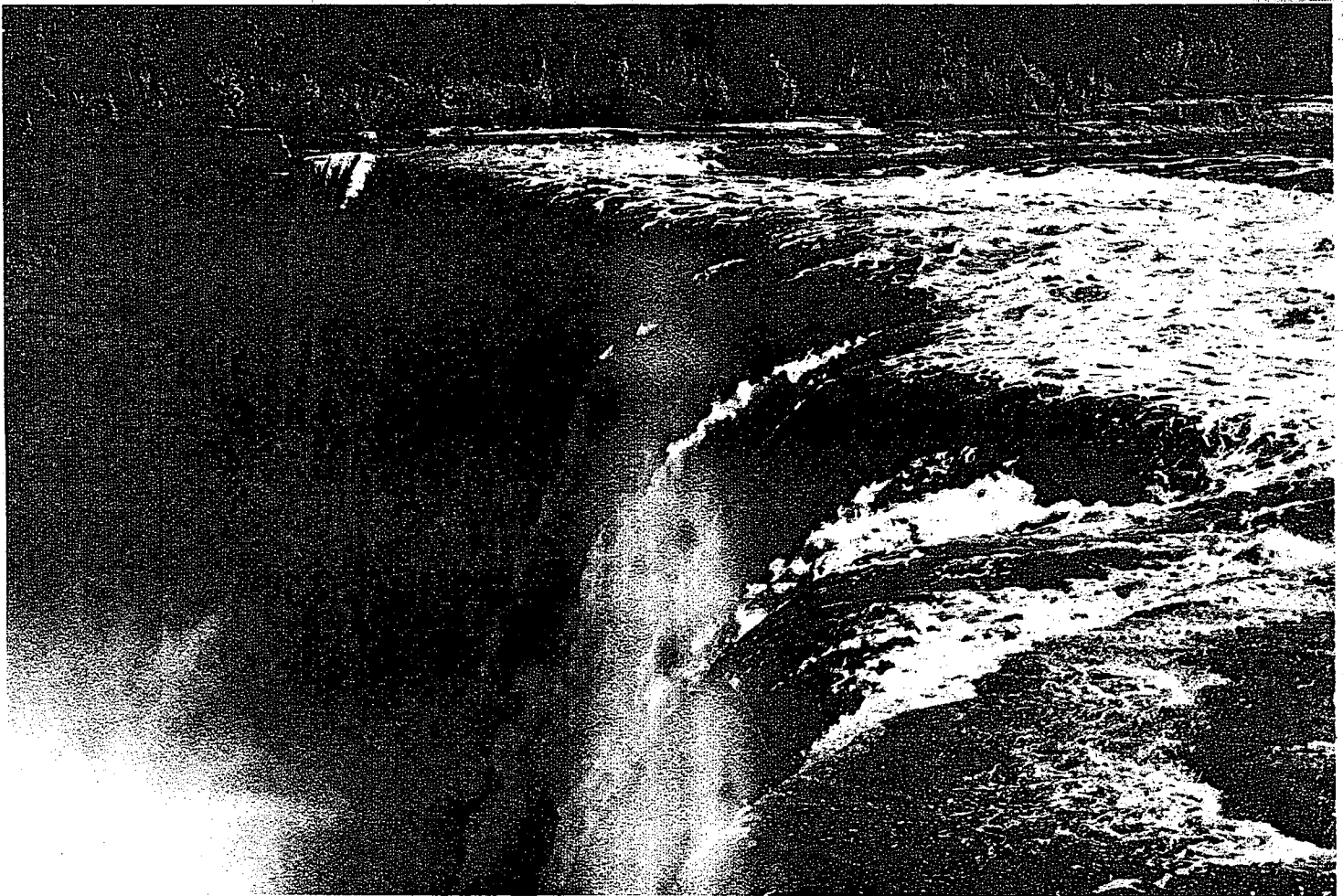


# Limitations of Single Water Samples in Representing Mean Water Quality

I. Thompson River at Shaw Spring,  
British Columbia

E. Oguss and W. E. Erlebach



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TECHNICAL BULLETIN NO. 95  
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INLAND WATER DIVISION, FISH AND WILDLIFE  
WATER QUALITY BRANCH  
VANCOUVER, BRITISH COLUMBIA, CANADA



Environment  
Canada

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*(Résumé en français)*

**INLAND WATERS DIRECTORATE, PACIFIC AND YUKON REGION,  
WATER QUALITY BRANCH,  
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# Contents

	Page
ABSTRACT .....	v
RÉSUMÉ .....	v
STATION DESCRIPTION .....	1
STATISTICAL AND SAMPLING METHODS .....	1
1) Instantaneous error .....	1
a) Short-range heterogeneity .....	1
b) Sample handling errors .....	1
c) Analytical variations .....	1
2) Spatial distribution .....	3
3) Temporal variability .....	3
a) Short-term variability .....	3
b) Monthly and quarterly variability .....	4
ANALYTICAL METHODS .....	4
RESULTS AND DISCUSSION .....	4
CONCLUSIONS .....	6
ACKNOWLEDGMENTS .....	6
REFERENCES .....	6
APPENDIX A. RESULTS OF CHEMICAL ANALYSES .....	9
APPENDIX B. PRECISION AND ACCURACY OF CHEMICAL ANALYSES .....	19

## Table

1. Results of statistical analysis of Shaw Spring data .....	5
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## Illustrations

Figure 1. Location of Shaw Spring station on the Thompson River .....	2
Figure 2. Flow record at Spences Bridge, April 1 to August 27, 1974 .....	2
Figure 3. Inland Waters Directorate replicate sampler .....	3

## **Abstract**

This study was undertaken to determine the degree to which infrequent single grab samples are representative of the monthly or quarterly mean water quality of the Thompson River in the vicinity of the station at Spences Bridge. It contributes to a continuing evaluation of the overall effectiveness of routine water quality monitoring performed by the Inland Waters Directorate in British Columbia. The study was designed to determine the magnitude of spatial and temporal variability in the concentrations of the following parameters: total phosphorus, nitrate plus nitrite, iron, fluoride, lead, zinc, silica and pH. These parameters were selected because they had shown marked variation in previous quarterly sampling.

## **Résumé**

La présente étude avait pour objet de déterminer dans quelle mesure les échantillons uniques prélevés au hasard et peu fréquemment sont représentatifs de la valeur mensuelle ou trimestrielle moyenne de la qualité des eaux de la rivière Thompson, à proximité de la station Spences Bridge. Elle sert de complément à l'évaluation continue de l'efficacité globale du contrôle régulier de la qualité des eaux exercé, en Colombie-Britannique, par la Direction générale des eaux intérieures. L'étude visait à déterminer les variations spatio-temporelles dans les concentrations des paramètres suivants: phosphore total, nitrate et nitrite, fer, fluorure, plomb, zinc, silice et pH. On a choisi ces paramètres parce qu'ils ont fait preuve d'une variation marquée lors du dernier échantillonnage trimestriel.

# Limitations of Single Water Samples in Representing Mean Water Quality

## I. Thompson River at Shaw Spring, British Columbia

E. Oguss and W. E. Erlebach

### STATION DESCRIPTION

The Spences Bridge station<sup>1</sup> is located in Shaw Spring, where a cableway crosses the Thompson River seven miles west of the town of Spences Bridge. Figure 1 shows the location north of the confluence of the Thompson and Fraser rivers. The river in this section has a rock base and is swift and turbulent in the vicinity of gravel bars and rock projections. The river was in freshet during the period of study (June 13 to August 22, 1974). Figure 2 shows the recorded flows (measured at Spences Bridge) from April 1 to August 27; the dates on which water samples were collected are indicated. Samples were taken from the cableway at three substations evenly spaced across the river channel about 15 m apart. There are no known point sources of wastes flowing into the river between the station and Spences Bridge.

