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STATISTICAL ANALYSES OF COLUMBIA RIVER WATER CHEMICAL DATA

Prepared for

Inland Waters Directorate
Water Quality Branch
Pacific and Yukon Region
Vancouver, B. C.

Under contract number 06SB.KW601-6-9042 by

Annette L. Smith

October, 1986



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I. Introduction

Levels of nutrients, metals and other parameters were measured in water collected from the Columbia River at Waneta and Birchbank, 1978-1984. This report describes statistical analyses of some of the data. The following questions have been addressed:

1. Is the river cross section at Waneta well-mixed, or do levels of chemical parameters measured at various points and depths differ? Are any observed differences among points real, or are they an artefact of the time it takes to sample the cross section?
2. Which parameters measured during 24 to 93 hour time series studies exhibit temporal variability, and what patterns of variability do they exhibit?
3. With what frequency (if any) do levels of parameters measured during the time series studies exceed guide lines for drinking water and/or aquatic life?
4. What is the relationship between dissolved, extractable and total metals?

II. Variability on the Cross Section

Six sets of samples were collected on the cross section in 1978 and 1979. Differences in each parameter measured at the various cross sectional points and depths initially were compared by two-way factorial analyses of variance (ANOVAs). The results are summarized in Tables 1 and 2.

A. Violations of ANOVA Assumptions

The ANOVA results should be viewed with caution. Although the organization of the samples into cross sectional points and depths was consistent with the two-way ANOVA, some of the assumptions of ANOVA were not met by the sampling design or by the nature of the data. Violations of the ANOVA assumptions and their potential effects on the statistical tests are discussed below:

1. Non-additivity of Main Effects

Since all of the 1978 samples as well as the 1979 samples for As, Se, Hg and physical parameters were taken without replication, it was necessary to analyze these data sets with the an ANOVA design which assumes that the main effects are additive (ie., that there is no interaction). However, there is no theoretical reason to assume lack of interaction between depth

Table 1. ANOVA results for 1978 cross sections. Significance ($P < .05$) of cross-sectional variability is indicated by X; significance of depth is indicated by D; NS = Not Significant

Parameter	June	July	November
Dissolved P	NS	X	X
Total P	NS	NS	NS
NO ₃ + NO ₂	NS	NS	X
NH ₃	X	NS	X
Total N	X	NS	X
TIC	X	-	-
TOC	X	-	-
Total Sb	X	-	-
Dissolved Sb	NS	-	-
Total As	NS	-	-
Dissolved As	NS	-	-
Total Cu	NS	X, D	NS
Dissolved Cu	NS	-	-
Extractable Cu	NS	-	-
Total Fe	NS	NS	X
Dissolved Fe	NS	-	-
Extractable Fe	NS	-	-
Total Pb	X	NS	NS
Dissolved Pb	NS	-	-
Extractable Pb	X	-	-
Total Mn	-	NS	X
Total Ni	-	X	NS
Total Se	NS	-	-
Dissolved Se	NS	-	-
Total Zn	NS	X	X
Dissolved Zn	NS	-	-
Extractable Zn	NS	-	-

Table 2. ANOVA results for 1979 cross sections. Significance ($P < .05$) of cross-sectional variability is indicated by X; significance of depth is indicated by D; significance of interaction by XD. NS = None Significant, A = All Significant

Parameter	May	June	July
Dissolved P	A	A	A
Total P	A	X	A
NO3 + NO2	NS	X,D	X
NH3	A	A	X
Total N	A	X,XD	X,XD
Ca	NS	XD	NS
F	X	X,XD	X
SO4	A	X	A
Total Cd	-	-	A
Total Cu	X,D	A	A
Total Fe	X,D	A	X,D
Total Pb	A	X,D	A
Total Mn	X	X	NS
Total Ni	-	X	NS
Total Zn	A	A	X,D

Sampled in randomized blocks:

Specific Conductivity	NS	NS	NS
Turbidity	NS	NS	NS
Alkalinity	NS	NS	NS
pH	NS	NS	NS
Hardness	D	NS	NS
Extractable As	X	X,D	X
Extractable Se	NS	NS	NS

stratification and cross sectional non-mixing. (For example, input from a small tributary could alter the relationship between depth and concentrations of various substances at any point on the cross section affected by the input.) The presence of an actual cross section X depth interaction would increase the error term and reduce the power of the ANOVA to detect significant main (cross section and depth) effects.

2. Heteroscedasticity

The 1979 replicate data do not meet the assumption of homogeneity of variances, which probably does not seriously affect the overall ANOVAs. Levene's test (Brown and Forsythe 1974) showed significant heteroscedasticity for all parameters except fluoride in all data sets. Since heteroscedasticity often results from a correlation between mean and variance (increasing variance with increasing mean), a log-transformation was applied but failed to produce homoscedasticity in any parameter except iron. Inspection of the data suggests that the primary reason for unequal variances was that for most parameters, in at least one set of replicates, all three values were identical (zero variance). This type of heteroscedasticity should affect only the test for the interaction. Further, Levene's test appears overly sensitive for the small cell sizes (three replicates) involved. When cells having zero variance were not considered, the F-max test (Sokol and Rohlf 1969) showed significant heterogeneity of variances only for iron (May and June data sets) and calcium (July data).

3. Non-Independence of Errors

Since sampling the cross section took several hours and since in a river over time, the water masses passing a given point are different, time dependence of the data was possible. As time dependence would be a violation of the assumption of independence of errors, runs tests above and below the median (Sokol and Rohlf 1969) were performed to test for independence. Results of the runs tests are summarized in Tables 3 and 4. The tests suggest significant time dependence for some (often most) parameters in each data set.

Time dependence of the data may seriously have affected the validity of the ANOVAs. Significant tests for cross-sectional differences could have been caused by changes in concentrations over time. No transformation or nonparametric statistical test is capable of remedying this problem. The only real solution would be to resample the cross section, taking all samples simultaneously or sampling the different points randomly over time.

However, results of the runs test could be misleading. Since samples were taken progressively across the river, real spatial differences (eg., an effluent flowing down one side of the river) rather than time dependence could have been responsible for the significant runs tests.

Table 3. Runs test above and below the median for 1978 cross sectional data. * $P < .05$, ** $P < .01$, NS = Not Significant

Parameter	June	July	November
Dissolved P	*	**	**
Total P	NS	*	NS
NO3 + NO2	NS	-	**
NH3	**	NS	*
Total N	NS	NS	**
Total Cu	NS	NS	-
Dissolved Cu	NS	-	-
Total Fe	*	NS	**
Dissolved Fe	NS	-	-
Total Pb	**	NS	*
Dissolved Pb	*	-	-
Total Mn	-	NS	-
Total Ni	-	NS	NS
Total Zn	**	NS	NS

Table 4. Runs test above and below the median for
1979 cross sectional data. * $P < .05$, ** $P < .01$,
NS = Not Significant

Parameter	May	June	July
Dissolved P	**	**	NS
Total P	**	**	**
NO3 + NO2	-	NS	**
NH3	**	**	*
Total N	**	**	**
Ca	NS	NS	*
F	**	**	*
SO4	**	**	**
Total Cd	-	-	**
Total Cu	*	NS	NS
Total Fe	**	NS	*
Total Pb	NS	NS	**
Total Mn	**	*	-
Total Zn	**	**	**

B. Spatial or Temporal Variability?

It may be possible at least partially to resolve the question of whether observed differences on the cross section are due to spatial or temporal variability. In 1979, half-hourly samples were taken at the left bank while the cross section was being sampled. If the river is well mixed, concentrations of chemicals measured at any point on the cross section should be equal to concentrations measured at the bank at the corresponding time. Temporal differences should be reflected in changes at the bank station.

The relation between bank and cross sectional samples was tested by Pearson product-moment correlation (Sokal and Rohlf 1969). In order to maximize the number of data points available for this analysis, bank and cross section samples were paired as shown in the following example. If a point on the cross section were sampled from 11:12-11:32, the measurements at that point were paired with bank samples taken at 11:25. The first bank replicate was matched with the mean of the three replicates from the first depth sampled, the second bank replicate with the mean at the second depth sampled, etc. Sometimes the sampling times of a cross sectional point did not encompass any bank sampling time. That point was then paired with the bank sample whose sampling time most nearly corresponded but which had not been paired with any other point. If a point had been sampled between two bank samples which matched the sampling times of other points, the data from that cross section were not included in the analysis.

Since bank and cross section sampling times did not match precisely, exact equivalence of concentrations was not expected, but significant positive correlations should have resulted if changes in concentrations occurred at the same time on both bank and cross section. Results of the correlation analyses are summarized in Table 5. Significant positive correlations were present for some but not all parameters in each month. Inspection of the data suggests that correlations were most pronounced when large changes in concentrations (probably due to upstream discharges) occurred over the sampling period. *

No explanation is apparent for the significant negative correlation between bank and cross sectional concentrations of iron in May.

When bank and cross sectional data were positively correlated, this relationship was used to remove the effect of time from the ANOVAs. If concentrations of a given substance measured at the left bank (l) and on the cross section (x) at the same time were equal, the relationship could be described by the regression

$$x = a + bl$$

where $a=0$ and $b=1$. If real differences in concentrations between the bank and the cross section occurred, b would not equal ~~zero~~ ^{one} and would be a measure of the effect due to cross section. Thus, the cross sectional data (including all replicates) were divided

Table 5. Correlation between concentrations measured at the bank and on the cross section at corresponding times. * $P < .05$, ** $P < .01$, NS Not Significant

Parameter	May	June	July
Total P	**	**	**
NO3 + NO2	-	NS	NS
NH3	NS	**	NS
Total N	NS	NS	NS
Ca	NS	NS	NS
F	**	NS	NS
SO4	**	NS	NS
Total Cd	-	-	**
Total Cu	NS	NS	NS
Total Fe	* (-ve)	NS	NS
Total Pb	NS	NS	**
Total Mn	NS	NS	NS
Total Zn	**	NS	NS

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by the corresponding bank values, and the ANOVAs were repeated using the quotients.

Results of these ANOVAs are listed in Table 6. Transformation removed the effect of cross section only from the total phosphorus data for June and the cadmium data for July. This suggests that for the remaining parameters, differences along the cross section were not artefacts of time dependence. *

C. Importance of Cross Sectional Variability

Several patterns of variability in concentrations of chemicals at various points on the cross section can be identified.

1. Large scale, persistent. When large scale incomplete mixing occurs, high concentrations of substances flow downstream from their discharge point along one side of the river. The general pattern of variability will be present under all flow regimes.

2. Small scale, persistent. Localized high concentrations of certain chemicals may be caused by ground or surface water inputs or by currents and eddies resulting from bottom configuration. The pattern of non-mixing can persist from day to day but may be altered by changes in water levels.

3. Small scale, transitory. At any time and point, concentrations of some substances may be altered by biological activities such as nutrient uptake by algal blooms or excretions by schools of fish.

(Refer to Ph. 5-12)

The effect of these types of incomplete mixing on water quality monitoring differs. Only the first type of non-mixing would cause the Waneta cross section to be an unsuitable site at which to monitor changes caused by upstream industrial discharges, but one would wish to avoid sampling at a point where a local (type 2) aberration occurred.

Three-way (point X depth X month) ANOVAs were used to look for persistent patterns of non-mixing. Because of similarity of sampling designs, data from July and November, 1978, were combined for one set of analyses, while all 1979 data were combined for another set.

Results of the three-way ANOVAs are listed in Table 7. They should be viewed with caution, as the time-dependence discussed previously is still present.

Significant tests for variability due to cross section combined with not significant results for the cross section X month interaction is evidence for a persistent pattern of non-mixing. This combination of results was found in the 1978 copper and zinc data and in the 1979 nitrate + nitrite and manganese data.

Normally, a posteriori tests (eg., multiple range tests) would be used to determine which points on the cross section had significantly different concentrations of each substance. However, since these tests are often more sensitive to violations

TABLE 5

~~Table 6~~. Significance of ANOVA results for 1979 cross sections on values transformed by dividing by the corresponding bank data to remove the temporal factor. Notation as in Table 2.4

Parameter	May	June	July
Total P	X, XD	NS	A
NH3	-	A	-
F	X, XD	-	-
SO4	A	-	-
Total Cd	-	-	NS
Total Pb	-	-	A
Total Zn	A	-	-

Table 2. Significance of 3-way ANOVA results for 1979 cross sections on untransformed values. XMD = 3-way interaction (possible for 1979 data only), other notation as in Table 2.

Parameter	1978	1979
Dissolved P	X, M, XM	X, M, XM, XD, XMD X
Total P	M	X, M, XM X
NO3 + NO2	X, M, XM X	X, M ✓
NH3	X, M, XM	X, M, XM, XD, XMD X
Total N	X, M, D, XM X	A
Ca	-	M, D, XD, MD, XMD X
F	-	X, M, XM, XD X
SO4	-	X, M, XM X
Total Cd	-	X, XM, XD, XMD X
Total Cu	X ✓	XM X
Total Fe	X, XM	X, M, D, XM X
Total Pb	M	A
Total Mn	NS	X, M
Total Ni	M	X, M, XM, MD
Total Zn	X, M ✓	X, M, XM, XD

of the assumptions of ANOVA than the tests for main effects, multiple range tests would be of little value for the Waneta data.

On the other hand, graphing concentrations of various chemicals along the cross section (Figures 1-7) and tabulating locations where the highest concentration of each substance was collected (Table 8) provide a picture of the pattern of incomplete mixing. There is no evidence of large-scale non-mixing that would confine an effluent to one side of the river, but there does appear to be an anomaly at point R2 characterized by higher concentrations of metals and sometimes other substances at the 80% depth. Variability also tends to be high at R2.8. The anomaly is present in both years but not in all months, suggesting that the mixing pattern changes under different flow conditions.

D. Cross Section Variability: Conclusions

1. Time dependence in the data is strong. This factor probably accounts for much of the variability and causes the validity of any statistical tests to be questionable.
2. There is no evidence for large-scale non-mixing across the river, but there does appear to be some localized non-mixing at point R2, which is most noticeable at the greatest depth.
3. Correlations between bank and cross sectional data suggest that samples taken at the bank will show the passage of effluents (as in the July, 1979, cadmium and lead data), but bank samples may not be representative of baseline conditions across the river.

E. 1984 Cross Sections

The cross section at Waneta was sampled at a single depth during controlled discharges on two successive days in March, 1984. Since the cross section again was sampled systematically from left to right bank, the data are not independent of time, but as the sampling was accomplished in only 15 min, the time effect should be minimal.

The data were analyzed by one-way and two-way (cross section X day) ANOVAs. The results (Table 9) support the conclusions derived from the more detailed cross sections. Concentrations of most substances varied among points, but in all parameters except Zn, the day X cross section interaction was significant ($P < .05$), suggesting that the pattern of variability was not consistent from day to day. *

Graphs of the data (Figures 8-10) illustrate these patterns of variability. They do not show an anomaly in Zn levels similar to the pattern observed in the 1978 and 1979 data.

