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Distributional Properties of Selected Water Quality Variables in the St. Mary River (B.C.)

1975 and 1980 to 1982

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DISTRIBUTIONAL PROPERTIES OF SELECTED WATER QUALITY VARIABLES IN THE ST. MARY RIVER (B.C.) FOR 1975 AND 1980-1982

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ABSTRACT

A number of statistical techniques applied to the St. Mary River water quality data indicate a significant difference between data sets for year 1975 and 1980 through 1982. These differences are very evident in the frequency distributions of each variable. A definite change in concentrations of phosphorus, fluoride and silicate is noted between 1975 and the years 1980-82 which corresponds to the the start-up of the waste water treatment facility at Cominco's Kimberly operation.

RESUME

Les résultats selon obtenus diverses méthodes statistiques utilisées pour analyser les données de la qualité de l'eau de la rivière St. Mary, indiquent une différence importante entre l' année 1975 et la période de 1980 à 1982. Cette différence est surtout évidente sur la courbe de distribution de fréquences de chaque variable. Notamment la concentration du phosphore, des chlorures et des silicates a varié de façon appréciable entre l'année 1975 et la période de 1980 à 1982, què correspond au début du traitement des eaux usées de la compagnie Cominco à Kimberly.

INTRODUCTION

Historically, the St. Mary River exhibited high levels of phosphorus and other variables as the result of the effluent disposal practices of Cominco's mining and fertilizer operations at Kimberly. Changes in these practices, most notably the start up of a wastewater treatment facility, occurred between 1975 and 1980. Since only limited monitoring has been undertaken over this period, the preferred statistical techniques of time series analysis cannot be applied in determining whether or not changes in water quality concentrations did result from changes in the Cominco operation.

Data was collected data during 1975, and between April 1980 and June 1982 to establish the levels of selected water quality variables. The objective of this study was to compare these data sets to determine if changes in the concentration of some water quality variables had occurred. This report describes how the distributions of total phosphorus, fluoride, and silicate changed between 1975 and 1980. Much of the emphasis of this report is on methods which may be used for considering differences in distributions of variables.

STUDY AREA

The St. Mary River is one of the major tributaries of the Kootenay River. Located in the southwestern region of the lower Kootenay River basin (Figure 1), the system is approximately 100 km in length with a drainage area estimated at 2400 km^2. The headwaters are located in the Purcell Mountain Range. Maximum flows of 100-250 m^3/s occur during freshet and minimum flows of 9-11 m^3/s occur during December through March (Environment Canada, 1980)

The major source of contamination to the system is from the Cominco operation located near Kimberley. Industrial effluents from the Sullivan mine, ore concentrator and phosphate fertilizer plant discharge into Mark, Kimberley, and James creeks. All of these ultimately flow into the St. Mary River. To upgrade effluent quality a treatment facility was installed and several inplant changes were carried out. These changes, including installation of the treatment plant, were completed and in operation by the spring of 1980.

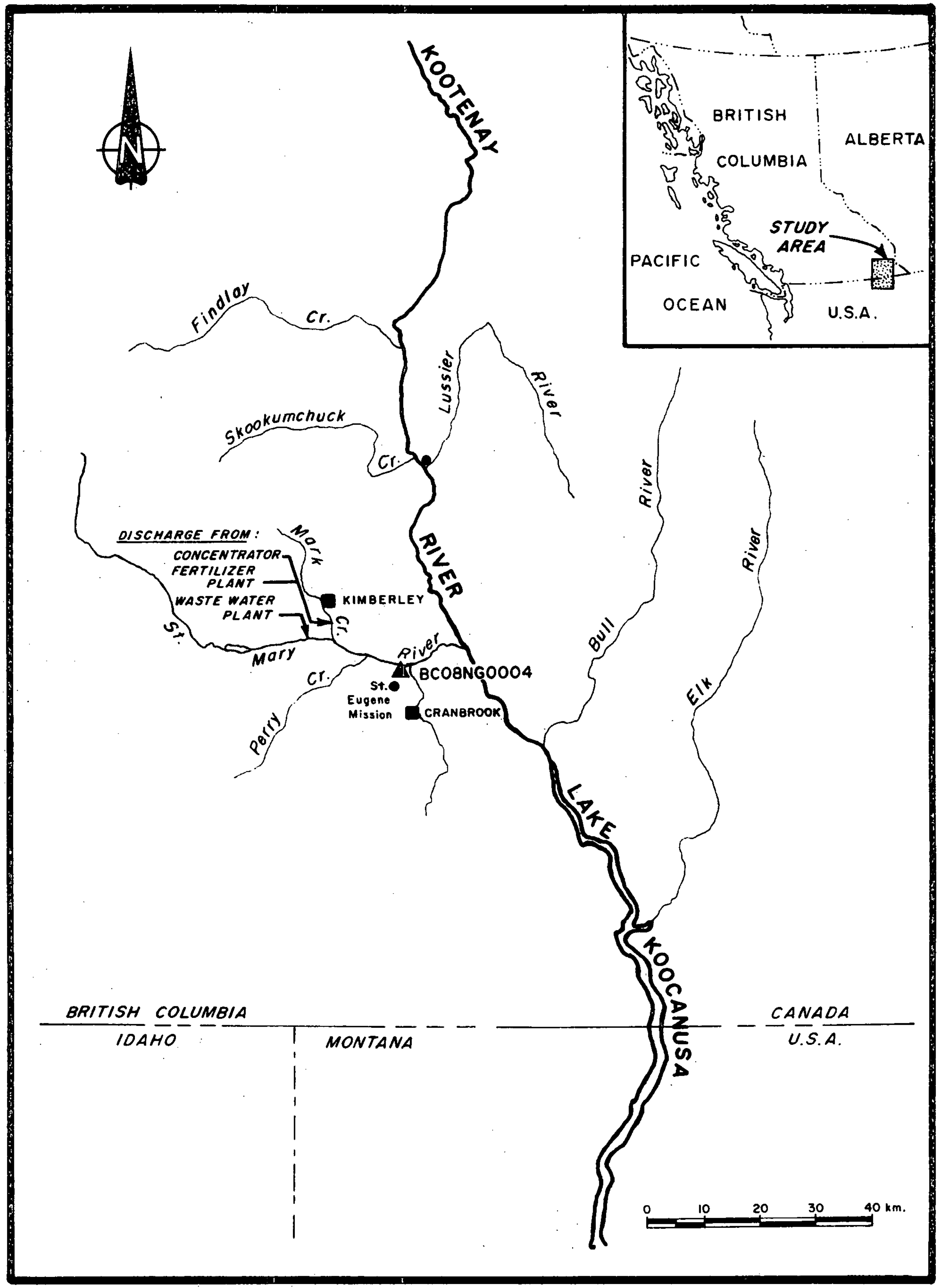

Figure 1. St. Mary River study area.