A station was also established on a bridge crossing the Nicola River (at Spences Bridge) to investigate the influence of Nicola River water on spatial and temporal variability at Shaw Spring. Samples were taken from two substations 5 m apart on the bridge. Samples of the Thompson River at Savona, collected during the same period as part of a separate study of Kamloops Lake, were used as an indication of water quality above the confluence of the Nicola River.

### STATISTICAL AND SAMPLING METHODS

The confidence with which a single sample can be accepted as an indicator of water quality depends on the variability of the water quality. If the sample is assumed to define the quality in a reach of a river at a given instant of time, the spatial variation must be established longitudinally, laterally and vertically. If the sample is to be used to define quality over a period at one point, the temporal variability must be assessed. Before detected variations can be assigned to spatial or temporal changes, the

instantaneous variability of the water quality must first be established by collecting multiple samples simultaneously from one point in a river.

#### 1) Instantaneous Error

A close approximation to single-point single-time multiple sampling is achieved with the multi-sampler shown in Figure 3. This sampler, holding as many as six bottles ranging in size from 50 ml to 250 ml, is rapidly dropped to a depth of up to 1 m. The bulk of the samples is collected in the lower third of the sampling depth. Filling time is less than five seconds. Differences between the concentrations of materials in these multiple samples can be accounted for by the following three factors.

##### *a) Short-Range Heterogeneity*

Since the bottle openings in the holder are separated by about 10 cm, each bottle samples a different mass of water over the short interval of time required to fill the sample bottle. The suspended and dissolved materials in the water may not be homogeneously distributed, particularly in waters that are turbid and turbulent. Consequently, samples that are taken simultaneously and side-by-side may contain different concentrations of materials.

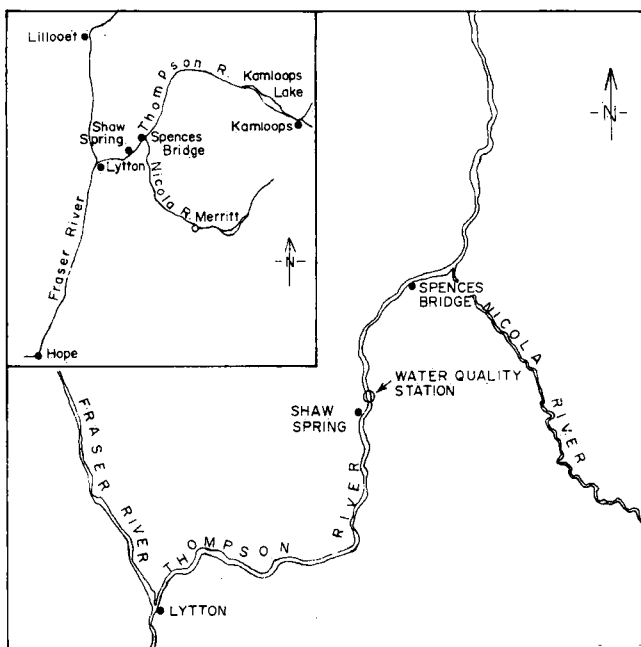
##### *b) Sample Handling Errors*

Different amounts of contaminants may be added to each of the simultaneous samples. Airborne particulates can settle into open bottles. Suspended particles and other surfaces in bottles may in time adsorb or release materials. Preservatives or other reagents added to samples may contribute contaminants. Biological or chemical reactions in the samples may differ in degree from one bottle to another. Some of these potential sources of variation were assessed by dispensing distilled water into sample bottles in the field and then analyzing for parameters of interest.

##### *c) Analytical Variations*

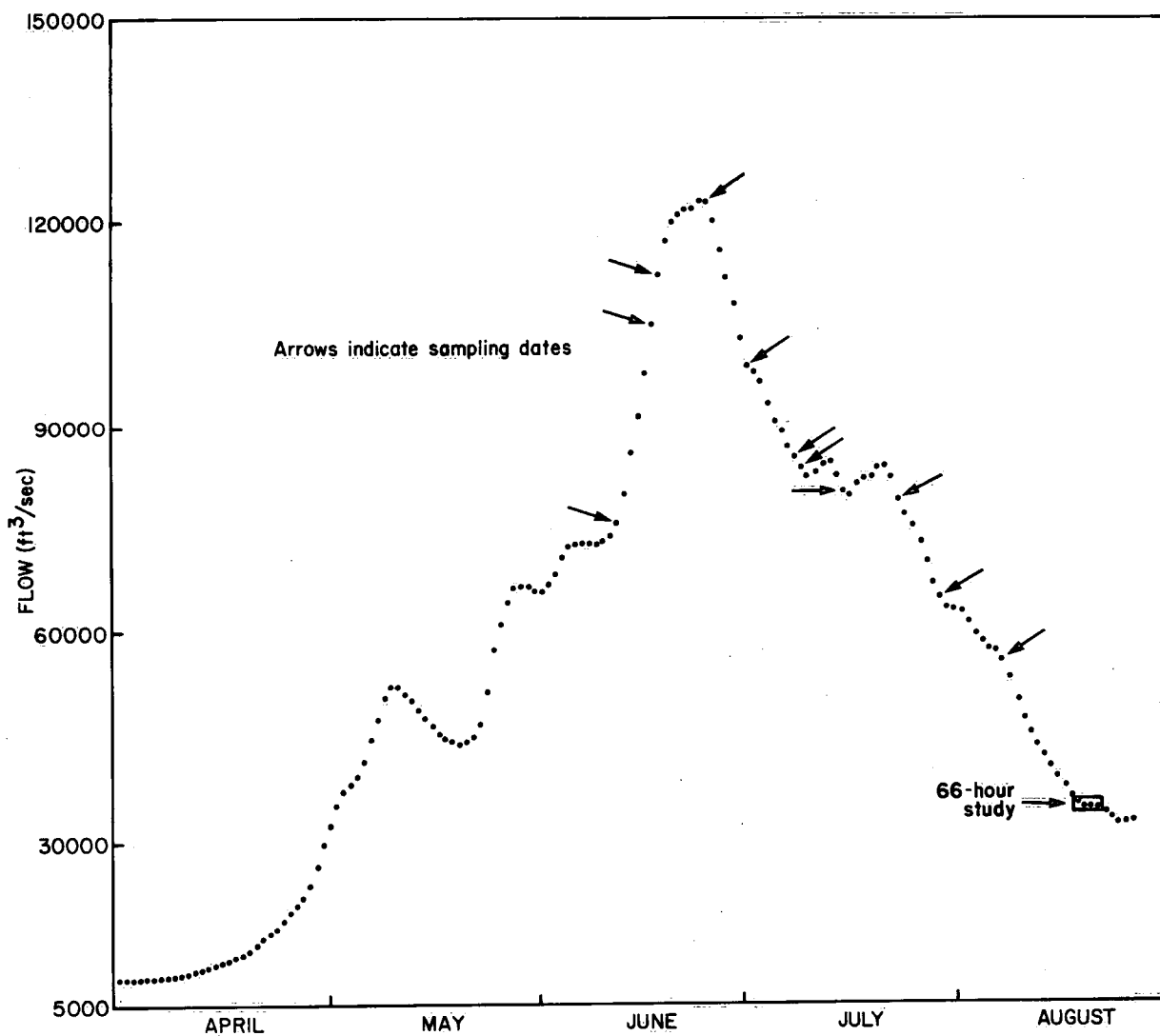
Aliquots or sub-samples removed from samples contain differing amounts of the material to be analyzed,

<sup>1</sup>NAQUADAT station No. 00BC08LF0001,  
Latitude 50° 21' 17", Longitude 121° 23' 35"



← Figure 1. Location of Shaw Spring station on the Thompson River.