Figure 1. Variability of total phosphorus on the cross section
at Waneta

Variability of Total Phosphorus

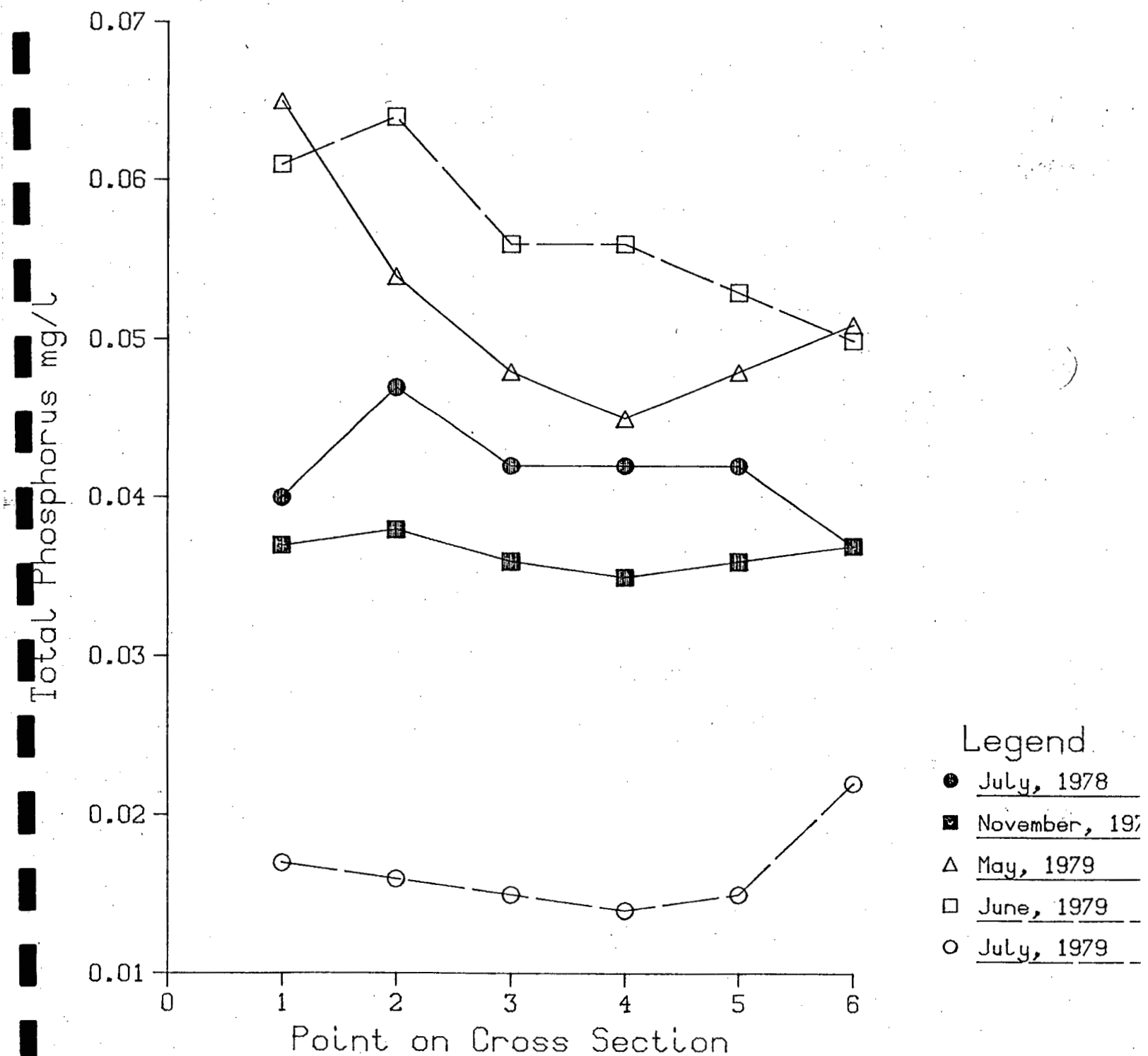


Figure 2. Variability of nitrate plus nitrite on the cross section at Waneta

Variability of $\text{NO}_3 + \text{NO}_2$

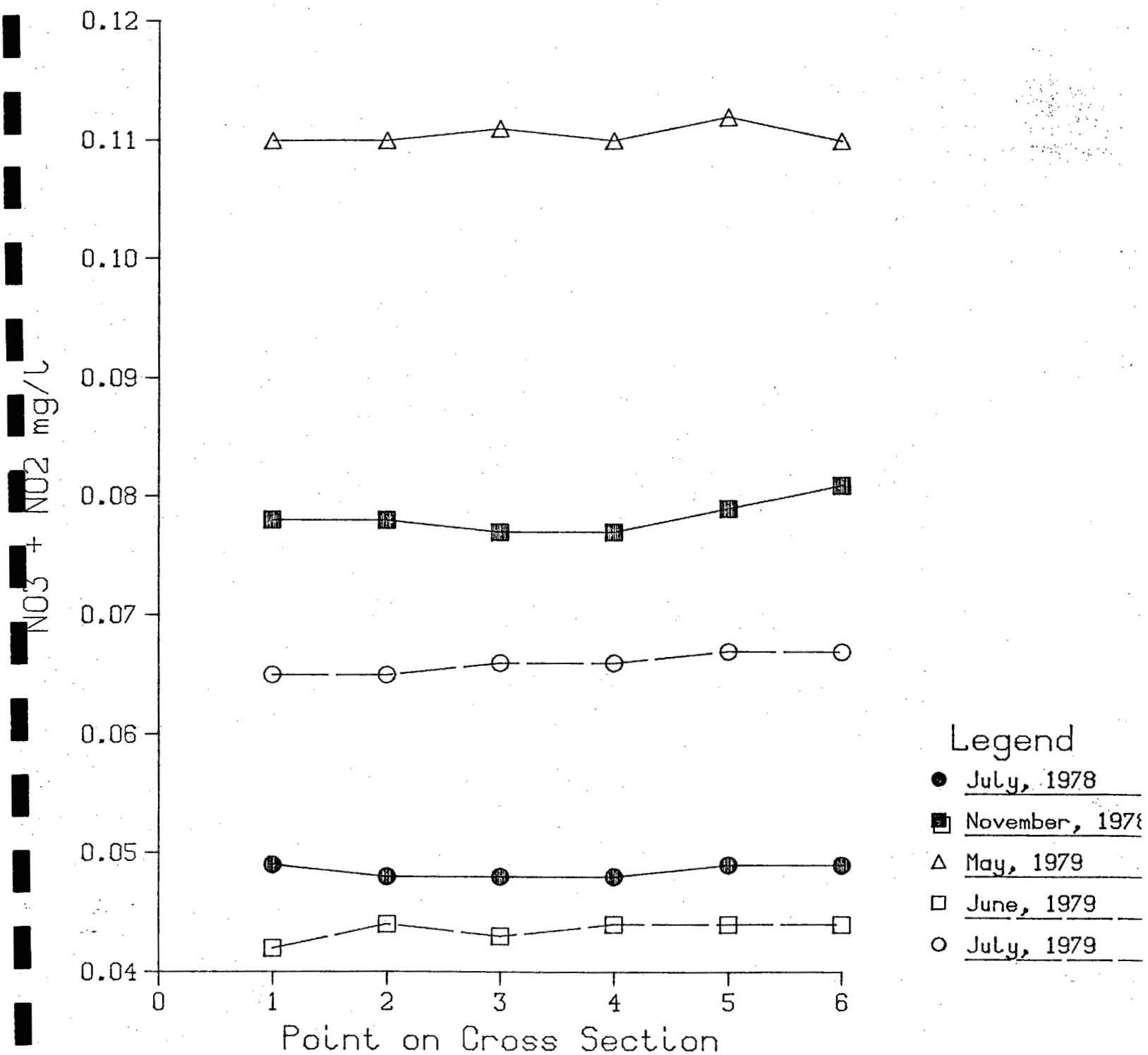
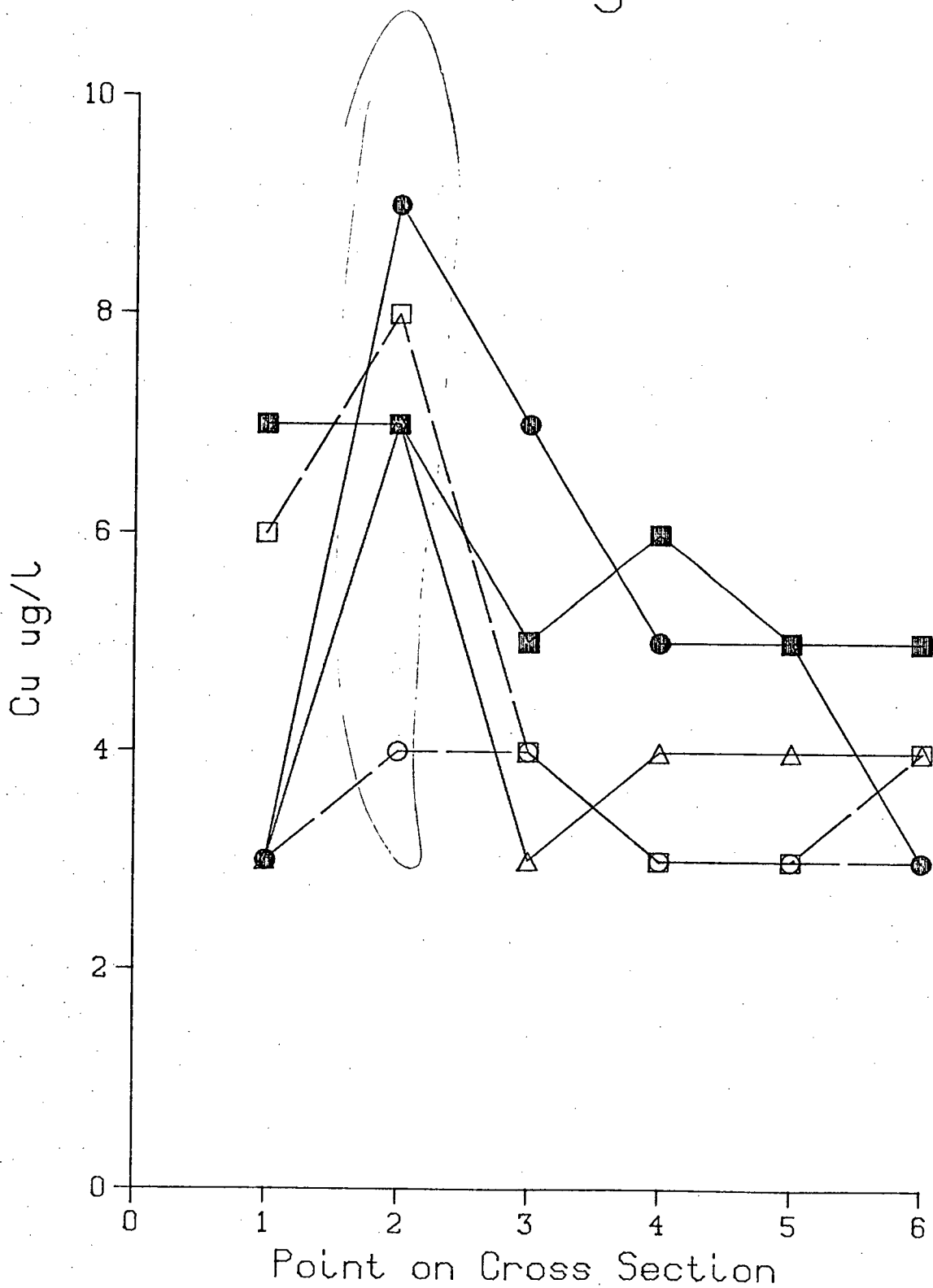


