

**WATER RESEARCH**

97/11



R. Gregory

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392-S

**GALVANIC CORROSION OF LEAD IN  
COPPER PIPEWORK: PHASE I,  
MEASUREMENT OF GALVANIC CORROSION  
POTENTIALS IN SELECTED WATERS**

Interim Report to the Department of the  
Environment for the period December 1983  
to November 1984

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## **SUMMARY**

### **OBJECT**

The objective of the work reported was to survey selected water supplies, in collaboration with water undertakings, to assess the level of galvanic corrosion of lead solder coupled to copper using voltage measurements from corrosion cells. This report presents the work done during the period December 1983 to November 1984.

### **APPROACH**

The galvanic corrosion potential of thirty-eight different waters were measured using corrosion cells. The waters were selected to represent typical extremes of water quality parameters previously established to have significant effects on the galvanic corrosion.

### **RESULTS**

A wide range in corrosion potential, greater than 85:1, was found. The value of corrosion potential was dependent on water quality. Multiple regression analysis established the most significant effects on voltage are associated with the chloride to sulphate concentration ratio and the chloride and nitrate concentrations. For data sub-groups significant effects are associated also with alkalinity, sulphate and silicate concentrations. No significant effect is associated with pH.

Strong intercorrelations were found between water quality parameters which accounts for the significant effect on voltage associated with alkalinity.

The extent to which variance was accounted for in the multiple regression analyses was poor and dependent on the data group. This suggests that other water quality parameters, not measured in this work, may also significantly affect corrosion potential.

Three waters produced voltages significantly greater than the other waters and some reasons for these are given. Eight waters produced voltages lower than the general distribution in voltages. The distinctive water quality features of this sub-group have not been identified.

### **CONCLUSIONS**

The results generally substantiate the conclusions of previous work by WRc. Dosing to increase sulphate or silicate concentrations might reduce corrosion potential. Further work should be done to test these and other treatments for reducing corrosion potentials.

# WARNING OF CONFIDENTIALITY

To maintain the anonymity of the waters measured, as part of the obligation to undertakings in return for the assistance given, this sheet must be removed before the report is released by either the DOE or WRc to a third party.

## KEY TO WATERS

A	1	Loch Lomond (before pH adj)	CSWDB
	2	Watchgate (before pH adj)	NWWA
	3	Katrine	SRC
	4	Frankley	STWA
	5	Derwent	STWA
	6	Crownhill	SWWA
B	1	Glenfarg (slow sand)	FRC
	2	Linacre	STWA
	3	Holl (raw)	FRC
	4	Seafield	LRC
	5	Fairmilehead	LRC
	6	Glendevon	FRC
	7	Broadside	CRC
C	1	Lound	EAWCo
	2	Ynysyfro	WWA
	3	Durleigh	WxWA
	4	Jellyholm	CRC
	5	Saltersford	AWA
	6	Purton	BWWCo
D	1	Medmenham (WRc)	AWA
	2	Stevenage (WRc)	LVWCo
	3	Irton	YWA
	4	Somerford	SSWWCo
	5	Elkesley	AWA
	6	Winterton Holmes	AWA
E	1	Bishop Cannings	WxWA
	2	Lacock	WxWA
	3	Grafham (LVWCo)	AWA
	4	Paines Hill	ESWCo
	5	Burham (MKWCo)	SWA
	6	Forstal	MKWCo
	7	Mill Gap 2	EWWCo
	8	Hazards Green	EWWCo
	9	Langford	ExWCo
	10	Denton	NWWA
	11	Littlehempston	SWWA
	12	Barrow	AWA
	13	Hartlepool	HWC0

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## 1. OBJECTIVE

The objective of the work reported was:

"To survey selected water supplies in collaboration with authorities to assess the level of galvanic corrosion of lead coupled to copper which might give rise to unacceptable high lead concentrations in water at consumers' taps".

The programme of work to be carried out was:

- (i) Produce 250 lead-copper corrosion cells (Oliphant cells to the design of WRc developed in earlier work under contract to DOE).
- (ii) Select 44 water supplies nationally for study.
- (iii) Provide 12 sets of equipment (thermostatically controlled water baths, voltmeters, etc), to be fitted with corrosion cells.
- (iv) Install this equipment in turn at the 44 selected supply works, obtain voltmeter readings over a period of one month at each installation.
- (v) Collate and analyse results, identify water supplies with high corrosion potential.
- (vi) Provide progress and final contract reports to the Department.



## 2. BACKGROUND

The work was concerned with determining the relative galvanic corrosion rate of lead solder coupled to copper in a selected range of water supplies. This work is relevant to the application of the New Model Water Byelaws and was welcomed by the water undertakings.

Previous work by WRc under contract to DOE on the contamination of water by domestic plumbing fittings\* showed that high lead concentrations in tap water may arise from the galvanic corrosion of lead solder coupled to copper. That work was based mostly on measurements made on synthetic waters with quality parameter concentrations changed systematically.

It was decided from subsequent discussions that equivalent field measurements of a wide range of selected real waters were required to underwrite the previous work as follows:

- (i) To check that the results obtained from synthetic waters agree with results obtained for "real" waters in supply.
- (ii) To identify the water types for which galvanic corrosion of lead solder in copper plumbing is relatively high to help water undertakings apply the New Model Water Byelaws and take other appropriate action to reduce lead levels.
- (iii) To identify water supply areas where it might be appropriate to carry out sampling exercises on copper plumbed properties to establish the magnitude and duration of unacceptably high lead concentrations arising from galvanic corrosion of lead solder.

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\*Oliphant R.J., "Summary report on the contamination of potable water by lead from soldered joints" WRc Engineering, Swindon, External Report No. 125E, November 1983.

- (iv) To produce information to help the DOE develop guidelines for reducing lead in tap water.

The work was carried out by WRc Processes as the main contractor with Dr J Gardiner, Consultant in Environmental Science, as the sub-contractor for the field work and with the active co-operation of individual water undertakings within the limits of their resources. The water undertakings were asked to operate the corrosion rigs for the specified periods and provide the required water quality analyses. The waters were selected in part on the basis of convenience to the water undertakings.

This report covers work carried out during the period December 1983 to November 1984.

### 3. MEASUREMENT OF VOLTAGES

The level of galvanic corrosion of lead coupled to copper was measured for each water in a standard way. The test water was continuously sampled and passed through five corrosion cells arranged in series.

Each corrosion cell was made to a design developed in earlier work under contract to DOE. The cathode in each cell was made from copper foil. The anode was made from copper foil coated in tin-lead solder.

Water temperature was standardised at 25°C by passing the water through a preheat coil before the corrosion cells and by holding the coil and cells in a water bath. A flow diagram is given in Figure 1. As in the previous work by WRc the corrosivity of each water was monitored for four weeks with specific attention to the fourth week.

The level of galvanic corrosion was assessed from the average value of the voltages measured across each of the corrosion cells.

Further details of the cells and the other equipment used and the methods and problems of usage are given in Appendix A1.

#### 4. SELECTION OF WATERS

The planned programme of work required 44 water supplies, with a national distribution, to be selected for study. This number of waters had been decided on the basis of agreed selection criteria. These were pH, chloride concentration, sulphate to chloride concentration ratio and alkalinity. The earlier work by WRc had shown that corrosion rate is sensitive to the first three parameters and likely to be insensitive to alkalinity.

The agreed aim of the measurements was to show as simply as possible that the conclusions from the earlier work by WRc, carried out under laboratory conditions mostly with "synthetic" waters are applicable to field measurements of "real" waters.

Once the selection of test waters had started it became evident that the selection criteria needed to be expanded. The revised "shopping list" for waters also took account of nitrate concentration and distinguished between ground and surface waters. The revision was based on a factorial design of the selection criteria matrix to facilitate statistical analysis of the data and avoid problems of inter-correlations.

Waters satisfying the shopping list were selected with the help of water undertakings. An important additional selection criterion was that each water should be convenient for measurement: this limitation made it increasingly difficult to complete the shopping list. Consequently, following a provisional assessment of the data available for the first twenty-four waters measured, the remaining waters measured were selected with the aim of improving the distribution of the values for the quality parameters of interest.

The outcome is that this report is based on the measurements of thirty-eight different waters which represent wide ranges in values of the quality parameters of interest.

Full details of the selection criteria are given in Appendix B. Details of the characteristics of the waters measured are given in Section 6.

## 5. EVALUATION OF DATA

Cell voltage measurements and the results of water quality analyses were recorded on a proforma by the participant undertakings. WRc itself carried out all the necessary voltage measurements and quality analyses for two waters.

The proforma were collected by the sub-contractor who checked that all the information requested had been provided. He then determined individual cell mean day voltages and, for each water, prepared plots of these voltages. From a visual inspection of the corrosion cells and these plots he made a preliminary identification of failed cells, Section A1. Taking account of these failures he made a determination for each water of the combined cell fourth-week mean voltage. All this information was then forwarded to WRc.

As the data became available scatter and frequency distribution diagrams, of the fourth-week mean voltages and principal water quality parameters for each water, were updated to monitor the likely overall outcome. This activity was particularly important when it was decided the waters selected by means of the shopping lists needed to be supplemented to improve the distribution of waters measured with respect to water quality.

Once most of the data had been received and it was evident that data evaluation based on the factorial approach of the revised selection criteria, Section 4, was no longer appropriate, a preliminary regression analysis was carried out. This showed that great care was needed in further processing of the data for coping with failed cells and checking cell voltages and water qualities which appeared to be unrepresentative of or contrary to the general picture. It also became evident from the way in which voltages could develop and vary with time that assessment of corrosion levels should not be confined to use of fourth-week mean values alone.

Because the preliminary evaluation indicated that evaluation of the data should not be confined to the fourth-week data, it was decided to computerise all voltage and water quality measurements. Two series of data files were set up: one series was for water quality, with one file for each water, and the other series for voltage measurements. Included in the files of voltage measurements was identification of which cells were regarded as having failed during the four week period of measurement. A cell was judged as having failed only if both visual inspection found that the separation of the epoxy resin backing from the lead soldered electrode had obviously started or was well established and the voltages for that cell had been very high, relative to the others for that water, continuously for at least some of the time. Either criterion on its own was not acceptable. This is because with a few waters measurements continued or cells remained full of water for longer than the required four weeks which led to some cells failing after the test period. Alternatively, for some waters relatively high voltages were plainly associated with visual evidence of greater corrosion.

## 6. RESULTS SUMMARY: WATER QUALITY

The water quality parameters measured for all the waters throughout the four week measurement periods were pH, alkalinity and concentrations of chloride, sulphate, nitrate-nitrogen and silicate. Water temperature was standardised at 25°C.

The frequency distributions of each quality parameter between waters reflect no major bias for any parameter. The distributions of chloride, sulphate and nitrate concentrations are positively skewed.

Visual examination of the data and comparison of the four-week and fourth-week arithmetic means for each parameter show that most waters had relatively stable water qualities throughout their four week measurement periods.

The average qualities for each water during the four week and fourth week periods are given in Tables 6 and 7, Appendix C.

Significant correlation was found between some pairs of quality parameters. The extent of intercorrelation depended on which waters were included in the sample group and whether the natural or log values of the qualities were used, as reflected in Tables 8, 9 and 10.

The chloride to sulphate concentration ratio was also examined as a water quality parameter. (This ratio was found superior to the ratio of sulphate to chloride, as detailed in Section 8.) The majority of the significant correlations between any two quality parameters involved either alkalinity or this ratio as one of the two parameters.



The proportional rates of increase in chloride and sulphate concentrations with increase in alkalinity are different. The effect of this is that a high alkalinity water is more likely to have a lower value of chloride to sulphate concentration ratio than a low alkalinity water.

Further details of the evaluation of the water quality data are given in Appendix C.

## 7. RESULTS SUMMARY: VOLTAGES

Corrosion rates have not been calculated. Results are expressed simply in terms of voltage which is the parameter which was actually measured to assess the galvanic action in each corrosion cell. Voltage is a relative measure of galvanic corrosion rate.

Voltage developments of each cell within a group of five cells, used for measuring any one water, were generally the same during the four week measurement period. The principal exceptions were for those cells which failed.

Initial cell voltage and subsequent development of voltage varied from water to water but typical development patterns occurred. Generally the day to day variation of voltage for a cell and within a group of five cells was relatively small. The two waters with the highest nitrate concentrations exhibited relatively unstable voltages. Some other waters which exhibited some instability also tended to have higher than average nitrate concentrations.

Each group of five cells was used with flow of the test water through the cells in series. The relationship between cell voltage and cell order was significant: the first and fifth cells tended to produce the highest and lowest voltages respectively.

Failed cells were identified from visual inspection and their voltage trends. For each group of five cells the average voltage of the failed cells was compared with that of the good cells but no relationship between the two was evident.

The average voltages of the good cells in each group for the whole four week period and the fourth week are given in Table 11, Appendix D.

Comparisons between the four-week and fourth-week and the fourth-week and three-week voltages indicated that a four week period was long enough to establish

stable corrosion and that this could be represented by the fourth-week voltages.

The frequency distributions of the average voltages are positively skewed. The spread in the fourth-week average voltages is slightly greater than for the four-week values. This greater spread is associated with a sub-group of eight waters which produced the lowest voltages and is highlighted by the distribution of log average voltage. No water produced an average fourth-week log-voltage which was greater or less than two standard deviations from the mean of the average log-voltage for all waters.

The average fourth-week log-voltage was equivalent to 18.6 mV.

The median fourth-week log-voltage was about 22.4 mV. The largest and smallest fourth week voltages were 194 mV and 2.24 mV respectively, a ratio of greater than 85:1.

Further details of the evaluation of the voltage data are given in Appendix D.

## 8. RESULTS SUMMARY: CORRELATION OF VOLTAGE WITH QUALITY

The effect on voltage by each water quality parameter was examined in the presence of the variability in the other parameters. Because of the significant intercorrelation between some parameters some effects appear to contradict the results of the earlier work by WRc. Multiple regression analysis was used with the hope of overcoming this problem.

Multiple regression analysis was carried out on the four-week and fourth-week data for all waters. The best fit found, with 64% variance accounted for, was for fourth-week data:

$$\text{mV} = -15.76 + 24.0 R + 0.294 \text{ Cl} + 2.99 \text{ NO}_3\text{-N}$$

where R is the chloride to sulphate concentration ratio. This ratio was found to be superior to using its inverse, sulphate to chloride concentration ratio, as used in the previous work by WRc.

The scatter diagrams of voltage versus the individual water quality parameters, particularly log-value of alkalinity, highlighted the sub-group of eight waters with very low voltages. Multiple regression analysis was carried out on the fourth-week data for this sub-group and on the main group of waters which also excluded the three waters with the highest voltages.

The best fit found, with 99.7% variance accounted for, for the very low voltage sub-group was:

$$\begin{aligned} \text{mV} = 4.696 & - 1.737 \log \text{Alk} \\ & + 0.990 \log \text{SO}_4 \\ & - 0.345 \log \text{NO}_3\text{-N} \\ & - 0.112 \log \text{SiO}_2 \end{aligned}$$

Alkalinity alone accounted for 56.5% of the variance.

This low voltage sub-group consists of waters of very different types with wide ranges in values for each quality

parameter such that no common factor is evident for these waters, except the extent of inter-correlation between water quality parameters. Consequently the viability of this regression result and the reality of this sub-group must remain questionable until established for a larger sample.

Multiple regression analysis was least successful for the main group of data. The best fit found, with only 40% variance accounted for, was:

$$\begin{aligned} \text{mV} = & 56.89 - 11.86 \log \text{SO}_4 \\ & - 14.39 \log \text{SiO}_2 \end{aligned}$$

Because of the significant correlation between water quality parameters, the presence of quality parameters in the regression equations and the magnitude of their coefficients cannot be interpreted as being the sole and true effect on voltage by those parameters. However, other than for the sub-group, conclusions can be drawn as to the general effect on voltage of the individual water quality parameters:

- \* No significant association was found between pH and voltage although pH is significantly correlated with alkalinity and silicate.
- \* Waters with high alkalinity are associated with low voltages but this is more likely due to significant correlation of alkalinity with other parameters rather than a direct effect.
- \* High chloride concentrations are generally associated with high voltages and the extent of the effect is comparable with, though slightly less, than that found previously by WRc.
- \* High sulphate concentrations are generally associated with low voltages which is the effect found previously by WRc.
- \* Chloride and sulphate concentrations are better represented by their ratio. High values of this ratio are associated with high voltages and the extent of the effect is greater than found previously.

- \* High nitrate concentrations are associated with high voltages whereas the previous work by WRc did not find a significant effect on voltage by nitrate. As with the previous work, increase in nitrate is associated with increase in instability of corrosion cell voltages.
- \* High silicate concentrations are associated with low voltages though not to the extent found in the previous work.

In most of the multiple regression analyses a substantial proportion of the variance in voltages was unaccounted for by the water quality parameters measured. This suggests that other water quality parameters and factors which were not measured may significantly affect voltage. Some of the variance could also be due to metalurgical variation on electrode surfaces between cells or quite simply lots of noise in the voltages.

Further details of the analysis of the effects of water quality on voltage are given in Appendix E.

## 9. IMPLICATIONS

The measurements have shown that a wide range in values of galvanic corrosion potential exists for real waters. Corrosion potential depends very much on water quality.

If the quality of the water is known the likely relative level of corrosion potential can be estimated using the regression equations which have been determined. The accuracy of the estimates is such that they are suitable only for judging priority for making more detailed assessment of the need for action to reduce lead concentrations. Better equations could possibly be developed by taking account of a larger number of water quality parameters.