↓ Figure 2. Flow record at Spences Bridge, April 1 to August 27, 1974.



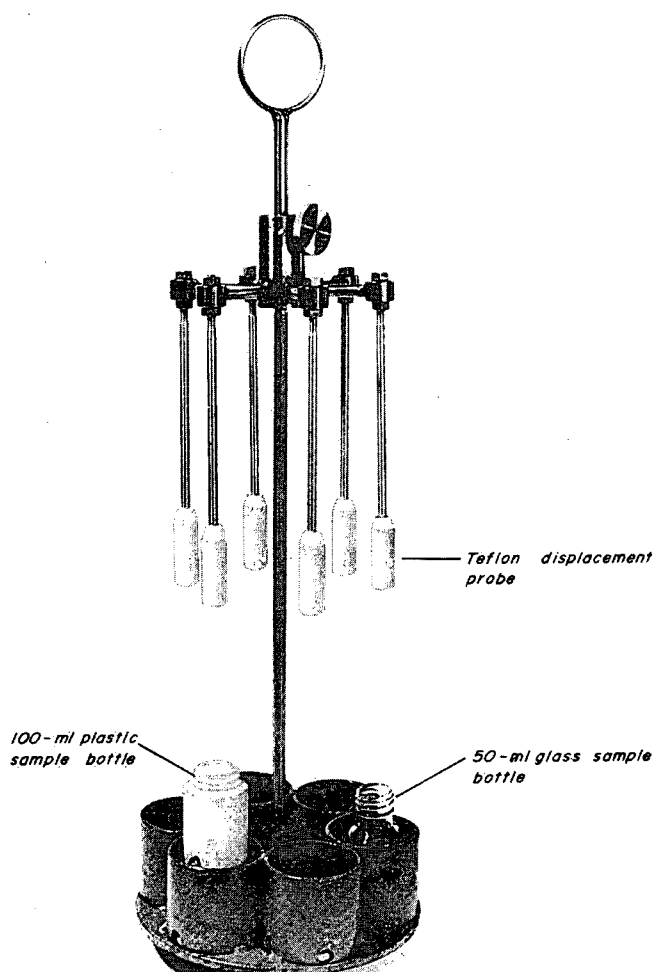


Figure 3. Inland Waters Directorate replicate sampler with Teflon displacement probes in raised position allowing access to cups holding sample bottles.

particularly when suspended solids are present. The analysis of the aliquot is also subject to variation. The procedure followed to determine the magnitude of the analytical variation, a component of the instantaneous error, is given in the section on "Analytical Methods."

To estimate the combined variability associated with these three factors, six simultaneous samples were taken at each substation for the most variable materials (total phosphorus and nitrate plus nitrite) and three simultaneous samples were taken for most of the other materials measured. The interval between samplings at adjacent substations was approximately five minutes. The standard deviation within each set of samples is the estimate of the instantaneous error. This deviation between these instantaneous samples establishes the limit of precision with which spatial or temporal changes can be measured for a given number of samples. When analysis of the results from substations showed no significant ( $p \geq 0.1$ ) difference among the substations, the sample analyses from all

substations were pooled, and the standard deviation of the pooled results was used to estimate the total instantaneous error. It is well illustrated in this study that the combined variability excluding significant temporal and spatial variations is not a constant feature but is itself variable. It appears to increase as the turbidity and turbulence of the water increase.

## 2) Spatial Distribution

The uniformity of distribution of materials across the channel and at different depths greatly influences the reliability of a single sample. Lateral gradients, usually created by the addition of water carrying different concentrations of materials to one side of the channel, are a common form of non-uniform distribution of materials. Throughout this study samples were collected at three substations across the Thompson River in order to detect a lateral gradient. Substations were compared using analysis of variance; when the results are significant ( $p \leq 0.1$ ), the measure of variation associated with non-uniform spatial distribution is the mean squares between substations.

Although no quantitative information is available concerning possible changes in concentration with depth, significant vertical gradients were not expected at the station. During the period of the study, boiling at the surface made it quite apparent that vertical mixing was thorough. This mixing was produced by the upward deflection of fast-flowing water striking large broken rocks in the riverbed.

The 95% confidence limits placed on a single sample as an indication of instantaneous water quality are calculated as  $\pm 1.96$  times the total instantaneous error (standard deviation).

## 3) Temporal Variability

No matter how accurately water quality can be measured at any given instant, it is well known that concentrations of materials in flowing water may change from hour to hour and day to day. Using a single grab sample as an estimate of water quality for the day, month or quarter in which it was taken must account for temporal variability as a source of error.

### a) Short-Term Variability

Variations measured hourly in the absence of local point sources of waste effluents frequently occur as a result of diurnal temperature changes or biological activity. These causes of variability are often very significant in lakes and small streams, but are less likely to be important



in rivers. A one-way analysis of variance was used to test for significant short-term variability at Shaw Spring; samples were taken at six-hour intervals for 66 hours. The mean squares between sampling times was used as the estimate of short-term temporal variability. The results of this 66-hour study are probably conservative because of the relatively constant discharge during this period.

#### *b) Monthly and Quarterly Variability*

The concept of quarterly sampling assumes that a single sample can be used as an estimate of water quality over a three-month period. As a matter of interest, the 95% confidence limits of using single samples for one-month and three-month estimates have been calculated. They are presently considered to be applicable to grab samples of the same size as the multiple samples. A study of the effect of sample size on short-range heterogeneity is planned. Work is also under way to examine the distribution of concentrations measured almost simultaneously close to a single point. Since this study was conducted during the freshet period, the results obtained by these calculations are applicable only to freshet conditions.

### **ANALYTICAL METHODS**

Copper, iron, zinc, fluoride and pH were analyzed according to the methods described in the *Analytical Methods Manual*, published by the Department of the Environment (1974).

Total phosphate was determined by the automated Murphy-Riley method (Murphy and Riley, 1962; Technicon Instruments Corp., 1971), after the entire field sample was digested with sulphuric acid and potassium persulphate.

The concentrations of nitrate plus nitrite were measured by an automated method (Technicon Instruments Corp., 1972). After being transferred to the AutoAnalyzer an aliquot of the sample was buffered at a pH of 8.5 with  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ , and then reduced by passage through a column packed with particles of copper-coated cadmium. A solution of sulphanilamide, N-1-naphthylene-diamine dihydrochloride, and phosphoric acid was added to the reduced aliquot to develop the azo dye. The dye concentration was determined spectrophotometrically at 550 nm.

Reactive silica concentrations were determined with a Technicon AutoAnalyzer II. The sample aliquot was mixed in the AutoAnalyzer with a solution of  $(\text{NH}_4)_6\text{MO}_7\text{O}_{24}$  in dilute  $\text{H}_2\text{SO}_4$  and reacted successively with oxalic acid and ascorbic acid to obtain the heteropoly blue. The colour intensity was measured spectrophotometrically at 660 nm.