Figure 3. Variability of Cu on the cross section at Waneta

Variability of Cu

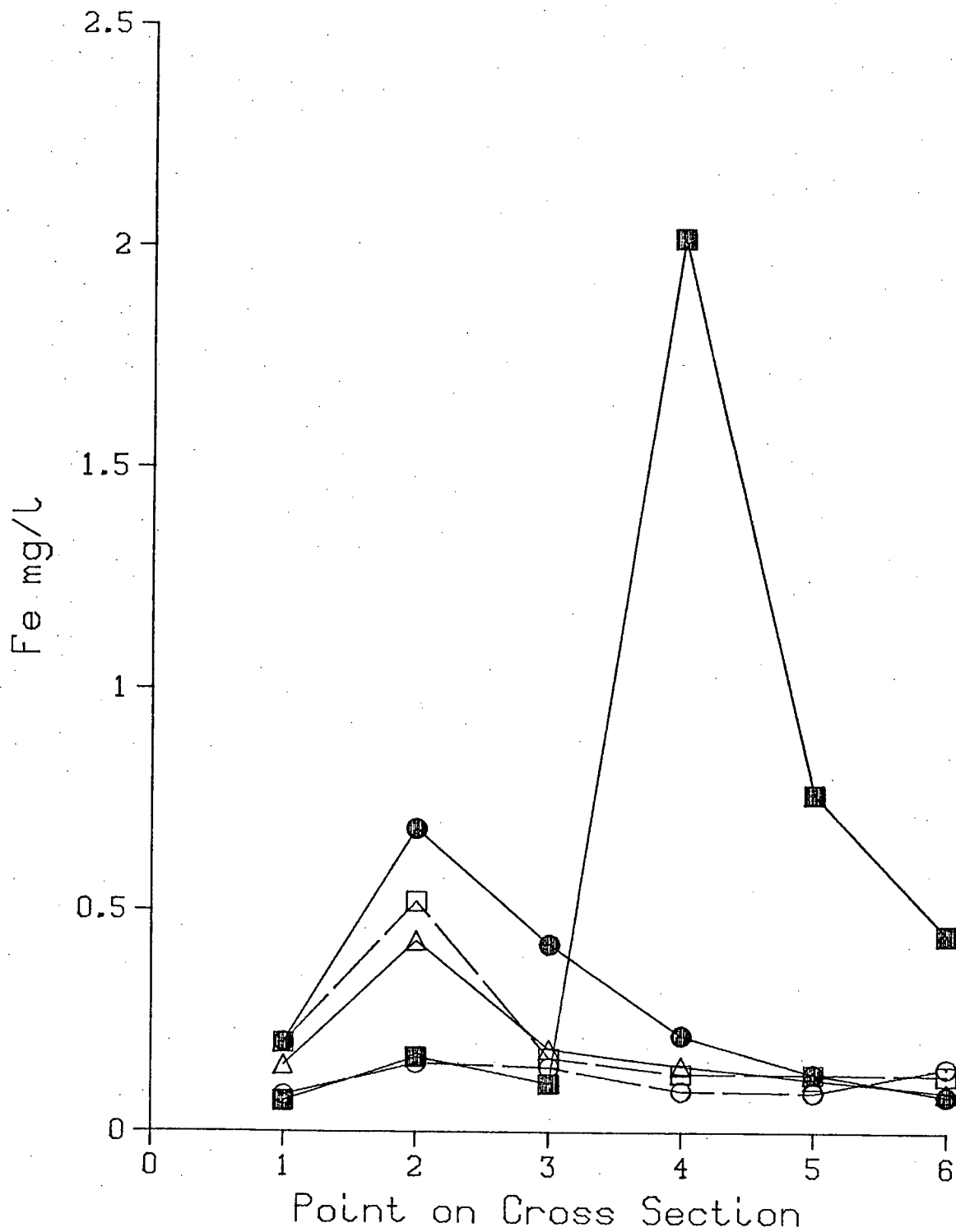


Legend

- July, 1978
- November, 1977
- △ May, 1979
- June, 1979
- July, 1979

Figure 4. Variability of Fe on the cross section at Waneta

Variability of Fe

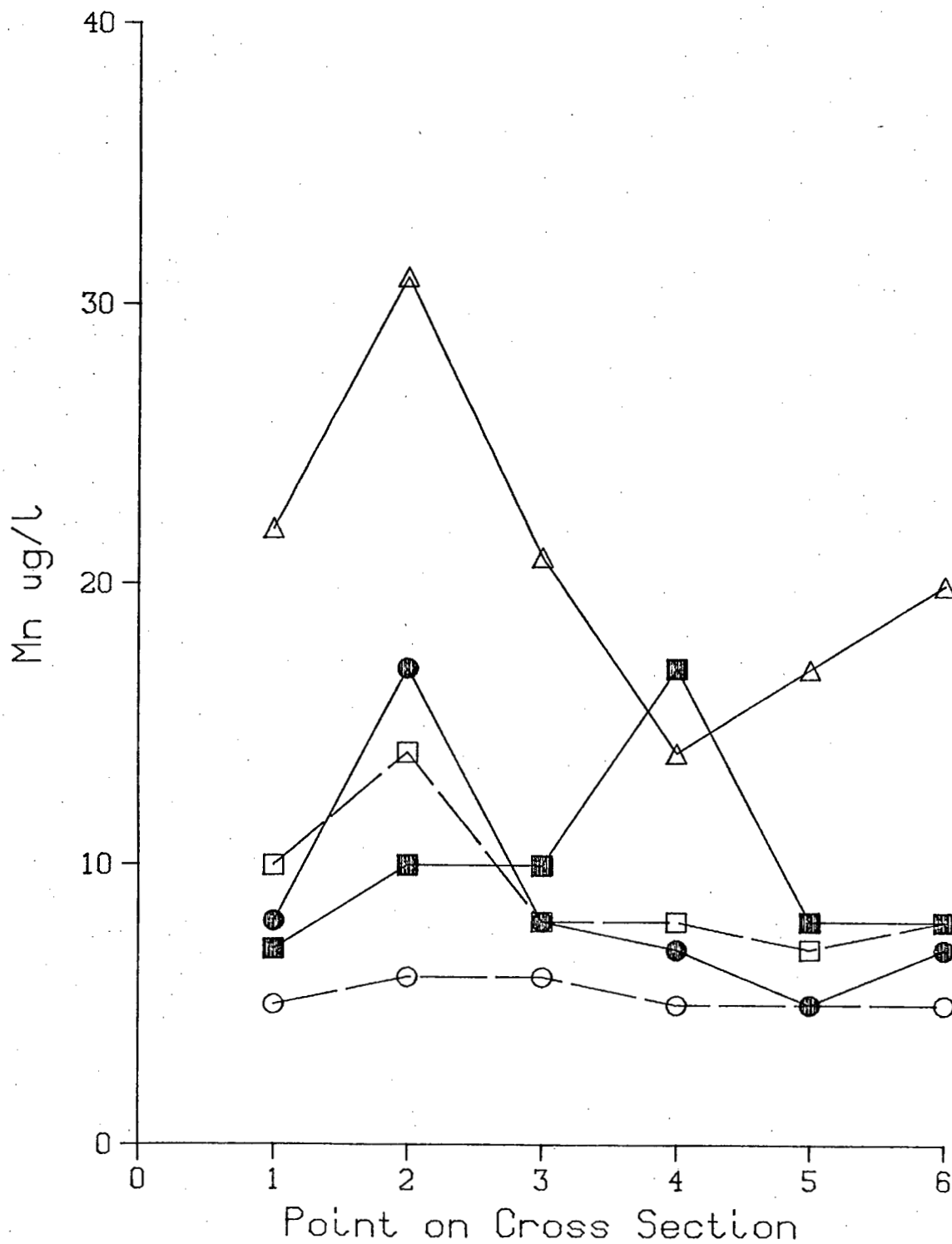


Legend

- July, 1978
- November, 1978
- △ May, 1979
- June, 1979
- July, 1979

Figure 5. Variability of Mn on the cross section at Waneta

Variability of Mn

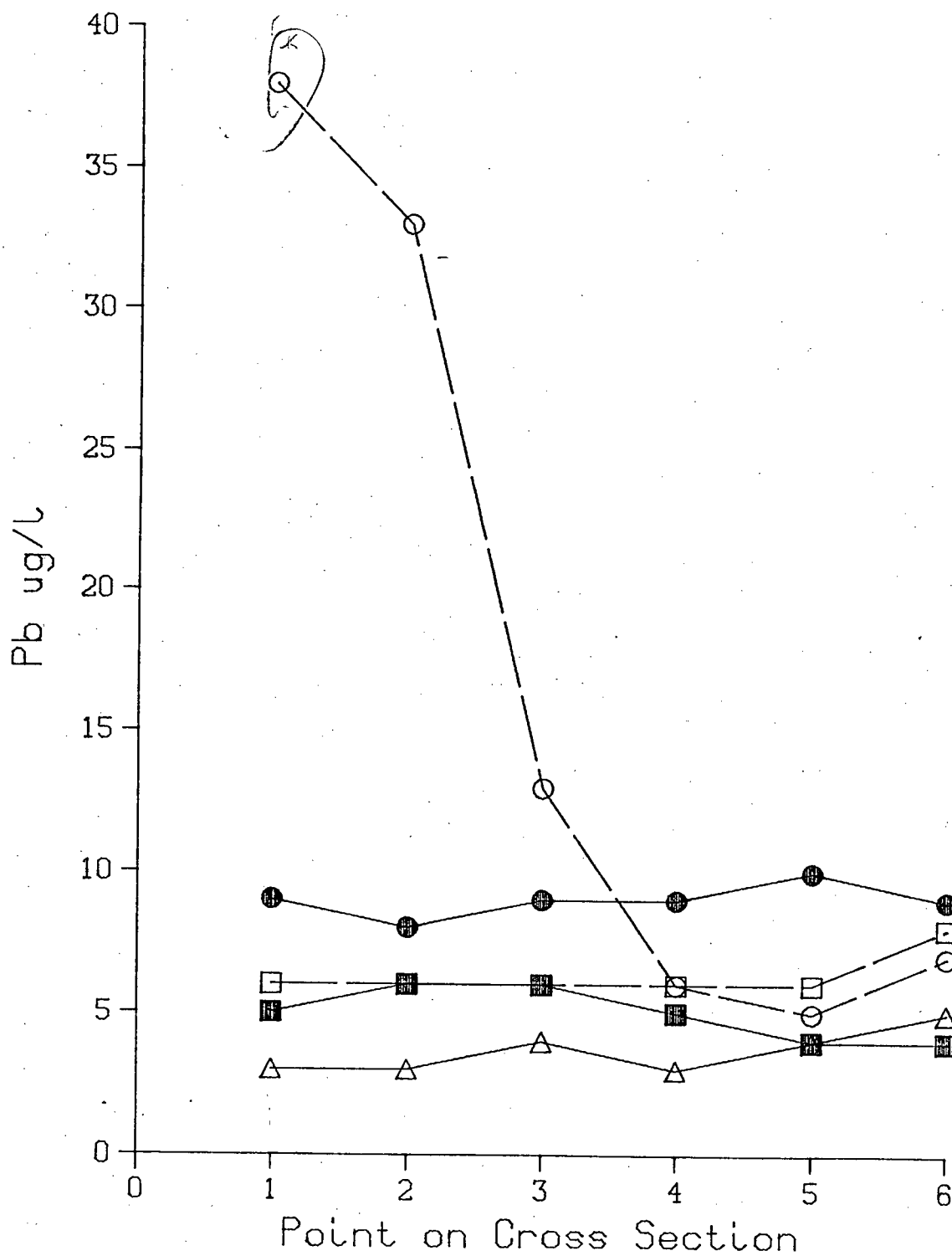


Legend

- July, 1978
- November, 1978
- △ May, 1979
- June, 1979
- July, 1979

Figure 6. Variability of Pb on the cross section at Waneta

Variability of Pb

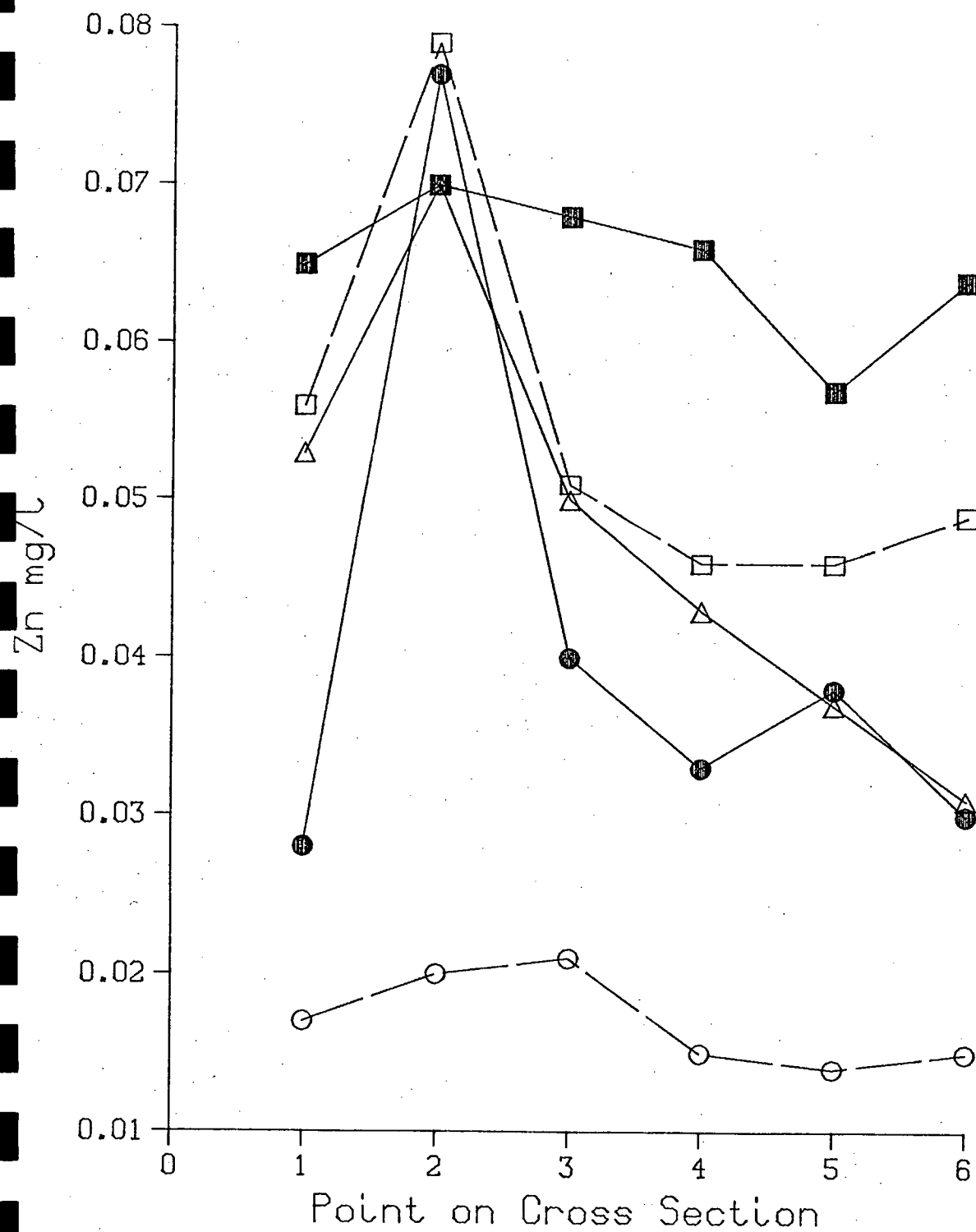


Legend

- July, 1978
- November, 1977
- △ May, 1979
- June, 1979
- July, 1979

Figure 7. Variability of Zn on the cross section at Waneta

Variability of Zn



- Legend
- July, 1978
 - November, 1978
 - △ May, 1979
 - June, 1979
 - July, 1979

Table 8. Cell containing highest mean, 1979 cross sections. NU = Not Unique, * indicates cell also had the highest variance.

Parameter	May	June	July
Dissolved P	R 1.8	R 1.2	NU
Total P	R 1.8	R 2.5	R 6.5
NO3 + NO2	NU	R 2.8*	NU
NH3	R 6.2	R 4.8	NU
Total N	R 6.2	NU	R 6.8
Ca	R 3.8	R 5.8	R 1.8
F	R 1.8	R 2.8	R 2.2*
SO4	R 2.8	R 1.5	NU
Total Cd	NU	NU	R 1.2
Total Cu	R 2.8*	R 2.8*	R 2.8
Total Fe	R 2.8*	R 2.8*	R 2.8
Total Pb	NU	NU	R 1.2
Total Mn	R 2.8	R 2.8*	NU
Total Ni	NU	R 5.2	NU
Total Zn	R 2.8*	R 2.8*	R 3.8

Table 9. ANOVA results for 1984 cross sections.
 * $P < .05$, ** $P < .01$, NS Not Significant

One-way ANOVAs (cross section only):

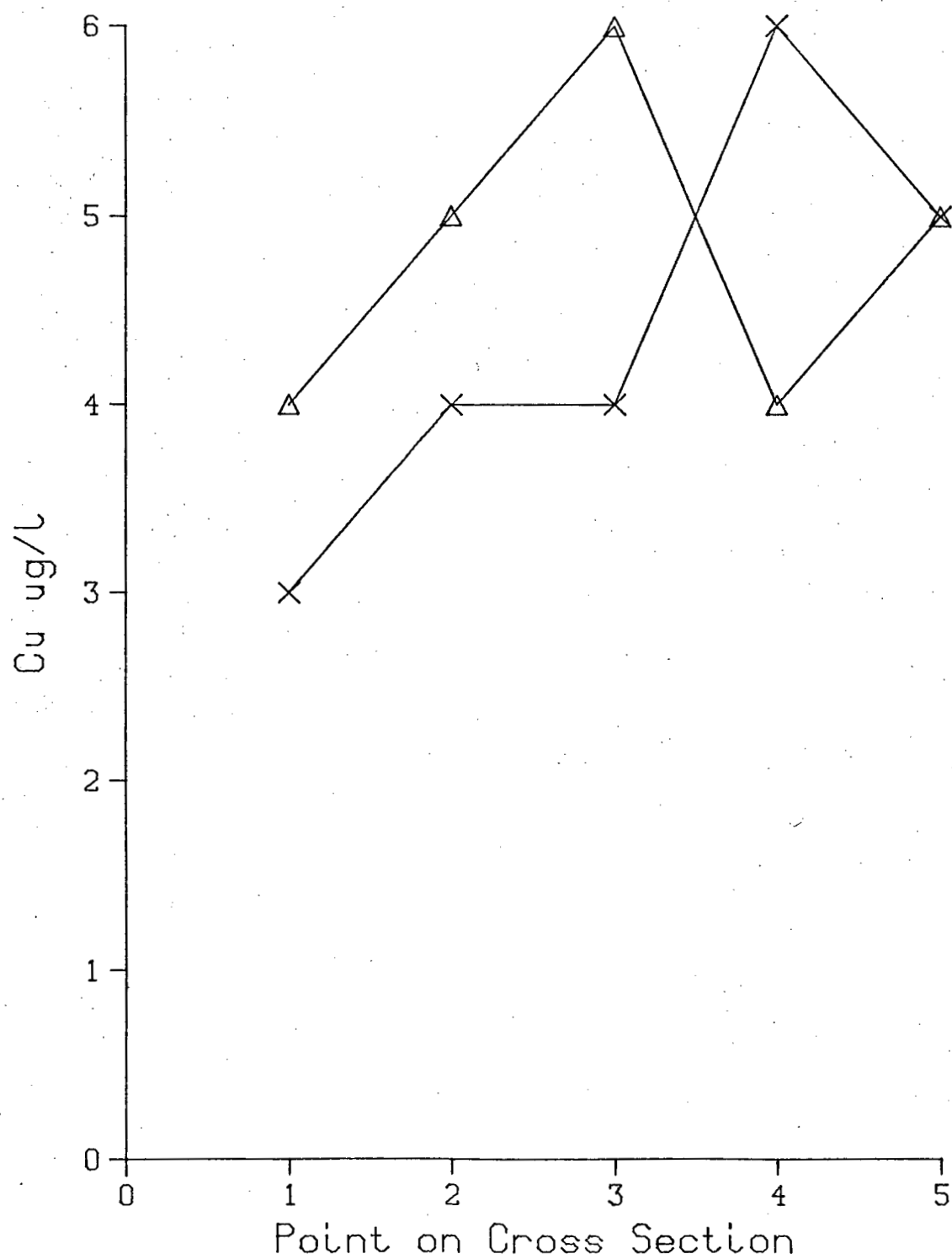
Parameter	Day 1	Day 2
As	NS	NS
Cd	NS	**
Cu	**	**
Fe	NS	**
Pb	*	NS
Zn	NS	NS
pH	*	*
SO ₄	*	**

Two-way ANOVAs:

Parameter	XS	Day	XS X Day
As	NS	**	NS
Cd	NS	**	NS
Cu	NS	NS	**
Fe	NS	NS	NS
Pb	*	**	*
Zn	*	**	NS
pH	NS	*	*
SO ₄	**	**	NS

Figure 8. Variability of Cu measured on the cross section at Waneta during the 1984 controlled-discharge study

Variability of Cu, 1984



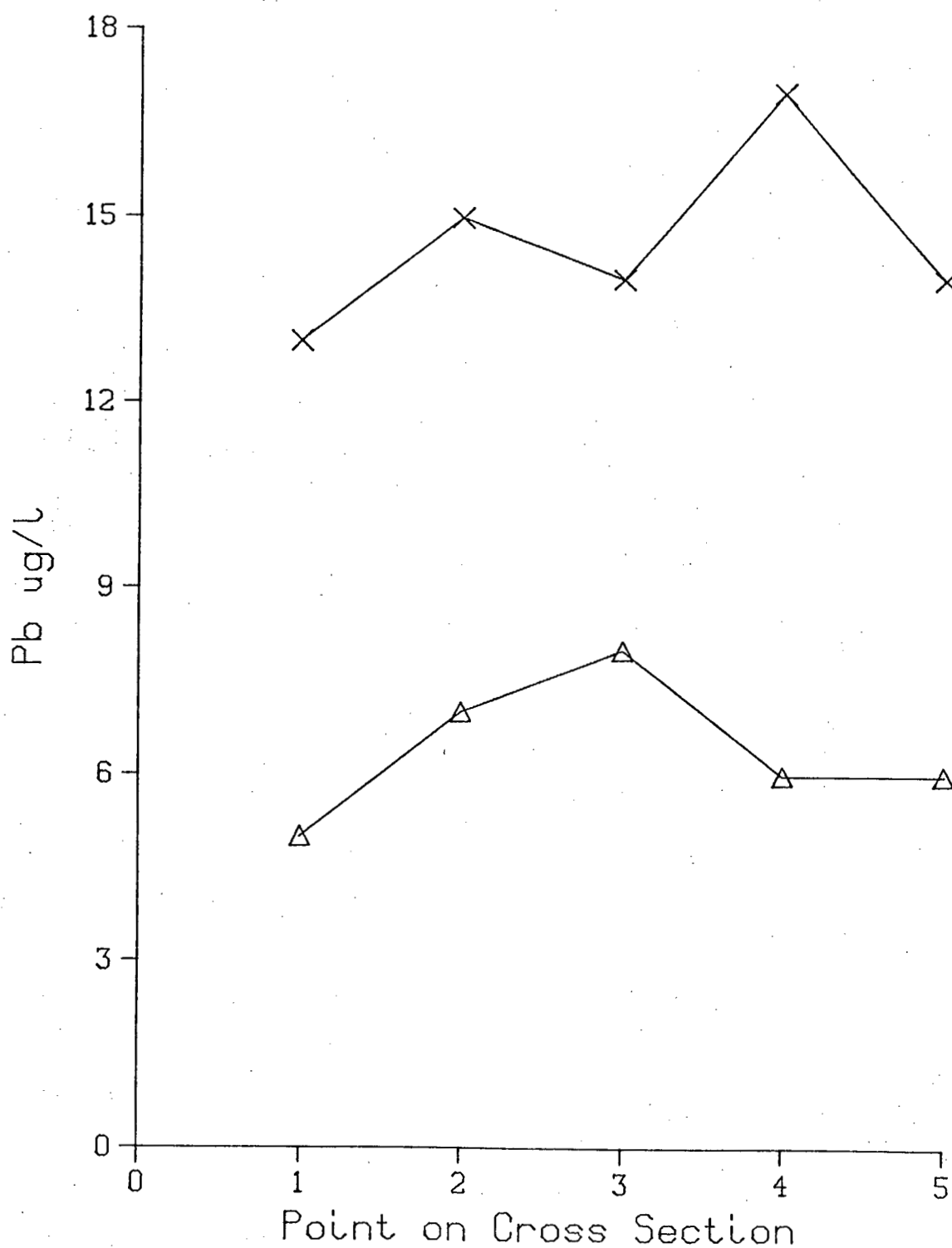
Legend

Δ Day 1

\times Day 2

Figure 9. Variability of Pb measured on the cross section at Waneta during the 1984 controlled-discharge study

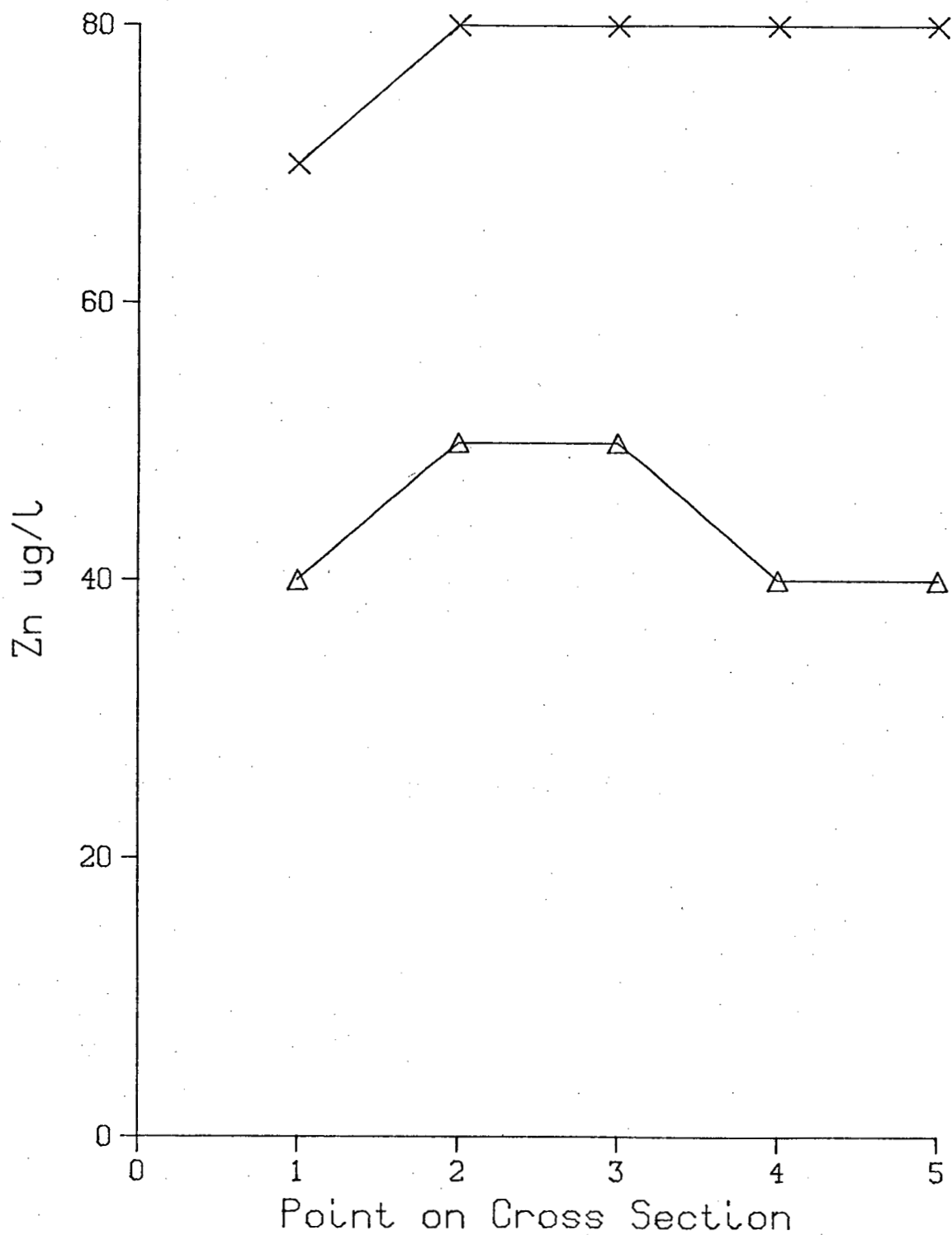
Variability of Pb, 1984



Legend
 Δ Day 1
 \times Day 2

Figure 10. Variability of Zn measured on the cross section at Waneta during the 1984 controlled-discharge study

Variability of Zn, 1984



Legend
 Δ Day 1
 \times Day 2

III. Time Series

A. Relative Variability of Metal Concentrations

Relative variability of the different metals measured during the 72 to 94-h time series studies was determined by using the coefficient of variability. This statistic makes it possible to compare variances of concentrations of each substance measured at different times and sites independently of the concentration means.

Results are summarized in Table 10. Lowest variabilities were measured for metals whose concentrations were near detection limits (As, Se and usually Hg and Mn). These metals might not appear less variable than others if detection limits were lowered so that their full concentration ranges could be measured. *

? There was no consistent pattern of high or low variabilities at either site or in any time series. Highest variabilities for most parameters were recorded at Waneta, but within any time series, variability of a given parameter was often higher at Birchbank.

The coefficients of variability were also calculated for parameters measured during the 24-h time series and the 72-h nutrient study. These values are listed in Table 11.

B. Patterns of Variability

Frequency distributions of levels of each parameter measured during each time series study were determined. From these distributions, medians (50%iles) and 75%iles were calculated. These values, along with minimum and maximum concentrations of each metal are listed in Table 12. A similar tabulation has been made for nutrients (Table 13). The distributions illustrate the range of concentrations and the levels of nutrients and metals most commonly encountered during the time series studies.

Time series plots of concentrations of each metal and nutrient have also been made (Figures 11-30). Median and 75%ile are illustrated on each plot. Viewing these plots leads to some conclusions about variability patterns.

✓ 1. Concentrations above the 75%ile do not usually occur randomly in time but tend to be clustered together in distinct peaks, often with both a rising and a descending portion.

✓ 2. There was a trend toward increasing lead levels in the 1984 time series. During this time series, controlled discharges of acid and spent electrolyte were being monitored. Apparently the lead concentrations in the river never returned to their previous level after the acid discharges. They increased even further following the electrolyte discharge and gave no indication of dropping for the duration of the study.

Table 10. Coefficients of variability of metals measured during the 1981-1984 time series studies.