Information on lead concentration in water from copper plumbing is available for a few of the waters measured in this exercise: high lead concentrations have been found in tap water from relatively short plumbing during the first three months of use in association with corrosion cell voltages of 30 to 60 mV. Since the average voltage is about 20 mV this suggests that perhaps more than a quarter of all waters might give rise to unacceptable lead concentrations from new lead soldered copper plumbing. Further work is needed to substantiate this.

The results reinforce the observation in the previous work by WRc that corrosion cell voltages can be decreased by dosing waters to increase sulphate concentration or to increase silicate concentration. The results also suggest that reduction of nitrate concentration will reduce and stabilise corrosion cell voltages. These and other treatments should be tested for reducing corrosion potentials.

## 10. CONCLUSIONS

- \* Corrosion cell voltages were measured for thirty eight different waters representing wide ranges in values for the water quality parameters of interest.
- \* Significant correlations were found between some water quality parameters especially alkalinity and the chloride to sulphate concentration ratio.
- \* Average fourth-week voltage values measured covered the range 2.24 to 194 mV, a ratio of greater than 85:1. The average voltage was about 20 mV.
- \* Multiple regression analyses were carried out which produced some "best fit" equations. The regression equation with the most substantial fit, 99.7 per cent variance accounted for, was for the sub-group of eight waters with very low voltages. The correlations for this small sub-group are different from those for the bulk of the data and must remain questionable until established for a larger sample.
- \* The extent to which variance in voltage was accounted for in the regression analyses, excepting the low voltage sub-group, was generally low and implies that there are other factors additional to those water quality parameters measured in this work which may significantly affect voltage.
- \* The most significant effects on voltage, established by regression analyses, are associated with the chloride to sulphate concentration ratio and the chloride and nitrate concentrations. pH was not found to have a significant effect. The effect of alkalinity was most significant for the sub-group of very low voltage waters.
- \* The results of the regression analyses generally substantiate the conclusions of the previous work by WRc:



- high chloride concentration tends to be associated with high voltage
  - high chloride to sulphate concentration ratio tends to be associated with high voltage
  - high nitrate concentration tends to be associated with high and unstable voltage
  - high silicate concentration tends to be associated with low voltage.
- \* Treatments to change water quality which might reduce corrosion potentials should be tested.

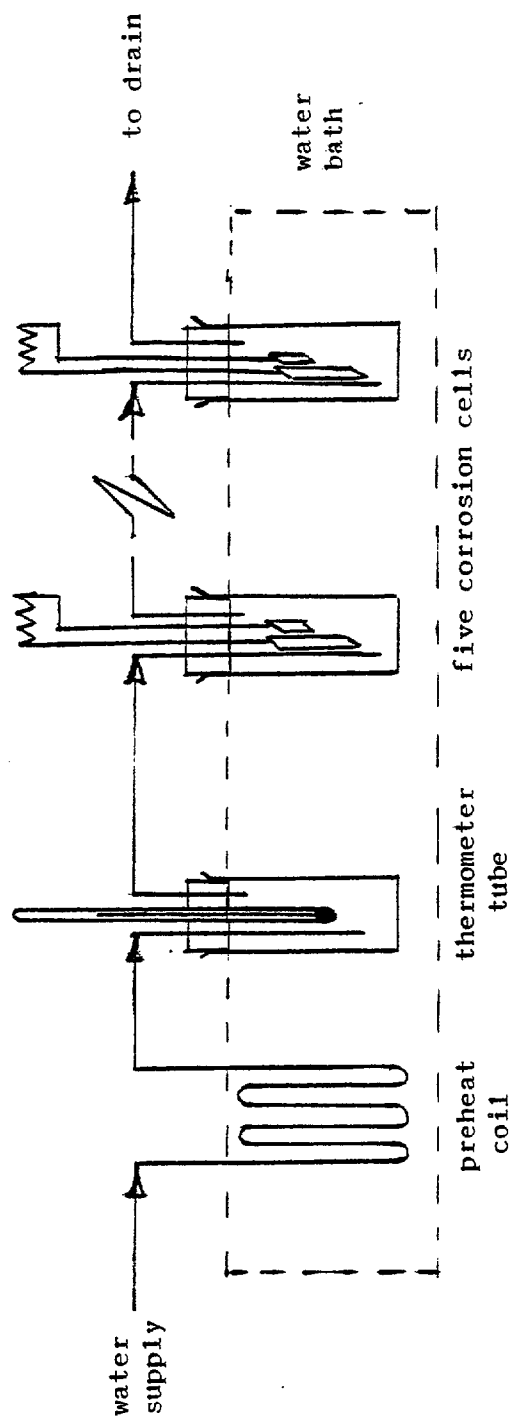


Figure 1. Diagram of flow arrangement through the corrosion cells

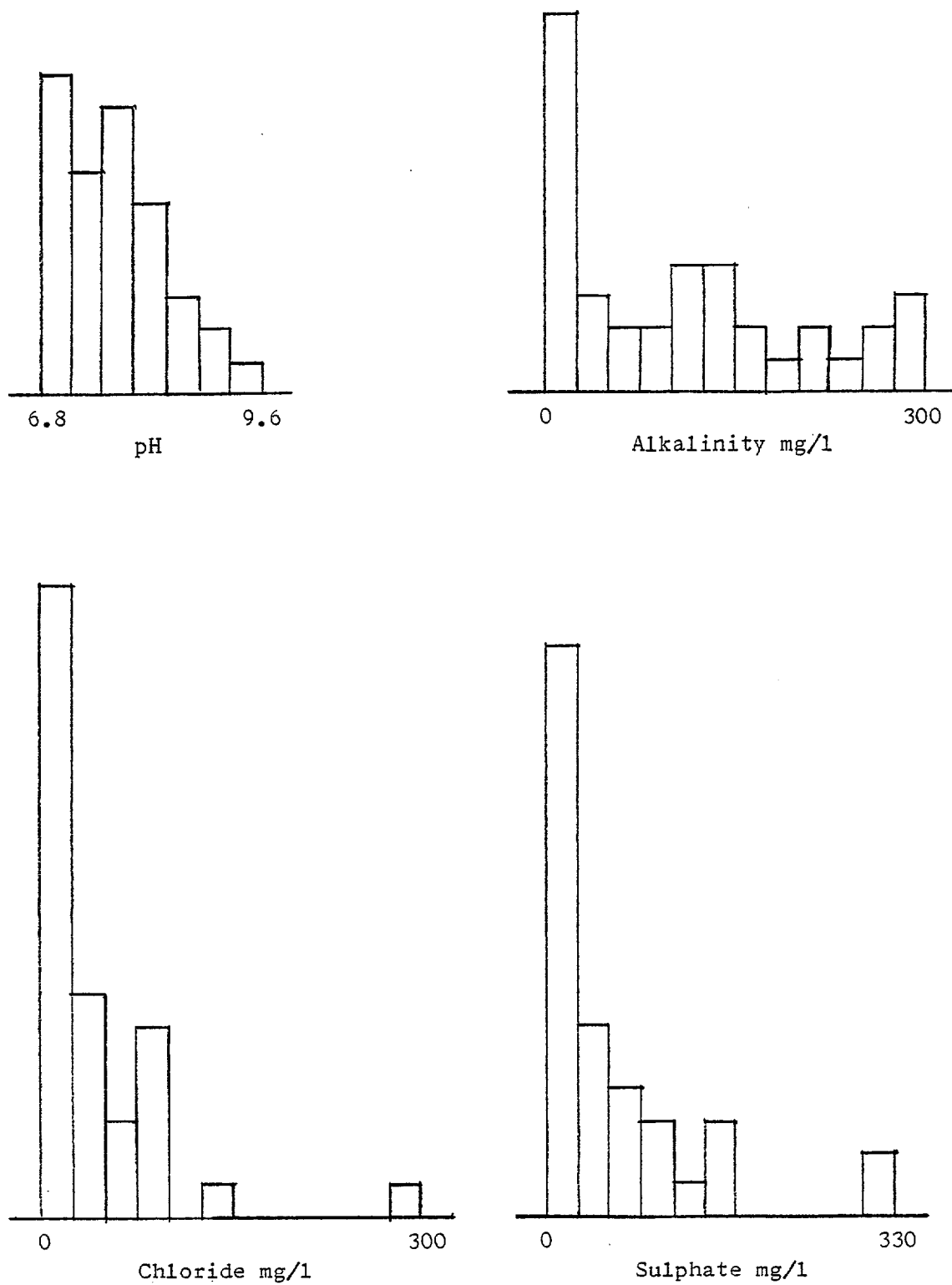


Figure 2. Histograms of four-week mean water qualities

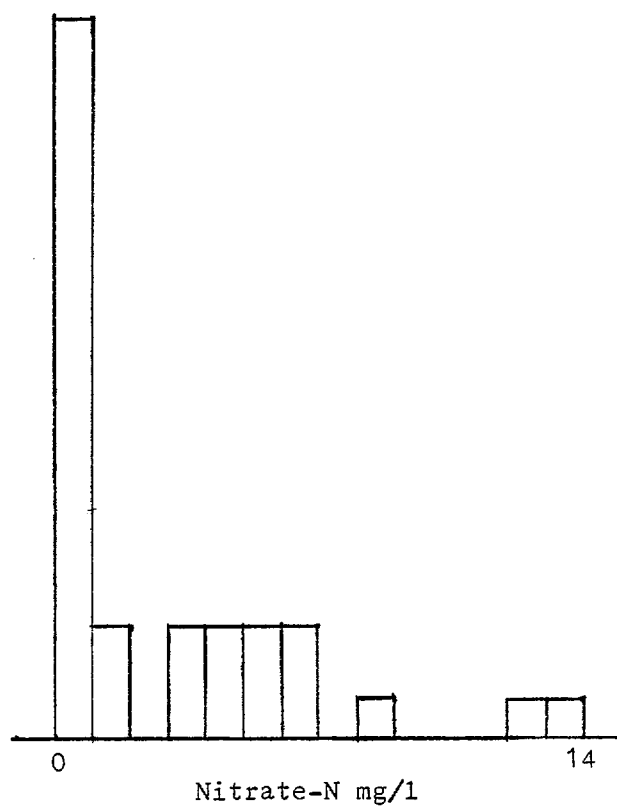
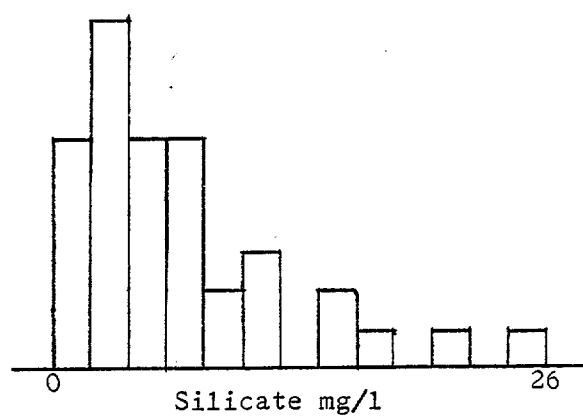