In a separate study by Mah *et al.* (in preparation), the precision and accuracy of the analyses of water samples were estimated by analyzing seven sub-samples poured from a well-mixed sample of natural water. Spiked sub-samples were prepared by the addition of a small volume of a standard solution to increase the concentration of the material in the water by a known amount. The sequence of analysis was arranged to promote possible cross-contamination in the automated equipment, that is, high concentration and low concentration samples were alternated.

The sub-samples analyzed for total phosphate were taken from a natural water sample after rough filtration. This procedure reduced the error contributed by a non-uniform distribution among the sub-samples of settleable particles. Each sub-sample was then digested to produce a homogeneous solution, and a single aliquot was analyzed for phosphate.

Mean concentrations, standard deviations, coefficients of variation and percent recovery were calculated for each group of sub-samples. The percent recovery was determined from the ratio of the measured increase in concentration over the original mean value and the calculated increase based on the amount of spike added.

A variation in the aliquots of a single sample exceeding the anticipated analytical error resulted in the rejection of the sample. Less than one percent of the samples were rejected.

### **RESULTS AND DISCUSSION**

The results of the station evaluation including the analytical errors are presented in Table 1. Concentration measurements for the individual samples are given in Appendix A, and the analytical precision and accuracy data are listed in Appendix B.

The observed range of each material is given to indicate the applicability of the error estimates and 95% confidence limits shown. These statistics do not apply to single grab samples with values outside the range indicated.

In the case of total phosphorus and nitrate plus nitrite measurements, relatively high single values were occasionally encountered, for example, the  $\text{NO}_3$  plus  $\text{NO}_2$  results of June 13 (Appendix A). Ordinarily when many samples are collected, such occasional high numbers can be rejected as outliers, assuming that the figure is an artifact caused by contamination or technical error. Rejecting outliers in these data would reduce the estimated

Table 1. Results of Statistical Analysis of Shaw Spring Data

	Nitrate plus nitrite	Total phosphorus	Reactive silica	Copper	Iron	Zinc	Fluoride	pH
Analytical error* (standard deviation)	.0005-.0015	.0004	.08	.0001	.008	.0001	.02	<.01
Instantaneous error (standard deviation)								
Average	.023	.007	0	.001	.07	.005	.004	0
Maximum	.100	.025	0.1	.002	.14	.039	.013	0.1
Spatial error	NS	NS	NS	NS	NS	NS	NS	NS
Range of data, June 13 - August 22	.035-.470	.002-.145	4.6-6.4	<.001-.006	.05-1.20	<.001-.040	.040-.120	7.6-8.0
Total instantaneous error								
Average	.023	.007	0	.001	.07	.005	.004	0
Maximum	.100	.025	0.1	.002	.14	.039	.013	0.1
95% Confidence limits† on estimates of instantaneous concentration	±.045	±.014	±0.1	±.002	±.14	±.010	±.008	±0.1
Short-term temporal error								
Mean square	.007	<.001	<.1	<.001	<.01	.001	NTS	NTS
(Mean square) <sup>1/2</sup>	.084	.016	.1	.001	.03	.013	NTS	NTS
95% Confidence limits† on estimates of concentration for a 66-hour period	±.087	±.017	±.1	±.001	±.08	±.014	NTS	NTS
Monthly errors								
June								
range of data	.075-.206	.071-.145	5.4-6.4	.002-.006	.26-1.20	<.001-.010	.046-.066	7.7-7.9
(mean squares) <sup>1/2</sup>	.015	.032	1.0	.002	.70	.003	.010	0.2
July								
range of data	.056-.184	.019-.109	4.7-5.4	<.001-.004	.05-.45	<.001-.006	.040-.120	7.6-8.0
(mean squares) <sup>1/2</sup>	.032	.055	0.6	.001	.26	.002	.042	0.2
August								
range of data	.035-.470	.002-.051	4.6-4.8	<.001-.004	.05-.15	<.001-.040	.059-.086	7.8-7.9
(mean squares) <sup>1/2</sup>	.032	.023	0.2	.001	.14	.012	.020	<0.1
95% Confidence limits† on estimates of mean monthly concentration								
June	±.088	±.036	±1.0	±.002	±.70	±.014	±.011	±0.2
July	±.093	±.057	±0.6	±.002	±.27	±.014	±.042	±0.2
August	±.093	±.028	±0.2	±.002	±.16	±.018	±.020	0
95% Confidence limits† on estimates of mean concentration for the 3-month period June through August	±.158	±.073	±1.2	±.004	±.77	±.027	±.048	±0.3

\* See Appendix B

† 95% Confidence that the true mean concentration for the period indicated lies in a range between the value of a single sample plus and minus the quantity shown; for example, if a single sample has a total phosphorus value of 0.054 mg/l, one can conclude with 95% confidence that the true instantaneous mean value is between 0.040 mg/l and 0.068 mg/l and that the true quarterly mean value is between 0.0 mg/l and 0.127 mg/l.

Note: All quantities shown are in mg/l, except pH.

Legend: NS — not significant ( $p = <.90$ )

< — less than (i.e., less than the detection limit)

NTS — not measured during 66-hour study

instantaneous error. Outliers were not eliminated from these calculations for two reasons:

- 1) Single grab samples offer no means of identifying outliers as such. Thus the chance that the single sample will be unusually high should be included in calculating errors and confidence limits.
- 2) There is at present no explanation for these high figures that links them to field technique, contamination or analytical error. Numerous possible sources of contamination have been investigated and found "innocent." Repeated analysis of the outlier confirmed the absence of significant analytical error. On the other hand, the high figures may be explained by excess organic or inorganic particulates in outliers that dissolve or become uniformly distributed during the interval between sampling and analysis.

Since Nicola River water was found to have no identifiable impact on variability at Shaw Spring, data from the Nicola were not analyzed further. No significant lateral gradients were found at Shaw Spring, indicating that the water is well mixed during freshet as well as showing that no significant temporal variation occurs during the five-minute interval between samples. This does not exclude the possibility of a lateral gradient developing during low-water periods.

Some of the instantaneous and temporal errors appear to be quite large, especially for materials that are consistently present in amounts greater than the detection limit. When concentrations are close to the detection limit, the variability of the concentration is artificially reduced because part of it cannot be detected. Fortunately, when this occurs, the variability is of limited importance because the concentrations are considerably below levels having a significant impact on water quality.

## CONCLUSIONS

The magnitude of the 95% confidence limits with which a single grab sample at the Shaw Spring station can be accepted as an estimate of the mean daily, monthly or quarterly concentration clearly shows the need for establishing the limits. These confidence limits are probably conservative because the water was well mixed during the 11 weeks of the study, and there was very little variation in flow rates during the 66-hour study of short-term temporal variability. The results illustrate the uncertainties associated with single grab samples as indicators of quarterly mean concentrations. For example, if a single sample has a total phosphorus concentration of

0.054 mg/l, one can conclude with 95 percent confidence that the true instantaneous mean value is between 0.040 mg/l and 0.068 mg/l and that the true quarterly mean value is between 0.0 mg/l and 0.127 mg/l. Furthermore, the need for caution in inferring the presence of a trend on the basis of single samples taken quarterly is apparent.