Metal	1981		1983		1984	
	Birchbank	Waneta	Birchbank	Waneta	Birchbank	Waneta
As	9.75	19.3	0	12.6	0	28.1
Cd	87.9	47.0	355.	181.	179.	288.
Cr	82.0	220.	-	-	-	-
Cu	81.4	149.	58.0	89.5	54.8	48.2
Fe	-	-	35.3	113.	23.3	43.4
Hg	63.6	130.	0	34.6	0	33.1
Pb	92.5	61.3	41.1	85.7	120.	70.7
Mn	-	-	0	63.1	10.7	0
Se	0	10.4	0	0	0	35.3
Zn	55.1	36.4	90.7	117.	86.3	51.7

Table 11. Descriptive statistics and coefficient of variability for parameters measured during the 1978 and 1979 time series studies. Mean concentrations and their standard deviations are given in mg/L.

Parameter/ Year	Mean	S. D	C. V.
1978:			
pH	7.56	.087	1.15
Spec. Cond.	109.	3.66	3.36
Turbidity	.446	.093	20.80
Dissolved P	.037	.048	128.77
Total P	.044	.052	117.71
NO3 +NO2	.061	.001	2.12
NH3	.029	.004	13.79
Total N	.111	.005	4.74
Particulate N	.025	.003	12.34
Particulate C	.209	.023	11.10
Ca	16.0	.614	3.84
F	.091	.020	21.85
SO4	10.0	1.96	19.59
Cd	.0003	.0002	51.52
Cu	.004	.001	15.92
Fe	.079	.024	30.26
Pb	.005	.001	25.22
Mn	.010	.003	28.80
Ni	.001	.001	61.26
Zn	.039	.007	18.19
1979:			
Total P	.077	.031	39.82
NO3 +NO2	.056	.004	7.55
NH3	.059	.036	60.07
Total N	.154	.037	23.78
F	.142	.022	15.55

Table 12. Descriptive statistics for metals sampled during the 24 to 94-h time series studies. 1978 values are based on means of three replicates; all other values are computed from automatic sampler data (single samples).

Metal/ Year	Station	n	Minimum	Median	75%ile	Maximum
Cd:						
1978	Waneta	13	<.0005	<.0005	<.0005	.0008
1981	Waneta	47	<.0005	.0005	.0007	.0009
	Birchbank	72	<.0005	<.0005	<.0005	.0024
1983	Waneta	66	<.001	<.001	.001	.012
	Birchbank	68	<.0005	<.0005	.0005	.028
1984	Waneta	92	<.0005	.001	.0014	.046
	Birchbank	86	<.0005	<.0005	<.0005	.0055
Cr:						
1981	Waneta	28	<.001	.001	.0025	.05
	Birchbank	72	<.001	.002	.004	.008
Cu:						
1978	Waneta	13	.0027	.0037	.004	.0043
1981	Waneta	47	<.001	.003	.004	.04
	Birchbank	72	<.001	<.001	.001	.005
1983	Waneta	66	.002	.005	.009	.04
	Birchbank	68	.001	.004	.005	.016
1984	Waneta	92	.001	.004	.0055	.017
	Birchbank	86	.002	.003	.004	.016
Fe:						
1978	Waneta	13	.04	.077	.10	.11
1983	Waneta	66	.038	.10	.17	.88
	Birchbank	68	.015	.029	.038	.07
1984	Waneta	92	.028	.06	.07	.24
	Birchbank	86	.020	.037	.042	.07

Table 12 (Cont'd)

Metal/ Year	Station	n	Minimum	Median	75%ile	Maximum
Pb:						
1978	Waneta	13	.0027	.005	.006	.0067
1981	Waneta	47	<.001	.004	.005	.012
	Birchbank	72	<.001	<.001	.001	.005
1983	Waneta	66	.003	.007	.010	.056
	Birchbank	68	.001	.003	.004	.007
1984	Waneta	92	<.001	.006	.0095	.022
	Birchbank	86	<.001	.001	.003	.017
Mn:						
1978	Waneta	13	<.01	.01	.01	.017
1983	Waneta	66	<.01	<.01	<.01	.02
	Birchbank	68	<.01	<.01	<.01	<.01
1984	Waneta	92	.01	.01	.01	.01
	Birchbank	86	<.01	<.01	<.01	.01
Ni:						
1978	Waneta	13	<.001	.001	.0017	.0037
Zn:						
1978	Waneta	13	.030	.040	.043	.05
1981	Waneta	47	.014	.027	.036	.07
	Birchbank	72	<.001	.002	.003	.007
1983	Waneta	66	.014	.024	.037	.303
	Birchbank	68	.001	.003	.005	.030
1984	Waneta	92	.017	.030	.035	.10
	Birchbank	86	.002	.005	.007	.040

Table 13. Descriptive statistics for nutrients and fluoride sampled at Waneta during the time series studies. 1978 values are based on means of three replicates; all other values are computed from automatic sampler data (single samples).

Chemical	Year	n	Minimum	Median	75%ile	Maximum
Dissolved P	1978	13	.0043	.0213	.0503	.1737
Total P	1978	13	.009	.028	.0543	.1963
	1979	69	.028	.069	.095	.186
NO3 + NO2	1978	13	.059	.060	.0617	.0627
	1979	72	.050	.054	.060	.068
NH3	1978	13	.0237	.0297	.0333	.0347
	1979	72	.028	.0485	.0575	.236
Total N*	1978	13	.10	.11	.113	.12
	1979	72	.128	.144	.157	.383
Particulate N	1978	13	.0183	.0257	.0263	.0303
Particulate C	1978	13	.163	.210	.223	.163
F	1978	13	.067	.090	.108	.122
	1979	72	.092	.1435	.158	.200

* 1978 nitrogen samples were filtered in the field; 1979 samples were not.

Figure 11. Variability in Cd concentrations (ug/L) measured at Waneta during the 1981 time series study

WANETA, 1981

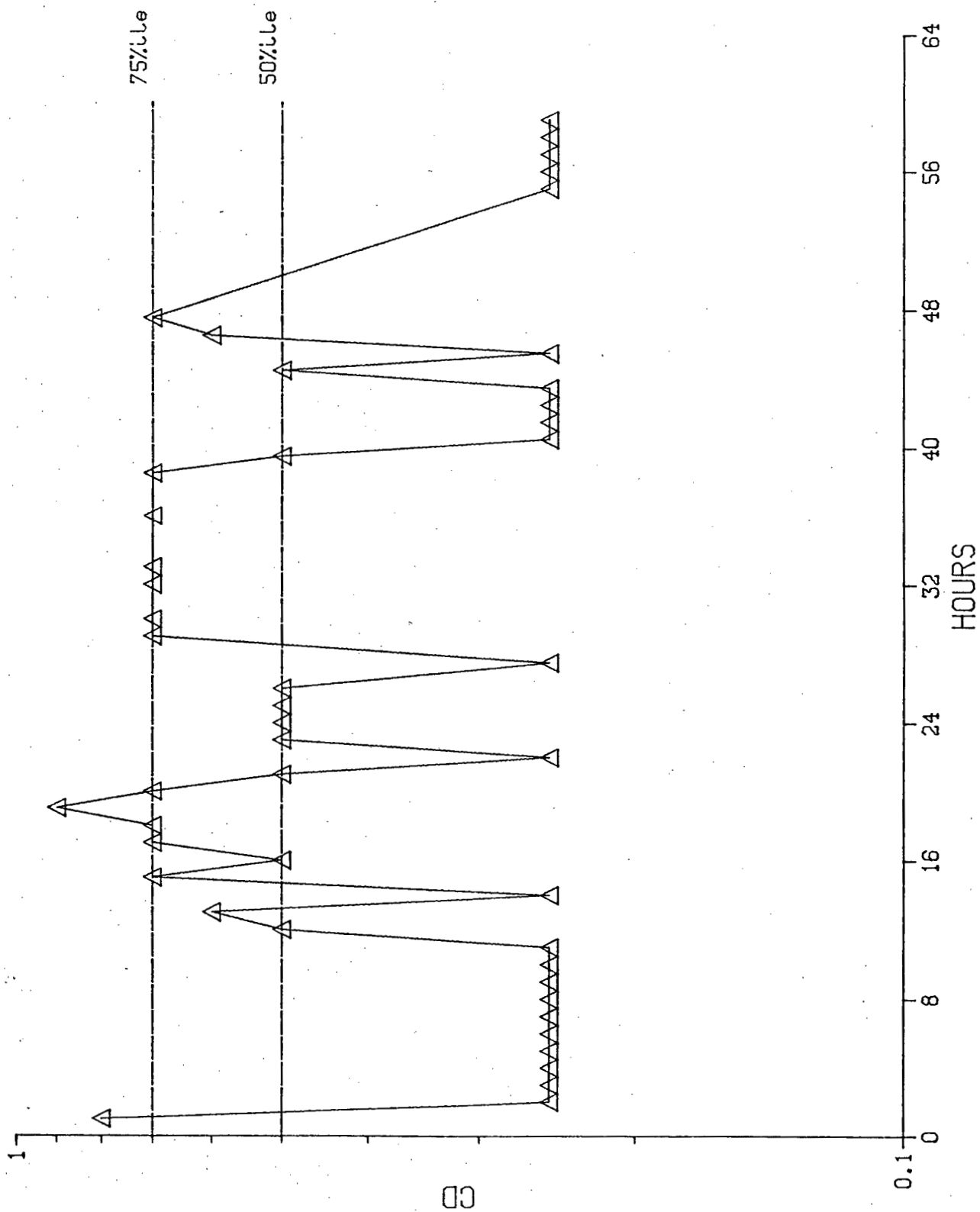


Figure 12. Variability in Cr concentrations (ug/L) measured at Waneta during the 1981 time series study

WANE TA, 1981

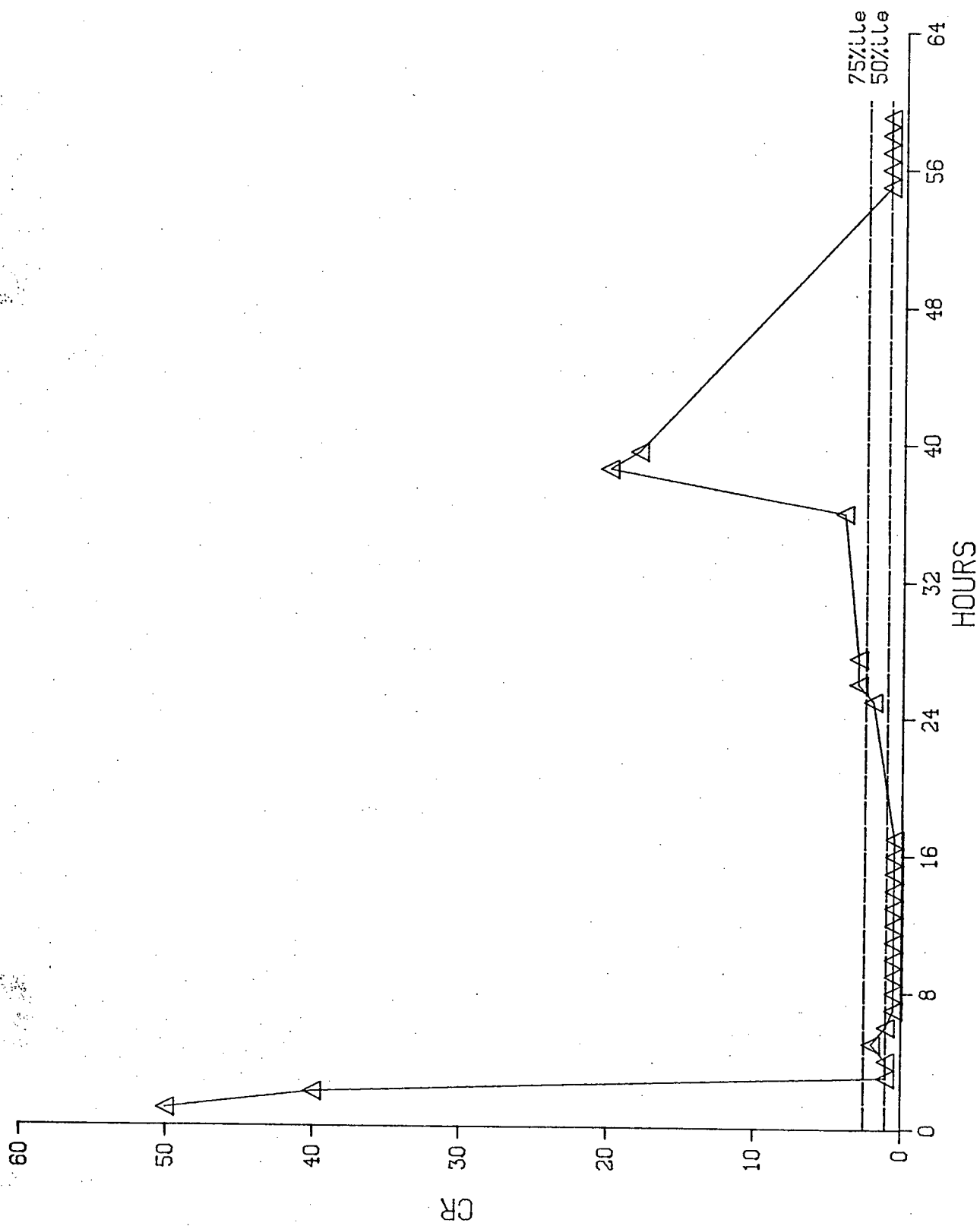


Figure 13. Variability in Cu concentrations (ug/L) measured at Waneta during the 1981 time series study

WANETA, 1981

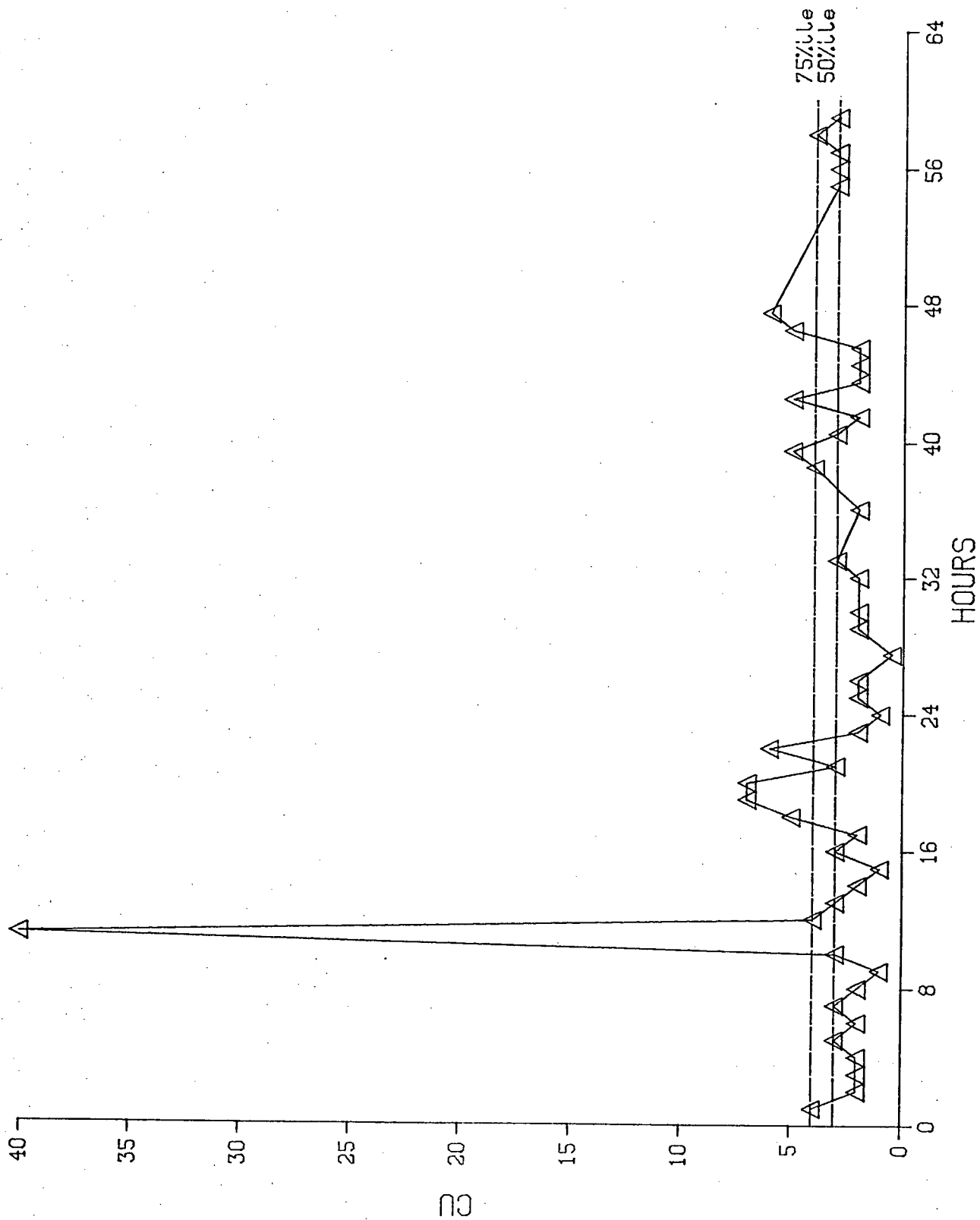


Figure 14. Variability in Pb concentrations (ug/L) measured at Waneta during the 1981 time series study

WANETA, 1981

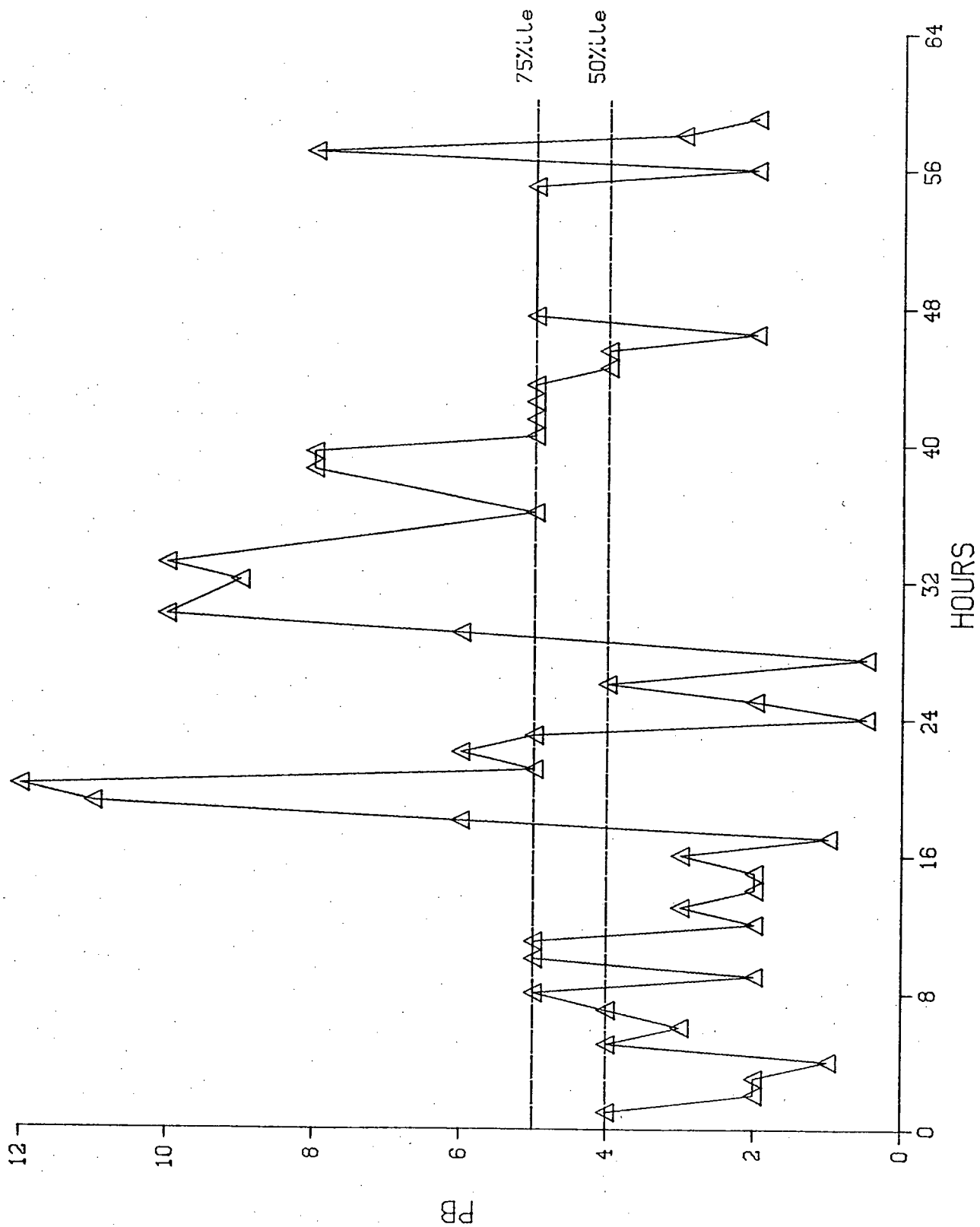


Figure 15. Variability in Zn concentrations (mg/L) measured at Waneta during the 1981 time series study