METHODS

Sampling Techniques

All samples discussed in this report were collected downstream from the industrial discharges at the bridge crossing the St. Mary River near the St. Eugene Mission (00BC08NG0004). Samples were collected at three points equidistant across the river using a IWD replicate sampler (Oguss and Erlebach, 1976). A set of six replicate samples were collected directly into glass bottles (50 ml) for the determination of total phosphorus, and a set of six into polyethylene bottles (250 ml) for fluoride and silicate determinations. Analytical work was performed by the Pacific and Yukon Region, Water Quality Branch Laboratory in Vancouver. The methods and procedures used in the chemical determinations are described in the Analytical Methods Manual (Environment Canada, 1979).

Sampling Frequency

A preliminary study of the Kootenay River Basin was carried out during 1975. The main objective of that study was to determine the mass transport of nutrients and establish input levels. In that study, samples were collected two times per day for approximately one week every other month. This sampling frequency began in April and continued until November 1975. With the installation of a wastewater treatment facility in August 1979 a subsequent monitoring program was initiated with samples collected every other month from April 1980 through June 1982. During both programs several variables were monitored, however this report considers only three. Additional data from this study can be obtained from the Data Systems Section of the Water Quality Branch, Inland Waters Directorate in Ottawa.

Statistical Techniques

Transformations

For the purpose of this study all data for each year were treated as a group. Statistical analyses were then performed on these groups. Where distributions were found to be non-normal a transformation which results in a more normal distribution was performed. In particular natural logarithmic transforms of raw data often result in increased normality of water quality data (Whitfield, 1983). This transformation was used extensively in the analysis of the data considered in this report.

Distributions

Histograms were prepared by plotting the number of occurrences expressed as a fraction of the total number of samples on the ordinate against the upper limit of each interval on a logarithmic scale. This type of plot will show differences in both distribution and magnitude.

A second method of graphing distribution is a plot of the cumulative probability distribution. These are prepared in the following manner. The total range of observations for each variable is divided into 100 equal intervals. The cumulative frequency distribution was then obtained by successive summation and expressed as percent of the total sample size. The upper limit of each interval is then plotted in linear scale on the abscissa against percent cumulative frequency in probability scale on the ordinate. Plots of this type allow visual determination of distributional properties of the data in particular the underlying distributions.

Test Statistics

The following statistical analyses were applied to the water quality data.

A. Kruskal-Wallis Test (Dixon, 1983)

The Kruskal-Wallis statistic is a nonparametric test of the equality of the location parameter (mean) for two or more independent samples. Let the N observations be classified into g groups, the jth group contains n observations. All the values for each variable are ranked from 1 to N; tied values are assigned the average rank for the tied values. Let R be the sum of the ranks for each group. The Kruskal-Wallis statistic (H) is:

$$H = \frac{12}{N(N+1)} \sum_{j=1}^{g} \frac{R_j}{n_j} - 3(N+1)$$

If ties exist, H is modified to:

$$H' = H \Big/ \left[1 - \frac{\Sigma^* (t_i^3 - t_i)}{N^3 - N} \right]$$

where t_i equals the number of observations tied with a single value and Σ^* is the sum over all distinct values for which a tie exists. The level of significance of the H statistic is obtained from the chi-square distribution with g-1 degrees of freedom.

Since no assumptions are made regarding the normality of the data or the equality of variances the test is robust. This test then is a simple method for determining whether or not the various groups have equal means.

B. One-Way Analysis of Variance (Sokal and Rohlf, 1969)

A one-way analysis of variance (ANOVA) tests the equality of group means. Let x_{ij} be the jth observation in the ith group, x_i the mean and N_i the number of observations in the ith group. The between sum of squares (BSS) is then:

$$BSS = \Sigma_i N_i (\overline{x}_i - x)^2$$

where $$\overline{x} = \Sigma_i N_i \overline{x}_i / \Sigma N_i$$

The between degrees of freedom are g-1 where g is the number of groups. The between mean square (BMS) is:

$$BMS = BSS/ (g-1)$$

The within sum of squares (WSS) is:

$$WSS = \Sigma_i \Sigma_j (x_{ij}-\bar{x}_i)^2$$

with degrees of freedom / $\Sigma_i(N_i-1)$.

The within mean square (WMS) is:

$$WMS = WSS/\Sigma_i (N_i-1)$$

and the F ratio is:

$$F = BMS/WMS$$

The tail probability is the probability of exceeding the F ratio when the group means are equal. This method is appropriate when the data are sampled from normal distributions with equal population variances. The distribution of the F ratio is particularly sensitive to the assumption of equal population variances. The F value is a test of the equality of group means.

C. Levene's Test for Equal Variances (Brown and Forsythe, 1974a)

Levene's test is a robust test of the equality of variances provided by a one-way analysis of variance computed on the absolute value of deviations from the group means:

$$\text{Let} \qquad Z_{ij} = |x_{ij}-\bar{x}_i|$$

Then the one-way anova statistic w_0 is formed as

$$w_0 = \frac{\Sigma_i N_i \ (Z_i - Z)^2/(g-1)}{\Sigma_i \Sigma_j \ (Z_{ij} - Z_i)^2/\Sigma_i \ (N_i - 1)}$$

where $Z_i = \Sigma Z_{ij}/N_i$ and $Z = \Sigma\Sigma Z_{ij}/\Sigma n_i$

The critical values are obtained from tables of F values with g-1 and $\Sigma_i \ (N_i-1)$ degrees of freedom.