The errors calculated at Shaw Spring during freshet are probably less than the errors that would be found at other stations where the water may be less "pristine" and not as well mixed. Variability of water quality is probably the greatest at Shaw Spring during freshet; errors associated with single grab samples during more constant flow periods are probably less than those calculated for the freshet period.

Since the short-term temporal errors were measured during a period of relatively constant flow, they are probably conservative. The thorough lateral mixing associated with turbulent freshet flow would also reduce spatial variance. Nevertheless, increases in instantaneous errors associated with outliers could accompany high turbidity during freshet conditions.

The use of quarterly sampling data as a means of "flagging" water quality impairment or measuring trends must include a consideration of both alpha and beta errors. Errors associated with getting a high single sample when the mean concentration is in fact low ("alpha error" or "false positive") and errors associated with getting a low single sample when the mean concentration is in fact high ("beta error" or "false negative") could lead to erroneous conclusions. Improvements in analytical technique and sample handling cannot increase the precision with which a single sample measurement represents mean instantaneous, temporal or spatial concentrations.

## ACKNOWLEDGMENTS

The contributions of Mr. James Taylor, who planned and implemented the field program, and those of the staff of the Analytical Services Division, who expeditiously analyzed the large and intermittent sample load, are gratefully acknowledged. Comments and criticisms from a number of associates have also been helpful.

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**Appendix A**  
**Results of Chemical Analyses**

Table A-1. Nitrate Plus Nitrite (mg/l)

Date	Time	Shaw Spring						Nicola				Savona			
		Substation A East		Substation B Centre		Substation C West		Substation A West		Substation B East		Substation A South		Substation B North	
June 13	15:00	.076	.206	.075	.076	.084	.077	—	—	—	—	.087	.087	.087	.086
												.087	.086	.086	.086
June 18	14:15	.090		.095		.118		—	—	—	—	.087	.090	.085	SL
June 19	4:15	.096		.098		.094		—	—	—	—	.082	.082	.087	.085
												.088	.084	.085	.083
												.082	.082	.086	.085
June 26	16:30	.084	.085	.075	.117	.076	.078	—	—	—	—	.073	.073	.072	.082
												.072	.073	.070	.096
												.074	.075	.073	SL
July 2 (Savona, July 3)	13:00	.081	.077	.127	.076	.075	.077	.128	.029	.023	.019	.015	.010	.010	.065
												.067	.067	.067	.065
July 9 (Savona, July 10)	14:40	.064	.065	.072	.062	.069	.066	.068	.062	.069	.010	.019	.052	.011	.012
July 16 (Savona, July 17)	14:20	.060	.061	.062	.061	.061	.061	.065	.062	.060	.012	.020	.018	.162	.018
July 24	—	.061	.085	.057	.184	.056	.059	.065	.060	.066	.029	.177	.027	.030	.030
												.037	.066	.067	.060
July 30 (Savona, July 31)	13:20	.064	.060	.057	.056	.059	.105	.019	.024	.011	.011	.051	.050	.061	.044
August 8 (Savona, August 7)	12:30	.071	.065	.066	.065	.058	.060	.019	.014	.007	.005	.047	.056	.046	.054
		.070	.049	.073	.059	.114	.072	.014	.016	.012	.009	.054	.060	.076	.056
		.076	.069	.066	.055	.080	.068	.007	.390	.118	.007	.058	.058	.055	.055
		.054	.065	.067	.064	.069	.156	.005	.014	.008	.345	.060	SL	.070	.066

SL — Sample lost

Table A-2. Short-Term Temporal Study of Nitrate Plus Nitrite, August 19-22, 1974, Shaw Spring Stations

Date	Time	Substation A			Substation B			Substation C		
		East			Centre			West		
August 19	16:30	.054	.055	.057	.058	.055	.056	.053	.057	.060
		.090	.058	.057	.059	.063	.057	.056	.056	.058
August 19	22:00	.055	.052	.058	.052	.054	.061	.061	.058	.055
		.055	.060	.053	.054	.055	.050	.056	.055	.058
August 20	5:00	.056	.058	.055	.059	.057	.061	.049	.050	.058
		.055	.115	.057	.061	.059	.051	.051	.072	.050
August 20	10:00	.045	.045	.045	.043	.045	.046	.045	.045	.051
		.046	.045	.047	.044	.045	.045	.046	.045	.062
August 20	16:00	.052	.051	.071	.055	.054	.053	.055	.056	.058
		.055	.051	.057	.184	.053	.052	.050	.061	.090
August 20	22:00	.049	.049	.054	.050	.054	.048	.048	.052	.048
		.046	.047	.052	.050	.050	.053	.059	.051	.053
August 21	5:00	.055	.055	.049	.052	.050	.060	.045	.045	.052
		.065	.050	.048	.055	.049	.046	.057	.051	.050
August 21	10:00	.085	.076	.064	.091	.100	.090	.078	.080	.077
		.069	.067	.062	.064	.095	.065	.068	.059	.095
August 21	16:00	.091	.075	.103	.265	.061	.470	.077	.078	.088
		.068	.086	.128	.099	.063	.061	.056	.120	.073
August 21	22:00	.052	.054	.057	.047	.043	.044	.055	.042	.061
		.050	.055	.052	.042	.044	.048	.054	.063	.059
August 22	5:00	.046	.040	.042	.040	.045	.039	.047	.045	.038
		.041	.048	.041	.046	.040	.039	.040	.042	.044
August 22	10:00	.039	.037	.039	.035	.046	.040	.050	.076	.045
		.048	.039	.037	.040	.038	.039	.080	.052	.045

Table A-3. Total Phosphorus (mg/l)

Date	Time	Shaw Spring						Nicola				Savona			
		Substation A East		Substation B Centre		Substation C West		Substation A West		Substation B East		Substation A South		Substation B North	
June 13	15:00	.095	.105	.128	.123	.110	.072	—	—	—	—	.087	.087	.087	.086
												.087	.086	.086	.086
												.094	.094	.087	.090
June 18	14:15	(.145	.146)*	(.106	.105)*	(.094	.094)*	—	—	—	—	—	—	—	—
		(.123	.135)*	(.098	.109)*	(.100	.100)*								
June 19	4:15	(.102	.101)*	(.102	.101)*	(.127	.144)*	—	—	—	—	.020	.018	.014	.013
		(.093	.091)*	(.098	.097)*	(.114	.115)*					.020	.019	.013	.015
												.014	.015	.030	.034
June 26	16:30	.072	.071	.082	.087	.073	.080	—	—	—	—	.018	.018	.015	.015
												.018	.018	.015	.015
												.017	.016	.015	.015
July 2		.046	.056	.051	.056	.064	.061	.133	.134	.159	.161	.015	.008	.011	.014
(Savona, July 3)	13:00	.052	.056	.047	.056	.081	.072	.145	.151	.164	.167	.011	.013	.016	.015
		.053	.054	.045	.054	.064	.070	.130	.149	.178	.156				
July 9		.057	.052	.053	.049	.036	.046	.101	.155	.094	.124	.020	.018	.013	.010
(Savona, July 10)	14:40	.058	.061	.061	.064	.039	.048	.090	.109	.109	.134	.022	.019	.010	.012
		.046	.072	.054	.050	.045	.045	.102	.129	.101	.110				
July 16		.029	.034	.035	.029	.030	.031	.043	.047	.036	.040	.008	.007	.002	.005
(Savona, July 17)	14:20	.033	.033	.035	.034	.036	.109	.043	.047	.035	.032	.007	.007	.009	.005
		.029	.028	.064	.043	.031	.034	.048	.054	.039	.038	.008	.004	.008	SL
July 24	—	.035	.034	.034	.024	.039	.026	.036	.037	.036	.048	.004	.008	.004	.002
		.038	.037	.019	.024	.032	.026	.032	.039	.036	.040	.008	.004	.003	.005
		.070	.028	.025	.029	.028	.036	.035	.038	.035	.032	.005	.004	.006	.002
July 30		.026	.034	.036	.027	.023	.028	.030	.033	.034	.027	.022	.014	.017	.016
(Savona, July 31)	13:20	.028	.028	.029	.026	.027	.037	.030	.033	.033	.038	.016	.016	.016	.014
		.027	.022	.032	.024	.030	.032	.030	.033	.036	.032	.017	.018	.015	.015
August 8		.024	.016	.020	.012	.047	.014	.132	.021	.015	.017	.008	.011	.029	.009
(Savona, August 7)	12:30	.014	.010	.016	.015	.051	.014	.023	.022	.013	.017	.025	.011	.007	.018
		.009	SL	.015	.016	.016	SL	.054	.018	.012	.014	.011	.012	.007	.010