WANETA, 1981

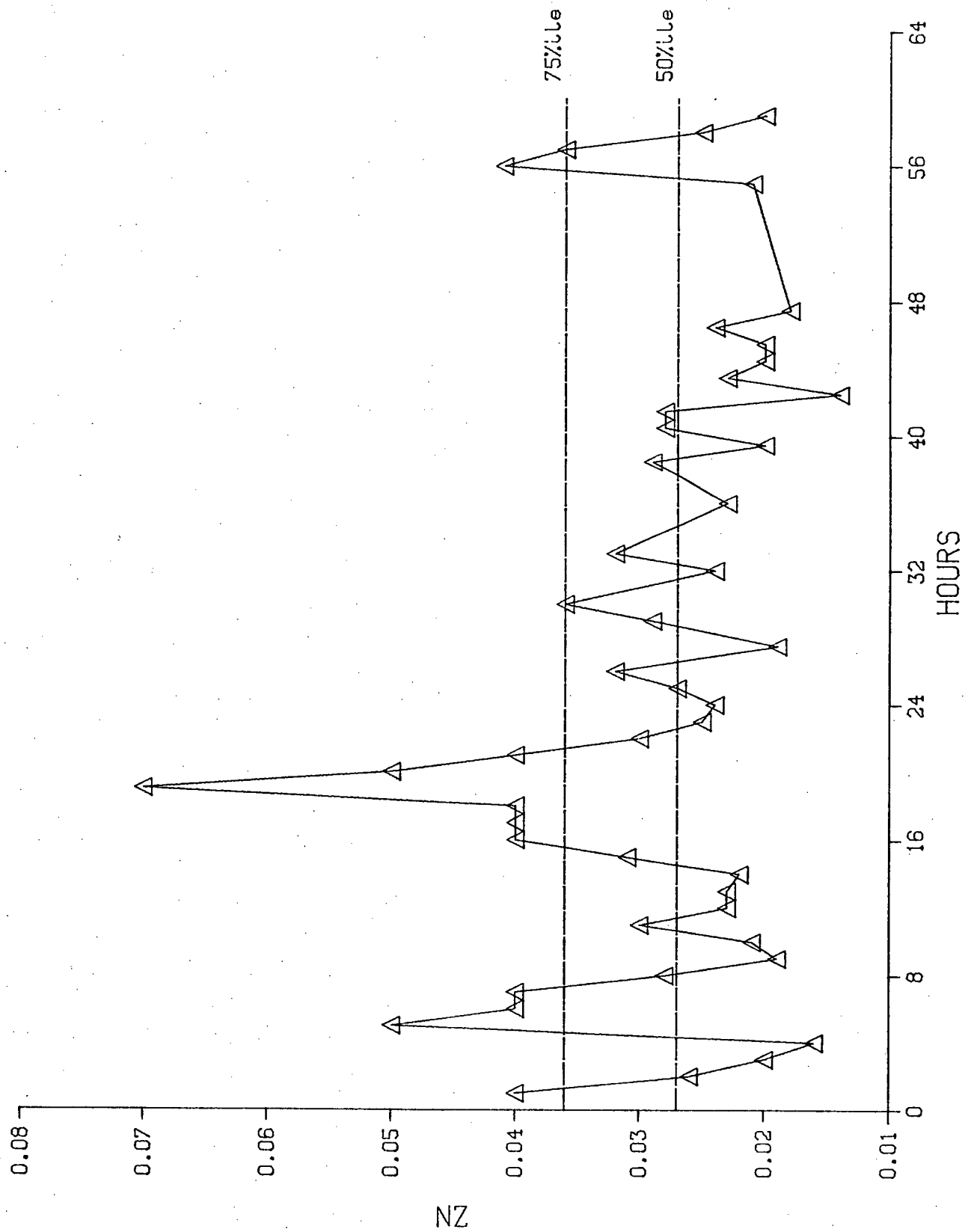


Figure 16. Variability in Cd concentrations (ug/L) measured at Waneta during the 1983 time series study

WANETA, 1983

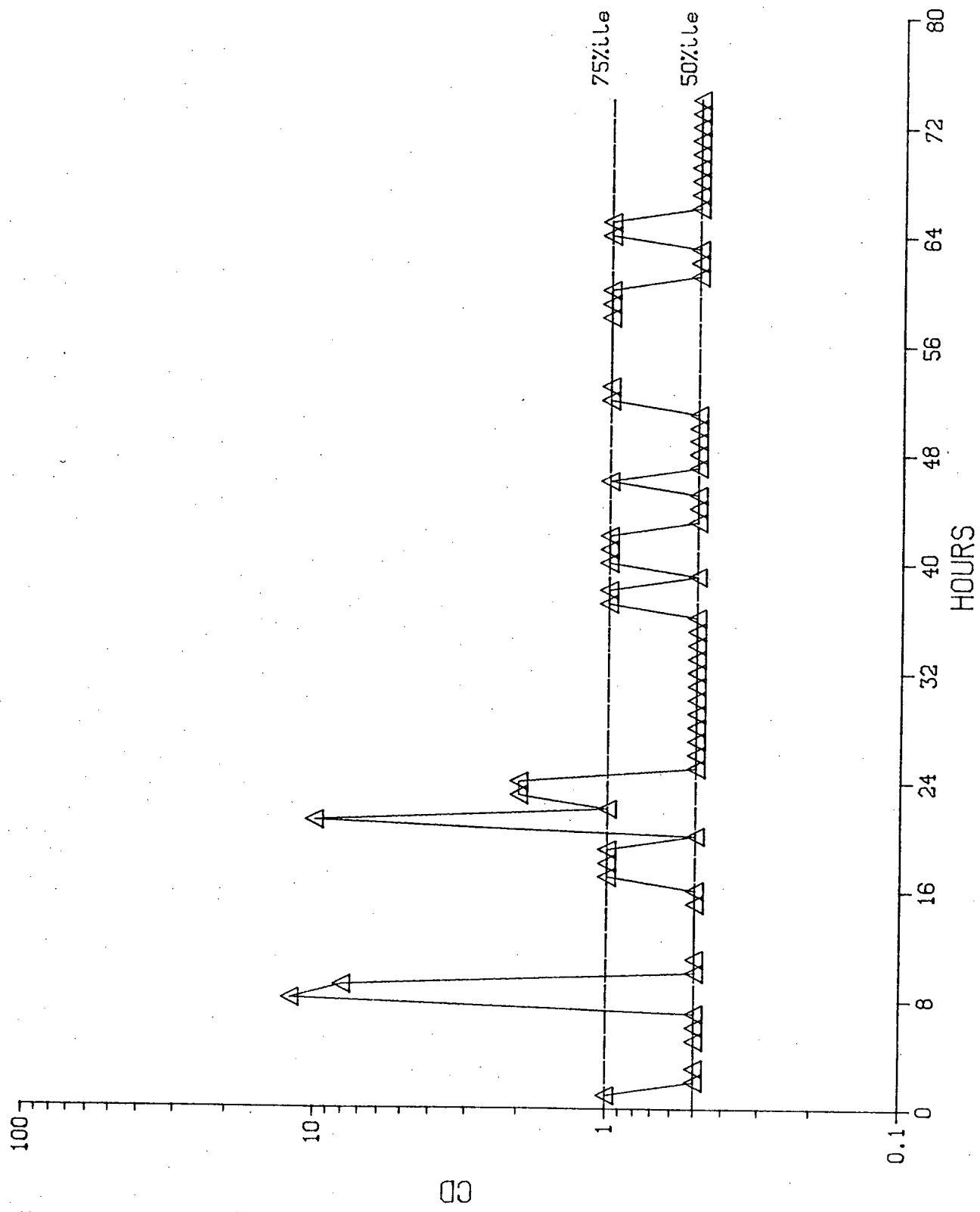


Figure 17. Variability in Cu concentrations ($\mu\text{g/L}$) measured at Waneta during the 1983 time series study

WANETA, 1983

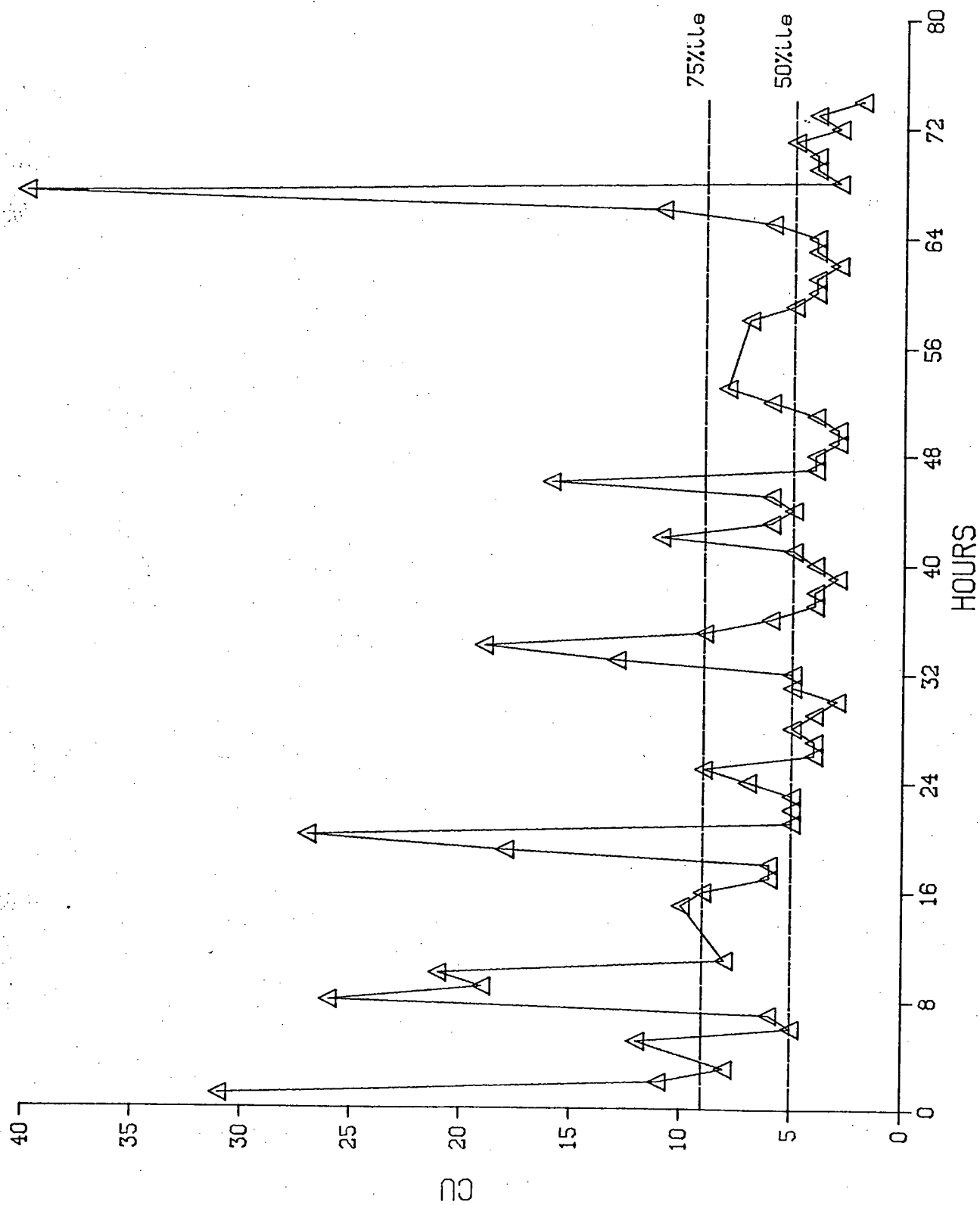


Figure 18. Variability in Fe concentrations (mg/L) measured at Waneta during the 1983 time series study

WANETA, 1983

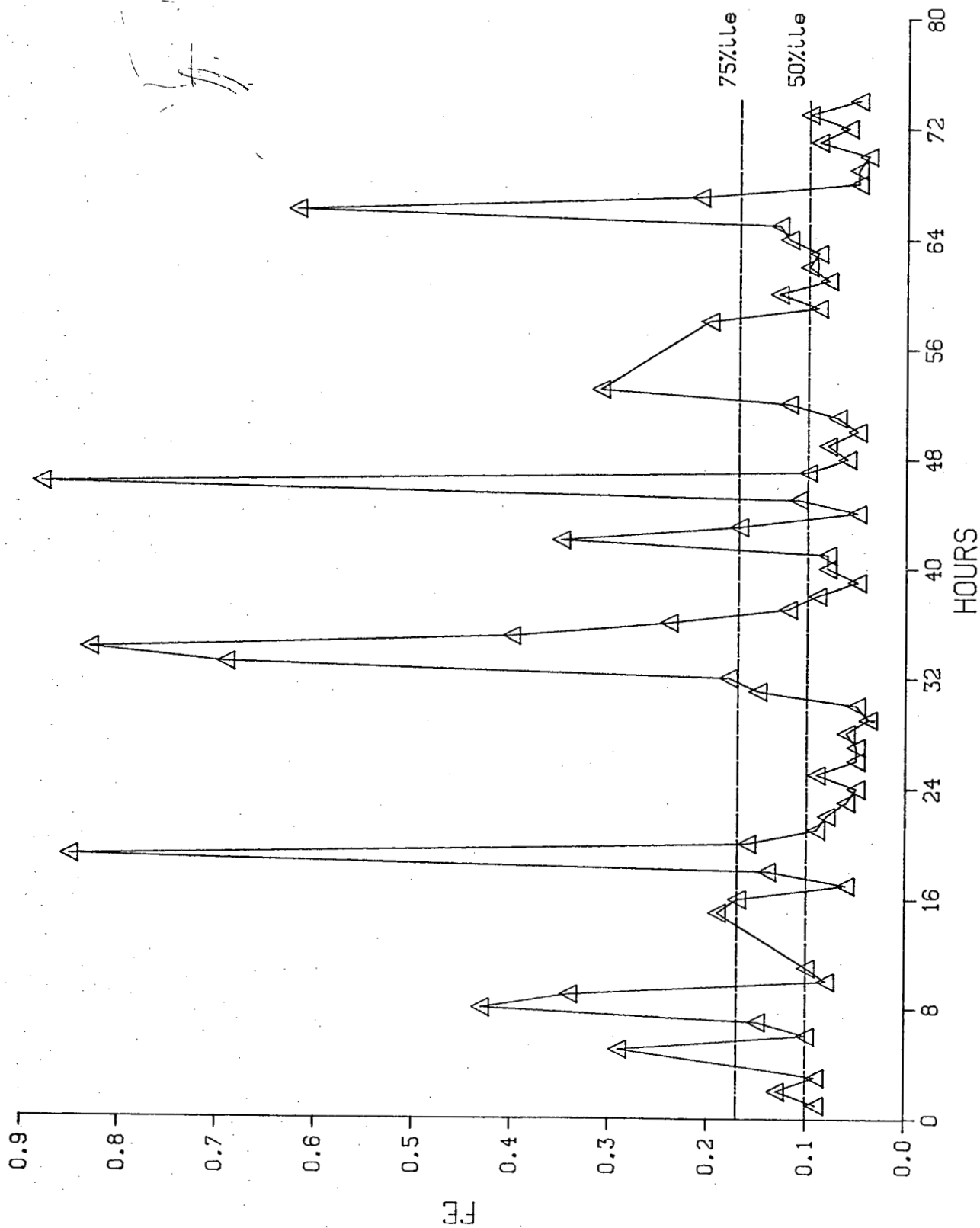


Figure 19. Variability in Pb concentrations (ug/L) measured at Waneta during the 1983 time series study

WANETA, 1983

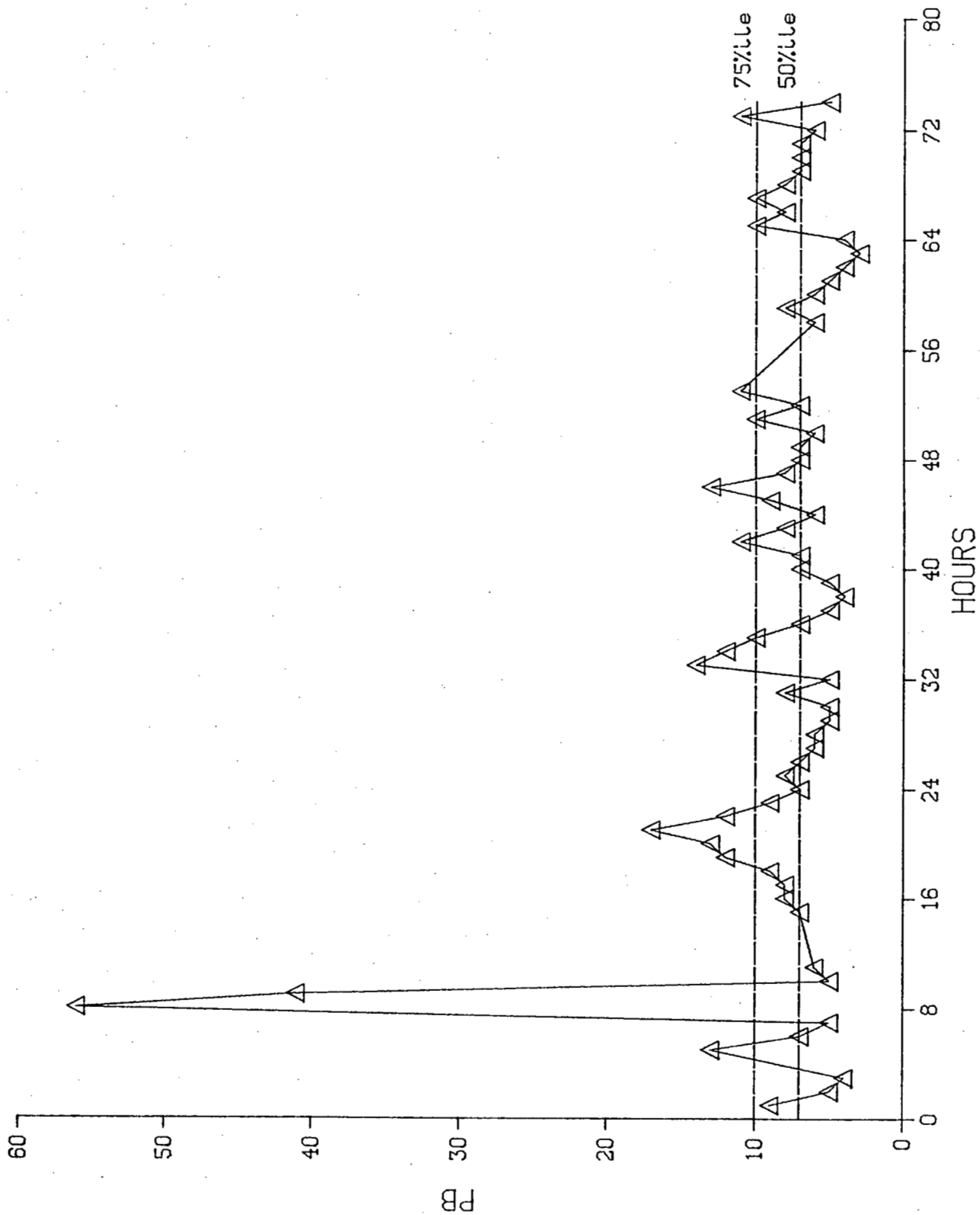


Figure 20. Variability in Zn concentrations (mg/L) measured at Waneta during the 1983 time series study

