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1977

Inland Waters Directorate
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INTRODUCTION

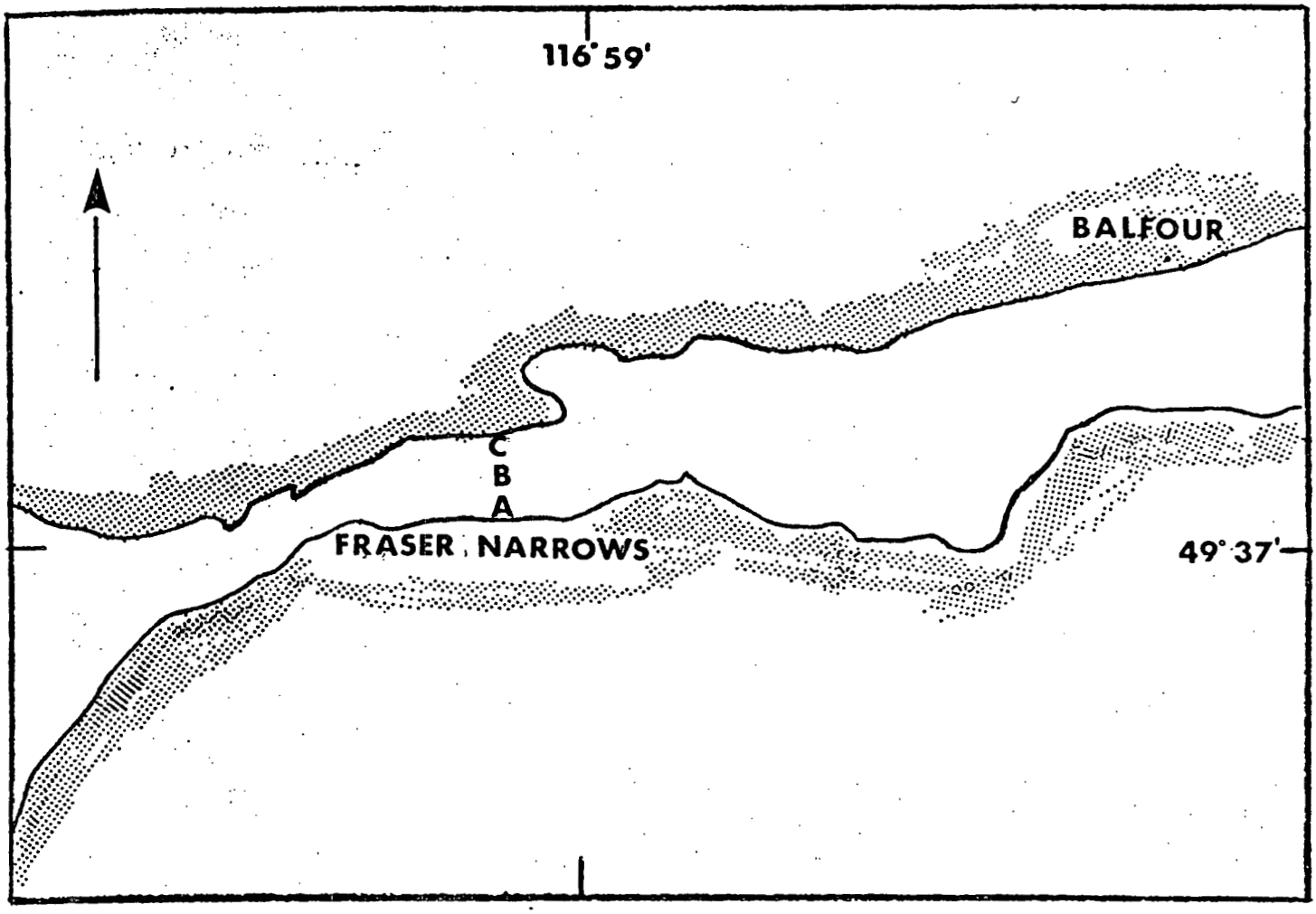
A question has been raised as to the validity of results for certain nitrogen species (Total nitrogen $[N]_T$, nitrate plus nitrite $[N]_{NO_3-NO_2}$, and ammonia $[N]_{NH_3}$) in view of the varying time lapses between sample collection and analysis. This question was brought to the attention of the Water Quality Branch during our Kootenay Lake Loading Study which is in support of the research being conducted on the lake by the Canadian Centre for Inland Waters.