Figure 3. Histograms of four-week mean water qualities

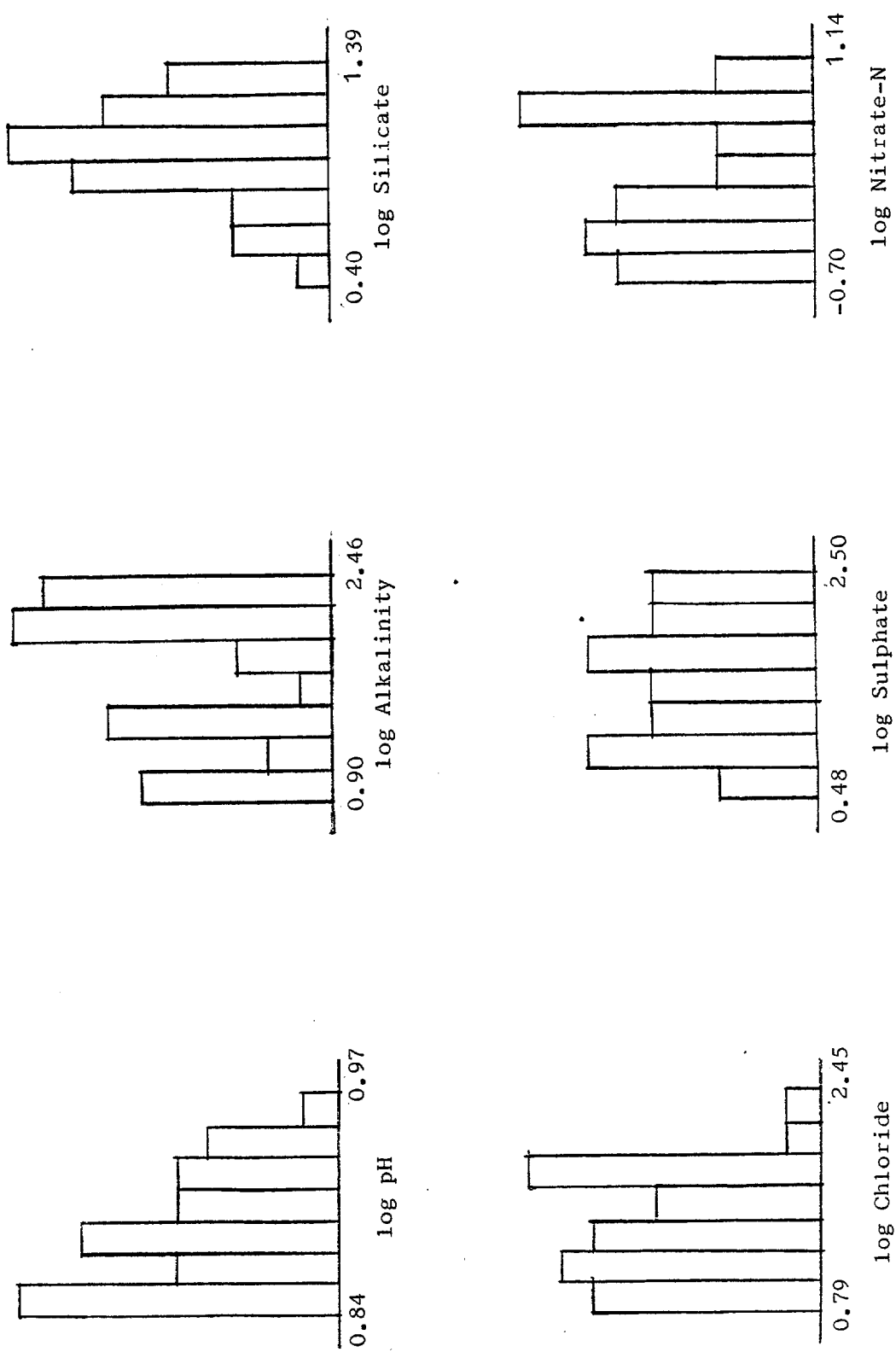


Figure 4. Histograms of four-week log-mean water qualities

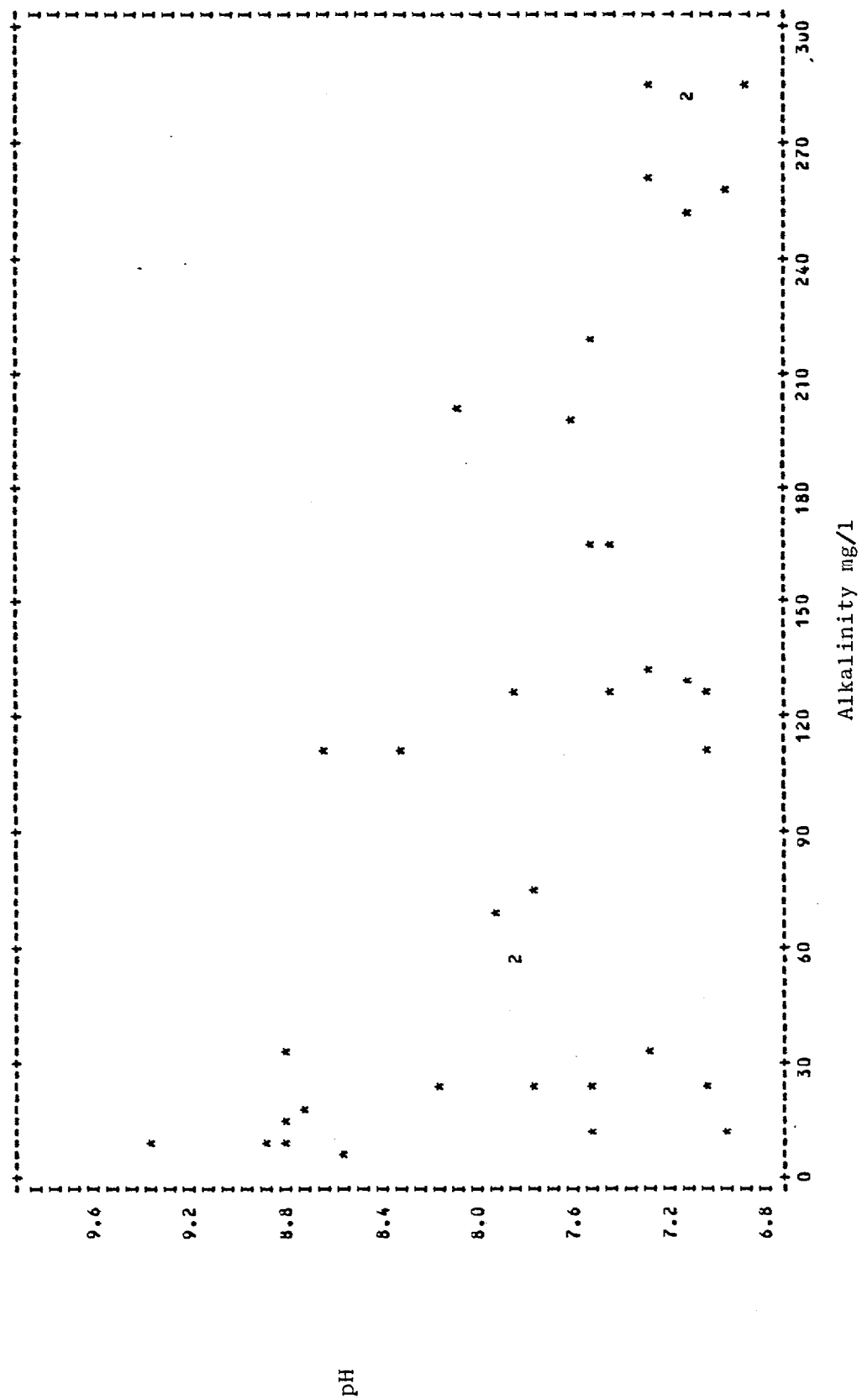


Figure 5. Scatter diagram of pH versus alkalinity fourth-week mean values

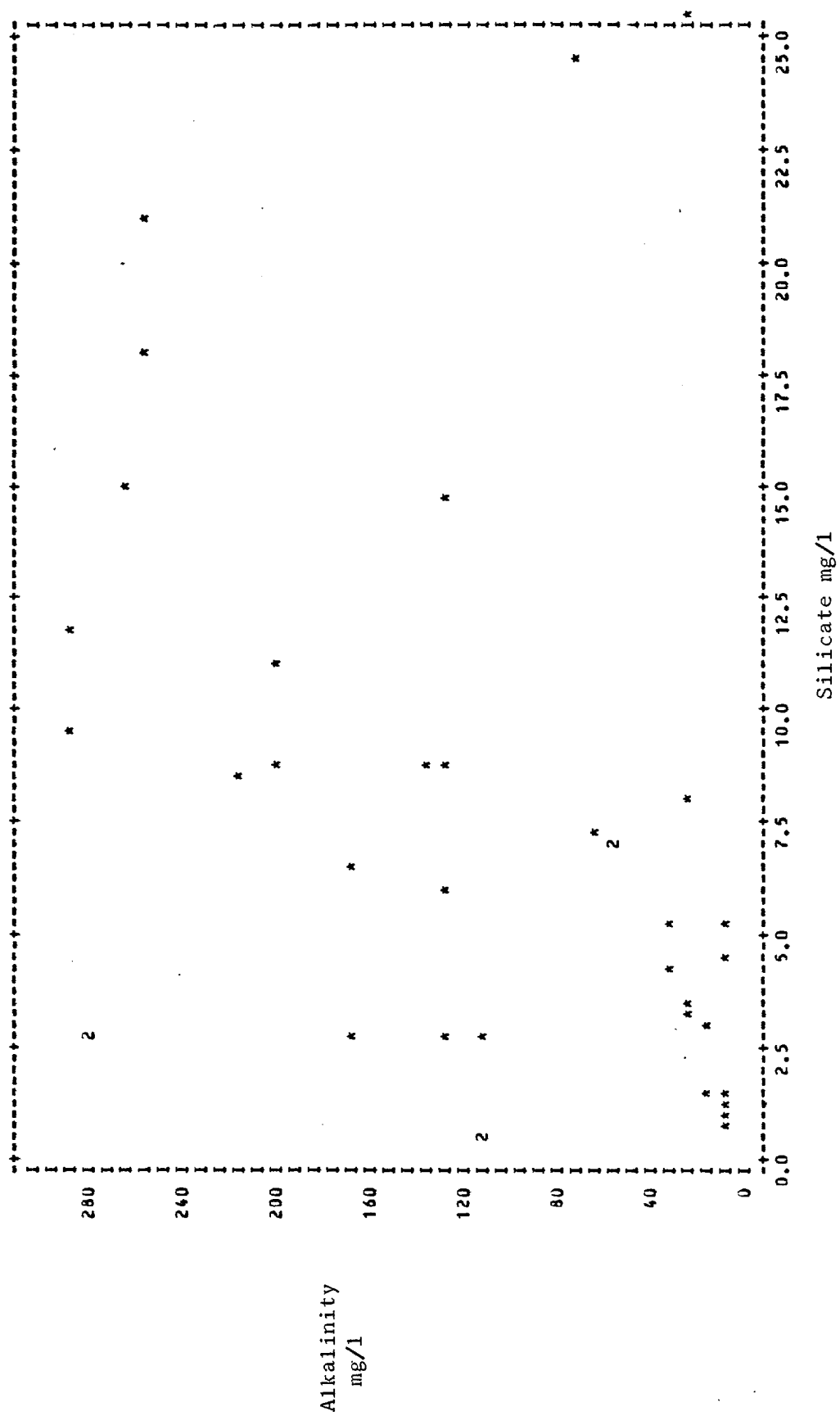
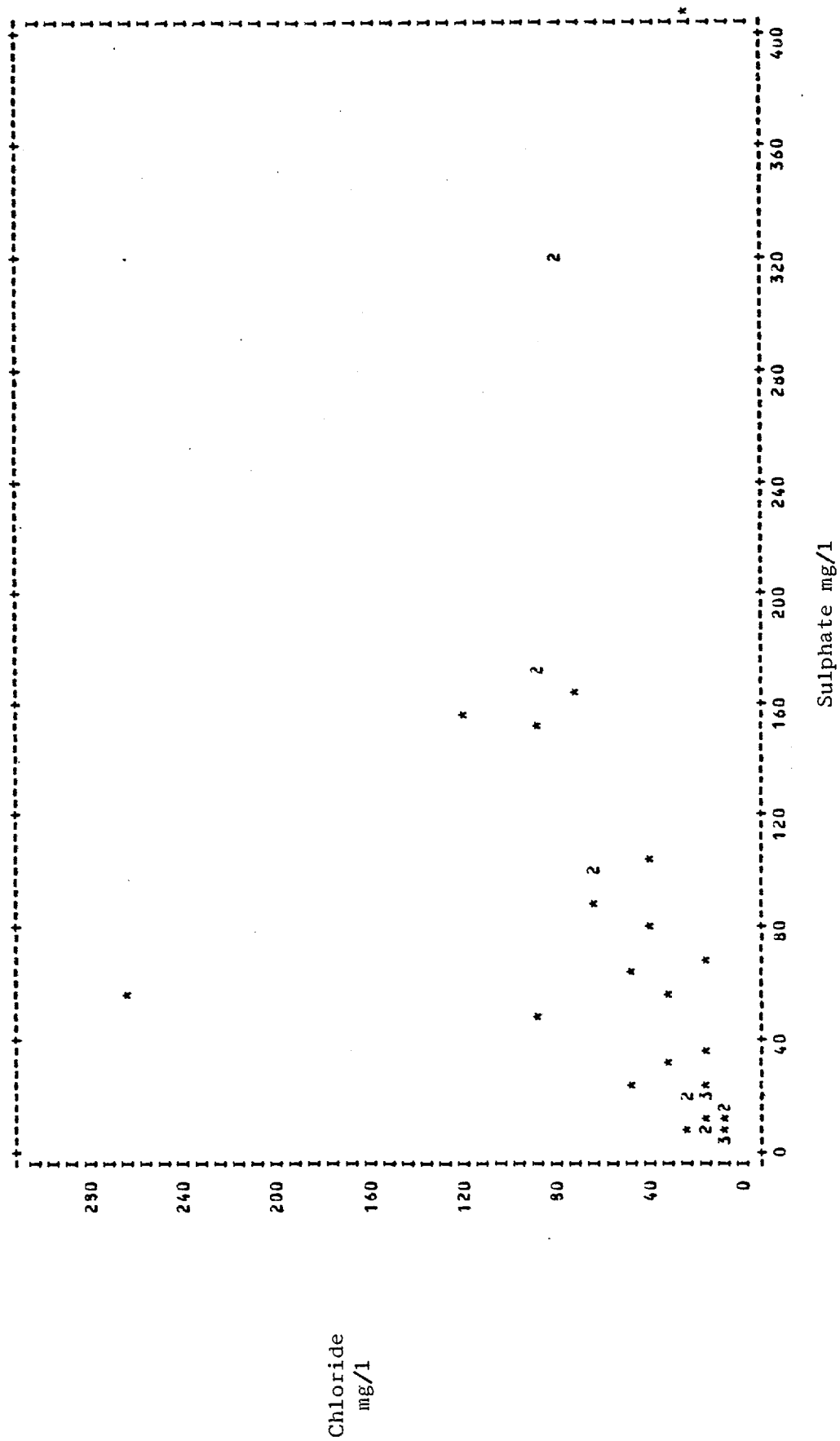


Figure 6. Scatter diagram of alkalinity versus silicate fourth-week mean concentrations





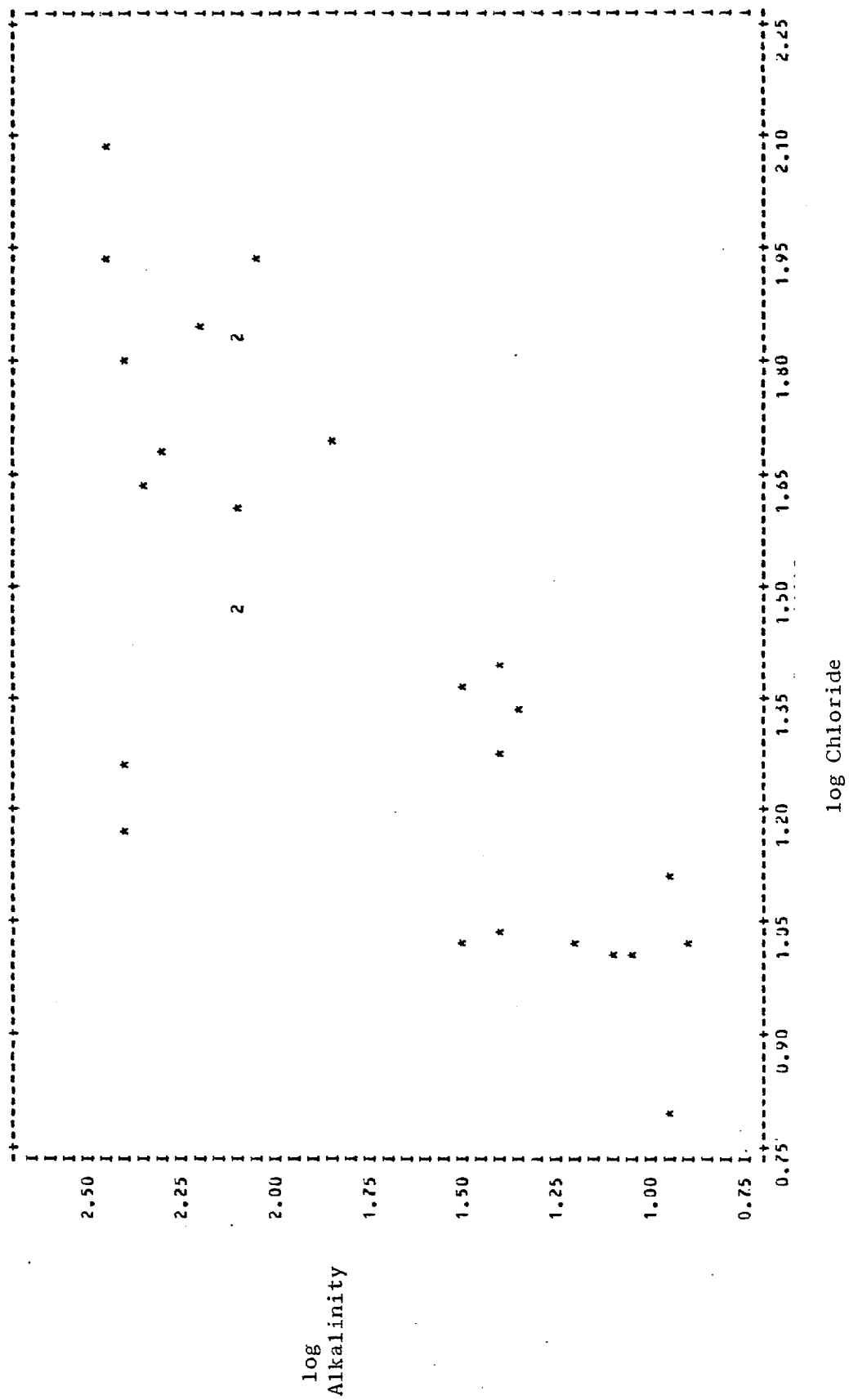


Figure 8. Scatter diagram of alkalinity versus chloride log of fourth-week mean concentrations

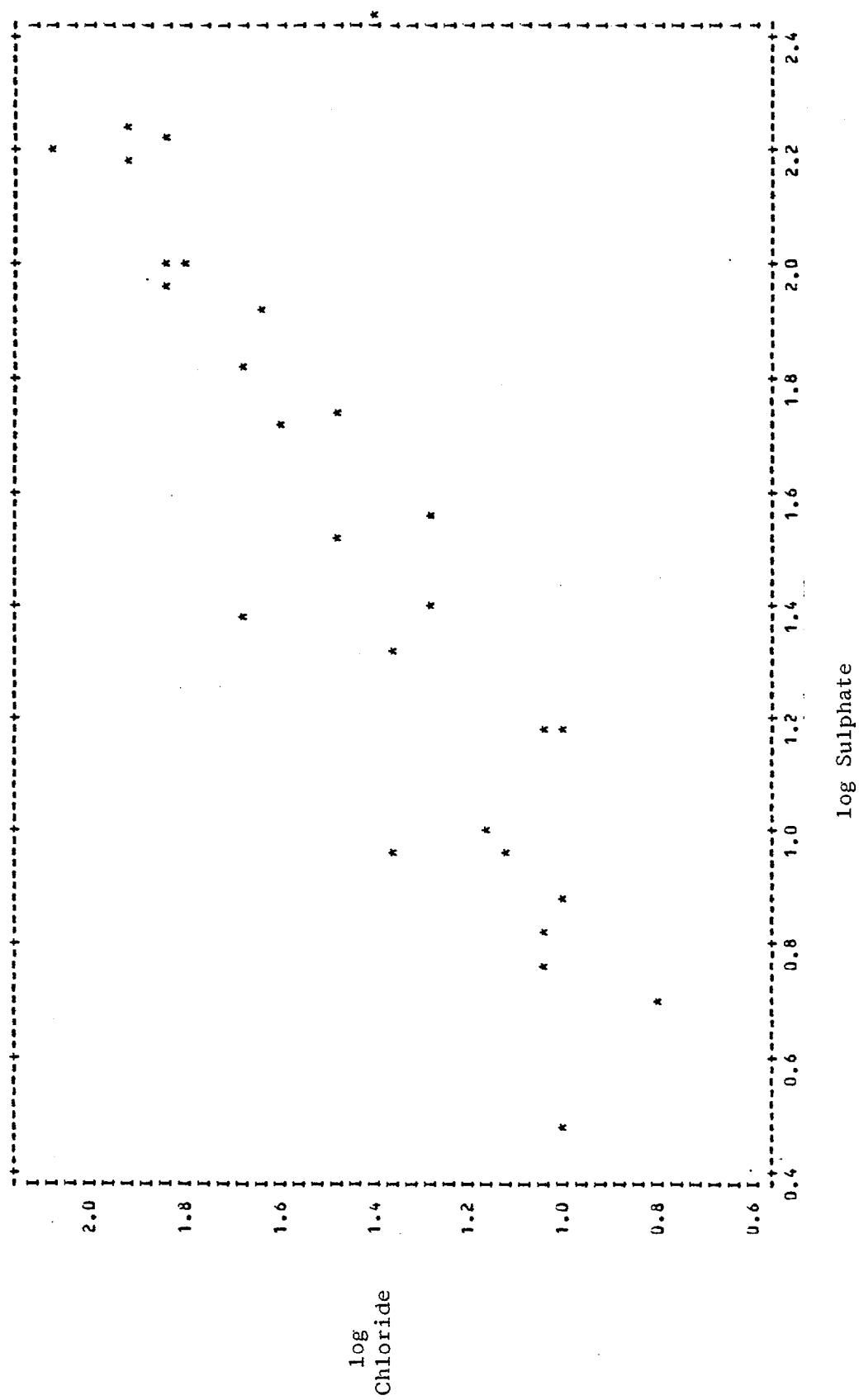
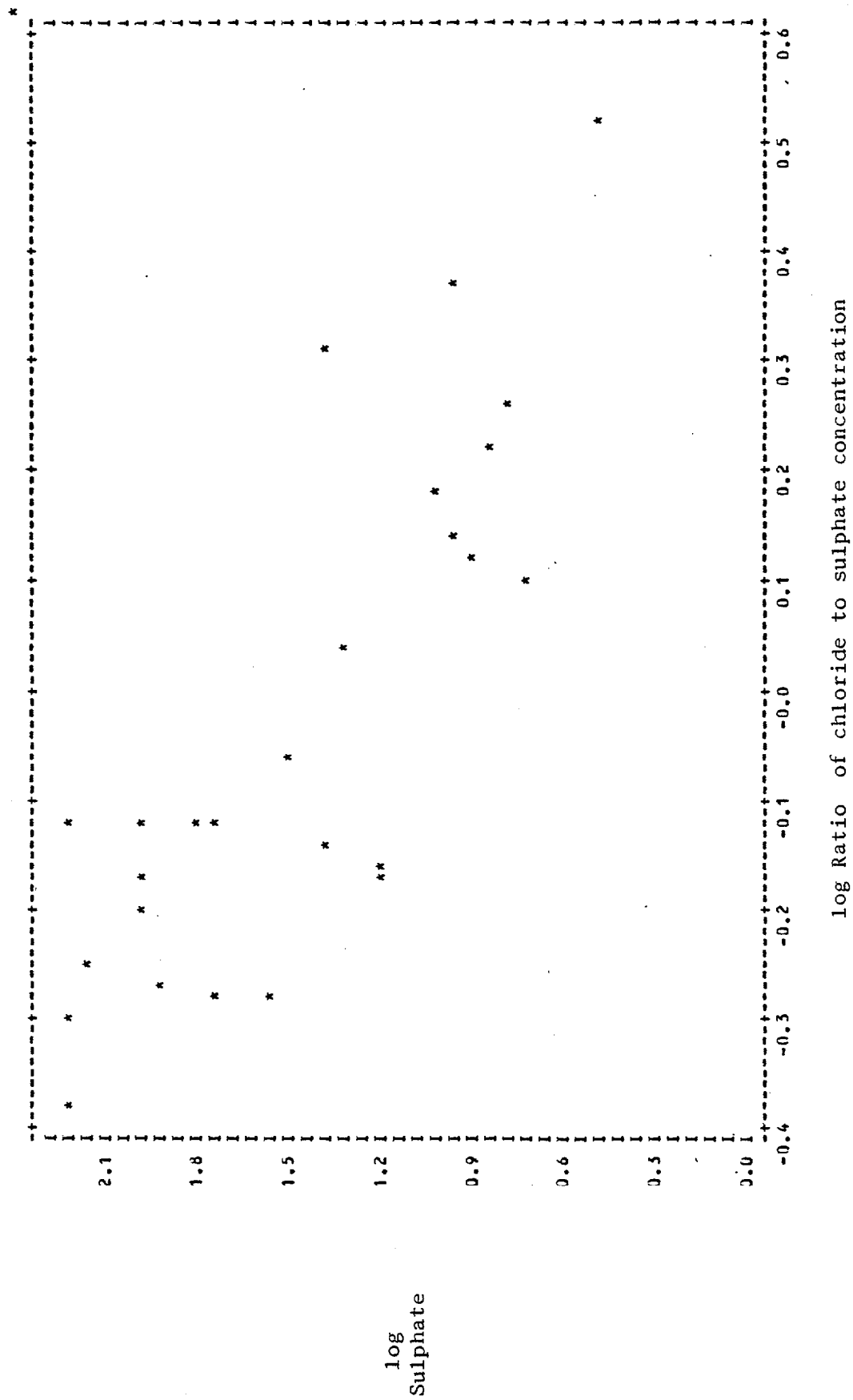