WANETA, 1983

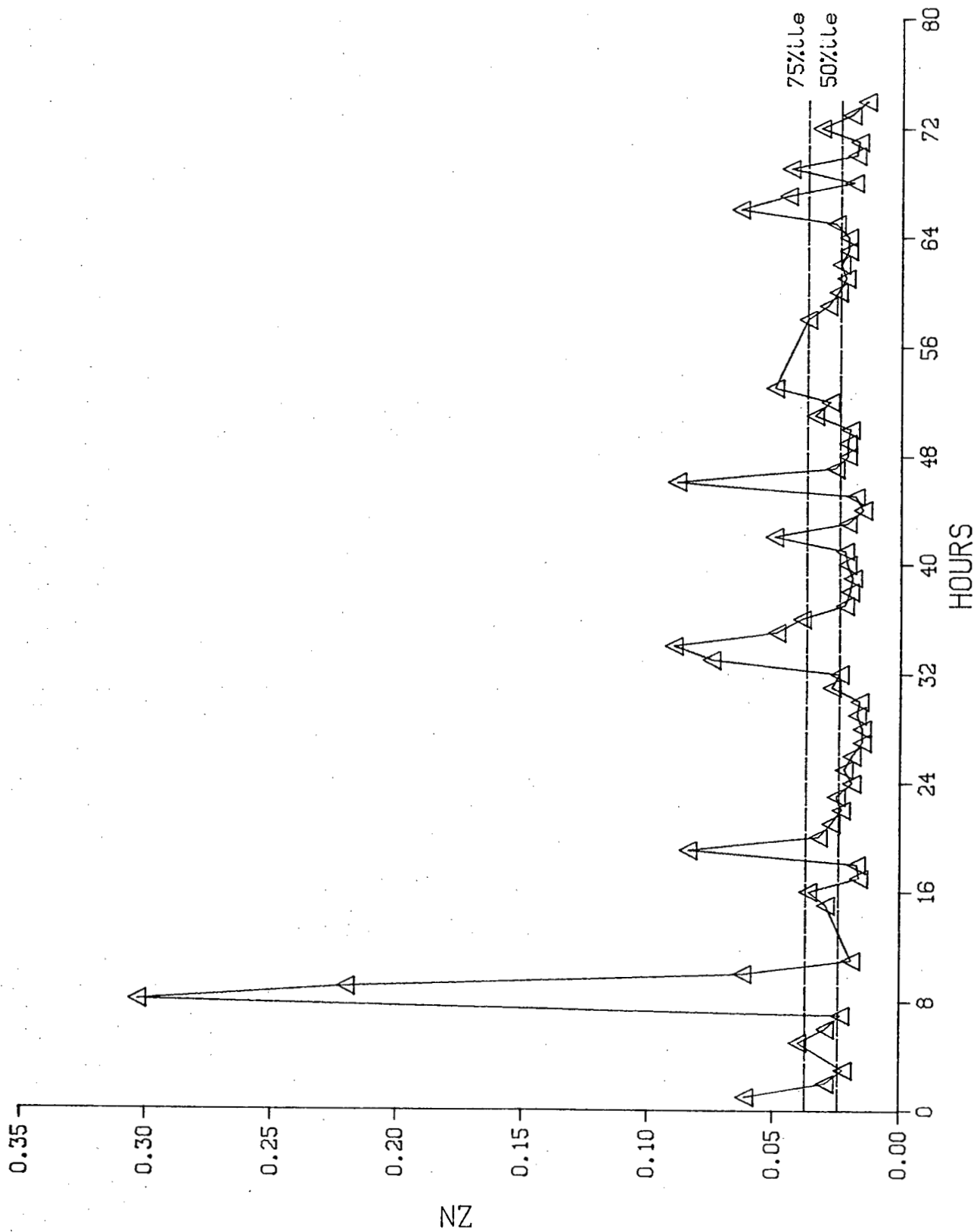


Figure 21. Variability in Cd concentrations (ug/L) measured at Waneta during the 1984 time series study

WANETA, 1984

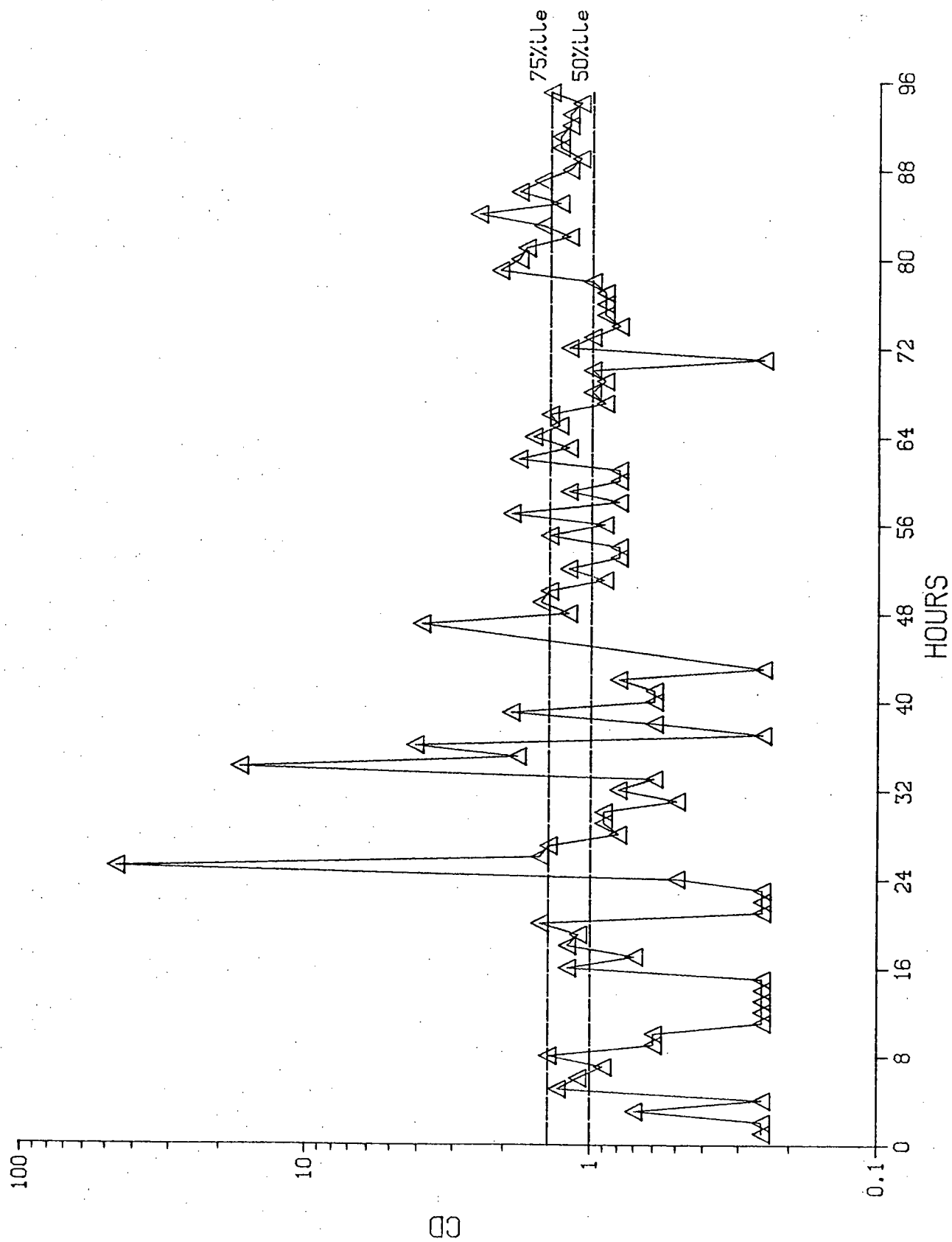


Figure 22. Variability in Cu concentrations (ug/L) measured at Waneta during the 1984 time series study

WANETA, 1984

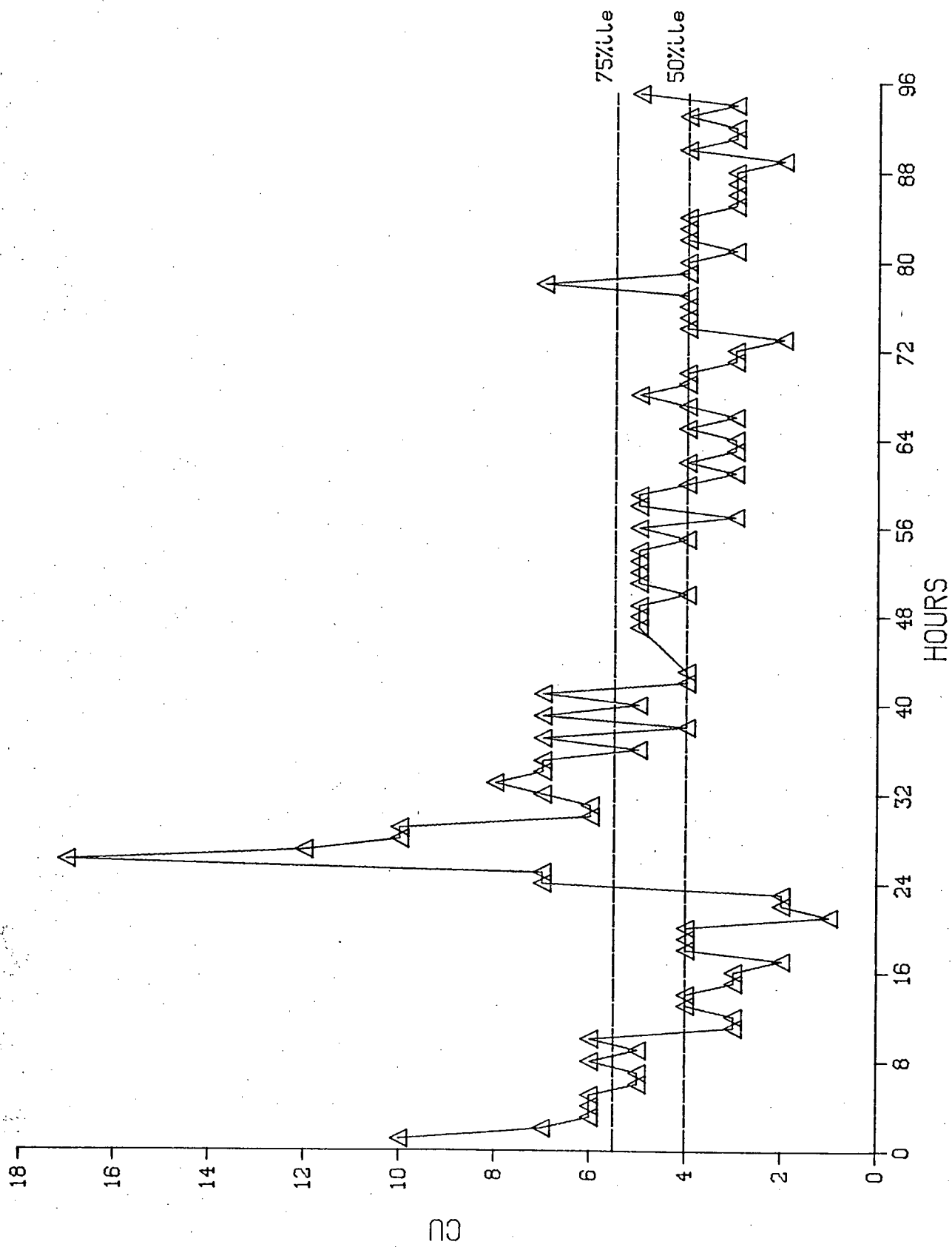


Figure 23. Variability in Fe concentrations (mg/L) measured at Waneta during the 1984 time series study

WANE TA, 1984

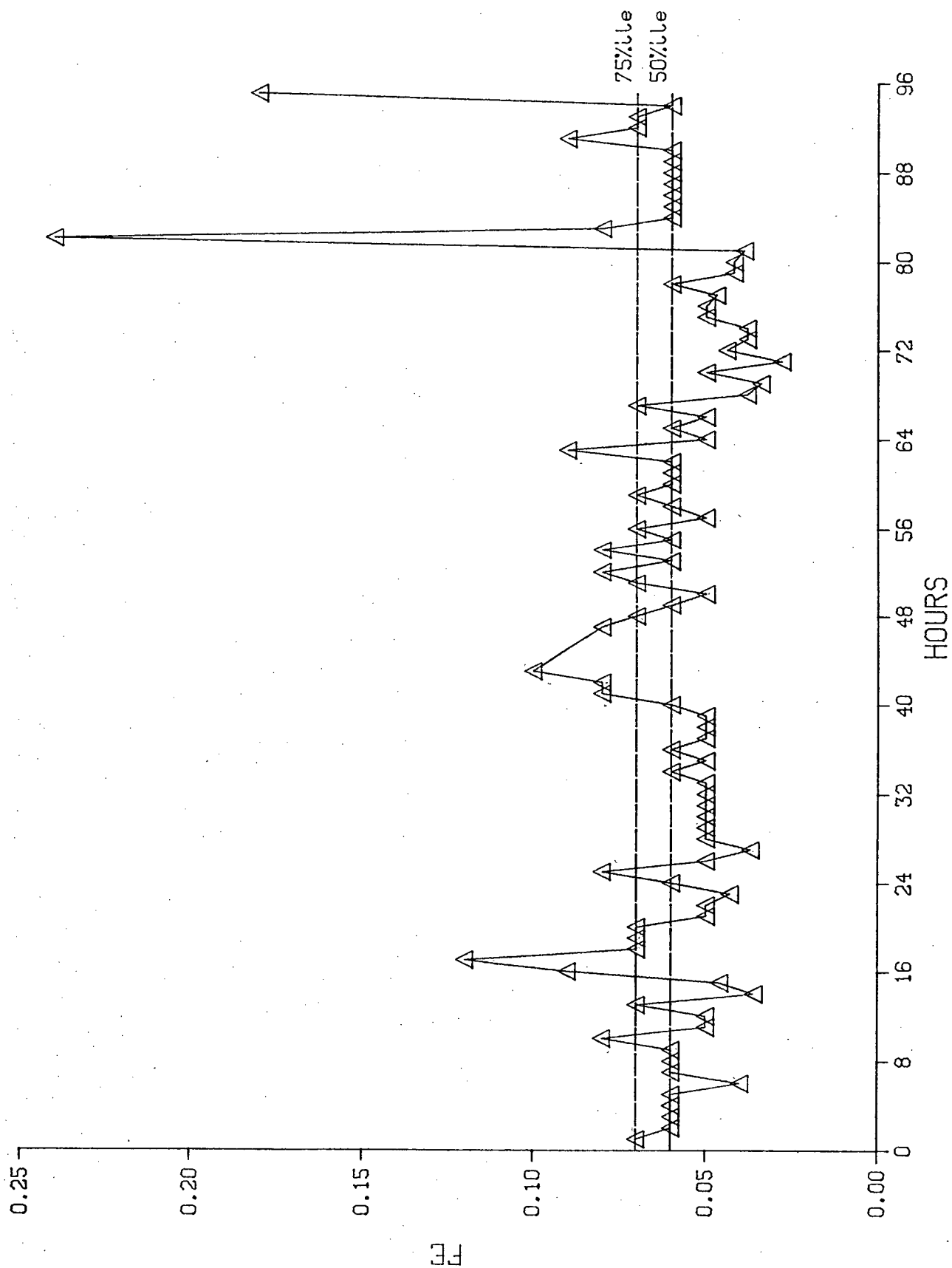


Figure 24. Variability in Pb concentrations (ug/L) measured at Waneta during the 1984 time series study

WANETA, 1984

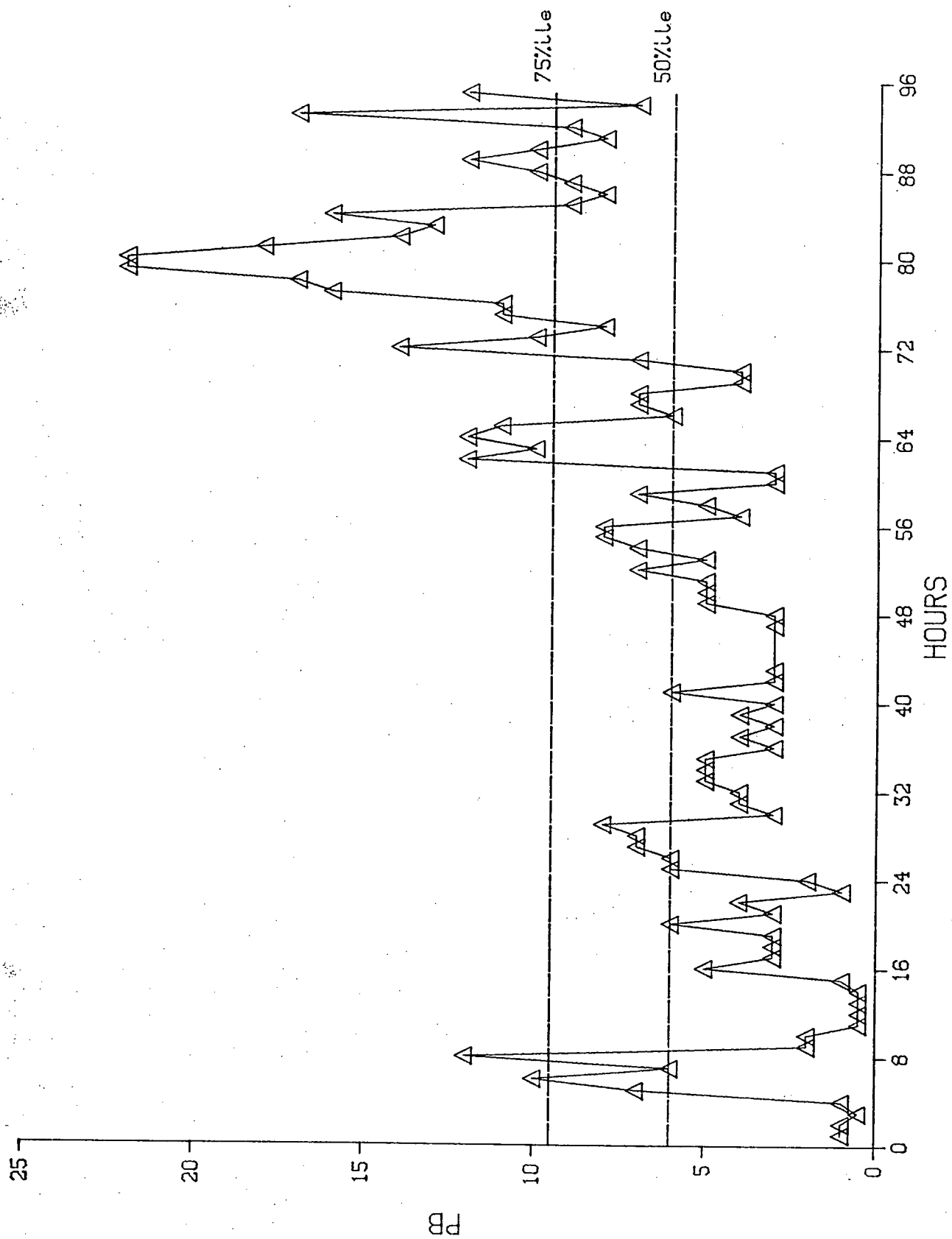


Figure 25. Variability in Zn concentrations (mg/L) measured at Waneta during the 1984 time series study