D. Brown-Forsythe Statistic (Brown and Forsythe, 1974b)

Another robust test for equality of means, the Brown-Forsythe statistic (F*), is a modification of F which substitutes a denominator which has an expectation equal to the numerator when all means are equal.

$$F^* = \frac{\Sigma_i N_i \ (\bar{x}_i - \bar{x})^2}{\Sigma_i \ (1 - N_i/\Sigma N_i) \ S_i^2}$$

Critical values are obtained from the F-distribution with g-1 and f degrees of freedom where f is defined by the approximation:

$$\frac{1}{f} = \Sigma_i C_i{}^2/(N_i - 1)$$

where $C_i = (1 - N_i/\Sigma N_i) \ S_i^2 \ /[\Sigma_i \ (1-(N_i/\Sigma N_i) \ S_i^2]$

There is a small loss in power when using F* rather than F, however the protection against the distortions of F when the variances are unequal commends it's use.

E. Welch Statistic (Brown and Forsythe, 1974b)

The Welch statistic (W) is a further test of the equality of means. However unlike the one-way anova this statistic is robust under the inequality of variances:

$$W = \frac{\Sigma_i w_i(\bar{x}_i-\tilde{x})^2/(g-1)}{\left[1 + \frac{2(g-2)}{(g^2-1)} \Sigma(1-w_i/u)^2/(N_i-1) \right]}$$

where

$$w_i = N_i/s_i^2$$

$$s_i^2 = \Sigma_i (x_{ij}-x_j)^2/(N_i-1)$$

$$u = \Sigma_i \omega_i$$

$$\tilde{x} = \Sigma w_i \bar{x}_i/u$$

When all population means are equal (even if the variances are unequal), W is approximately distributed as a F statistic with g-1 and f degrees of freedom where f is implicitly defined as:

$$\frac{1}{f} = [3/(g^2-1)]\ \Sigma_i (1-w_i/u)^2/(N_i-1)$$

As with the Brown-Forsythe statistic, there is a small loss of power in using this statistic rather than F, however the protection against the distortion in size of F from unequal variances warrents the use of W.

RESULTS AND DISCUSSION

The intention of this paper was to compare distributional properties of the phosphorus, fluoride and silicate data, and examine some possible methods of analysis.

Distributions

Each frequency distribution is graphically represented as Figures 2 to 7. A histogram and a cumulative probability distribution were plotted for each variable for each year. Both types of distributions are graphic techniques in determining the normality of a sampled population as well as allowing us to graphically estimate the mean and standard deviation.

In a histogram a normal distribution curve would appear symmetrical or bell shaped with the observations equidistant from a central maximum. The shape or distribution of total phosphorus shown in Figure 2 departs from the normality and demonstrates a skewed distribution to the right in 1975 and to the left in the 1980, 1981 and 1982 distributions. Note that during the 1975 sampling period more than 50 percent of the samples contained concentrations ranging from 0.55 to 1.82 mg/l. Comparison with later years (1980-82) shows a marked decrease in concentration with a large percentage of samples having values between 0.09 to 0.30 mg/l.

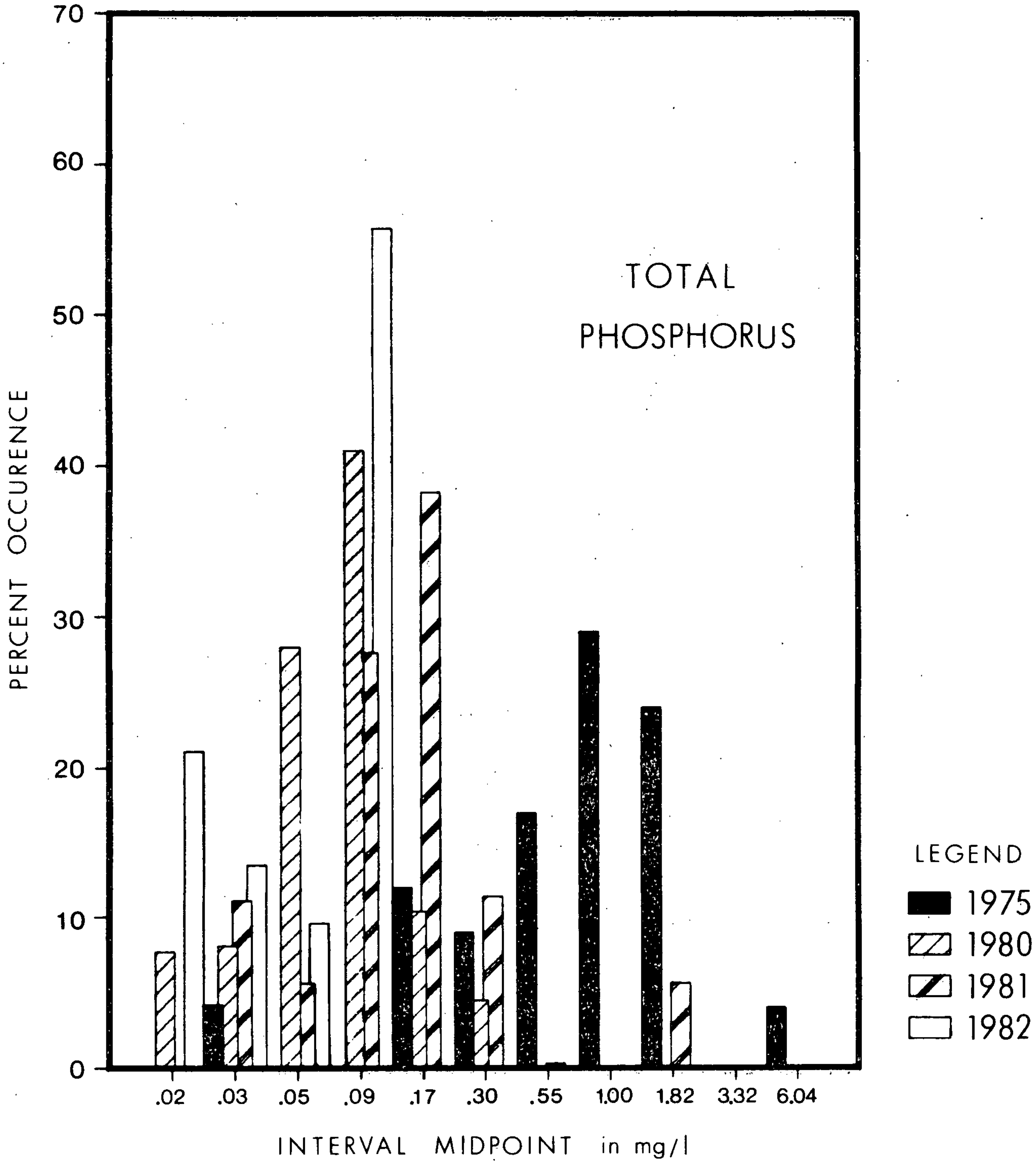

Figure 2.
Histogram of total phosphorus concentrations in the St. Mary River.