Figure 9. Scatter diagram of chloride versus sulphate log of fourth-week mean concentrations



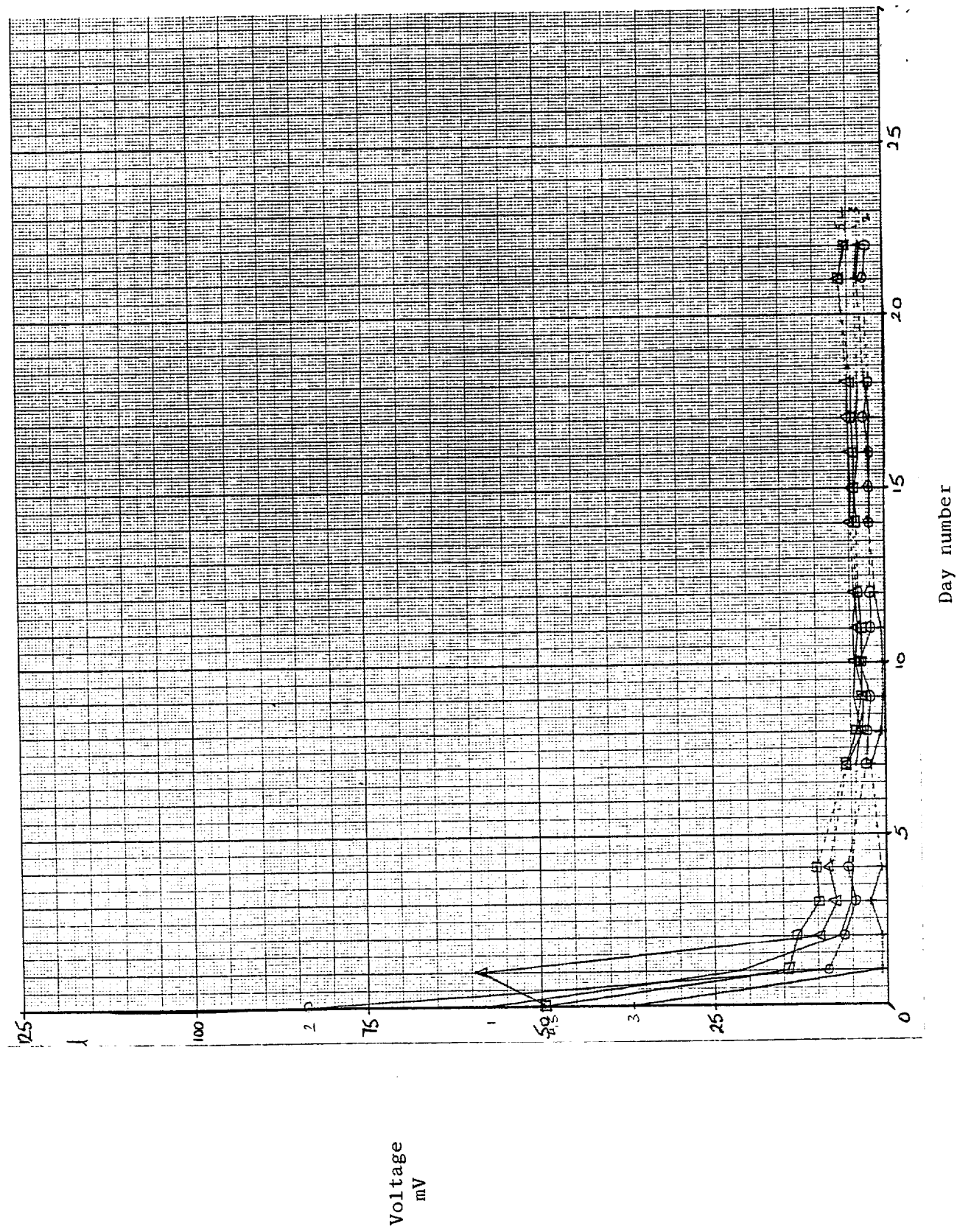


Figure 11. Voltage development for water D6

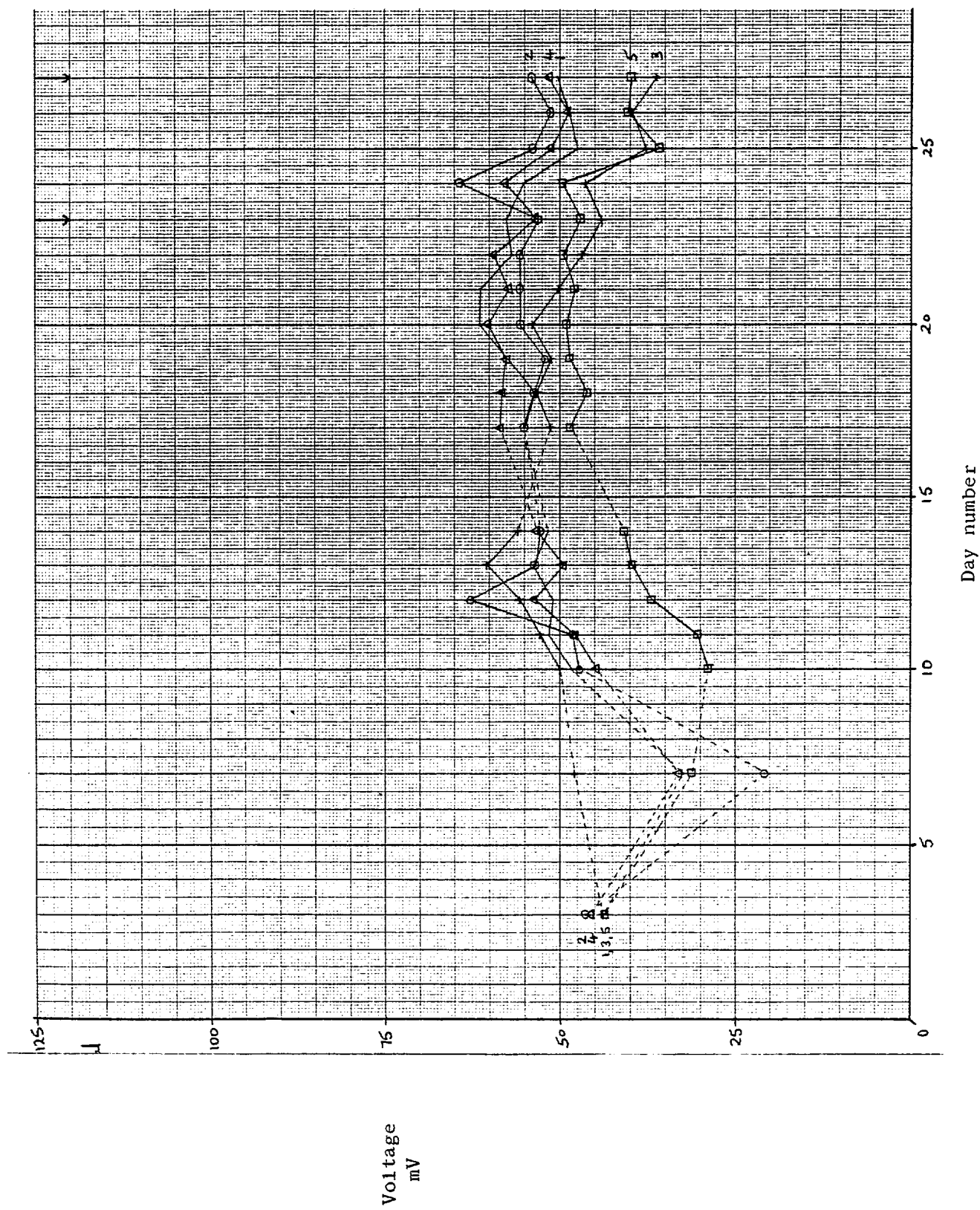


Figure 12. Voltage development for water A4

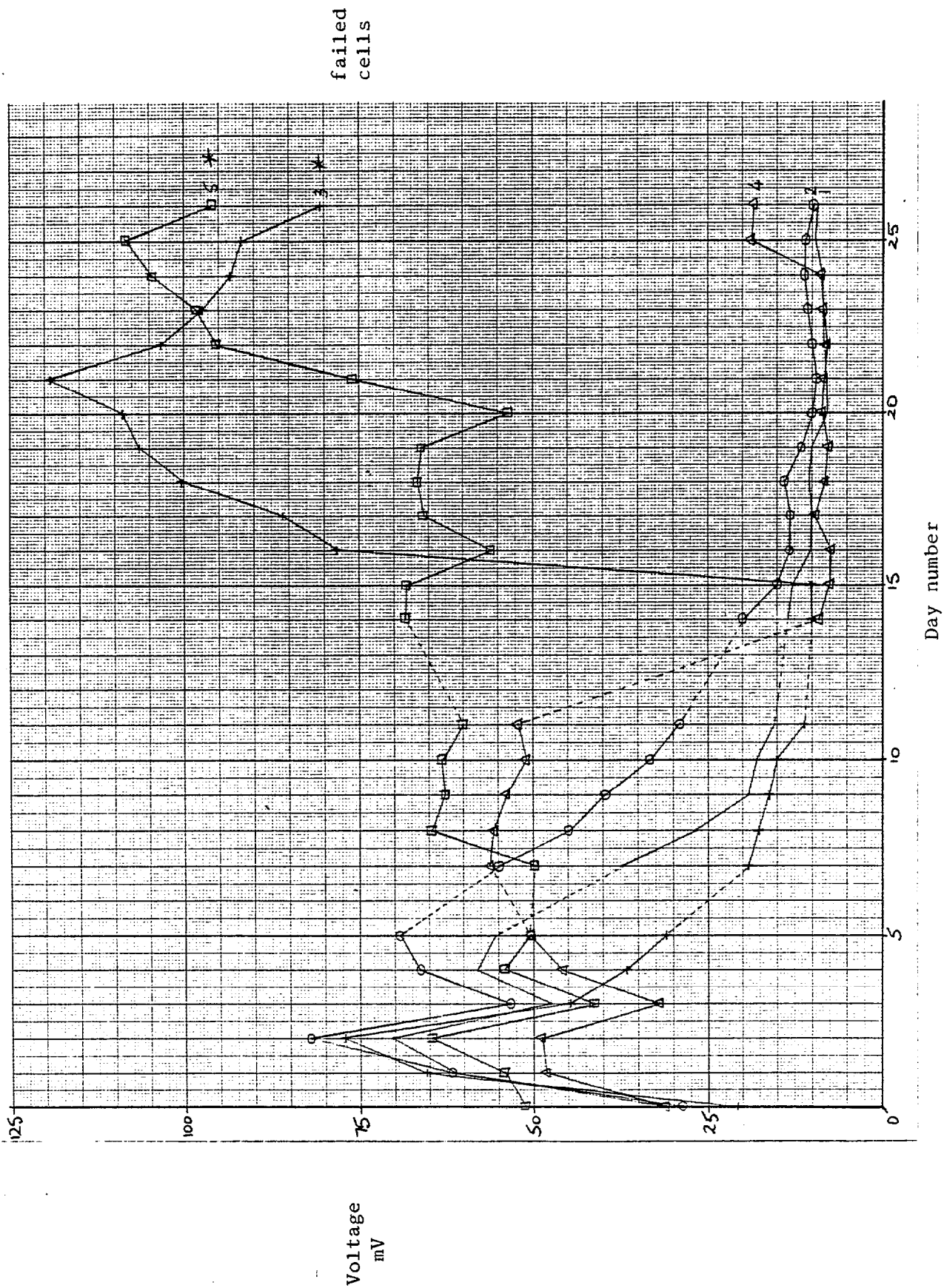


Figure 13. Voltage development for water B3

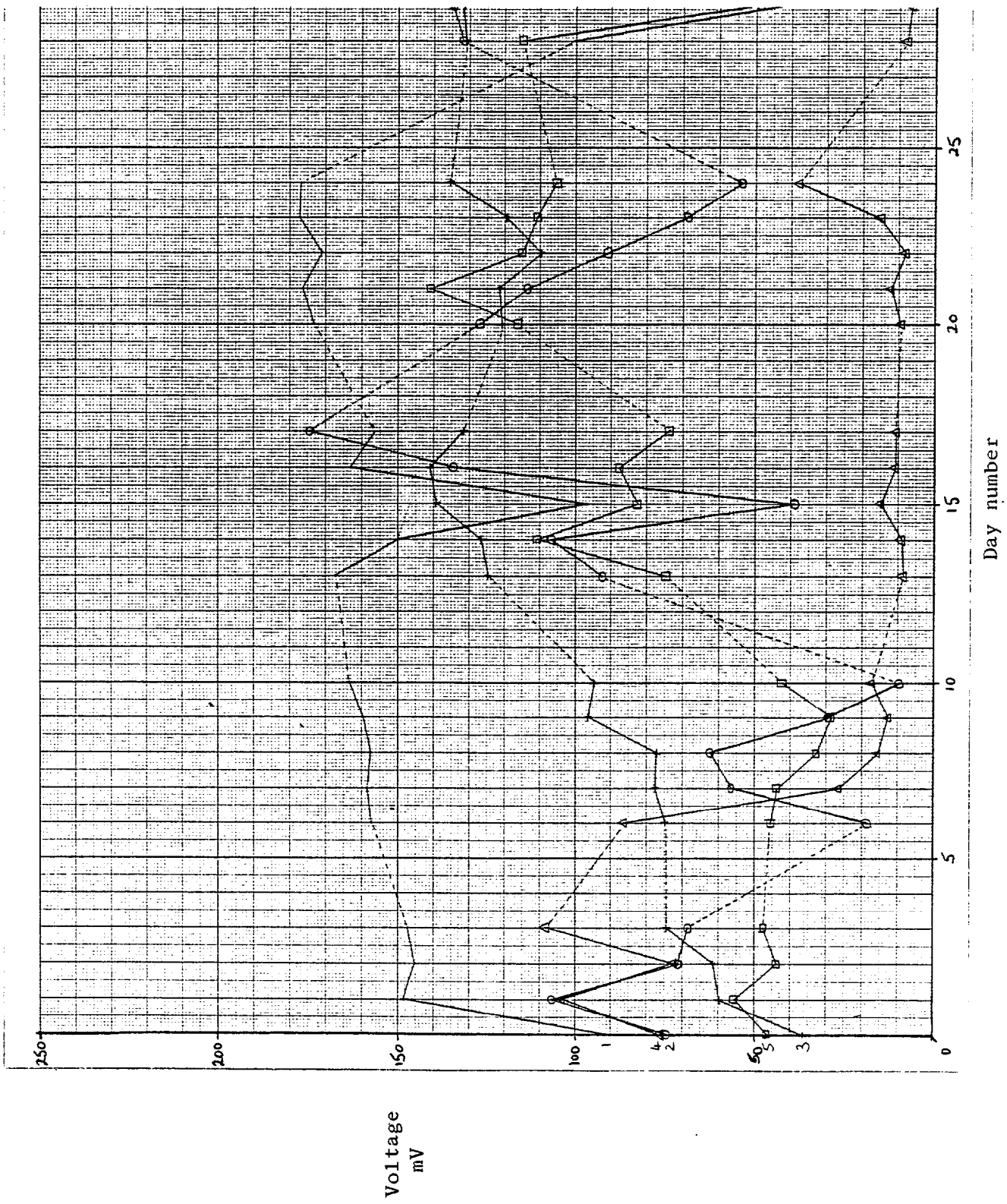


Figure 14. Voltage development for water C5

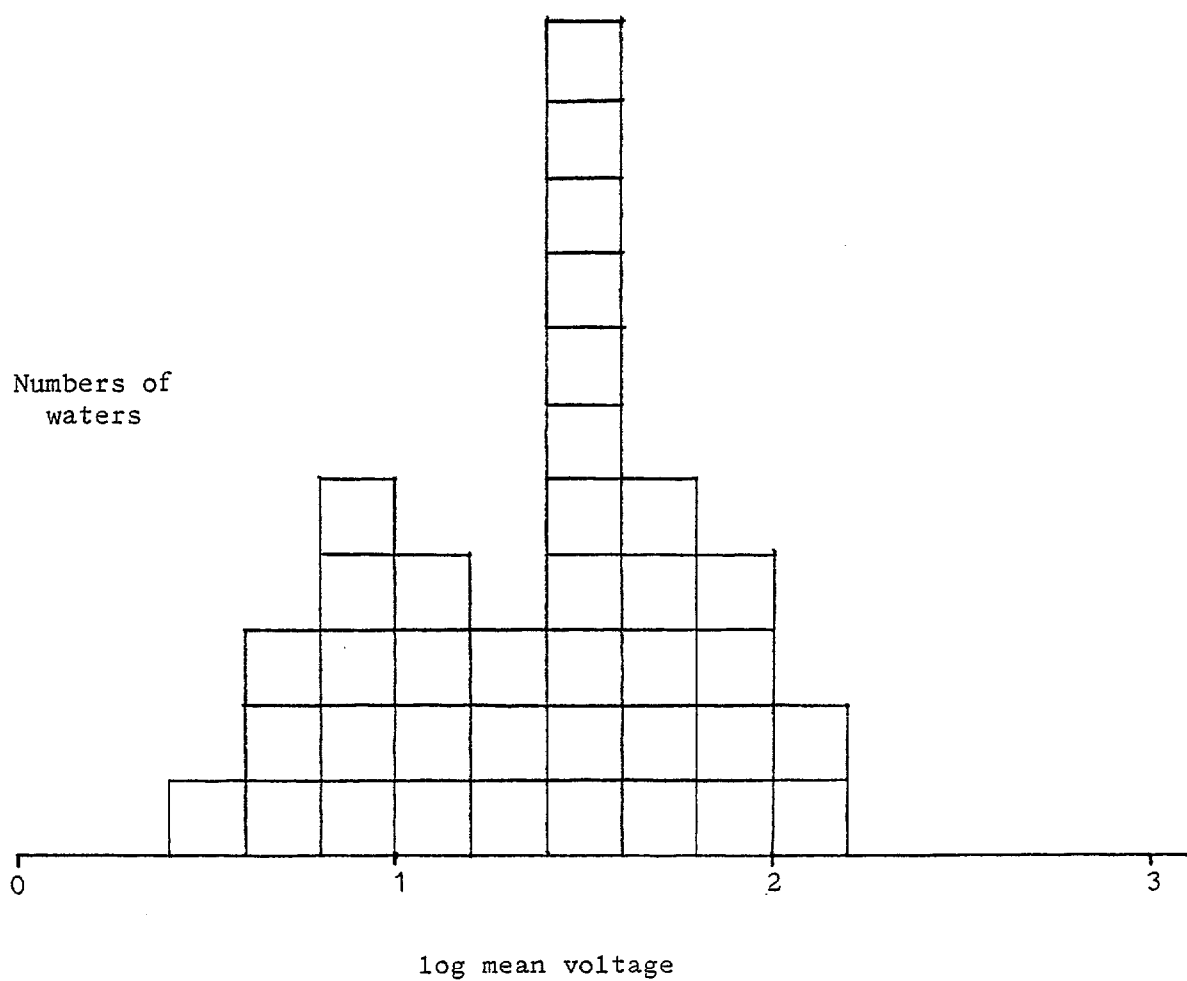
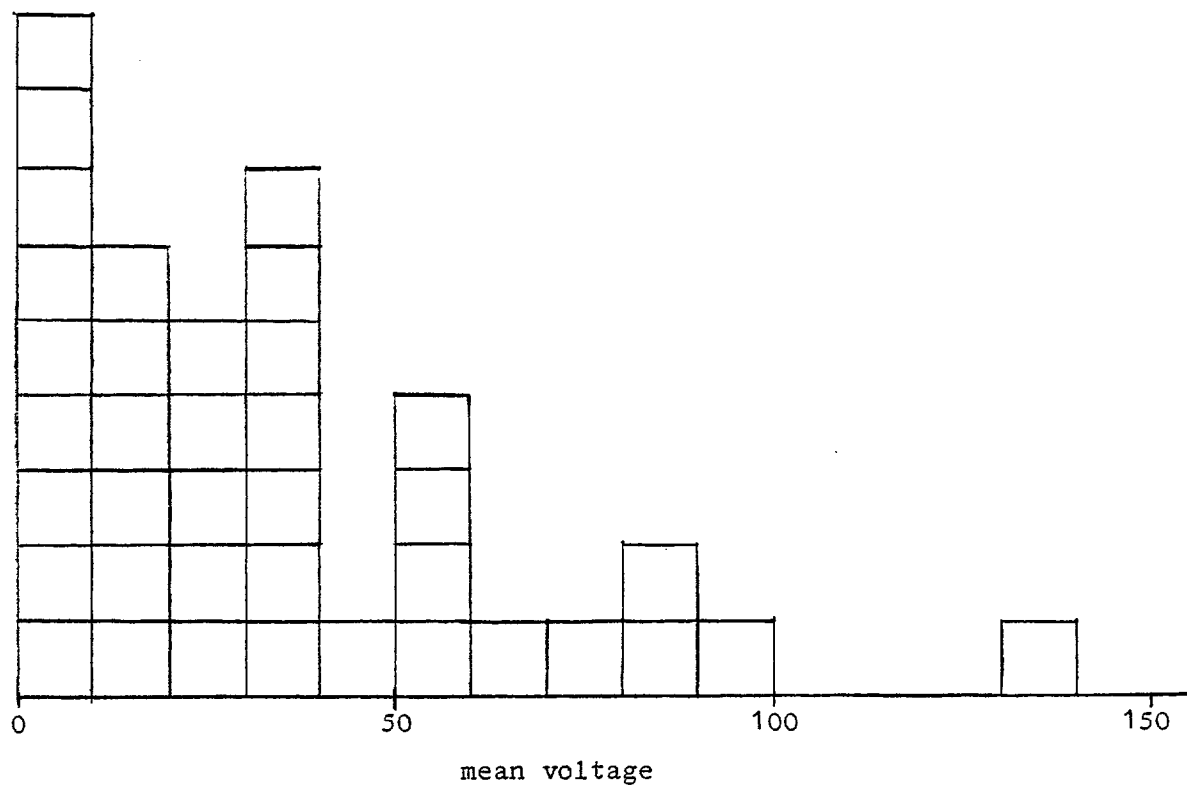


Figure 15. Distributions of four-week mean voltage values



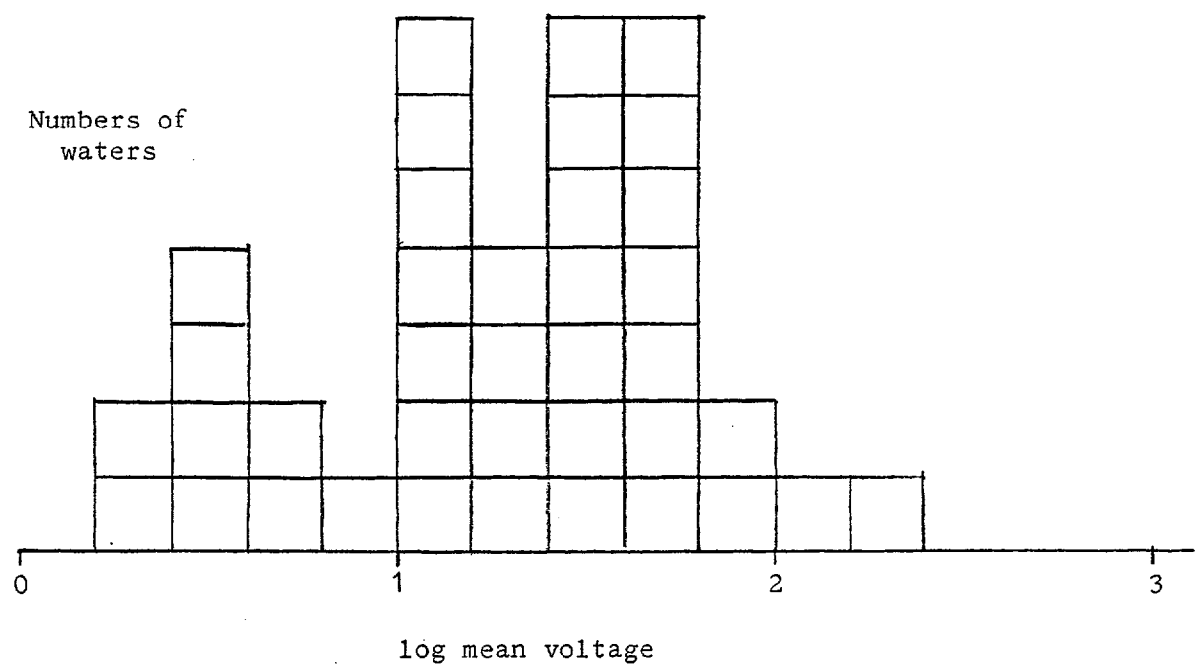