\* Duplicate laboratory samples  
SL — Sample lost

Table A-4. Short-Term Temporal Study of Total Phosphorus, August 19-22, 1974, Shaw Spring Stations

Date	Time	Substation A			Substation B			Substation C		
		East			Centre			West		
August 19	16:30	.014	.013	.011	.011	.017	.018	.018	.022	.018
		.010	.014	.010	.015	.012	.013	.016	.030	.119
August 19	22:00	.014	.027	.015	.013	.013	.020	.012	.017	.016
		.013	.015	.015	.013	.014	.012	.011	.012	.012
August 20	5:00	.012	.011	.008	.010	.014	.011	.011	.010	.013
		.013	.011	.010	.008	.008	.008	.011	.010	.014
August 20	10:00	.017	.011	.016	.013	.010	.007	.006	.004	.007
		.012	.028	.014	.011	.014	.007	.005	.005	.007
August 20	16:00	.010	.009	.010	.008	.010	.010	.013	.010	.012
		.008	.030	.009	.009	.015	.010	.016	.012	.014
August 20	22:00	.019	.012	.011	.013	.009	.014	.010	.010	.011
		.011	.011	.013	.012	.038	.018	.011	.014	.011
August 21	5:00	.009	.013	.011	.009	.009	.009	.008	.009	.010
		.014	.011	.009	.014	.010	.009	.011	.012	.010
August 21	10:00	.010	.010	.009	.011	.015	.013	.011	.012	.012
		.013	.009	.008	.008	.009	.012	.010	.023	.010
August 21	16:00	.004	.010	.009	.006	.007	.006	.007	.009	.010
		.005	.004	.006	.014	.008	.007	.008	.009	.008
August 21	22:00	.007	.007	.002	.004	.003	.006	.010	.013	.009
		.008	.008	.004	.004	.003	.007	.011	.009	.019
August 22	5:00	.011	.010	.008	.017	.010	.011	.006	.006	.012
		.009	.008	.013	.009	.009	.008	.008	.008	.007
August 22	10:00	.011	.008	.009	.009	.013	.008	.008	.010	.008
		.008	.009	.009	.015	.008	.009	.012	.009	.007

Table A-5. Silica (mg/l)

Date	Time	Shaw Spring						Nicola				Savona			
		Substation A East		Substation B Centre		Substation C West		Substation A West		Substation B East		Substation A South		Substation B North	
June 13	15:00	6.4	6.4	6.4	6.4	6.4	6.4	—	—	—	—	5.9	5.9	5.9	5.9
June 18	14:15	6.2	6.2	6.2	6.2	6.2	6.2	—	—	—	—	—	—	—	—
June 19	4:15	6.1	6.1	6.1	6.1	6.1	6.1	—	—	—	—	5.8	5.8	5.8	5.8
June 26	16:30	5.4	5.4	5.4	5.4	5.4	5.4	—	—	—	—	5.3	5.3	5.3	5.3
July 2															
(Savona, July 3)	13:00	5.3	5.3	5.3	5.3	5.3	5.3	6.0	6.0	6.0	6.0	5.2	5.2	5.2	5.2
July 9															
(Savona, July 10)	14:40	5.4	5.4	5.4	5.4	5.4	5.4	6.3	6.3	6.4	6.4	5.4	5.4	5.4	5.4
July 16															
(Savona, July 17)	14:20	5.2	5.2	5.2	5.2	5.2	5.2	6.2	6.1	6.1	6.1	5.2	5.2	5.2	5.2
July 24	—	5.0	5.0	5.0	5.0	5.0	5.0	5.1	5.1	6.1	6.1	4.8	4.8	4.9	4.9
July 30															
(Savona, July 31)	13:20	4.8	4.8	4.7	4.7	4.8	4.8	6.1	6.1	6.2	6.2	4.8	4.8	4.8	4.7
August 8															
(Savona, August 7)	12:30	4.6	4.6	4.6	4.6	4.6	4.6	6.9	6.9	6.9	6.9	4.4	4.4	4.2	4.5

Table A-6. Short-Term Temporal Study of Silica, August 19-22, 1974, Shaw Spring Stations

Date	Time	Substation A		Substation B		Substation C	
		East	Centre	Centre	West	West	West
August 19	16:30	4.7	4.7	4.7	4.7	4.7	4.7
August 19	22:00	4.7	4.7	4.7	4.7	4.7	4.7
August 20	5:00	4.7	4.7	4.7	4.7	4.7	4.7
August 20	10:00	4.7	4.7	4.7	4.7	4.7	4.7
August 20	16:00	4.7	4.7	4.7	4.7	4.7	4.7
August 20	22:00	4.7	4.7	4.7	4.7	4.7	4.7
August 21	5:00	4.75	4.75	4.75	4.75	4.75	4.75
August 21	10:00	4.75	4.75	4.75	4.75	4.75	4.75
August 21	16:00	4.75	4.75	4.8	4.75	4.75	4.8
August 21	22:00	4.75	4.75	4.8	4.75	4.75	4.75
August 22	5:00	4.7	4.7	4.8	4.75	4.75	4.75
August 22	10:00	4.75	4.65	4.75	4.75	4.75	4.75



Table A-7. Copper (mg/l)

Date	Time	Shaw Spring									Nicola						Savona					
		Substation A East			Substation B Centre			Substation C West			Substation A West			Substation B East			Substation A South			Substation B North		
June 13	15:00	.002		.002	.003	.002	.002		.002		—				—		—				—	
June 18	14:15		.003			.003			.004		—				—		—				—	
June 19	4:15		.002			.003			.002		—				—		—				—	
June 26	6:30	.003		.003	.003		.003	.005		.006												
		.003		.003	.003		.003	.003		.003		—			—		—				—	
		.003		.003	.004		.003	.003		.003												
July 2	13:00	.002	.002	.002	.002	.002	.002	.002	.002	.002	.003	.003	.003	.003	.003	.003		—			—	
July 9	14:40	.001	.001	.002	<.001	.001	<.001	.001	.004	.001	.002	.002	.002	.002	.004	.002		—			—	
July 10	14:40																<.001	<.001	<.001	<.001	<.001	.001
July 16	14:20	.001	.001	.001	.001	.001	.001	.001	.001	.001	.001	.001	.001	.001	.001	.001		—			—	
July 24	—	<.001	<.001	<.001	<.001	.001	.001	.002	.002	.001	<.001	<.001	.001	<.001	<.001	<.001		—			—	
July 30	13:20	.001	SL	.001	.001	.001	.001	.001	.001	.001	.002	.002	.002	.002	.002	.002		—			—	
August 8	12:30	<.001	.001	<.001	.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	.001	.001	<.001	<.001		—			—	