These patterns are also evident in the frequency distributions of fluoride (Figure 3). A large percentage of the sampled population in 1975 had concentrations greater than 4 mg/l, somewhat higher than those indicated for 1980-82. Another interesting observation is the characteristic bimodal distribution of each frequency curve. Instead of having just one peak or maximum these curves illustrate two reflecting periods of increased dilution during freshet and intense concentration during the low flow periods of winter.

The percent occurences of silicate, Figure 4, again signifies changes in river chemistry possibly due to treatment processes. The median observed in each of the annual distributions from 1980 to 1982 fall approximately in the same area or interval. Actually these distributions appear very similar in both location and dispersion. In 1975 the median is observed slightly higher than determined in the subsequent years, however, the amount of variation is significantly different. Prior to proper effluent disposal practices a substantial percentage of samples had concentrations in the range of 9-12 mg/l. In the later years, the dispersion pattern is reduced and variability due more to seasonal flux than to a point source variability.

A cumulative probability distribution is an alternate method used to describe or graphically display data. Such a technique again allows us to analyse the data graphically for normality and to estimate visually the mean and standard deviation. When a cumulative normal distribution is plotted on probability paper the plot will roughly lie on a straight

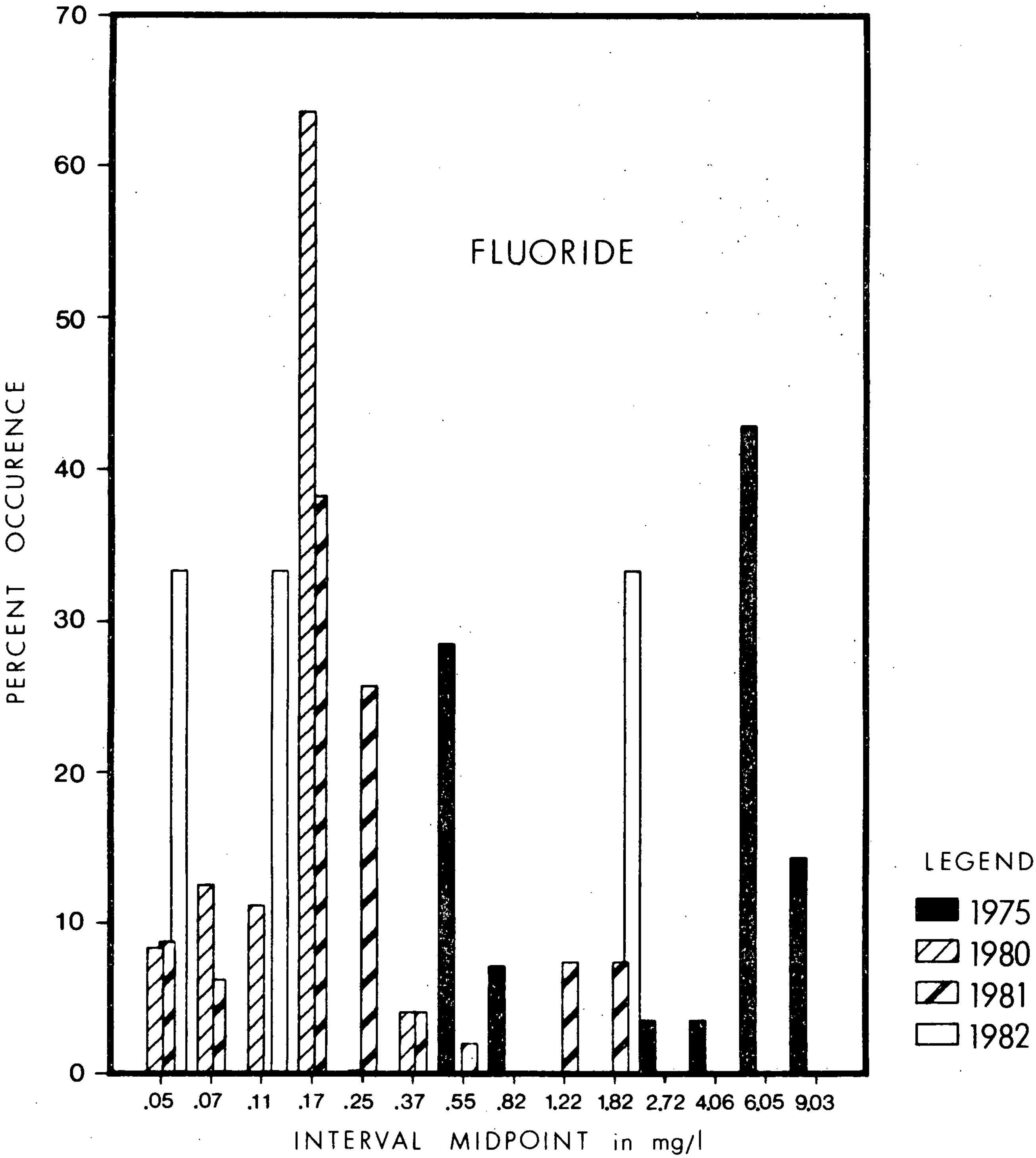

Figure 3.
Histogram of fluoride concentrations in the St. Mary River.

