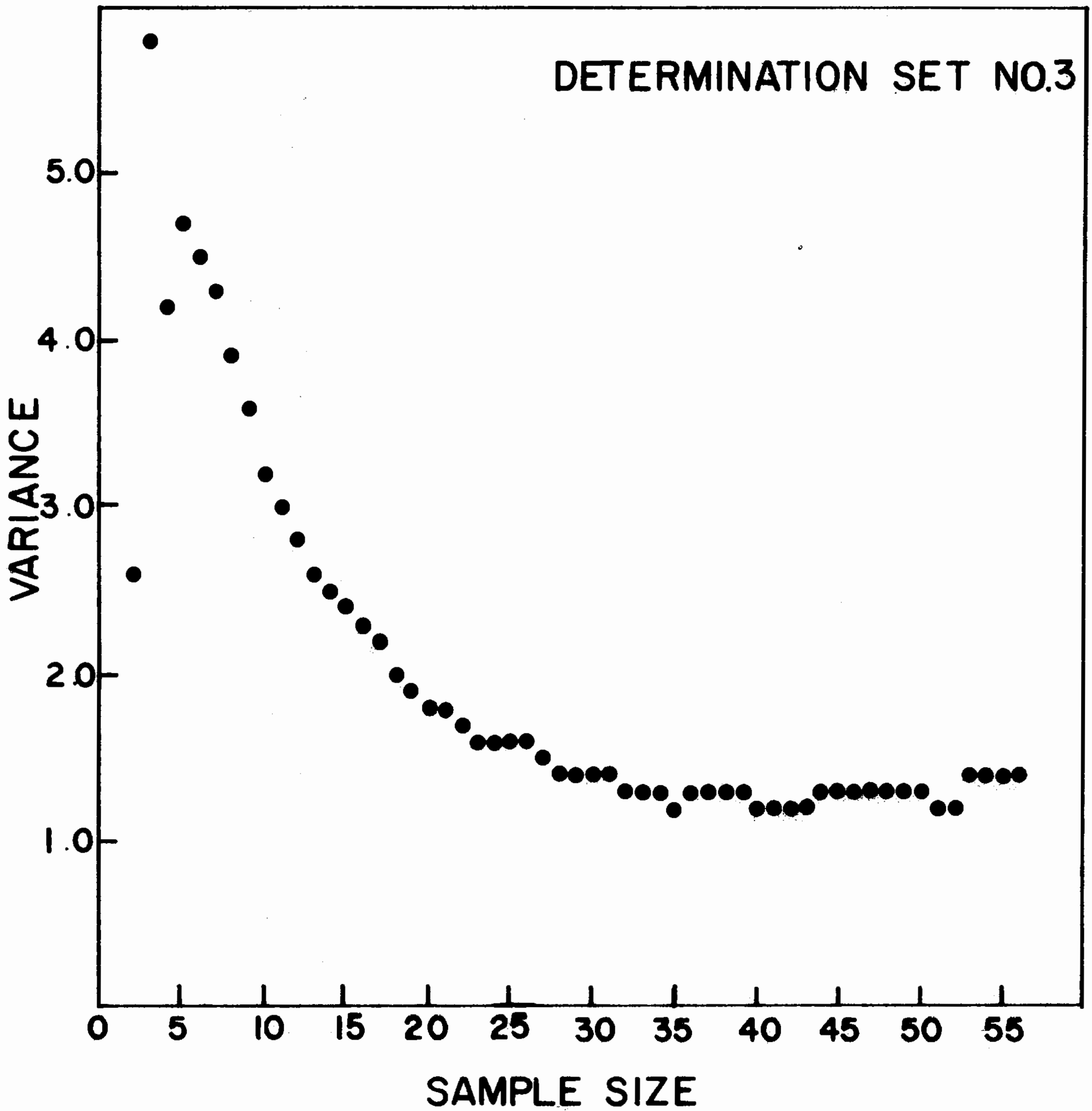

Figure 3.--Cumulative variance of mercury content versus cumulative sample size for 56 walleyes from Lake St. Clair, August 1970