SL — Sample lost

Table A-8. Short-Term Temporal Study of Copper, August 19-22, 1974, Shaw Spring Stations

Date	Time	Substation A			Substation B			Substation C		
		East			Centre			West		
August 19	16:30	.001	<.001	.001	<.001	.001	.001	.002	.002	.001
August 19	22:00	.001	.001	<.001	.001	.001	.001	.001	.003	.002
August 20	5:00	.002	<.001	<.001	.001	.001	<.001	.001	.001	.002
August 20	10:00	.002	<.001	<.001	<.001	.001	.001	<.001	.002	<.001
August 20	16:00	<.001	<.001	.003	.001	<.001	<.001	<.001	<.001	.001
August 20	22:00	<.001	.001	<.001	.003	.001	<.001	<.001	.002	.004
August 21	5:00	<.001	.001	<.001	<.001	<.001	<.001	.001	<.001	<.001
August 21	10:00	<.001	.001	.001	<.001	.002	.001	.003	.001	.001
August 21	16:00	<.001	<.001	<.001	<.001	<.001	.001	.001	<.001	.002
August 21	22:00	.002	.006	.002	.001	.001	.001	.003	.002	<.001
August 22	5:00	<.001	.002	<.001	<.001	.001	.003	.002	<.001	.002
August 22	10:00	<.001	<.001	.001	.001	.001	.002	.001	<.001	.001

Table A-9. Iron (mg/l)

Date	Time	Shaw Spring									Nicola						Savona			
		Substation A East			Substation B Centre			Substation C West			Substation A West			Substation B East			Substation A South		Substation B North	
June 13	15:00	.31	.29	.32		.26	.31	.38			—		—			—			—	
June 18	14:15		.82			.82		1.06			—		—			—			—	
June 19	4:15		.69			.83		.71			—		—			—			—	
June 26	16:30	.90		.82	.76		.80	1.08	1.20		—		—			—			—	
		.82		.82	.84		.84	.76	.80											
		.82		.84	.92		.90	.86	.80											
July 2	13:00	.40	.38	.40	.38	.38	.36	.38	.39	.53	.55	.56	.53	.59	.52				—	
July 9 (Savona, July 10)	14:40	.24	.45	.25	.05	.25	.26	.27	.26	.40	.62	.76	.39	.43	.46	.09	.09	.09	.09	.10
July 16	14:20	.14	.14	.16	.14	.15	.14	.15	.16	.18	.18	.14	.17	.17	.17				—	
July 24	—	.19	.11	.18	.22	.23	.43	.20	.19	.22	.06	.06	.06	.07	.06				—	
July 30	13:20	.19	SL	.23	.24	.24	.25	.24	.24	.25	.21	.18	.18	.21	.21	.19			—	
August 8	12:30	.14	.11	.15	.14	.12	.11	.10	.12	.07	.05	.05	.05	.07	.07				—	

SL — Sample lost

Table A-10. Short-Term Temporal Study of Iron, August 19-22, 1974, Shaw Spring Stations

Date	Time	Substation A			Substation B			Substation C		
		East			Centre			West		
August 19	16:30	.08	.08	.07	.10	.06	.09	.10	.12	.09
August 19	22:00	.10	.10	.08	.12	.07	.12	.12	.10	.12
August 20	5:00	.14	.11	.11	.06	.11	.12	.11	.11	.10
August 20	10:00	.10	.10	.10	.14	.10	.12	.10	.11	.10
August 20	16:00	.12	.11	.11	.12	.10	.10	.11	.12	.12
August 20	22:00	.11	.10	.10	.12	.11	.11	.10	.11	.14
August 21	5:00	.09	.11	.10	.11	.14	.10	.11	.11	.12
August 21	10:00	.09	.10	.12	.11	.12	.12	.10	.10	.10
August 21	16:00	.09	.10	.11	.11	.12	.08	.10	.11	.08
August 21	22:00	.09	.10	.09	.14	.14	.12	.11	.14	.12
August 22	5:00	.06	.06	.10	.10	.11	.11	.06	.08	.08
August 22	10:00	.10	.11	.10	.08	.10	.10	.09	.10	.10

Table A-11. Zinc (mg/l)

Date	Time	Shaw Spring									Nicola						Savona					
		Substation A East			Substation B Centre			Substation C West			Substation A West			Substation B East			Substation A South			Substation B North		
June 13	15:00	.002		.002	.004		.010	.002		.001	—			—			—			—		
June 18	14:15		.002			.003			.002		—			—			—			—		
June 19	4:15		.001			.002			.001		—			—			—			—		
June 26	16:30	.001		<.001	.001		.002	<.001		.003	—			—			—			—		
		<.001		<.001	.002		.002	<.001		.001												
		<.001		<.001	.003		.002	.002		.003												
July 2	13:00	.002	<.001	.003	.003	.001	.001	.005	.003	.005	.002	.003	.005	.002	.009	.001	—			—		
July 9 (Savona, July 10)	14:40	.001	.001	.006	<.001	<.001	<.001	.003	.002	.004	.001	.001	.002	.003	.002	.001	.002	<.001	<.001	.003	.001	<.001
July 16	14:20	.001	.002	.004	<.001	.004	<.001	<.001	.002	<.001	.003	.002	.001	<.001	<.001	<.001	—			—		
July 24	—	.001	<.001	<.001	.002	.004	<.001	.005	.005	.003	<.001	<.001	<.001	<.001	<.001	<.001	—			—		
July 30	13:20	.001	SL	<.001	<.001	.002	.001	.001	.001	.002	.001	.001	.001	.001	.001	.001	—			—		
August 8	12:30	.003	.002	.002	.002	.003	.001	.002	.002	.003	.003	.002	.001	.009	.002	.002	—			—		

SL — Sample lost

Table A-12. Short-Term Temporal Study of Zinc, August 19-22, 1974, Shaw Spring Stations

Date	Time	Substation A			Substation B			Substation C		
		East			Centre			West		
August 19	16:30	<.001	.003	.020	.009	.010	.001	.040	.001	.002
August 19	22:00	.005	.003	.006	.003	.004	.002	.002	<.001	.004
August 20	5:00	<.001	<.001	<.001	.007	<.001	<.001	.002	<.001	.003
August 20	10:00	<.001	<.001	<.001	.003	<.001	<.001	.002	<.001	.005
August 20	16:00	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	.006
August 20	22:00	<.001	<.001	<.001	<.001	<.001	<.001	<.001	.002	.004
August 21	5:00	<.001	<.001	.003	<.001	<.001	.002	.007	.010	.010
August 21	10:00	.020	.005	.010	.001	.005	.003	.004	.012	.005
August 21	16:00	<.001	.006	<.001	.020	<.001	.003	<.001	.009	<.001
August 21	22:00	.003	.006	.006	<.001	<.001	.007	.004	.002	<.001
August 22	5:00	<.001	.002	.003	.006	.005	<.001	.009	.009	<.001
August 22	10:00	<.001	.005	.003	<.001	.006	.002	.010	.003	.004