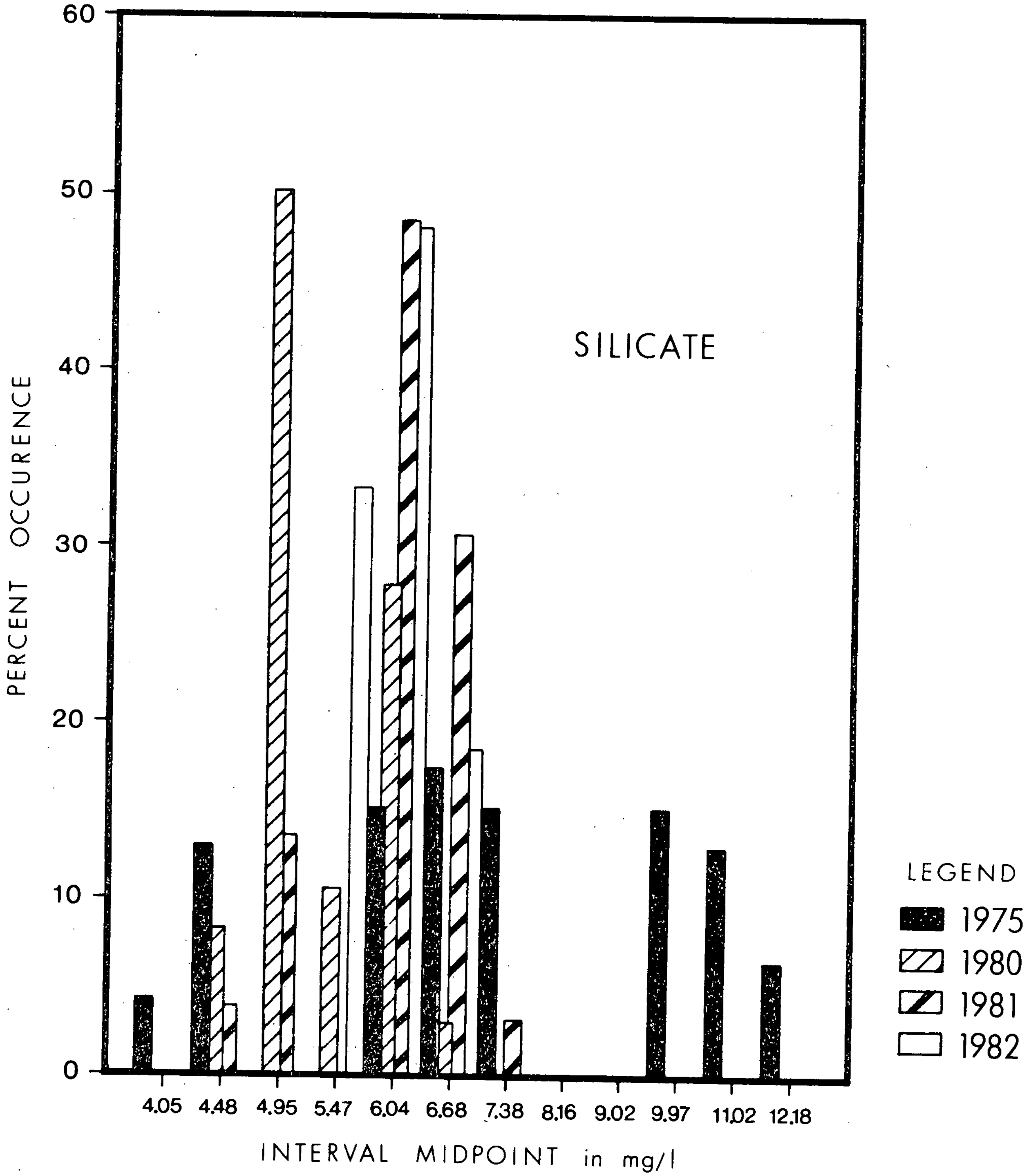

Figure 4.
Histogram of silicate concentrations in the St. Mary River.

line. As shown in Figure 5 the untransformed total phosphorus distributions are far from normal, however they do indicate departures from normality and the underlying distributions.

An estimation of the mean is approximated by a graphic measure of the median. This is accomplished by drawing a perpendicular line from the 50 percent mark on the probability scale (ordinate) to the cumulative frequency curve and then to the corresponding concentration listed along the abscissa. The standard deviation is obtained by similar methods using instead the intersections of 15.9 percent and 84.1 percent with the cumulative curve (Sokal and Rohlf, 1969). In Figure 5, the cumulative distribution of total phosphorus estimated in 1975 before upgrading and implementation of treatment facilities is significantly different than the 1980-82 distributions signifying the post treatment period. In 1975 the estimated median was approximately 0.85 mg/l compared to about 0.10 mg/l shown in the 1980-82 distributions. Graphically analysing the data shows a similarity between the cumulative frequencies calculated in 1980-82. Each distribution demonstrates the same pattern with comparable means (medians) and standard deviations except for the slight departure at higher concentrations. However, in this region single values or outliers can make appreciably changes in the tail percentages, therefore the region between the cumulative frequencies of 25 to 75 percent are far more significant. In the 1975 distribution higher levels of total phosphorus are noted was found using the histogram.

This pattern is also shown in the cumulative distributions of fluoride (Figure 6). The probability or chance that a sample taken at random had