Figure 16. Distributions of fourth-week mean voltage values

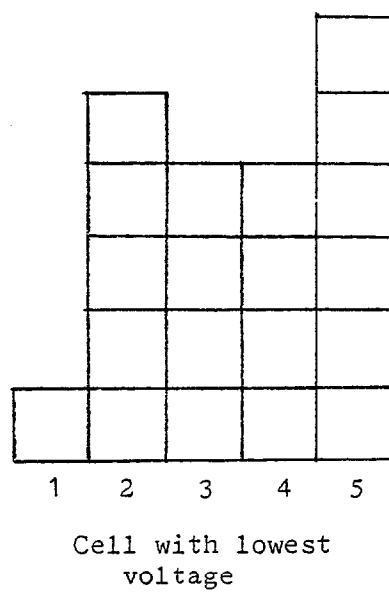
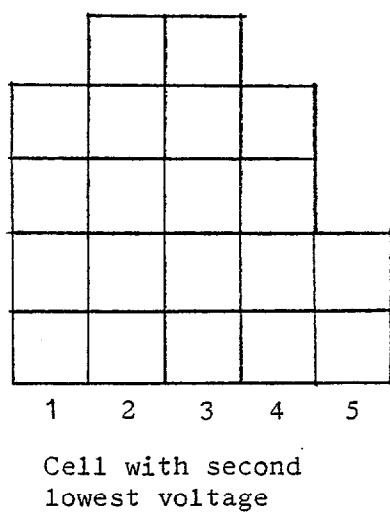
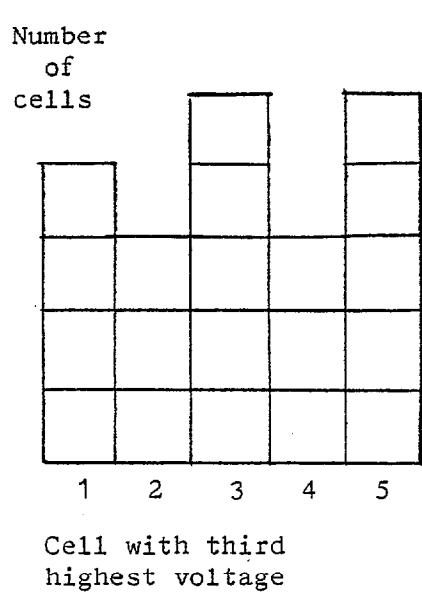
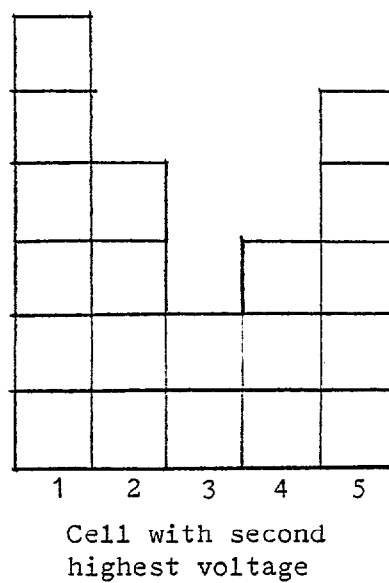
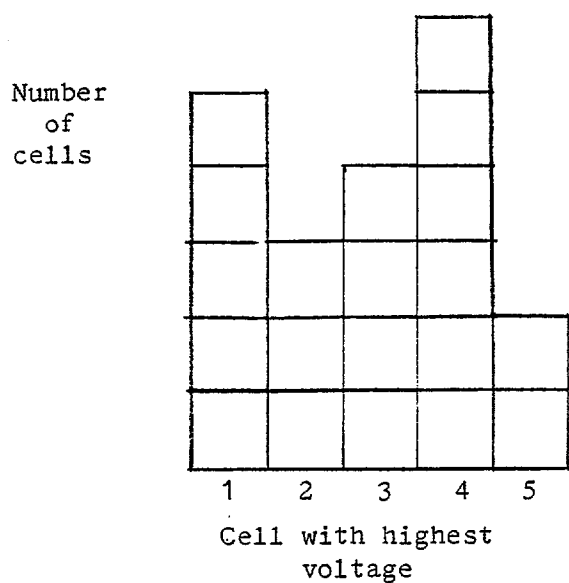
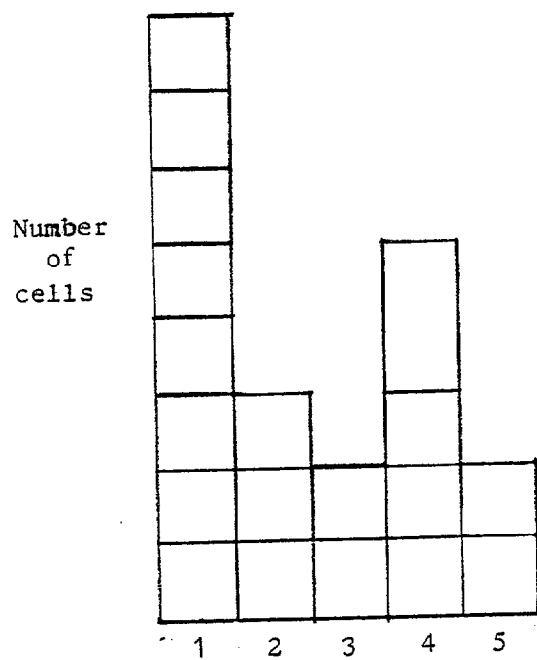
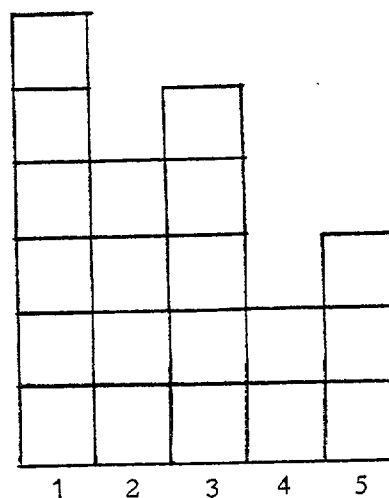


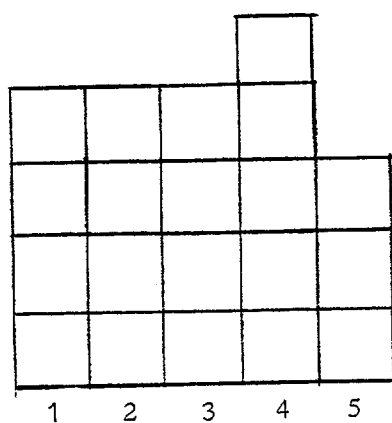
Figure 17. Effect of cell order on cell fourth-week voltage



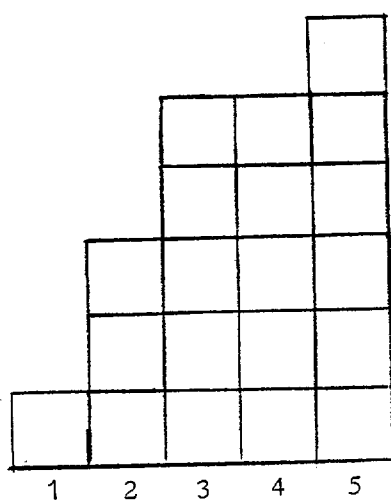
Cell with highest  
voltage



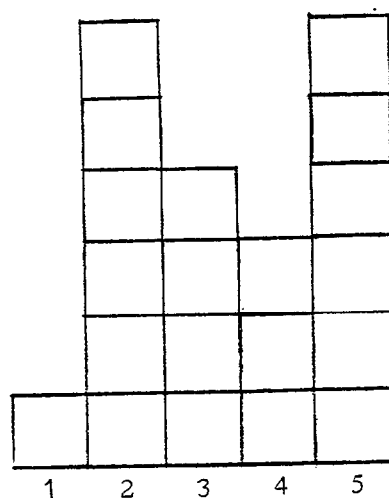
Cell with second  
highest voltage



Cell with third  
highest voltage



Cell with second lowest  
voltage .