Table A-13. Fluoride (mg/l)

Date	Time	Shaw Spring						Nicola		Savona
		Substation A East		Substation B Centre		Substation C West		Substation A West	Substation B East	Centre
June 13	15:00	.058	.058	.058	.058	.055	.062	—	—	—
June 18	14:15	.056		.056		.054		—	—	—
June 19	4:15	.056		.058		.066		—	—	—
June 26	16:30	.050	.050	.048	.046	.054	.050	—	—	—
July 9	14:40	.060		.055		.055		.057	.057	—
July 16	14:20	.059		.062		.064		.067	.062	.059
July 24	—	—		.04		—		.05	—	—
July 30	13:20	.094		.10		.12		.105	.105	.086
August 8	12:30	.086		.086		.081		.115	.115	.090
August 19	—	—		.073	.062	—		—	—	—
August 21	—	—		.059	.059	—		—	—	—

Table A-14. pH

Date	Time	Shaw Spring						Nicola		Savona
		Substation A East		Substation B Centre		Substation C West		Substation A West	Substation B East	Centre
June 13	15:00	7.9	7.8	7.9	7.9	7.9	7.9	—	—	—
June 18	14:15	7.8		7.8		7.8		—	—	—
June 19	4:15	7.8		7.8		7.8		—	—	—
June 26	16:30	7.7	7.7	7.7	7.7	7.7	7.7	—	—	—
July 2	13:00	7.7	7.7	7.7	7.7	7.7	7.7	7.9	7.9	7.9
July 9	14:40	7.8		7.7		7.7		8.0	8.1	—
July 16	14:20	7.8		7.7		7.6		8.0	8.0	7.7
July 24	—	—		7.8		—		7.6	—	—
July 30	13:20	7.9		8.0		7.9		8.2	8.2	7.8
August 8	12:30	7.8		7.8		7.8		8.3	8.3	7.7
August 19	—	—		7.8	7.8	—		—	—	—
August 21	—	—		7.9	7.8	—		—	—	—

**Table A-15. Lead (mg/l)**

		Shaw Spring									Nicola						Savona					
Date	Time	Substation A East			Substation B Centre			Substation C West			Substation A West			Substation B East			Substation A South			Substation B North		
June 13	15:00	.001		<.001	.001		.002	.003		.002	—			—			—			—		
June 18	14:15	<.001		<.001		<.001		<.001			—			—			—			—		
June 19	4:15	<.001				<.001		<.001			—			—			—			—		
June 26	16:40	.001		.001	<.001		.001	.002		.001												
		.002		<.001	.001		<.001	<.001		.001	—			—			—			—		
		<.001		.001	.001		.001	.001		.002												
July 2	13:00	<.001	.002	.001	<.001	<.001	<.001	<.001	<.001	<.001	.001	<.001	<.001	.26	.001	<.001	—			—		
July 9 (Savona, July 10)	14:40	<.001	<.001	<.001	<.001	<.001	.006	<.001	<.001	<.001	<.001	<.001	.007	<.001	<.001	<.001	.025	<.001	<.001	<.001	<.001	<.001
July 16	14:20	<.001	<.001	<.001	<.001	<.001	<.001	.001	<.001	.001	<.001	<.001	<.001	<.001	<.001	<.001	—			—		
July 24	—	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	—			—		
July 30	13:20	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	—			—		
August 8	12:30	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	.019	<.001	<.001	—			—		

**Table A-16 Nickel (mg/l)**[illegible]

**Appendix B**  
**Precision and Accuracy of**  
**Chemical Analyses**

Table B-1. Nitrate Plus Nitrite (Automated)

Sample	Spike	Mean	Standard deviation	Coefficient of variation	% Recovery
Low	—	0.0063	0.0005	7.8	—
Med-1	—	0.0714	0.0005	0.8	—
Med-2	—	0.1134	0.0008	0.7	—
High	—	0.1492	0.0015	1.0	—
Low spike	.005	0.0110	0.0000	0.0	100
Med-1 spike	.075	0.1464	0.0008	0.6	100

Table B-2. Total Phosphate

Sample	Spike	Mean	Standard deviation	Coefficient of variation	% Recovery
Low	—	0.0051	0.0003	6.33	—
Med-1	—	0.0131	0.0002	1.36	—
Med-2	—	0.0662	0.0004	0.64	—
High	—	0.1776	0.0002	0.12	—
Low spike	0.025 +0.025	0.0506	0.0005	0.94	101
Med-1 spike	0.175	0.1882	0.0005	0.28	100

Table B-3. Silica

Sample	Spike	Mean	Standard deviation	Coefficient of variation	% Recovery
Low	—	0.8500	0.0500	5.88	—
Med-1	—	7.4286	0.0759	1.02	—
Med-2	—	12.3741	0.1079	0.87	—
High	—	18.8500	0.1740	0.92	—
Low spike	1.0	1.7000	0.0015	0.09	91.9
Med-1 spike	5.0	16.9900	0.0751	0.44	97.8

Table B-4. Copper (Solvent Extraction)

Sample	Spike	Mean	Standard deviation	Coefficient of variation	% Recovery
Low	—	0.002	0.0001	6.45	—
Med-1	—	0.005	0.0001	1.55	—
Med-2	—	—	—	—	—
High	—	—	—	—	—
Low spike	0.002	0.004	—	—	100.0
Med-1 spike	0.005	0.0098	—	—	98.0

Table B-5. Iron (Direct Aspiration)

Sample	Spike	Mean	Standard deviation	Coefficient of variation	% Recovery
Low	—	0.13	0.007	5.38	—
Med-1	—	0.19	0.005	2.75	—
Med-2	—	0.55	0.008	1.42	—
High	—	0.74	0.007	0.93	—
Low spike	0.10	0.221	—	—	96.0
Med-1 spike	0.30	0.833	—	—	98.0

**Table B-6. Zinc (Direct Aspiration\*)**

Sample	Spike	Mean	Standard deviation	Coefficient of variation	% Recovery
Low	—	0.03	0.0021	7.20	—
Med-1	—	0.05	0.0010	0.74	—
Med-2	—	0.10	0.0022	2.15	—
High	—	0.20	0.0015	2.11	—
Low spike	0.02	0.489	—	—	97.8
Med-1 spike	0.05	0.103	—	—	103.0

\*Applied when concentration exceeds 0.020 mg/l

**Table B-7. Zinc (Solvent Extraction\*)**

Sample	Spike	Mean	Standard deviation	Coefficient of variation	% Recovery
Low	—	0.002	0.0002	11.0	—
Med-1	—	0.005	0.0001	2.7	—
Med-2	—	0.010	0.0003	2.5	—
High	—	0.012	0.0004	3.19	—
Low spike	0.001	0.0032	—	—	107.0
Med-1 spike	0.005	0.0107	—	—	93.0

\*Applied when concentration is less than 0.020 mg/l

**Table B-8. Fluoride**

Sample	Spike	Mean	Standard deviation	Coefficient of variation	% Recovery
Low	—	0.0172	0.0016	9.33	—
Med-1	—	0.2507	0.0034	1.36	—
Med-2	—	0.5300	0.0000	0.0000	—
High	—	0.9772	0.0214	2.19	—
Low spike	0.01	0.0242	0.0008	3.46	89.3
Med-1 spike	0.50	0.7243	0.0251	3.46	96.5



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