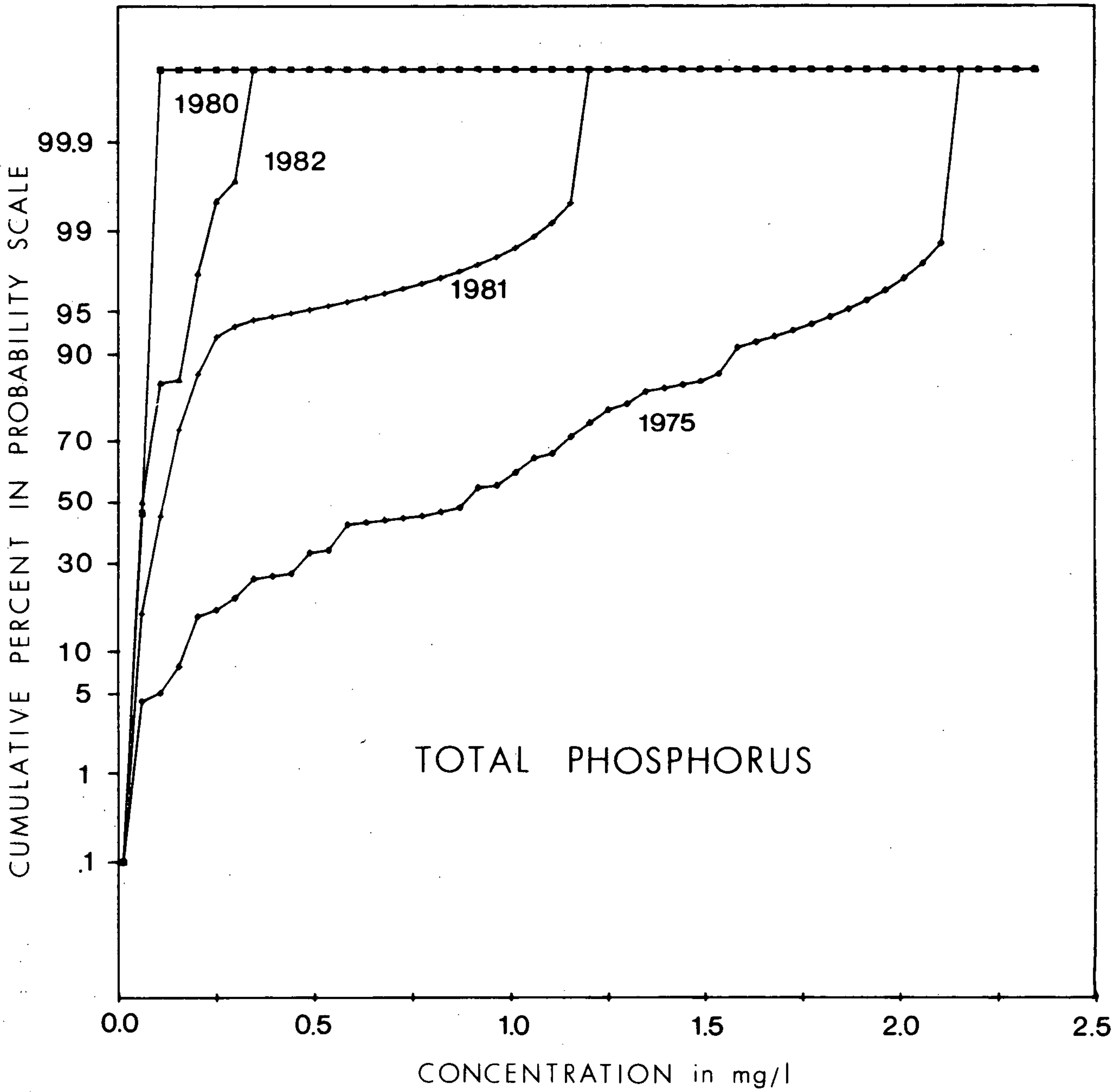

Figure 5.
Cumulative probability distributions of total phosphorus in the St. Mary River.

a fluoride concentration between 0.5 and 1.5 mg/l would be 40 percent in 1975; less than 0.1 percent in 1980; 13 percent in 1981; and 24 percent in 1982. Another way of expressing this would be the probability of samples with concentrations less than 1.5 mg/l are 65 percent in 1975; 99.9 percent in 1980; 93 percent in 1981 and 96 percent in 1982. For silicate (Figure 7) the results are not as graphic as those shown for phosphorus and fluoride or even in frequency polygons, however statistically as determined in the following section there is a significant difference.

Test Statistics

Determining the equality of means from independent samples is a common statistical analysis. Several methods can be utilized testing basically the same hypothesis however they are substantially different in the slopes of their power curve, critical values, and robustness. In this report five techniques were applied to the data sets to determine and identify distributional properties for each variable.

Non-parametric methods are generally not as powerful as their parametric equivalents especially when the assumptions of the parametric test hold true. Procedures such as the Kruskal-Wallis test are particularly useful when uncertainty exists concerning the satisfaction of assumptions or in looking at the form of the population frequency distribution instead of specific population parameters.