The investigation into this possible problem was initiated by collecting a number of samples using similar methods to those established on the Kootenay Lake Loading Study and under the same conditions (identical water sampling and shipping methods). In the Kootenay study there was a minimum time period of two to four days between sample collection and analysis; therefore it was uncertain if or how much the nitrogen concentrations changed during this time. To clarify this, samples were collected from a site immediately adjacent to an active station for the Kootenay Loading Study and transported to Vancouver where analysis was started the same day. Samples were analyzed at varying time intervals to reproduce the actual delays encountered under normal working conditions. The sample site was at Fraser Narrows on the west arm of Kootenay Lake near Balfour, B.C. (49° 37' N, 116° 59' W). This station is normally sampled at three sampling points on a transection across the river near the outflow from Kootenay Lake (Fig. 1). For this investigation, samples were collected only near point "C" on the transection, however

FIGURE 1

KOOTENAY LAKE (WEST ARM)

SAMPLING POINTS A, B AND C



samples for the Kootenay Loading Study were collected on the same day at the three points, A, B and C, and used for comparison in the investigation.

METHODS

At 0745 on November 23, 1976, using a water Quality Branch, Pacific and Yukon Region, replicate sampler (Oguss and Erlebach, 1976), a total of twenty-four 100 ml. samples were collected in polyethylene bottles at a point approximately 3 metres from the right bank (10 metres from "C" Fig. 1). These samples, together with an additional two 100 ml. sample bottles containing deionized water, were placed in an ice chest and shipped to our laboratory in North Vancouver.

The twenty-four samples were then, arbitrarily, divided into four groups of six samples each. One group of six (numbered 1-6) was analyzed immediately, that is at 1430 on November 23, (A_1),(Table 1). This group was subsequently analyzed at 1000 on November 24, (A_2) and at 1100 on November 25, (A_3). The second group of six (numbered 7-12), group B, was analyzed at 1000 on November 24, (B_1) and subsequently at 1100 on November 25, (B_2) and also at 1100 on November 29, (B_3). The third group (C), of six (numbered 13-18) was first analyzed at 1100 on November 25, (C_1) and again at 1100 on November 29, (C_2). The final group (numbered 19-24) was not analyzed until 1100 on November 29, (D_1). Blanks, that is, the 100 ml. samples containing deionized water, were analyzed at all times mentioned above. The mean, standard deviation, 95% confidence limit and a one-way analysis of variance were used to

statistically compare the analytical results.

Samples were collected at 1130 on the same day for the loading study (not the investigation) at the Fraser Narrows transection points A, B and C and were stored in an ice chest until the field trip was completed. They were then taken to our laboratory by car and analyzed on November 26. The analytical results from these samples were also checked statistically using the same methods as for the investigation, (Table 3).

Samples were not filtered in the field nor in the laboratory prior to analysis with a Technicon Autoanalyzer, model #AA2. Between analyses, samples were stored in the laboratory cooler at 2° C.

RESULTS AND DISCUSSION

Analytical results for this investigation (Table 1) when compared statistically at the 95% confidence level (Table 2) are not significantly different. This is evident when comparing results within each group and also results from the initial analyses of all groups. The initial analyses of each group, however, best indicates the result that would be obtained for the regular loading study as these samples would not be affected by repeated exposure to the laboratory atmosphere.

Of the three forms of nitrogen considered in this investigation, total nitrogen showed the greatest change between the initial analyses of each group and subsequent analyses over the six day period. The mean for $[N]_T$ of 0.141 mg/l in group A_1, analyzed six hours after collection, was 0.014 mg/l higher than the mean for group D_1 analyzed six days later.