WANETA, 1984

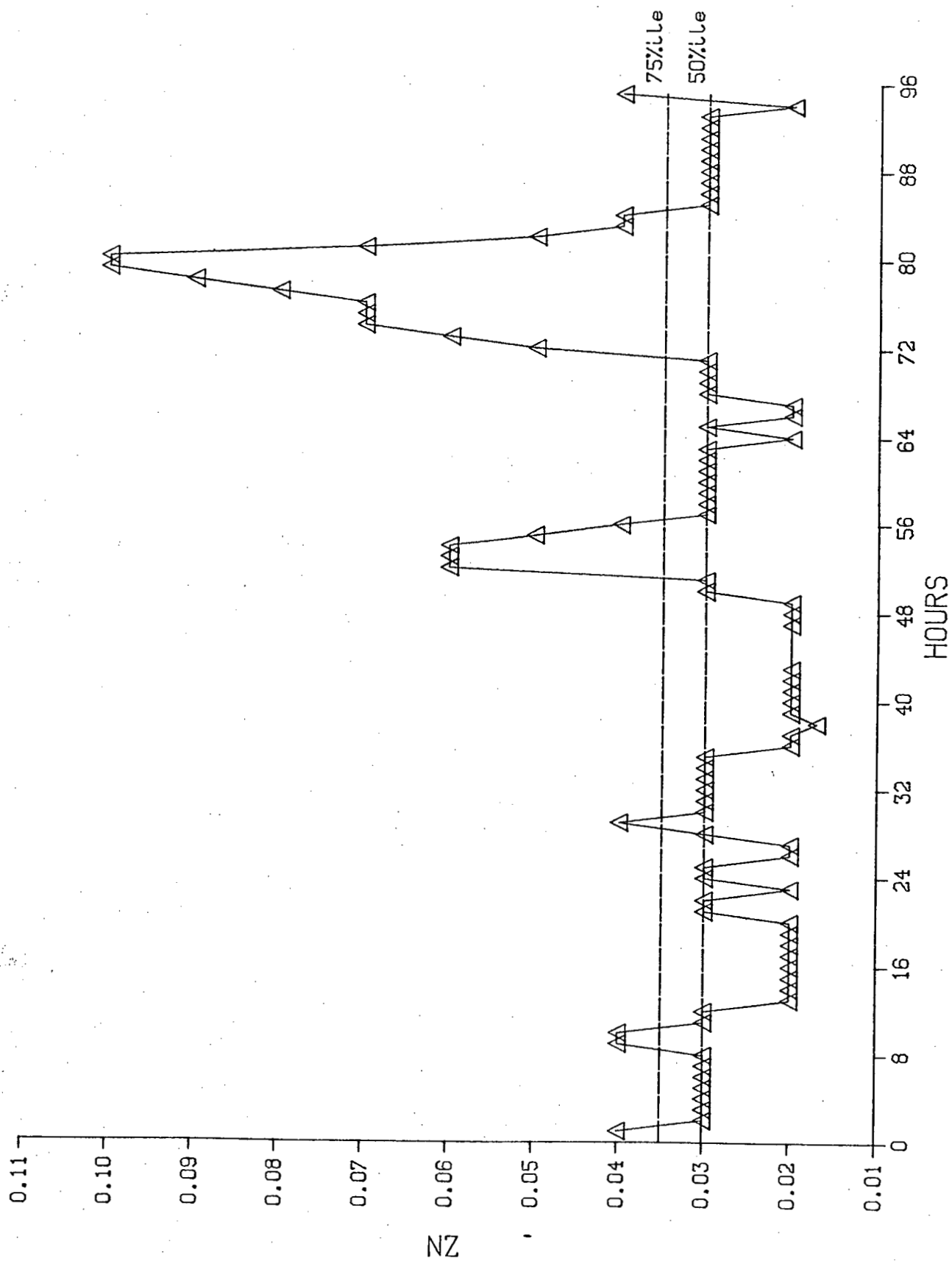


Figure 26. Variability in total phosphorus concentrations (mg/L) measured at Waneta during the 1978 time series study

Total Phosphorus at Waneta

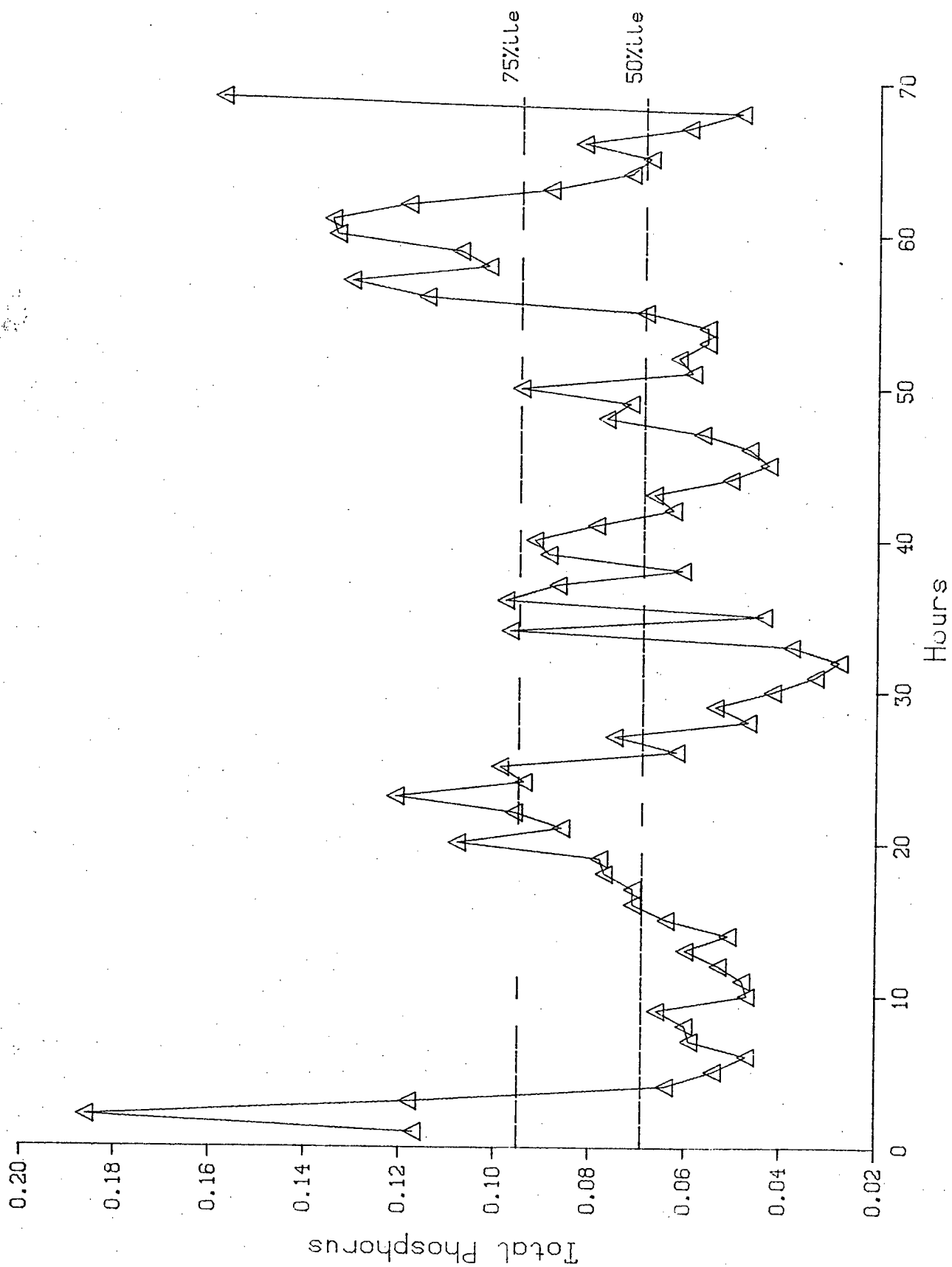


Figure 27. Variability in nitrate plus nitrite concentrations (mg/L) measured at Waneta during the 1978 time series study

N03 + N02 at Waneta

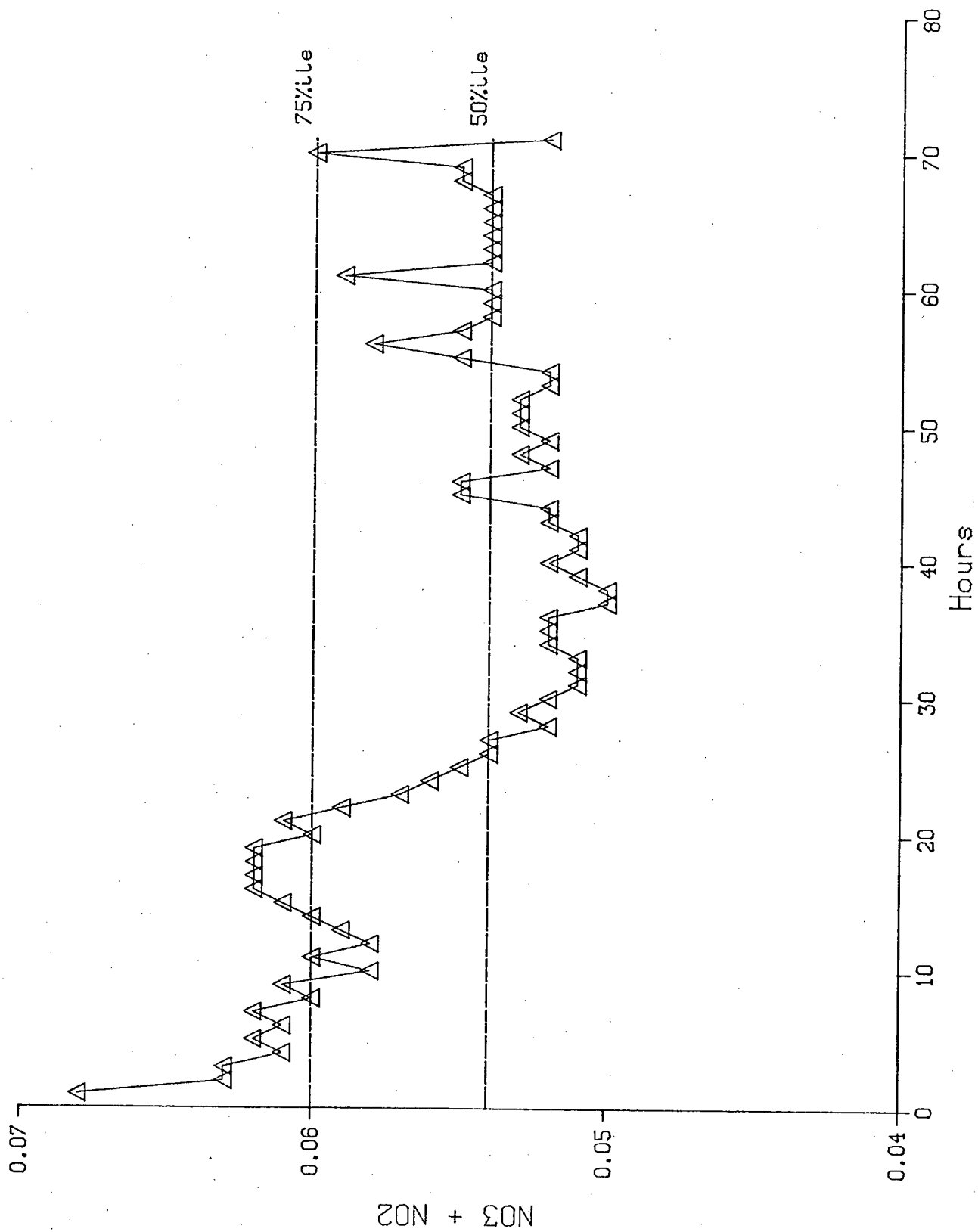


Figure 28. Variability in ammonia concentrations (mg/L) measured at Waneta during the 1978 time series study

NH3 at Waneta

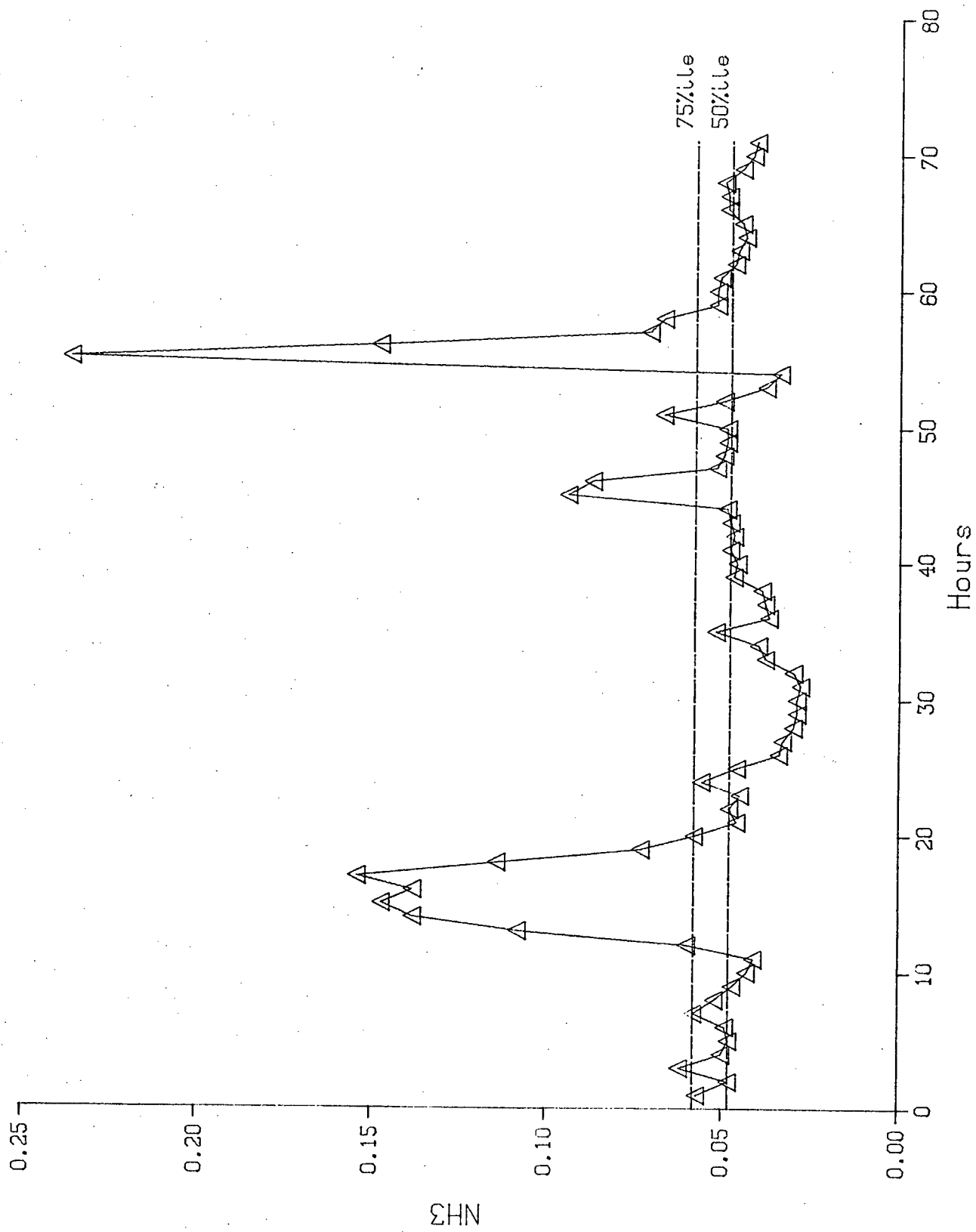


Figure 29. Variability in total nitrogen concentrations (mg/L)
measured at Waneta during the 1978 time series study