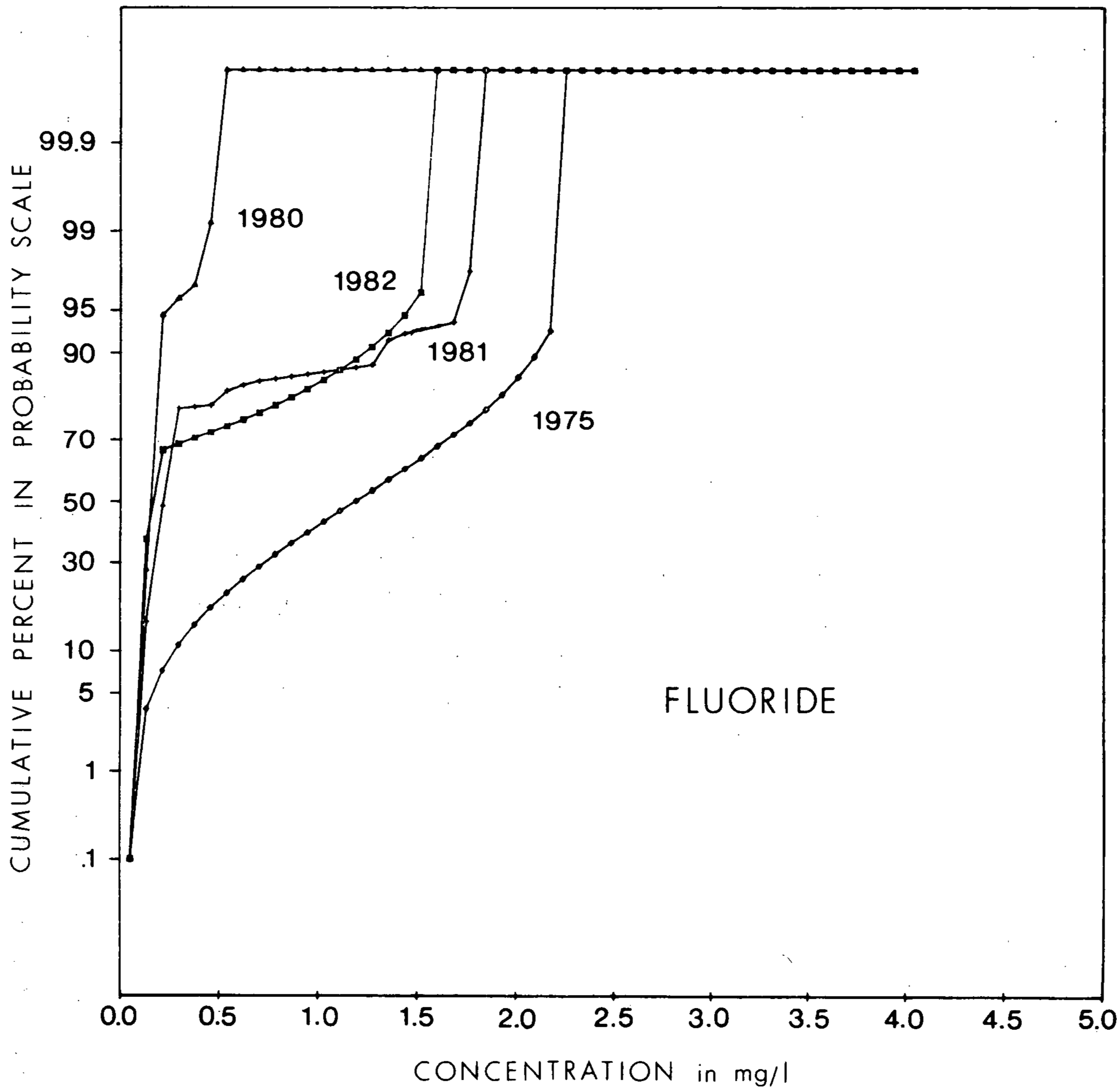

Figure 6.
Cumulative probability distributions of fluoride in the St. Mary River.

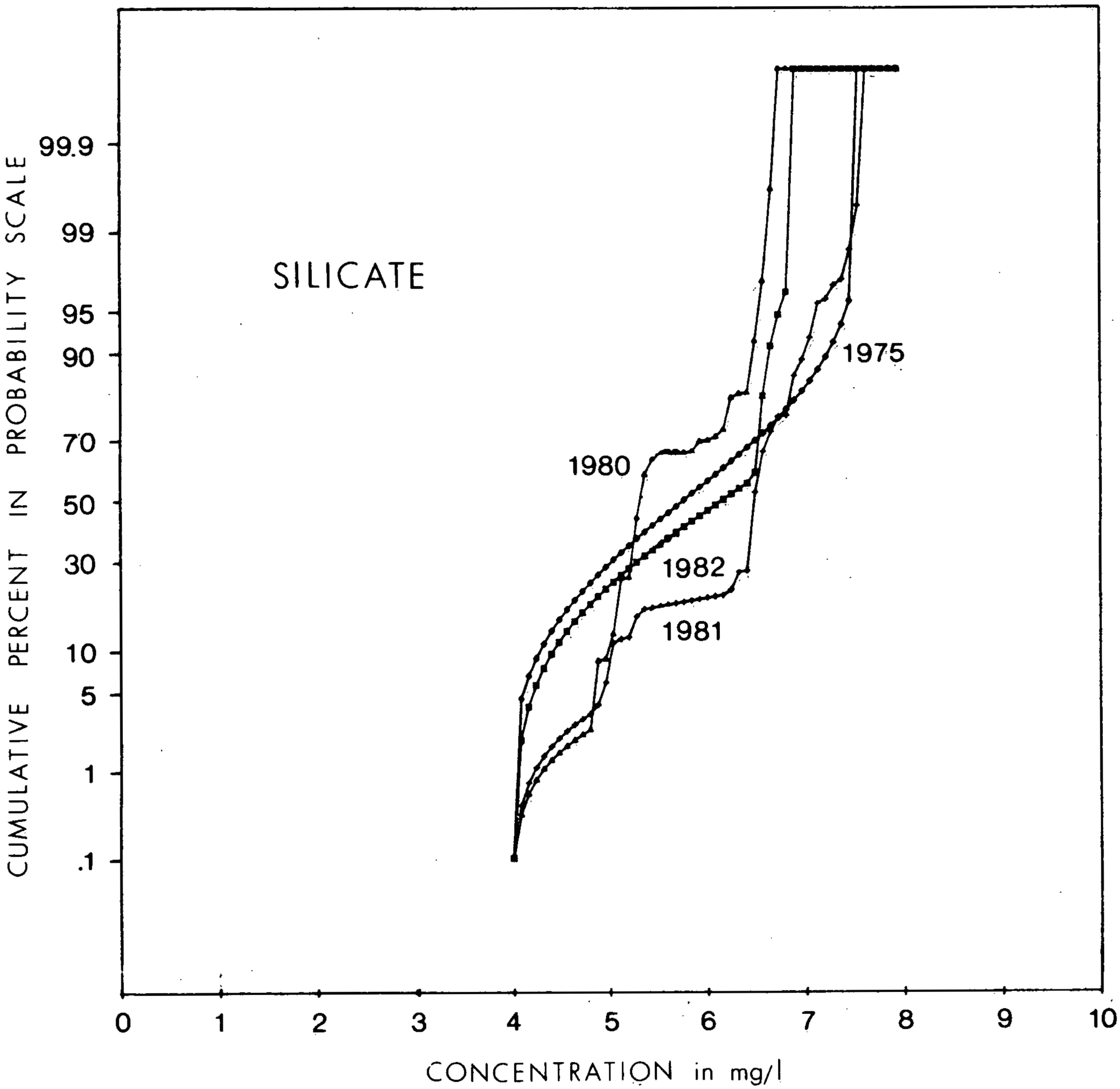

Figure 7.
Cumulative probability distributions of silicate in the St. Mary River.

The null hypothesis of the Kruskal-Wallis test states that the location parameters of the populations do not differ between the samples. For our data set, this hypothesis is rejected since each test statistic (H) calculated is greater than the level of significance determined from the chi-square distribution. The population distributions for each variable during each year is significantly different, indicating a definite change in the mean of total phosphorus, fluoride and silicate concentrations between the years.

The next statistic used to test the equality of the population means was the ANOVA F-statistic. This alternate approach again indicates a significant added variance component among the group means ($^{P}F_{S}$ $P < 0.05$) for all three variables. Unlike the Kruskal-Wallis test the ANOVA is a parametric statistic with underlying assumptions (i.e. homoscedasticity).

Levene's statistic is useful in testing the equality or homogeneity of variances, often assumed in many of the statistical procedures. Brown and Forsythe (1974b) determined that Levene's statistic was robust under non-normality. The variances of the data sets are significantly heterogeneous since $P < 0.05$.