Cell with lowest voltage

Figure 18. Effect of cell order on cell four-week mean voltage

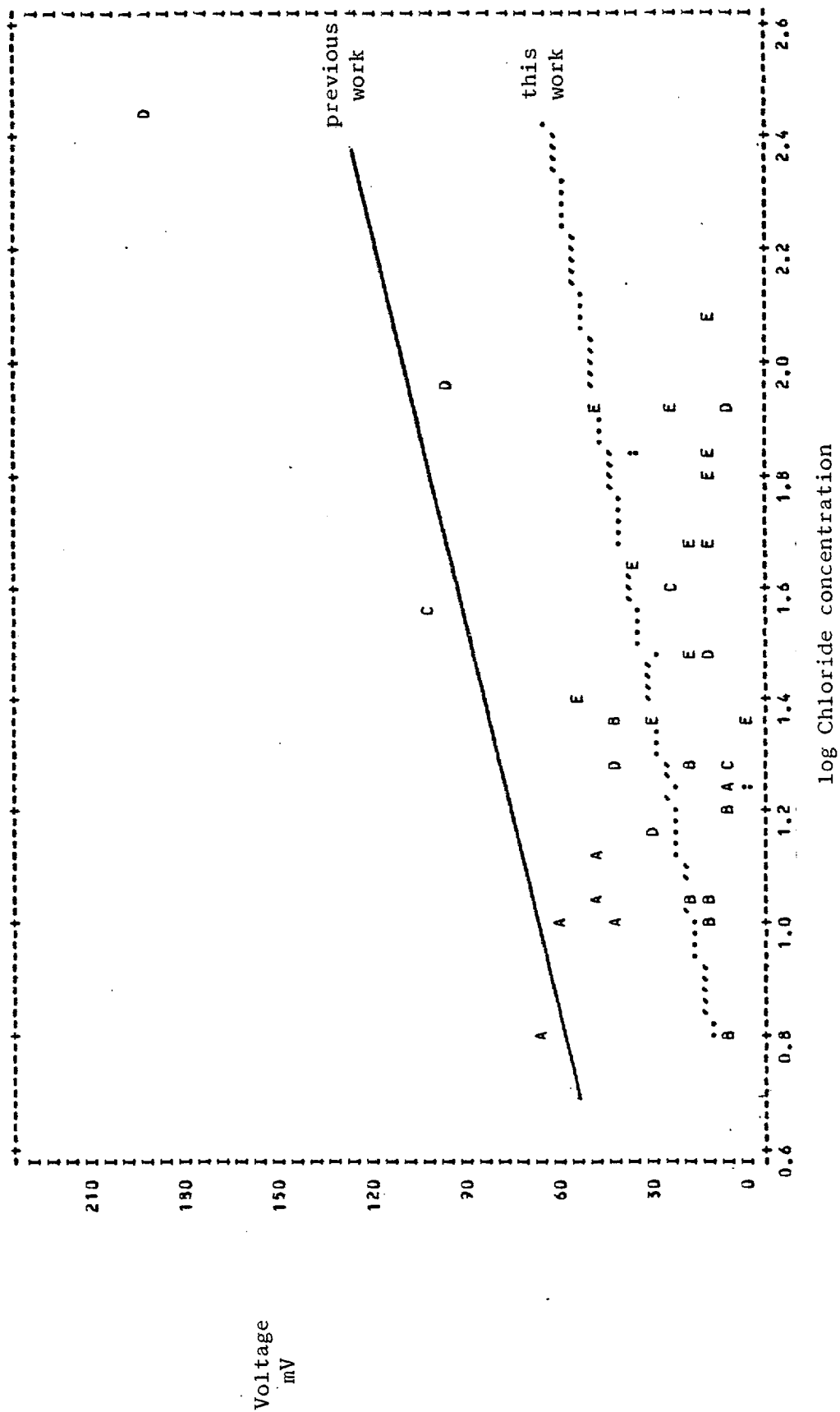
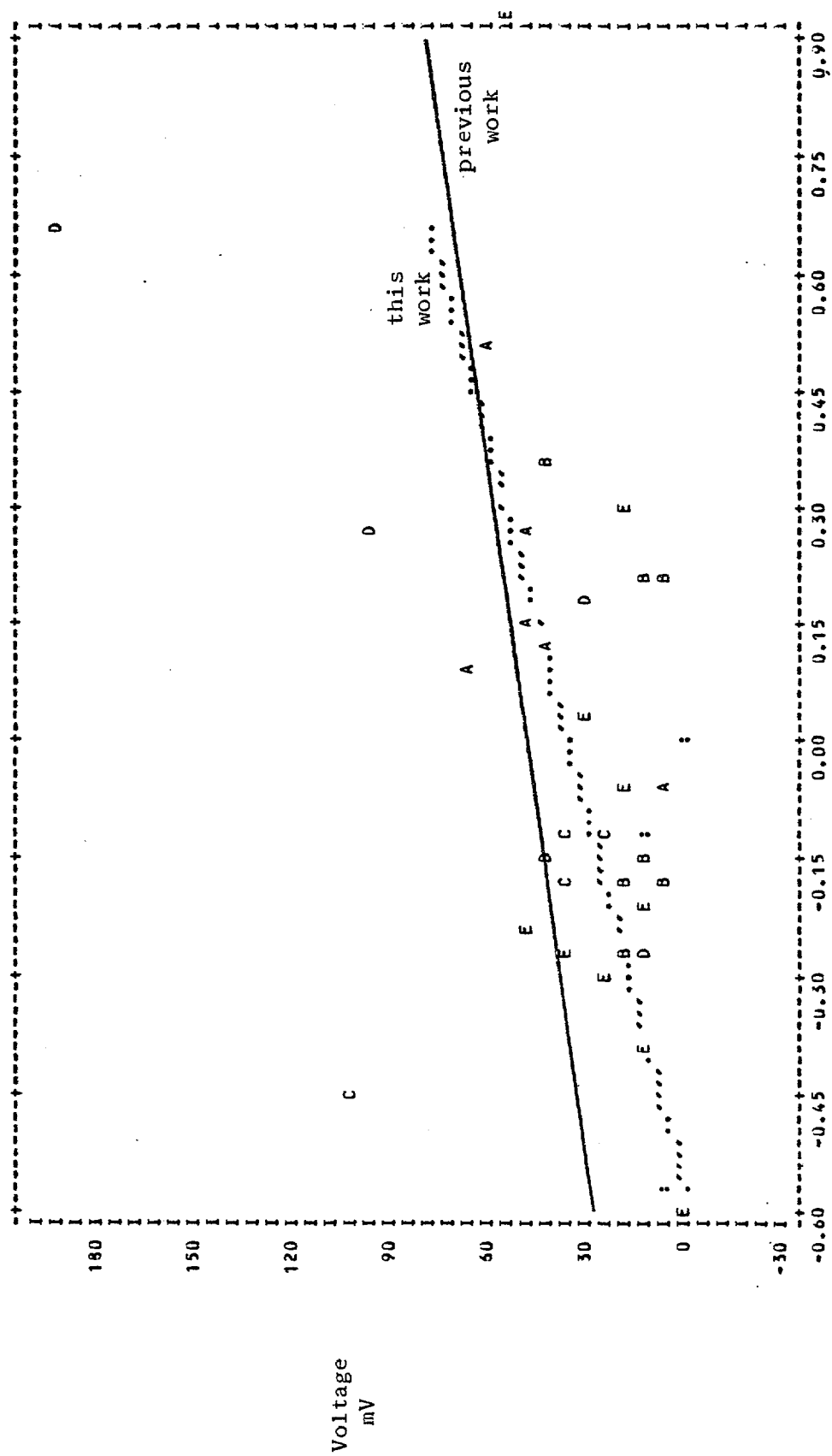


Figure 19. Comparison of the effect on voltage of chloride concentration for this work with results of previous work



log Ratio of chloride to sulphate concentration

Figure 20. Comparison of the effect on voltage of the chloride to sulphate concentration ratio for this work with results of previous work

## ACKNOWLEDGEMENTS

The work reported was carried out with the assistance of the following:

\* Water undertakings:

Anglian Water Authority  
North West Water Authority  
Severn Trent Water Authority  
South West Water Authority  
Welsh Water Authority  
Wessex Water Authority  
Yorkshire Water Authority  
Bristol Waterworks Company  
East Anglia Water Company  
East Surrey Water Company  
Eastbourne Waterworks Company  
East Surrey Water Company  
Lee Valley Water Company  
Mid Kent Water Company  
South Staffordshire Waterworks Company  
Central Regional Council  
Fife Regional Council  
Lothian Regional Council  
Strathclyde Regional Council  
Central Scotland Water Development Board

Other undertakings were also approached for help but whilst willing they were unable to provide assistance, within the criterion of convenience to themselves, for measuring the corrosion potential of waters which matched the selection criteria.

\* Sub-contractor to WRc:

J Gardiner, Consultant in Environmental Science

\* Colleagues throughout WRc.

## APPENDIX A - EQUIPMENT

### A.1

#### Corrosion cells

A total of 250 corrosion cells were manufactured by WRc Engineering. The design of the cells was the same as developed in the earlier work under contract to DOE\*. The cathode in each cell was made from copper foil with neither side masked. The anode was made from copper foil coated in tin-lead solder and with the side facing the cathode masked with epoxy resin. The two electrodes were coupled externally via a 10 kohm resistor.

A minor problem encountered with handling the cells was that a few of the glass boiling tubes containing the electrodes broke. The broken tubes were replaced by new tubes taking care not to touch the surfaces of the electrodes.

An important problem encountered was the separation of the epoxy resin masking of the lead-soldered electrodes in a proportion of the cells. It was evident for some cells during or after use that the epoxy resin masking and electrode "split" apart. Whilst the failure of some electrodes may have been due to simple failure of adhesion there was indication that corrosion, starting as edge corrosion, had penetrated and opened up the interface between the masking and the electrode.

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\* Walker, R. and Oliphant, R.J. "A cell to study corrosion of materials in the water supply industry" Jour. Instn. Water Engrs and Scientists 1983, 32 (2) 143-150.

Once it was apparent how high the failure rate was, eventually assessed as one in five, it was decided to strengthen the remaining unused cells. The method used to strengthen the bonding of the masking to the electrode was to apply a beading of epoxy resin very carefully round the edge of the electrode. The failure rate arising from strengthening was eventually assessed as one in twenty-five. The strengthened electrodes were used for measuring water Nos C3, D3, D5 and E1 to 13.

Cells after use were coded and stored for examination.

## **A.2 Water baths**

Twelve water baths were purchased. All were Grant FE15, 0 to 80°C, with preset temperature control. All of them were tested at Stevenage to work at a preset temperature of 25°C.

A PVC lid was made for each bath. In each lid was a set of holes to hold and suspend a stainless steel preheat coil, a thermometer tube and five corrosion cells. These items were connected in series in this order for the test water to continuously flow through them. A flow diagram is given in Figure 1.

The preheat coil was sized to allow test water at 5°C to reach 25°C, in a bath held at 25°C, at a maximum flow rate of 150 ml per min.

The thermometers used were short-stemmed, to minimise the risk of breakage, and graduated in 0.5°C.

The corrosion cell positions were numbered in order of flow.

Problems were reported by participants with two of the baths: in one case leakage from the base; in the other initial sticking of a relay in the temperature controller.

## **A.3 Digital multimeters**

Twelve Beckman T100 digital multimeters were purchased. All of the multimeters were checked at Stevenage before being distributed with the water baths. Problems with the multimeters were not reported by participants.



#### A.4

##### Use of equipment

After waters had been selected as appropriate for measurement of corrosion rate, the sub-contractor established contact with the participant and arranged to deliver the equipment, instal it if necessary and instruct the participant on the use of the equipment. The participant was also provided with a brief set of notes on the background and the methodology of the study as an aide-memoire, and copies of a proforma to record all the necessary data.

The participants were asked to operate the equipment, to assess relative corrosion rate, for four weeks on each of their waters selected. It was emphasised that the quantity and quality of the measurements made during the fourth week were the most important.

The participants were asked to send the results for each water measured to the sub-contractor who was responsible for the collation and preliminary assessment of the data. When the participant had measured all their waters selected then the sub-contractor collected the equipment and delivered it to the next participant.

New and unused cells were used for each water measured. Before use each cell was checked visually and suspect cells were put aside.

## APPENDIX B. SELECTION OF WATERS

### B.1

#### Original selection criteria

The earlier work by WRc showed that corrosion rate is sensitive to pH, chloride and sulphate to chloride concentration ratio but insensitive to alkalinity within the range of values for these parameters in "real" waters. Using this as a basis a "shopping list" of waters to be measured was prepared to cover likely high and low corrosion rates but with emphasis on high rates.

The list of water types to be selected was given by the matrix in Table 1. This matrix defines eighteen water types for measurement. The aim was to measure two examples of each water type with predicted low corrosion rate and three examples of each water type with predicted high corrosion rate. The total number of waters to be measured was therefore to be forty-four.

Even though the preparation of this matrix had taken into account knowledge about the inter-related distribution of pH and alkalinity little equivalent information was available on chloride, sulphate and nitrate. Following the initial approaches to some water undertakings it became evident that the criteria for selecting waters needed to be revised.

Table 1

Matrix of water types: original criteria

Alkalinity	pH	mg Cl/l	SO <sub>4</sub> :Cl ratio
<50	>8.0 )		
<50	7.5 to 8.0)		
<50	<7.5 )	( <15	<1
		( >30	<1
100 to 200	7.5 to 8.0)	( >30	>2
100 to 200	<7.5 )		
>200	<7.5 )		

Additionally: concentrations of phosphate, silicate and nitrate should be low.

## B.2

### Revised criteria

It was decided that the revised criteria had to not only allow for inter-relationships between chloride, sulphate and alkalinity but also accommodate nitrate, distinguish between very low and low alkalinity waters and distinguish between surface and ground waters. Because of the increased complexity it was decided also to adopt a straightforward factorial design for the selection matrix to facilitate the statistical analysis of the data and allow the assessment of inter-correlation of corrosion effect by the different quality parameters.

The revised "shopping list" is given by Tables 2 to 5. Even though values were assigned to each parameter to define the limits of their low and high values some of these were regarded as being targets and therefore were elastic. The final results depended on the conditions existing at the time of the measurements although some re-measurements were anticipated to be necessary for better alignment with the targets.

In Table 2, for very low alkalinity surface waters, Group A, three basic water types were identified. This is the only group, because of its size, for which two examples of each water type were to be measured. In Group B, low alkalinity surface waters, eight water types were identified. In both Group C, high alkalinity surface waters, and Group D, high alkalinity ground waters, sixteen water types were identified. The total number of waters sought for measurement therefore became forty-six.

The final column in each Table indicates whether an example of each water was found and measured.

Table 2

GROUP A. Very low alkalinity surface waters,  $<20 \text{ mg CaCO}_3/\text{l}$

pH <7.5, >8		Found
Low		/
Low		/
High	No coag	/
High	No coag	/
High	With coag	/
High	With coag	/
Total 6, all found		

Table 3

GROUP B. Low alkalinity surface waters,  
20 to 50 mg CaCO<sub>3</sub>/l

pH <7.5,>8.0	Cl mg/l <20,>40	SO <sub>4</sub> :Cl <1,>2	Found
Low	Low	Low	/
Low	Low	High	/
Low	High	Low	/*
Low	High	High	x
High	Low	Low	/
High	Low	High	/
High	High	Low	/
High	High	High	x

\*Two examples measured

Total, 6 found

Table 4

GROUP C. High alkalinity surface waters,  
100 to 200 mg CaCO<sub>3</sub>/l

pH <7.3,>7.7	Cl mg/l <30,>60	SO <sub>4</sub> :Cl <1,>2	NO <sub>3</sub> -N mg/l <3,>6	Found
Low	Low	Low	Low	x
Low	Low	Low	High	x
Low	Low	High	Low	x
Low	Low	High	High	x
Low	High	Low	Low	/
Low	High	Low	High	x
Low	High	High	Low	x
Low	High	High	High	x
High	Low	Low	Low	/
High	Low	Low	High	/
High	Low	High	Low	/
High	Low	High	High	/
High	High	Low	Low	x
High	High	Low	High	x
High	High	High	Low	x
High	High	High	High	/

Total 16, 6 found

Table 5

GROUP D. High alkalinity ground waters,  
150 to 250 mg CaCO<sub>3</sub>/l

pH <7.3,>7.7	Cl mg/l <30,>60	SO <sub>4</sub> :Cl <1,>2	NO <sub>3</sub> -N mg/l <3,>6	Found
Low	Low	Low	Low	x
Low	Low	Low	High	/
Low	Low	High	Low	x
Low	Low	High	High	/
Low	High	Low	Low	x
Low	High	Low	High	x
Low	High	High	Low	x
Low	High	High	High	x
High	Low	Low	Low	x
High	Low	Low	High	x
High	Low	High	Low	/
High	Low	High	High	x
High	High	Low	Low	/
High	High	Low	High	/
High	High	High	Low	/
High	High	High	High	x

Total 16, 6 found

### B.3

**Supplementary selection** Waters fitting the above "shopping list" and within the limitations of convenience for measurement were identified with the help of water undertakings. The selection of waters, even after the revision of the selection criteria, was found more difficult than expected for various reasons including:

- (i) The extensive centralisation by water undertakings of laboratory facilities substantially limits waters which are convenient to undertakings to measure corrosion rate under continuous sampling conditions.
- (ii) The extensive development of conjunctive use of supplies limits the reliability of water of relatively consistent quality being supplied where it would be convenient to operate the corrosion equipment.
- (iii) The large number of selection criteria for the high alkalinity waters results in greater exclusion of waters.