Total N at Waneta

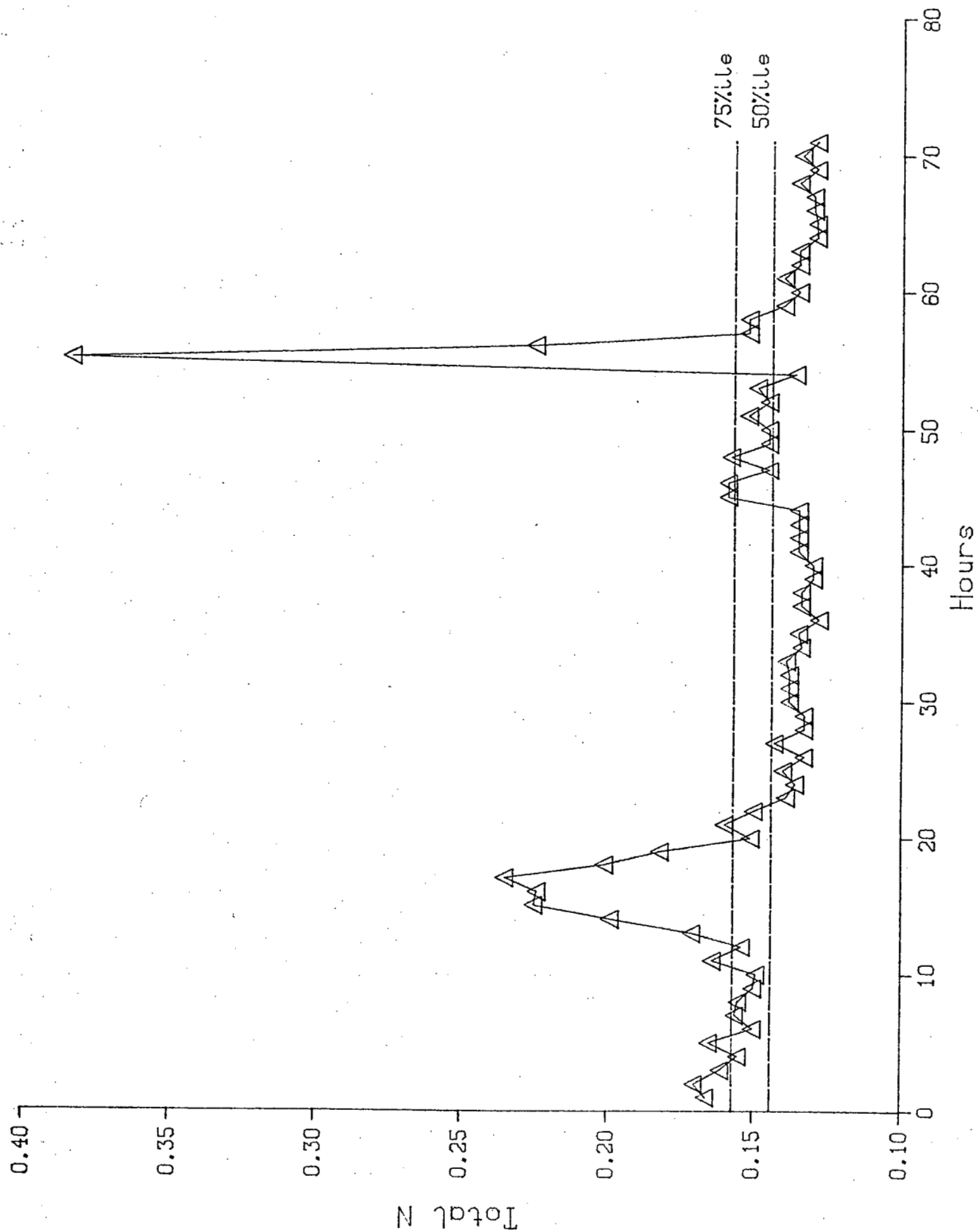
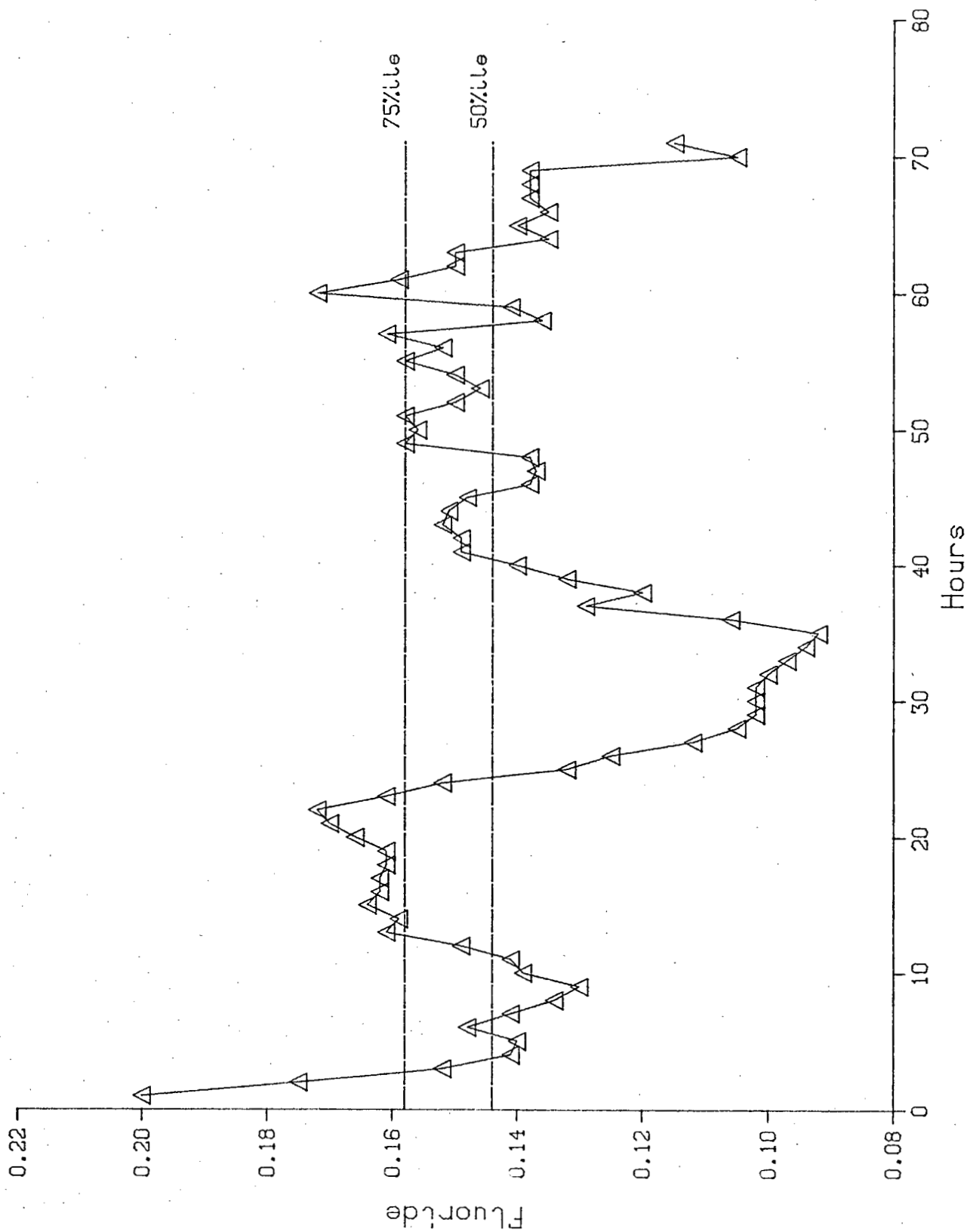


Figure 30. Variability in fluoride concentrations (mg/L)
measured at Waneta during the 1978 time series study

Fluoride at Waneta



IV. Metal Levels and Water Quality Guidelines

The frequency distributions calculated from the 1978-1984 time series data were used to determine how often (if ever) metal levels exceeded guidelines set for the protection of human health and aquatic life.

For human health, levels were compared with the Canadian drinking water guidelines (1978). These comparisons are given in Table 14.

Since metal levels recommended for the protection of aquatic life are generally more variable than those recommended for drinking water, two comparisons were made. Initially, levels were compared with the Canadian (1979) recommended objectives for aquatic life (Table 15). Further comparisons were made with the U. S. Environmental Protection Agency (EPA) water quality criteria (1980), which take into consideration the influence of water hardness on toxicity (Table 16).

IV. Relationship of Extractable, Dissolved and Total Metals and Dissolved: Total Phosphorus

A. Extractable: Total Metals

Correlation coefficients for extractable and total metals (Cu, Fe, Pb, Zn) were calculated using the June, 1978, cross sectional data, as this date was the only occasion on which extractable metals were measured. The correlations were highly significant ($P < .01$) in all cases. This relationship was expected, since extractable metals should form the major portion of the total metals present. However, the ratios of individual sample pairs were quite variable (Table 17).

Estimates of means and variances of total and extractable metals were compared. Variances were compared using the variance ratio F-test. Means were compared by two-way ANOVAs (Sokol and Rohlf 1969) for methods having equal variances. The variances of iron and zinc determined by the two methods were significantly different, while means of copper and lead determined by the two methods varied significantly.

Since the amount of data is limited (18 sample pairs, measured on only one occasion), it is risky to put much weight on these results, but some tentative conclusions can be drawn.

1. As long as only one method is used, total and extractable methods should be equally valid for experiments whose intent is to monitor changes in metal concentrations over time or space.

2. If the intent of a study is to report means and variances of metal concentrations, the methods are not equivalent. There is nothing in the present data to suggest a preferred method.

Table 14. Percent of samples exceeding Canadian Drinking Water Guidelines, 1978. Levels are given in mg/L. The number of samples from which these percentages were calculated may be found in Table 12.

	As	Cd	Cr	Pb	Hg	Se	Cu*	Fe*	Mn*	Zn*
Level	.05	.005*	.05**	.05	.001	.01**	1.0	.3	.05	5.0
Station/Date										
Waneta										
	% Exceeding Guidelines									
1978	-	0	-	0	0	-	0	0	0	0
1981	0	0	0	0	0	0	0	-	-	0
1983	0	4.5	-	1.5	0	0	0	15.2	0	0
1984	0	2.2	-	0	0	0	0	0	0	0
Birchbank										
1981	0	0	0	0	0	0	0	-	-	0
1983	0	3.0	-	0	0	0	0	0	0	0
1984	0	1.2	-	0	0	0	0	0	0	0

* Values based on aesthetics rather than health

** 1979 "Guidelines for Surface Water Quality" levels as follows:

Cd .01 mg/L
Cr .1 mg/L
Se .05 mg/L

Table 15. Percent of samples exceeding Canadian (1979) "recommended objectives" for aquatic life. Levels are given in mg/L. The number of samples on which these percentages are based can be found in Table 12.

	As	Cd	Cu	Cr	Pb	Hg	Se	Zn
Level	.05	.0002	.002	.04	.005	.0001*	.01	.05
Station/Date								
Waneta								
	% Exceeding Guidelines							
1978	-	14.4	100	-	46.2	0	-	23.1
1981	0	51.1	53.2	3.6	23.4	2.1	0	2.1
(✓) 1983	0	100	98.5	-	77.3	0	0	13.6
1984	0	84.8	93.5	-	90.2	0	0	13.0
Birchbank								
1981	0	20.8	2.8	0	0	1.4	0	0
1983	0	26.5	86.8	-	4.4	0	0	0
1984	0	15.1	80.2	-	5.8	0	0	0

* Hg guideline if fish are eaten;
if fish not eaten, level is .0002 mg/L

Table 16. Percent of samples exceeding US Environmental Protection Agency criteria, 1980. Levels are given in mg/L. The number of samples on which these percentages are based can be found in Table 12.

	Cd		Cu		Pb		Zn	
	Max.	24-h	Max.	24-h	Max.	24-h	Max.	24-h
Level	.0019	.00002	.015	.0056	.102	.0014	.225	.047

Station/Date

Waneta

% Exceeding Guidelines

1978	0	15.4	0	0	0	100. *	0	23.1
1981	0	51.1	2.1	6.4	0	91.5*	0	6.4
1983	7.6	100. *	13.6	47.0*	0	100. *	1.5	16.7
1984	6.5	84.8*	1.1	17.4	0	89.1*	0	13.0

Birchbank

1981	1.4	20.8	0	0	0	13.9	0	0
1983	8.8	16.2	1.5	13.2	0	92.6*	0	0
1984	2.4	15.1	1.2	8.1	0	41.9*	0	0

* Mean concentration over sampling period exceeded criterion for 24-h average.

Formulas used to calculate levels:

	Maximum	24-h Average
Cd	$e(1.05 \ln(H) - 3.73)$	$e(1.05 \ln(H) - 8.53)$
Cu	$e(0.94 \ln(H) - 1.23)$	
Pb	$e(1.22 \ln(H) - 0.47)$	$e(2.35 \ln(H) - 9.48)$
Zn	$e(0.83 \ln(H) + 1.95)$	

H = Hardness = 65 mg CaCO₃/L

2200-1
Sander

Table 17. Extractable: total ratios for metals measured at each point and depth on the cross section at Waneta during the June, 1978, sampling.

Point/ Depth	Ratio			
	CU	FE	PB	ZN
R1.8	.29	.63	1.00	.67
R1.2	.29	.72	1.50	.67
R2.8	1.11	1.85	1.50	2.22
R2.2	.38	.73	1.20	1.50
R3.8	.23	.64	1.00	.75
R3.2	.40	.40	1.00	.83
R4.8	.56	1.79	1.00	1.00
R4.2	.29	.14	.83	.70
R5.8	.71	.60	1.67	.83
R5.2	.33	.44	1.00	.70
R6.8	.29	.34	1.33	.82
R6.2	.33	.25	1.33	.61
R7.8	.29	.71	1.33	.93
R7.2	.67	.56	2.00	.80
R8.8	.29	.91	2.00	1.10
R8.2	.50	.54	1.67	1.09
R9.8	.40	.71	1.33	1.20
R9.2	.17	.75	1.33	.83

B. Dissolved: Total Metals

Ratios of dissolved to total metals were calculated for the three data sets which contained dissolved values (the June, 1978, cross sections and the 1983 and 1984 time series). The calculations were done as follows. In the June, 1978, data one dissolved and one total determination were made at each point and depth; ratios were calculated for each pair. In the time series studies, three replicates each of dissolved and total metals were measured at each time; ratios of the replicate means were calculated. If values below detection limits appeared in any data pair or set of replicates, no ratio was calculated because the handling of undetectable values (ie., whether to use the value as the detection limit, half the detection limit or zero) had a major influence on the ratio.

Ratios for some metals (Table 18) were highly variable and may not be meaningful because values were low and concentrations were measured to only one significant figure. This problem was especially evident for arsenic in 1978, when all total values were either 0.3 or 0.4 ug/L, and dissolved levels ranged from 0.1 to 0.3 ug/L. Variability in these levels, which could as easily have been due to analytical error as to real differences in levels, resulted in ratios ranging from 0.67 to 1.

It may be possible to calculate an overall dissolved: total ratio for each metal as the slope of dissolved on total metal from a Model II (Sokal and Rohlf 1969) regression through zero. However, this technique assumes that the ratio remains constant over all concentrations of metal in the river. Based on the chemistry of solutions, it seems unlikely that this assumption will be true, although it might be if soluble and insoluble forms of a metal were put into the river in constant proportion.

A test was performed to determine whether dissolved: total ratios remained constant over all concentrations of metal. Correlation between the dissolved: total ratio and the total of each metal were calculated. If the ratio remains constant over all concentrations of total metal, the correlation should be zero; significant correlations are evidence that the ratio varies.

Correlation coefficients and their significances are listed in Table 19. Generally, there was a negative relationship between the ratios and the total metals. Correlations were not significant for most metals in individual data sets but were significant when all data were pooled. This relationship implies that inputs which raise metal levels are mainly in particulate (insoluble) forms or that metal levels in the river are approaching saturation for the compounds present.

Zinc ratios behaved somewhat differently than the general pattern in that correlations were significant in individual data sets, but the correlation for pooled data was not significant. This paradox may have arisen because the slopes of the regressions of ratio on total zinc were significantly different in different data sets. Analysis of covariance should be used to test for equality of slopes, but it cannot be applied to the present data because of unequal sample sizes.

Table 18. Relationship between dissolved and total metals. Concentrations are given in mg/L. * indicates ratio not calculated because some values were below detection limits. 1978 ratios were calculated for each point and depth on the cross section (as in Table 17). 1983 and 1984 ratios were calculated from the means of the quality control samples taken during time series studies.

Total As	Diss/Tot Ratio	Total Cu	Diss/Tot Ratio	Total Fe	Diss/Tot Ratio	Total Pb	Diss/Tot Ratio	Total Zn	Diss/Tot Ratio
1978:									
.0004	.75	.007	.286	.30	.017	.005	.20	.03	.267
.0004	.75	.007	.286	.29	.021	.004	.50	.03	.233
.0003	1.00	.018	.167	1.3	.005	.004	.25	.09	.067
.0004	.75	.008	*	.41	.015	.005	.20	.02	.35
.0003	1.00	.013	.077	.55	.045	.005	.40	.04	.20
.0004	.75	.005	.20	.25	.02	.005	.40	.018	.389
.0003	1.00	.009	.222	.38	.011	.005	.20	.03	.233
.0003	1.00	.007	.286	.70	.014	.006	.333	.02	.35
.0003	1.00	.007	.286	.25	.02	.003	.667	.018	.389
.0003	1.00	.006	.167	.27	.067	.004	.50	.02	.30
.0003	1.00	.007	.286	.35	.014	.003	*	.017	.353
.0003	1.00	.006	.167	.40	.015	.003	*	.018	.333
.0003	.67	.007	.143	.17	.024	.003	.667	.015	.40
.0003	.67	.006	.167	.16	.05	.002	*	.015	.40
.0003	1.00	.007	*	.11	.045	.002	*	.01	.60
.0004	.75	.004	*	.13	.023	.003	*	.011	.545
.0003	1.00	.005	.20	.14	.171	.003	*	.01	.50
.0003	1.00	.006	*	.12	.042	.003	.333	.012	.50
1983:									
		.004	.364	.12	.067	.004	.417	.019	.596
		.004	.455	.081	.123	.008	.36	.023	.478
		.004	*	.121	.063	.012	.297	.024	.493
		.003	.500	.442	.063	.007	.381	.022	.612
		.007	.350	.034	.373	.015	.156	.044	.366
		.002	.429	.126	.037	.003	.600	.015	.826
		.003	.500	.148	.036	.007	.350	.015	.756
		.003	.400	.238	.041	.007	.318	.016	.702
		.008	.313	.027	.353	.016	.125	.051	.275
		.004	.625	.186	.175	.010	.211	.032	.429
		.005	.438	.154	.123	.008	.261	.021	.484
		.004	.462	.091	.117	.008	*	.023	.456
1984:									
		.002	1.29	.319	.053	.003	.70	.023	1.29
		.003	1.00	.141	.073	.006	.444	.027	1.25
		.004	.75	.105	.057	.004	*	.023	1.00
		.002	.833	.246	.047	.003	.778	.020	1.02
		.003	.778	.197	.047	.003	.444	.037	1.00
		.002	*	.181	.042	.002	*	.020	1.02
		.002	*	.164	.049	.003	*	.016	.917
		.001	.75	.12	.067	.001	*	.015	1.14
		.002	*	.077	.087	.002	*	.018	.887
		.002	*	.147	.063	.004	*	.06	.833
		.002	.80	1.19	.057	.003	*	.037	.818
		.002	*	.118	.048	.003	*	.03	.667
		.004	*	.154	.058	.007	*	.03	.667
		.003	.75	.159	.036	.008	.375	.05	.867
		.004	.727	.252	.042	.020	.311	.093	.571
		.004	.909	.128	.060	.009	.296	.03	1.00

Table 19. Correlation of dissolved: total ratio with total metals at Waneta. * $P < .05$, ** $P < .01$

Metal	All	June 1978	October 1983	March 1984
Cu	-.557**	-.35	-.55	-.091
Fe	-.643**	-.357	-.523	-.098
Pb	-.331*	-.631*	-.652 ¹	-.268
Zn	-.16	-.825**	-.847**	-.585*

1 One set of Pb replicates contained a single value below the detection limit. When this value was set to half the detection limit and the resulting data pair included in the analysis, the correlation coefficient became $-.761^{**}$

C. Dissolved: Total Phosphorus

Ratios of dissolved and total phosphorus were calculated for all data sets which included dissolved measurements. For the 1979 data, only levels measured on the bank and not at the points on the cross section were used. All values from the remaining data sets were included.

Correlations of ratio with total phosphorus were calculated as described for metals and are summarized in Table 20. Both significant positive and significant negative correlations are present in different data sets, suggesting that different types of phosphorus discharges may be occurring or that different river conditions can alter the relationship between dissolved and total phosphorus.

Table 20. Correlation of dissolved: total ratio with total phosphorus at Waneta. * $P < .05$, ** $P < .01$

Date	n	r	Significance
June, 1978	18	-.068	NS
July, 1978	18	-.524	*
September, 1978	13	.658	*
November, 1978	18	-.799	**
1979 (Bank)	16	.392	NS
All	83	.325	**

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