To obtain an estimate of error (confidence limits of sample mean) and risk (probability of being wrong) in a sample of 25 walleyes, we used a procedure for estimating sample size described by Snedecor (1956). The technique assumes sampling from a normal distribution. Although the assumption is not valid for these data (Figure 2), rough estimates can be made. Sample size was estimated for errors of ± 0.10, ± 0.20, ± 0.50 and ± 1.00 ppm, and for risks of 2, 5 and 10 percent (Table 5). We conclude that (1) sample sizes which limit error to ± 0.10- 0.20 ppm are unreasonable, and (2) a sample of 25 walleyes provides an estimate of average mercury contamination with error of ± 0.5 ppm, and 2-5 percent chance of being wrong.

Alternate method of estimation

Because of the skewed distribution of mercury concentrations among walleyes (Figure 2), a mean or average mercury value is difficult to evaluate without a knowledge of variation and frequency distribution. If one is unfamiliar with statistical methods, an evaluation is even more difficult. The cumulative probability curve provides an alternate procedure to monitor mercury contamination which may be more useful (in terms of public health decision-making) than estimation of average values. The curve results from plotting values (e.g., mercury) against the percentage of individuals in the sample with less than those values, successively, until all individuals in the sample are included.

Data from the frequency distribution of determination number 3 (Figure 2) are the basis for the cumulative probability curve shown in Figure 4. Seven percent of the walleyes contained less than 0.5 ppm total mercury; 50 percent had less than 1.0 ppm, and nearly 80 percent less than 1.5 ppm. In about

Table 5.--Estimates of sample size (number of walleyes) required for various levels of error (precision) and risk (probability)

Error (ppm)	Risk (percent)		
	2	5	10
± 0.10	738	522	366
± 0.20	185	131	91
± 0.50	30	21	15
± 1.00	7	5	4