Twenty-four of the forty-six waters in the shopping list were found before it was decided not to keep to the shopping list any more because of the difficulties. Whilst examples of some waters could not be found this does not necessarily mean those waters do not exist. The waters found and measured are identified by the last column in Tables 2 to 5.

A provisional assessment of the results obtained for the waters selected according to the revised shopping list was carried out. The conclusion was that if additional waters to be measured were to be selected by some other means then the aim should be to improve the distribution of the values for the quality parameters of interest including silicate but still keeping the concentrations of orthophosphate insignificant. It was also decided to include waters associated with high lead concentrations found in water from copper plumbed systems. The purpose of this was to help develop the significance of the values of relative corrosion rate measured.

As a result an additional thirteen waters were selected, Group E, mainly arising from opportunity and not according to a rigid shopping list. Ultimately a total of thirty-eight waters were measured.

## APPENDIX C. RESULTS: WATER QUALITY

### C.1

#### Parameters measured

The investigation was concerned with concentrating on the parameters considered in the previous work by WRc. Therefore the water quality parameters measured consistently for all measurements were pH, alkalinity and chloride, sulphate, nitrate-nitrogen and silicate concentrations. Chloride and sulphate concentrations were considered also in combination as their ratio. All waters were selected to have low and insignificant orthophosphate concentrations. Water temperature was standardised at 25°C by holding the corrosion cells in water baths.

### C.2.

#### Average qualities

The arithmetic mean for each quality parameter was calculated for each water for the four week and fourth week periods. Generally there is little difference between the two sets of values. This indicates that most waters had relatively stable qualities during their four week measurement periods. The average qualities during the four week and fourth week periods are given in Tables 6 and 7.

The frequency distributions of each quality parameter between all the waters were examined to highlight any substantial bias. Figures 2, 3 and 4 are the histograms for the six quality parameters for their natural and log four-week mean values respectively. Whilst chloride, sulphate and nitrate have nominally unsatisfactory and skewed distributions for their mean values the distributions of their log-mean values reflect no substantial skew or extremes.

Table 6

Water Qualities: four week means

Water No	pH	Alk <sup>†</sup> mg/l	Cl mg/l	SO <sub>4</sub> mg/l	NO <sub>3</sub> -N mg/l	SiO <sub>2</sub> mg/l	R <sup>††</sup>
A.1	7.23	9.00	9.50	3.00	0.70	0.90	3.12
A.2	7.09	12.00	10.38	6.50	0.35	1.67	1.60
A.3	8.88	8.50	6.25	5.00	0.78	0.82	1.25
A.4	8.12	8.00	10.40	5.80	0.27	1.16	1.79
A.5	8.84	8.20	13.00	18.00	0.43	5.60	0.72
A.6	9.31	9.57	13.47	9.10	0.73	4.51	1.48
B.1	7.04	25.00	10.44	6.14	1.90	2.27	1.70
B.2	7.63	22.67	19.33	35.33	1.73	3.87	0.55
B.3	7.22	31.83	10.38	15.00	0.85	4.28	0.69
B.4	7.02	22.44	21.00	9.20	0.74	3.56	2.28
B.5	8.21	16.88	15.63	8.33	0.36	3.00	1.88
B.6	8.24	23.60	6.17	6.67	0.27	7.97	0.93
B.7	8.78	18.40	11.00	15.58	0.63	1.68	0.71
C.1	7.01	123.25	67.40	89.90	4.81	2.70	0.75
C.2	8.21	112.00	18.00	18.00	0.92	0.40	1.00
C.3	7.11	127.15	80.33	112.42	0.58	2.33	0.71
C.4	7.98	80.50	19.75	74.73	0.66	0.69	0.26
C.5	7.55	164.42	35.97	103.00	13.68	3.35	0.35
C.6	7.86	130.00	39.29	55.90	6.68	3.75	0.70
D.1	7.18	248.25	14.25	9.13	5.25	20.25	1.56
D.2	7.30	226.14	18.43	25.86	6.93	15.00	0.71
D.3	7.44	123.00	29.00	55.75	3.02	6.42	0.52
D.4	8.12	208.60	281.80	61.04	0.50	11.13	4.62
D.5	7.77	131.29	87.97	59.00	5.33	8.66	1.49
D.6	7.69	61.00	83.83	313.27	0.20	6.90	0.27
E.1	6.90	285.00	17.00	66.00	0.50	11.80	0.26
E.2	7.10	282.00	86.00	170.00	0.50	2.70	0.51
E.3	7.60	166.60	68.40	167.80	4.16	5.40	0.41
E.4	7.82	76.00	23.17	22.50	4.32	24.43	1.03
E.5	7.11	139.90	31.20	34.00	3.27	15.40	0.92
E.6	7.09	257.57	62.00	93.33	5.44	17.43	0.66
E.7	7.61	199.00	47.67	23.58	8.12	8.80	2.02
E.8	7.90	72.22	46.58	58.44	3.51	7.18	0.80
E.9	8.50	116.50	81.75	137.50	6.74	4.75	0.59
E.10	8.38	22.80	18.00	na	na	na	na
E.11	8.75	33.20	23.33	21.18	1.34	5.23	1.10
E.12	7.55	217.00	43.63	81.49	12.05	7.82	0.54
E.13	7.25	281.45	125.55	162.81	0.41	10.15	0.77

† as mg CaCO<sub>3</sub>/l

†† R: chloride to sulphate concentration ratio



Table 7

Water qualities: four week means

Water No	pH	Alk† mg/l	Cl mg/l	SO <sub>4</sub> mg/l	NO <sub>3</sub> -N mg/l	SiO <sub>2</sub> mg/l	R††
A.1	7.50	11.00	10.00	3.00	0.42	0.90	3.33
A.2	7.00	12.00	10.00	7.50	0.36	1.54	1.33
A.3	8.88	8.50	6.25	5.00	0.78	0.82	1.25
A.4	8.80	8.0*	10.50	5.8*	0.28	1.15	1.81
A.5	8.53	7.40	17.00	20.00	0.43*	5.30	0.85
A.6	9.37	9.33	13.00	9.33	0.80	4.47	1.39
B.1	7.07	24.75	10.88	6.50	1.83	2.03	1.67
B.2	7.50	24.00	19.00	36.00	1.50	3.50	0.53
B.3	7.25	32.75	10.38	15.00	0.83	4.28	0.69
B.4	7.07	23.33	22.00	9.33	0.93	3.33	2.36
B.5	8.70	16.50	15.50	9.50	0.40	3.00	1.63
B.6	8.20	23.33	6.50	10.00	0.20	7.97	0.65
B.7	8.80	16.00	10.50	15.45	0.66	1.60	0.68
C.1	7.05	124.50	68.00	89.90	5.24	2.67	0.76
C.2	8.30	112.00*	18.00*	18.00*	0.45	0.40*	1.00
C.3	7.25	132.75	67.33	98.50	0.87	2.05	0.68
C.4	8.10	82.00	19.00	71.40	0.72	0.30	0.27
C.5	7.55	166.13	37.00	102.00	12.94	2.65	0.36
C.6	7.81	128.75	39.75	52.70	5.60	2.40	0.75
D.1	7.10	253.00	15.00	10.00	5.00	21.00	1.50
D.2	7.26	262.00	18.25	25.00	7.00	15.00	0.73
D.3	7.43	125.00	29.33	55.50	2.90	5.90	0.53
D.4	8.10	202.00	265.00	57.75	0.55	11.00	4.59
D.5	7.85	126.00	88.00	46.00	4.70	8.66*	1.91
D.6	7.85	57.00	84.00	321.00	0.20	7.00	0.26
E.1	6.90	285.00	17.00	66.00	0.50	11.80	0.26
E.2	7.10*	282.00*	86.00*	170.00*	0.50*	2.70*	0.51
E.3	7.45	165.00	69.00	165.00	3.90	6.50	0.42
E.4	7.80	75.50	23.00	23.00	4.25	24.50	1.00
E.5	7.10	129.20	29.60	33.80	3.02	14.80	0.88
E.6	7.00	257.50	62.50	98.00	5.35	18.00	0.64
E.7	7.61	199.33	48.00	23.67	8.20	8.80*	2.03
E.8	7.90	67.50	49.05	65.00	4.18	7.35	0.75
E.9	8.60	110.00	86.00	152.00	6.30	2.83	0.57
E.10	7.80	24.00	25.00	na	na	na	na
E.11	8.77	32.50	23.53	21.23	1.40	5.30	1.11
E.12	7.56	219.50	43.50	81.49*	10.80	8.50	0.53
E.13	7.25	285.00	120.25	157.75	0.41	9.50	0.76

† as mg CaCO<sub>3</sub>/l

†† R chloride to sulphate concentration ratio

\* mean of value during the preceding three weeks

### C.3 Intercorrelation of parameters

The multiple regression analyses correlating voltage and quality, Sections 8 and E, drew attention to significant correlation between some of the water quality parameters. The significant correlation coefficients involved in these multiple regression analyses of the fourth-week data are given in Tables 8, 9 and 10.

Table 8 is the correlation matrix involving the natural average parameter values for all thirty-eight waters. Alkalinity is involved in five of the nine pairs of parameters with significant correlation.

Table 9 is the correlation matrix involving the log average parameter values for the main group of twenty-seven waters, which excludes the three waters with the highest voltages and the eight waters with the lowest voltages. For this group intercorrelation of quality is extensive amongst all parameters except pH.

Table 10 is the correlation matrix involving the log average parameter values for the sub-group of eight waters with the lowest voltages. For this group the extent of intercorrelation is least. The correlation is limited to the pairs: pH/alkalinity, pH/ratio, chloride/ sulphate and sulphate/ratio.

Scatter diagrams, Figures 5, 6 and 7 are presented for the three pairs of parameters with the most significant correlations for all waters and, Figures 8, 9 and 10, for the main group. To some extent a good correlation between sulphate and the chloride-sulphate ratio should be expected. However, the correlation is not as good as that simply between chloride and sulphate. This is done to provide further evidence of the extent of intercorrelation. These and the scatter diagrams for all other pairs of parameters reinforced the highlighting by the histograms of distribution in quality the waters with relatively high chloride, sulphate and nitrate concentrations.

There is some indication in the scatter diagrams of sub- groups which tended to be limited to specific pairs of parameters. However, no investigation was made to test whether these sub-groups might be real and have significant effects on corrosivity. A larger sample of results is needed to do this.

**Table 8** All waters, correlation matrix for water quality

	mV	pH	Alk	NO <sub>3</sub>	Cl	SO <sub>4</sub>	SiO <sub>2</sub>	R <sup>+</sup>
mV	1.00							
pH	-	1.00						
Alk	-	-.533*	1.00					
NO <sub>3</sub>	-	-	.438	1.00				
Cl	.622	-	.447	-	1.00			
SO <sub>4</sub>	-	-	.385	-	.483*	1.00		
SiO <sub>2</sub>	-	-.343	.522*	-	-	-	1.00	
R <sup>+</sup>	.677	-	-	-	.399	-.391	-	1.00

critical values of r:

2Q <	10	5	2	1	0.5	0.1%
r >	.275	.325	.381	.418	.452	.519

values of r < .275 have been excluded.

DF = 35

† R: chloride to sulphate concentration ratio.

**Table 9** Main group, correlation matrix for log of water quality

	mV	log pH	log Alk	log NO <sub>3</sub>	log Cl	log SO <sub>4</sub>	log SiO <sub>2</sub>	log R <sup>+</sup>
mV	1.00							
log pH	.345	1.00						
log Alk	-.579	-.525	1.00					
log NO <sub>3</sub>	-.381	-	.647	1.00				
log Cl	-.511	-	.792*	.412	1.00			
log SO <sub>4</sub>	-.587	-	.780	.435	.930*	1.00		
log SiO <sub>2</sub>	-.565	-.396	.758	.579	.484	.482	1.00	
log R <sup>+</sup>	.533	-	-.534	-.341	-.547	-.817*	-.337	1.00

critical values of r:

2Q <	10	5	2	1	0.5	0.1%
r >	.330	.389	.454	.497	.534	.607

values of r < .330 have been excluded.

DF = 24

† R:chloride to sulphate concentration ratio.

Table 10

Sub-group, intercorrelation matrix for log  
of water quality

	mV	log pH	log Alk	log NO <sub>3</sub>	log Cl	log SO <sub>4</sub>	log SiO <sub>2</sub>	log R <sup>†</sup>
mV	1.00							
log pH		1.00						
log Alk	-.800	-.797	1.00					
log NO <sub>3</sub>	-	-	-	1.00				
log Cl	-	-	-	-	1.00			
log SO <sub>4</sub>	-	-	-	-	.827	1.00		
log SiO <sub>2</sub>	-	-	-	-	-	-	1.00	
log R <sup>†</sup>	-	.669	-	-	-	-.840	-	1.00

critical values of r:

2Q <	10	5	2	1	0.5	0.1%
r >	.621	.707	.789	.834	.870	.925

values of r < .621 have been excluded

DF = 6

† R:chloride to sulphate concentration ratio.

## APPENDIX D RESULTS: VOLTAGES

### D.1

#### Introduction

The corrosion cells used were constructed to a standard design. The voltage across the electrodes in each cell was easily measured. From Ohm's and Faraday's laws the voltage is a relative measure of corrosion rate, corrosion current, corrosion potential or corrosivity. Because of this, within the context of this report there is no benefit in converting the voltage measurements to currents or corrosion rates.

Because all the corrosion cells were fitted with 10 kohm resistors, the conversion from voltages to currents is simple:

10 mV is equivalent to 1 uA.

### D.2

#### Variation with time

The previous work by Oliphant assessed the effect of water quality on corrosion from the effect on the corrosion voltage measurements during the fourth week of continued exposure of the corrosion cells. The fourth week was chosen because generally the short-term corrosion levels had stabilised. The results in this report also are based on voltage measurements made throughout four weeks of continuous exposure of the corrosion cells.

Voltage development of each cell within a group of five cells used for measuring any one water was generally the same during the four week measurement period. The exceptions tended to be those cells which failed, Section 5. Examination of voltage development with time was used to confirm the identity of the cells which failed during the four week measurement period. Typically these cells produced the highest voltages for some or most of the period usually following a sudden large increase in voltage.

Initial cell voltage and subsequent development of cell voltages varied from water to water but typical development patterns occurred. Examples of these are given in Figures 11 to 14.

- Figure 11 - Initial cell voltages are average, subsequently voltages quickly fall to consistently low values for the remainder of the period.
- Figure 12 - Initial cell voltages are relatively moderate, subsequently voltages slowly increase and then slowly decrease slightly, with all cells behaving very similarly.
- Figure 13 - Initial cell voltages are average, subsequent voltage development is slow compared with Figure 11. This example illustrates the voltage trends of cells which failed.
- Figure 14 - Obviously variants of the above typical patterns occurred. One pattern of particular concern, is when each cell is apparently unstable in its behaviour throughout the whole period covering a wide range in voltage. This instability is associated with relatively high nitrate concentration.

### D.3 Average voltages

The average of the combined voltage measurements of all the good cells in a group for the whole four week period and the fourth week are given in Table 11. The relative standard deviation for each average value are included. The table also gives the ratio of the four-week to the fourth-week average voltages.

The frequency distributions of the natural and log values of the four-week and fourth-week averages are given in Figures 15 and 16. The spread in fourth-week average voltages is marginally greater than for the four-week average voltages. The distributions of log voltages show that the very high voltage measured for water D4 cannot be regarded as unusual; the largest and smallest values both fall within two standard deviations of the overall average value. The distribution of the average voltages is positively skewed and approximates to log normal.

The eight waters which produced the lowest voltages measured are highlighted the most by the distribution of fourth-week log average voltage.