The consequences of heterogeneity of variances is a serious violation of the one way analysis of variance. When looking at the overall test of significance however, methods testing the equality of means on the assumption of heterogeneity of variances is an alternate approach to obtain a more powerful estimator. Two more robust tests are the modified F statistic proposed by Brown-Forsythe and the Welch statistic. Each test approximates the distribution of its estimate by that of Snedecor F with respect to unequal population variances.

Both statistics have been shown to be robust under heteroscedasticity (Brown and Forsythe 1974a). The choice between them depends on the magnitude of their means and standard errors. As shown in the Tables 1 to 3, both tests showed significant differences between means.

The results from each statistical test applied to the data sets indicate the means differ from each other to such an extent that we must assume they were sampled from different populations. These results are shown in Tables 1 to 3. The probability of each test statistic is calculated to be less than 0.001 within the rejection region of their specific frequency curves. Overall, the results indicate a definite change in the concentration of the three variables phosphorus, fluoride, and silicate during the sampled years 1975 and 1980-82.

The results show significant decreases in the concentration of total phosphorus from a mean in 1975 of 0.63 mg/l to less than 0.11 mg/l in the period 1980-82. The average concentrations of fluoride in 1975 was 2.86 mg/l and reduced to less than 0.25 mg/l in 1980-82. Silicate concentrations were also reduced from 7.47 mg/l (1975) to less than 6.29 mg/l (1980-82). These concentration decreases were the result of the changes in wastewater treatment and handling by the Cominco operations in the Kimberley area.

Table 1 Statistical Comparison of Total Phosphorus Concentrations Between Years. Numbers Shown in Parenthesis are in mg/l, All Other Values Are Natural Logarithmic Transforms

STATISTIC	1975	1980	1981	1982
Mean	-0.461 (0.630)	-2.807 (0.060)	-2.198 (0.111)	-3.153 (0.042)
Standard Deviation	1.045	0.695	0.937	0.758
Maximum Value	1.563 (4.775)	-0.654 (0.520)	0.652 (1.920)	-2.408 (0.089)
Minimum Value	-3.612 (0.027)	-4.382 (0.013)	-4.017 (0.018)	-4.423 (0.012)
Number of Observations	142	501	322	52

TEST STATISTIC	TESTS	VALUE	DEGREES OF FREEDOM	PROBABILITY
A. Kruskal-Wallis (H) (non-parametric)	equality of means	383.91	3	0.000
B. ANOVA (F) (parametric)	equality of means	310.95	3 1013	0.000
C. Levene (ω_0) (robust)	equality of variances	9.97	3 1013	0.000
D. Brown-Forsythe (F*) (robust)	equality of means	279.29	3 407	0.000
E. Welch (W) (robust)	equality of means	235.30	3 195	0.000

Table 2 Statistical Comparison of Fluoride Concentrations Between Years. Numbers Shown in Parenthesis are in mg/l, All Other Values Are Natural Logarithmic Transforms

STATISTIC	1975	1980	1981	1982
Mean	1.051 (2.86)	-1.947 (0.143)	-1.407 (0.245)	-1.431 (0.240)
Standard Deviation	1.151	0.435	0.921	1.551
Maximum Value	2.104 (8.20)	-0.744 (0.475)	0.626 (1.870)	0.693 (2.00)
Minimum Value	-0.580 (0.560)	-2.781 (0.062)	-2.996 (0.051)	-2.996 (0.051)
Number of Observations	28	432	241	54

TEST STATISTIC	TESTS	VALUE	DEGREES OF FREEDOM	PROBABILITY
A. Kruskal-Wallis (H) (non-parametric)	equality of means	179.81	3	0.000
B. ANOVA (F) (parametric)	equality of means	144.50	3 751	0.000
C. Levene (ω_0) (robust)	equality of variances	102.95	3 751	0.000
D. Brown-Forsythe (F*) (robust)	equality of means	62.08	3 111	0.000
E. Welch (W) (robust)	equality of means	89.94	3 86	0.000

Table 3 Statistical Comparison of Silicate Concentrations Between Years. Numbers Shown in Parenthesis are in mg/l, All Other Values Are Natural Logarithmic Transforms

STATISTIC	1975	1980	1981	1982
Mean	2.011 (7.47)	1.710 (5.52)	1.839 (6.29)	1.821 (6.17)
Standard Deviation	0.334	0.101	0.112	0.075
Maximum Value	2.485 (12.0)	1.917 (6.80)	2.028 (7.60)	1.917 (6.80)
Minimum Value	1.386 (3.90)	1.569 (4.80)	1.569 (4.80)	1.705 (5.50)
Number of Observations	46	432	309	54

TEST STATISTIC	TESTS	VALUE	DEGREES OF FREEDOM	PROBABILITY
A. Kruskal-Wallis (H) (non-parametric)	equality of means	232.25	3	0.000
B. ANOVA (F) (parametric)	equality of means	118.25	3 837	0.000
C. Levene (ω_0) (robust)	equality of variances	98.84	3 837	0.000
D. Brown-Forsythe (F*) (robust)	equality of means	46.44	3 62	0.000
E. Welch (W) (robust)	equality of means	105.22	3 130	0.000

SUMMARY

In summarizing the statistical methods used in this report, the one way analysis of variance (ANOVA) is a powerful statistic of test however it is sensitive to the lack of homogeneity within group variances. To test the homoscedasticity (i.e. lack of homogeneity within group variances) we used Levene's test statistic (ω_0) and found it to be significant. The Kruskal-Wallis test is a non-parametric statistical procedure particularly useful when uncertainty exists concerning assumptions underlying parametric tests. This method along with the Brown-Forsythe and Welch statistic are robust under conditions of non-normality and useful in determining the form of the population frequency distribution. The Brown-Forsythe or Welch tests are also effective considering the small loss in power, even when the population variances are equal.

All of the techniques described herein suggest a significant change in water quality, at least for the three variables we considered. These changes reflect decreases in phosphorus silicate and fluoride concentrations in the St. Mary River between 1975 and 1980-1982. During this interval effluent disposal practices were improved and a treatment facility was built. The concentration and distributional changes described here reflect the effectiveness of these action.

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