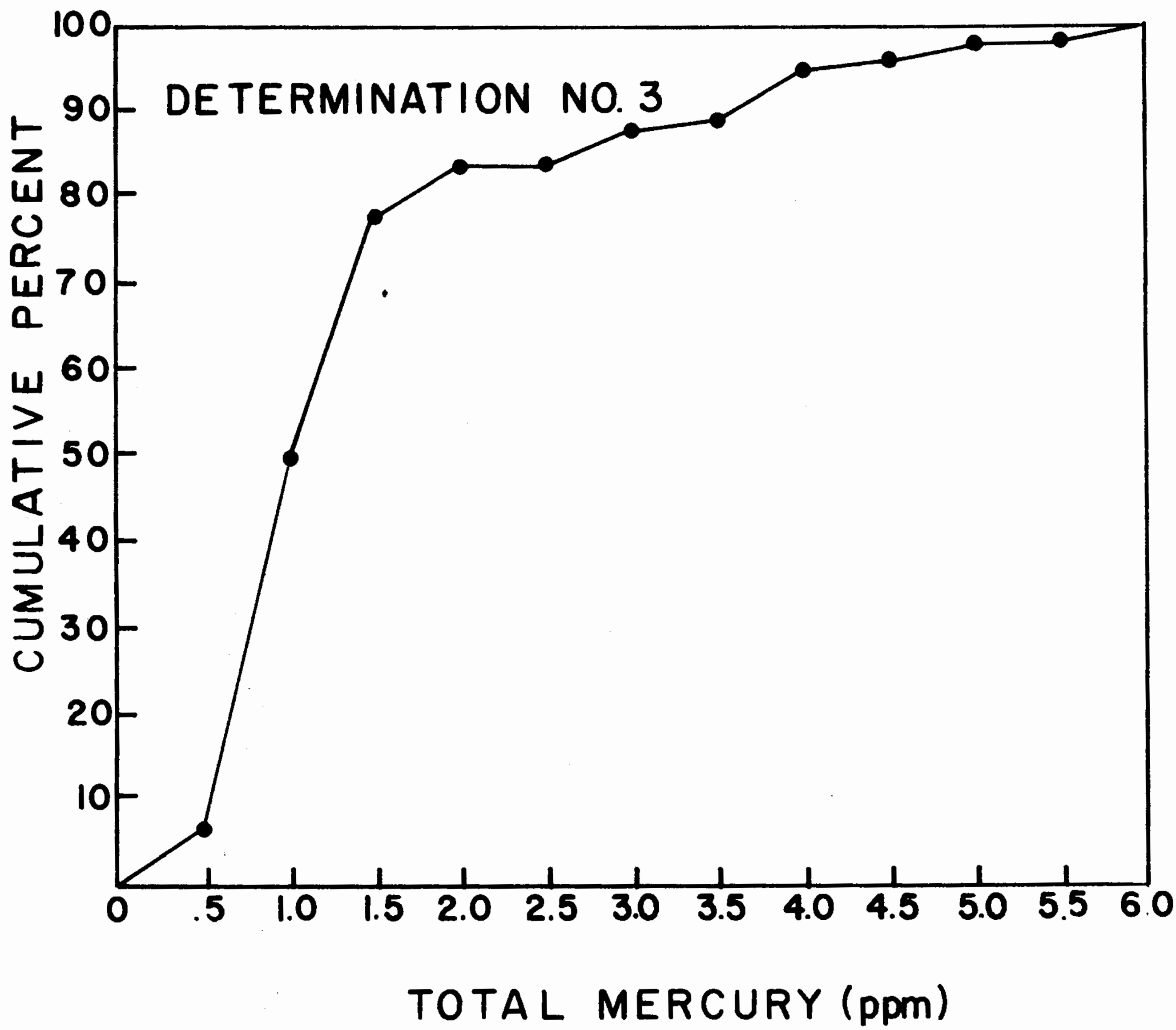

Figure 4.--Cumulative probability curve for mercury contamination in 56 walleyes from Lake St. Clair, August 1970

20 percent of the sampled walleyes, concentrations of total mercury were 1.5 ppm or greater.

If mercury contamination declines in future walleye samples, the probability curves will shift to the left; if the level of contamination increases, the curves will shift to the right. Governmental health agencies must decide the acceptable probabilities involved from a public health viewpoint.

Evaluation of the Results

Mercury is distributed unevenly throughout the physical environment of Lake St. Clair; concentrations are high near the discharge sources, and probably decrease progressively at increasing distances from these sources. Walleyes in Lake St. Clair are highly mobile, and probably are of various origins, including Lakes Huron and Erie (Regier et al., 1969). The skewness of distribution in mercury concentrations for the 56 walleyes studied is very likely an indication of mobility and mixing among Lake St. Clair walleyes, and reflects the resulting differences in their chances of being exposed to heavy doses of mercury. Although a few walleyes have a high mercury content, it is of greater consequence that the contamination of most of the fish in the population exceeds the tolerable level.

We did not attempt to determine the relationship, if one exists, between the size or age of walleyes and the amounts of mercury which they contain. A size range of walleyes presently abundant in Lake St. Clair, and desirable for food and sport was selected for estimating sample size. Future estimates of mercury should not be based on a different size group (particularly a smaller one) unless more is known about the relation between mercury and size of fish. Sex does not seem to have an important influence on mercury content, but may be ignored (for monitoring purposes) even if it does--a fisherman may not know or care about the sex of the walleyes he eats.

In summary, a sample of 25-30 walleyes, in the size range studied, will yield a mean value of mercury content which will be within ± 0.5 ppm of the true mean; about a 5 percent chance exists of the true mean being outside of the sample limits. It is possible that the cost of analyses could be somewhat reduced without loss in precision by compositing all fillets and taking fewer subsamples from the composite. However, since no data are yet available on this procedure, we recommend that the analyses be made on individual fish.

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Regier, Henry A., Vernon C. Applegate, and Richard A. Ryder. 1969. The ecology and management of the walleye in western Lake Erie. Great Lakes Fishery Comm., Tech. Rept. 15, 101 pp.

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Appendix. Size, sex and mercury content of 56 walleyes collected in Lake St. Clair, August 10-14, 1970.