**Table 11** Four-week and fourth-week averages of combined good cell voltages

Water No	No of good cells	FOUR-WEEK			FOURTH-WEEK			
		mV	RSD(1)	r(2)	mV	RSD(1)	R(3)	r/R(4)
A.1	3	84.61	0.18	0.88	62.33	0.27	1.36	0.65
A.2	5	57.65	0.15	0.89	42.90	0.27	1.34	0.66
A.3	5	55.08	0.17	1.14	64.57	0.13	0.85	1.34
A.4	5	49.01	0.09	1.00	48.82	0.13	1.00	1.00
A.5	3	4.00	0.39	1.03	4.57	0.87	0.88	1.17
A.6	5	37.76	0.22	1.10	48.14	0.28	0.78	1.41
B.1	3	31.13	0.34	0.85	14.33	0.39	2.17	0.39
B.2	3	24.01	0.16	0.88	15.97	0.52	1.50	0.59
B.3	3	26.00	0.13	0.84	9.67	0.10	2.69	0.31
B.4	4	37.03	0.45	1.16	41.69	0.54	0.89	1.30
B.5	4	7.42	0.55	0.80	3.58	0.46	2.07	0.39
B.6	3	6.22	0.63	0.87	3.45	0.72	1.80	0.48
B.7	3	13.79	0.21	1.12	15.97	0.22	0.86	1.30
C.1	5	28.79	0.34	1.06	33.42	0.80	0.86	1.23
C.2	4	5.27	0.48	0.84	2.55	0.82	2.07	0.41
C.3	5	76.42	0.50	0.78	37.14	0.55	2.06	0.38
C.4	2	6.24	0.19	0.76	3.32	0.47	1.88	0.40
C.5	5	89.11	0.50	1.04	102.55	0.56	0.87	1.20
C.6	4	30.06	0.42	0.82	21.19	0.35	1.42	0.58
D.1	4	36.44	0.78	1.21	27.92	0.98	1.31	0.82
D.2	5	62.79	0.61	0.89	39.14	1.12	1.60	0.56
D.3	5	29.46	0.55	0.87	12.47	1.63	2.36	0.37
D.4	5	132.35	0.21	1.29	193.99	0.25	0.68	1.90
D.5	5	99.93	0.59	0.98	95.46	0.57	1.05	0.93
D.6	5	7.80	0.33	0.95	4.25	0.34	1.84	0.52
E.1	5	3.35	1.30	0.85	2.24	0.53	1.50	0.57
E.2	5	17.50	1.01	1.45	26.32	1.39	0.66	2.20
E.3	5	9.77	0.79	1.09	11.09	0.93	0.88	1.24
E.4	4	8.29	0.93	0.73	2.40	0.35	3.45	0.21
E.5	5	29.81	1.48	0.85	20.58	1.53	1.45	0.59
E.6	4	15.56	0.99	0.91	10.76	1.12	1.45	0.63
E.7	5	18.17	0.47	0.93	15.33	1.58	1.19	0.78
E.8	4	14.39	0.15	1.01	14.88	0.57	0.97	1.04
E.9	5	38.47	0.40	1.13	46.58	0.76	0.83	1.36
E.10	5	55.46	0.35	0.98	53.77	0.56	1.03	0.95
E.11	5	30.52	0.51	0.97	28.63	1.10	1.07	0.91
E.12	4	59.73	0.54	0.89	33.11	0.81	1.80	0.49
E.13	4	14.09	0.45	0.95	12.18	0.81	1.16	0.82

1. RSD relative standard deviation.
2.  $r = (\text{Four-week average mV}) / (\text{Three-week average mV})$
3.  $R = (\text{Four-week average mV}) / (\text{Fourth-week average mV})$
4.  $r/R = (\text{Fourth-week average mV}) / (\text{Three-week average mV})$ .

The frequency distribution of the ratio of the four-week to the fourth-week average voltages is skewed but with a modal value of about 1.0. This distribution indicates that about 40 per cent of the groups of cells produced fourth-week average voltages which were significantly smaller than their related four-week value. This suggests that a four week period or greater is necessary to develop cell stability for some but not all waters.

This comparison was extended to include the average voltage during the first three weeks. This indicated that the contribution of the fourth week to the four-week average was only marginal. Hence, generally it is unlikely that there would have been little advantage from making the measurements for more than four weeks or from selecting the fifth or a subsequent week, instead of the fourth week, to reflect stabilised corrosion. For some waters corrosion stability deteriorated with time.

The relative standard deviations of the average voltages cover a wide range in values. Their distributions reflect a tendency for the higher values to occur for the lower values of average voltage. This is associated with those waters whose cell voltages decreased slowly with time from their initial moderate to their eventual low values. It is also associated with those waters whose cells generally produced low voltages but which occasionally for short periods produced high voltages.

#### D.4

#### Effect of cell order

Five new corrosion cells were exposed to each water. Each group of five cells was arranged for the water to flow through them in series. Oliphant, in his investigations, on the few occasions he used a similar number of cells in series with a similar flow of water did not observe a significant effect on the voltages.

In this work twenty of the groups of cells had no cells which failed. The results from these groups have been examined for the effect of cell order on cell voltage. This was done by comparing the extent to which the cell with the  $n$ th,  $n = 1$  to 5, highest voltage was likely to be the  $n$ th cell. The results are significant, chi-squared distribution  $P < 0.01$ , for the fourth-week average values comparing the probability of



cell 1 and cell 5 producing the highest and lowest voltages respectively, Figure 17.

The results are significant,  $P < 0.01$ , also for the four-week average values not only between cells 1 and 5 but also between cells 1 and 4, 2 and 4, as well as 2 and 5, Figure 18. Only a few groups of cells produced voltages with magnitude in sequence of cell position. Therefore the effect of cell order was not obvious and is established only because of the quantity of measurements made.

#### D.4

##### Failed cells

Failed cells were identified from visual inspection and their voltage trends. Because their voltage trends are distinct, though not necessarily characteristic solely of failed cells, the voltages of failed cells were compared with the voltages of the good cells in their groups. No consistent trend was evident, for example: the ratio of failed-cell voltage to good-cell voltage ranged from 1.5 to greater than 20 apparently independent of water type and good cell voltage.

The effect of reinforcing cells was to reduce the failure rate. For cells which were not reinforced approximately 1 in 5 cells failed. For cells which were reinforced approximately 1 in 25 cells failed. It is not possible to determine whether cells which were reinforced produced significantly different voltages than cells which were not reinforced. However, this may have been possible since the reinforcement might have increased the opportunity for edge corrosion to occur.

## APPENDIX E. RESULTS: CORRELATION OF VOLTAGE WITH QUALITY

### E.1 Preface

The principal water quality parameters measured were pH, alkalinity and the chloride, sulphate, nitrate-nitrogen and silicate concentrations together with the ratio of chloride to sulphate concentration.

Oliphant in his work controlled water quality to a great extent and examined much wider ranges in values of the parameters. As a result the graphical presentation of his results generally clearly reflect whether a water quality parameter affected cell voltage. In this work the examination of the effect of an individual quality parameter is hindered by the variability in the data due to the uncontrolled variability of the other quality parameters.

Oliphant found it most convenient to present his results graphically in the form voltage vs log-quality, partly because of the range in values of quality examined. In this work the scatter diagrams of voltage vs log-quality are certainly more visually useful than voltage vs quality and there is even some attraction in using diagrams of log-voltage vs log-quality because of the wide ranges in values involved. However, the strongest correlations have been found in the regressions of voltage vs quality for the combined data of all waters. There is little difference in the significance of the correlations for voltage vs log-quality and log-voltage vs log-quality; full details are given in Section E.2. Thus, whilst these latter two forms of correlations are used in the following sections any trends reflected by them must be regarded with caution.

In addition to the uncontrolled variability of the water quality parameters and the apparent presence of sub-groups, the interpretation of the results is affected also by the very significant inter-relationship between some water quality parameters and by possible

correlation with parameters which have not been accounted for. Some of the variance unaccounted for could also have been due to variation between cells of the metalurgy of the electrode surfaces or quite simply lots of noise in the voltage.

## E.2 Multiple regression analysis

Whilst it was not originally intended, as explained in Sections 4 and B, statistical analysis of the effect of water quality on voltage must rely mainly on multiple regression analysis. Multiple regression analysis was carried out for the effect of water quality on voltage for the four-week and fourth- week data. For each of these sets of data correlations were examined for voltage vs quality, voltage vs log-quality and log-voltage vs log-quality. The results are summarised in Table 12.

The conclusions which can be drawn from Table 12 are:

- \* The fourth-week data is better than the four-week data for developing correlations.
- \* Correlations are best developed from the natural values for voltage and water quality.
- \* The most comprehensive regression equation accounting for the most variance was produced by the fourth-week natural values for voltage and water quality. The regression equation with the best fit is:  
$$\begin{aligned} \text{fourth-week mV} = & - 15.76 + 24.0 R \\ & + 0.294 Cl \\ & + 2.99 NO_3-N \end{aligned}$$
- \* Alkalinity, pH and silicate do not represent significant effects on voltage.

The examination of voltages highlighted the three waters with very high voltages and the sub-group of eight waters with very low voltages, Section D. Therefore, multiple regression analyses were carried out also on this sub-group, even though it consisted of only eight observations, and the main group of waters, which excluded these very high and low values, for the fourth-week averages. The results of this for both groups are summarised in Table 13 and are quite different from the results of the combined data in Table 12.

**Table 12** Summary of results of multiple regression of the combined data for all waters

Regression	Four Week			Fourth Week		
	Quality Parameters	V <sup>†</sup>	F <sup>††</sup>	Quality Parameters	V <sup>†</sup>	F <sup>††</sup>
Natural vs Natural	Cl	18.8	0.5	Cl	37.0	0.1
	R	30.9	0.1	R	44.4	0.1
	R, NO <sub>3</sub> -N(1)	45.1	0.5	R, NO <sub>3</sub> -N(2)	52.3	5
				R, Cl R, Cl, NO <sub>3</sub> -N(3)	58.4 63.9	0.5 5
Natural vs Log	R	18.4	0.5	Cl	9.2	5
	R, Cl (4)	27.0	5	R	23.2	0.5
				R, SO <sub>4</sub> (5)	37.6	0.5
				R, Cl (6)	37.6	0.5
Log vs Log	R	18.2	0.5	R	20.3	0.5
	R, NO <sub>3</sub> -N(7)	30.4	5	R, NO <sub>3</sub> -N(8)	29.9	5

† V percentage variance accounted for

†† F percentage significance of F-test for introduction of parameter

Best fit regression equations:

- (1) mV = - 1.39 + 23.14 R + 3.63 NO<sub>3</sub>-N
- (2) mV = -12.34 + 30.73 R + 3.55 NO<sub>3</sub>-N
- (3) mV = -15.76 + 24.0 R + 0.294 Cl + 2.99 NO<sub>3</sub>-N
- (4) mV = 1.90 + 52.0 log R + 24.9 log Cl
- (5) mV = -18.6 + 105.7 log R + 37.6 log SO<sub>4</sub>
- (6) mV = -18.6 + 68.1 log R + 37.6 log Cl
- (7) log mV = 1.3622 + 0.718 log R + 0.291 log NO<sub>3</sub>-N
- (8) log mV = 1.2587 + 0.862 log R + 0.313 log NO<sub>3</sub>-N

where

R : chloride to sulphate concentration ratio

Table 13

Summary of results of multiple regression  
of the main group and sub-group data

Regression	Main Group			Sub Group		
	Quality Parameters	V <sup>†</sup>	F <sup>††</sup>	Quality Parameters	V <sup>†</sup>	F <sup>††</sup>
Natural vs Natural	SiO <sub>2</sub>	11.7	5	Alk (F almost 5%)	41.4	-
	Cl	11.7	5			
	Alk	16.7	5			
	R	25.1	1			
Natural vs Log	Cl	23.0	1	Alk	56.5	5
	R	25.5	0.5	Alk, R (2)	84.0	5
	SiO <sub>2</sub>	29.1	0.5	Alk, SO <sub>4</sub> (3)	94.3	0.1
	Alk	30.8	0.5			
	SO <sub>4</sub>	31.7	0.5	Alk, SO <sub>4</sub> , NO <sub>3</sub> -N	98.5	5
	SO <sub>4</sub> , SiO <sub>2</sub> (1)	40.0	5	Alk, SO <sub>4</sub> , NO <sub>3</sub> -N, SiO <sub>2</sub> (4)	99.7	5
Log vs Log	Cl	21.4	5	Alk	58	5
	R	22.7	1	Alk, SO <sub>4</sub>	91.5	0.5
	SiO <sub>2</sub>	23.0	1	Alk, SO <sub>4</sub> , NO <sub>3</sub> -N	96.4	5
	Alk	24.7	1	Alk, SO <sub>4</sub> ,	99.1	5
	SO <sub>4</sub>	29.0	0.5	NO <sub>3</sub> -N, SiO <sub>2</sub> (5)		

† V percentage variance accounted for

†† F percentage significance of F-test for introduction of parameter

Best fit regression equations:

- (1) mV = 56.89 - 11.86 log SO<sub>4</sub> - 14.39 log SiO<sub>2</sub>
- (2) mV = 6.10 - 1.88 log Alk - 1.63 log R
- (3) mV = 4.78 - 1.84 log Alk + 1.07 log SO<sub>4</sub>
- (4) mV = 4.696 - 1.737 log Alk + 0.990 log SO<sub>4</sub>  
- 0.345 log NO<sub>3</sub>-N - 0.112 log SiO<sub>2</sub>
- (5) log mV = 0.705 - 0.232 log Alk + 0.125 log SO<sub>4</sub>  
- 0.0498 log NO<sub>3</sub>-N - 0.0226 log SiO<sub>2</sub>

where

R : chloride to sulphate concentration ratio

For both groups alkalinity represents significant effects on voltage. Silicate can also represent significant effects whilst pH again does not. However, the viability of the regression result for and the reality of the sub-group must remain questionable until established for a larger sample.

Explanation for these contrasts is found in the correlation matrices given in Tables 8 to 10 and the extent to which correlation occurs between water quality parameters. The intercorrelation which occurs for the main group is so strong that it restricts the extent to which the regression analysis can demonstrate the effect of quality on voltage.

This difference between the combined data and the main group is another indication of the possible need to consider the low voltage sub-group as being real.

Some multiple regressions were carried out to compare various ratios of water quality parameters. The conclusions were that the ratio of chloride to sulphate concentration was the most superior and was superior to its inverse, sulphate to chloride, as used in the previous work, in the extent to which it could account for variance in voltage. Therefore all other multiple regressions considered only the ratio of chloride to sulphate. However, mathematically, whilst there is a great difference between the natural values of the ratio of chloride to sulphate and its inverse, the only difference between the logs of the ratios is a negative sign.

### **E.3 Comparison with previous work**

The present results can be compared with the previous work by comparing the gradients of the regression equations of the correlations between voltage and the water quality parameters. This is set out in Table 14.

In Table 14 the gradients found for the fourth-week data in the previous work are compared with those which relate to the results summarised in Tables 12 and 13. Results whose residual variance exceed the variance of the Y-variate and therefore are insignificant are included for completeness.

The observations from Table 14 are:

- \* Whilst the previous work indicated voltage decreases with pH the present results indicate pH increase can be associated also with an increase in voltage.

**Table 14** Comparison of the gradients from the correlations of voltage and quality

Parameter:	pH	log Cl	log R <sup>(1)</sup>	log NO <sub>3</sub> -N	SiO <sub>2</sub>
Previous work <sup>(2)</sup>	-20.6	45.3	33.9 <sup>(4)</sup>	12.5 <sup>(3)</sup>	-1.46
Single regression:					
Four-week	-3.48 <sup>(3)</sup>	19.4	47.2	9.24	-0.308
Fourth-week	6.47 <sup>(3)</sup>	32.3	63.0	6.0 <sup>(3)</sup>	-0.31 <sup>(3)</sup>
Main Group	7.66	-21.47	35.1	-12.2	-1.10
Sub-Group	0.87	0.69 <sup>(3)</sup>	0.01 <sup>(3)</sup>	-1.11	-0.044
Multiple regression:					
Four-week	-	24.9	52.0	-	-
Fourth-week	-	37.6	105.7, 68.1	-	-
Main Group	-	-	-	-	-
Sub Group	-	-	-1.63	-0.345	-

(1) R : chloride to sulphate concentration ratio.

(2) equivalent to present work after multiplying by 10 to convert to mV.

(3) residual variance exceeded variance of Y-variate.

(4) negative sign in previous work because inverse of R used.

\* The present results, for the combined data of all waters, indicate chloride increase is associated with voltage increase but at slightly less the rate found in the previous work.

\* The present results indicate that increase in ratio of chloride to sulphate concentration is associated with a greater rate of increase in voltage than found in the previous work.

\* The present results, for the combined data of all waters, indicate nitrate increase is associated with an increase in voltage but at a lesser rate than the previous work; however, both sets of results are not significant. This contrasts with the significant association of natural value of nitrate with increase in voltage. Analyses of the present results which have some significance for the main group and sub-group indicate voltage reduction can be associated with an increase in nitrate concentration.

\* The present results indicate an increase in silicate concentration is associated with decrease in voltage but at a lesser rate than found in the previous work.

The more contradictory observation for nitrate, of voltage decrease associated with nitrate increase, also contrasts with the significant roles of nitrate in the multiple regressions summarised in Table 12. In the best fit equation for the fourth-week data, natural values, the marginal effect of nitrate, at 10 mg  $\text{NO}_3\text{-N/l}$  on increasing voltage is about four times as great as that found in the previous work, based on log-values. A greater marginal rate occurs also for ratio of chloride to sulphate.

Visual comparison between the results of the previous and present work is most valid for the correlation of voltage with log-chloride and log-ratio of chloride to sulphate concentration for the combined fourth-week data for all waters. These two comparisons are shown in Figures 19 and 20. (The coding A to E is the same as used in Tables 6 etc.)

#### E.4

#### Waters with high voltages

Three waters produced voltages which are distinctly greater than other waters. These are:

Water D4 - This produced the highest voltage. It had the highest chloride concentration and also the highest value of chloride to sulphate concentration ratio.

Water C5 - It had the highest nitrate concentration encountered together with a relatively low silicate concentration. The variability of voltage within and between cells was very substantial. In contradiction, it had one of the smallest values of chloride to sulphate concentration ratio.

Water D5 - Its chloride to sulphate concentration ratio and concentrations of chloride and nitrate were relatively high. The variability of voltage within and between cells was very substantial.

The water with the next most highest voltages tended to be many of the low alkalinity waters. This appears to be associated with the tendency for low alkalinity waters to have high values of chloride to sulphate concentration ratio and low silicate concentrations.



The symptom of variability of voltage within and between cells was examined. From plots of voltage against time variability was obvious for some or all of the time for most but not all waters with nitrate concentrations greater than 1.0 mg NO<sub>3</sub>-N/l. Variability was negligible for most waters with nitrate concentrations less than this. The most substantial variability occurred for waters with the highest nitrate concentrations.

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