Length (inches)	Weight (pounds)	Total mercury (ppm), right fillet 1	2	3	4	Identification number
Males						
18.6	2.2	1.18	1.05	1.18	1.23	3038
18.7	2.0	1.22	1.21	1.17	1.13	3020
18.8	2.2	0.54	0.50	0.58	0.62	3019
19.1	2.3	0.58	0.59	0.57	0.59	3087
19.1	2.5	0.80	0.91	0.91	0.80	3101
19.2	2.1	3.35	3.30	3.50	3.22	3086
19.3	2.2	0.31	0.30	0.30	0.32	3007
19.4	2.4	1.24	1.08	1.10	1.01	3006
19.5	2.8	0.90	0.81	0.66	0.69	3030
19.6	2.2	1.29	1.28	1.26	1.25	3018
20.0	2.5	1.36	1.32	1.08	1.08	3022
20.1	2.6	4.10	4.78	4.40	4.55	3077
20.1	3.0	0.47	0.46	0.57	-	3034
20.3	2.9	0.49	0.54	0.41	0.48	3074
20.8	2.6	1.10	1.12	0.99	1.01	3046
21.1	2.2	1.37	1.51	1.30	1.37	3079
21.2	3.2	1.24	1.09	1.36	1.47	3023
21.7	2.9	1.38	1.17	0.97	0.94	3035
21.8	3.5	1.47	1.48	1.32	1.64	3076
22.2	2.6	0.95	0.97	0.96	0.88	3080
22.2	3.4	0.49	0.71	0.80	0.68	3015
Females						
18.4	2.1	4.85	5.70	5.80	-	3017
19.1	2.2	1.67	1.75	1.73	1.59	3085
19.1	2.4	3.30	3.86	3.95	3.40	3099
19.4	2.2	1.42	1.41	1.30	1.29	3098
19.6	2.1	1.40	1.19	1.42	1.45	3016
19.7	2.4	1.05	1.04	0.98	0.91	3028

Length (inches)	Weight (pounds)	Total mercury (ppm), right fillet 1	2	3	4	Identification number
19.7	2.5	2.70	2.31	2.64	3.38	3081
19.9	2.3	1.37	1.37	1.34	1.35	3084
19.9	2.5	1.44	1.41	1.33	1.42	3005
19.9	2.9	0.94	0.96	0.84	0.94	3029
20.0	2.2	1.57	1.51	1.59	1.62	3082
20.0	2.6	3.24	3.75	3.59	3.20	3083
20.1	2.6	1.06	1.18	1.34	1.01	3036
20.1	2.8	0.89	0.88	0.88	0.95	3027
20.2	2.8	0.89	0.96	0.95	0.87	3100
20.2	2.9	1.00	0.95	0.81	0.82	3037
20.3	2.6	2.46	3.00	3.05	2.84	3024
20.4	2.6	1.80	1.73	1.78	1.78	3026
20.4	2.8	0.82	0.98	0.82	1.01	3013
20.4	2.8	0.91	0.89	0.88	0.88	3078
20.4	2.8	0.55	0.63	0.56	0.60	3102
20.5	2.4	0.96	1.04	1.06	1.07	3010
20.5	2.4	0.76	0.71	0.70	0.73	3021
20.5	2.8	0.70	0.70	0.76	0.79	3014
20.5	2.9	1.49	1.38	1.30	1.29	3044
20.6	2.3	4.06	4.36	4.60	4.70	3033
20.6	2.8	2.68	2.44	2.66	2.66	3031
20.8	3.1	0.54	0.61	0.66	0.64	3045

Length (inches)	Weight (pounds)	Total mercury (ppm), right fillet 1	2	3	4	Identification number
20.8	3.3	1.49	1.45	1.30	0.90	3032
20.9	2.9	1.03	1.01	0.89	1.11	3008
21.4	3.2	0.95	0.96	0.96	1.10	3075
21.5	3.2	0.43	0.48	0.40	0.43	3004
21.7	3.0	0.65	0.59	0.59	0.54	3025
21.9	4.1	0.76	0.91	0.90	0.78	3073
23.2	3.9	0.26	0.24	0.25	0.27	3009