TABLE 1

LABORATORY RESULTS (MG/L)

Sample Number	Nov.23 1430 hrs.			Nov.24 1000 hrs.			Nov.25 1100 hrs.			Nov.29 1100 hrs.		
	$[N]_T$	$[N]_{NO_3-NO_2}$	$[N]_{NH_3}$	$[N]_T$	$[N]_{NO_3-NO_2}$	$[N]_{NH_3}$	$[N]_T$	$[N]_{NO_3-NO_2}$	$[N]_{NH_3}$	$[N]_T$	$[N]_{NO_3-NO_2}$	$[N]_{NH_3}$
		A_1			A_2			A_3				
1	.145	.050	.002	.152	.052	.003	.150	.049	.003			
2	.138	.051	.001	.133	.051	.003	.130	.050	.001			
3	.155	.051	.002	.160	.052	.003	.156	.051	.002			
4	.137	.051	.001	.130	.051	.001	.128	.050	L.001			
5	.131	.051	.001	.130	.051	.002	.130	.050	L.001			
6	.138	.052	.002	.128	.051	.002	.123	.050	.001			
					B_1			B_2			B_3	
7				.127	.052	.007	.127	.051	.002	.125	.049	.00
8				.128	.051	.002	.120	.050	.001	.115	.049	.00
9				.125	.051	.001	.120	.050	.001	.115	.049	L.00
10				.140	.052	.006	.150	.052	.004	.145	.050	.00
11				.135	.051	.004	.125	.050	.001	.115	.048	.00
12				.155	.051	.003	.141	.051	.002	.137	.049	.00
								C_1			C_2	
13							.125	.048	.001	.116	.049	.00
14							.128	.048	.001	.120	.049	.00
15							.152	.049	.002	.150	.052	.00
16							.130	.049	.001	.123	.051	L.00
17							.120	.048	.001	.115	.050	L.00
18							.140	.050	.003	.135	.051	.00
											D_1	
19										.118	.051	.00
20										.143	.051	.00
21										.137	.052	.00
22										.122	.050	.00
23										.115	.051	.00
24										.126	.050	.00
Blanks												
25	.013	L.001	L.001	.015	L.001	.002	.013	L.001	L.001	L.010		
26	.015	L.001	L.001	.015	L.001	.001	.015	L.001	L.001	L.010		

L = Less than

TABLE 2

Statistical Results (Means and 95% Confidence Levels) mg/l

	$[N]_T$		$[N]_{NO_3-NO_2}$		$[N]_{NH_3}$	
Group	Mean	95% Confidence Level	Mean	95% Confidence Level	Mean	95% Confidence Level
A_1	.141	.016	.051	.002	.002	.002
A_2	.139	.027	.051	.002	.002	.002
A_3	.136	.025	.050	.002	.002	.002
B_1	.135	.022	.051	.002	.004	.004
B_2	.131	.024	.051	.002	.002	.002
B_3	.125	.025	.049	.002	.002	.002
C_1	.133	.024	.049	.002	.002	.002
C_2	.127	.027	.050	.002	.002	.002
D_1	.127	.022	.051	.002	.002	.002

TABLE 3

KOOTENAY LOADING STUDY LABORATORY RESULTS (MG/L)
FRASER NARROWS TRANSECTION POINTS A, B AND C

SAMPLING DATE: NOVEMBER 23, 1976 AT 1130 PST
ANALYSIS DATE: NOVEMBER 26, 1976

	$[N]_T$	$[N]_{NO_3-NO_2}$	$[N]_{NH_3}$
SAMPLING POINT A	.340	.056	.114
	.322	.057	.100
	.247	.056	.042
	.160	.054	.016
	.224	.056	.051
	.260	.057	.071
Mean	.259	.056	.066
95% CONFIDENCE LEVEL	·129	·002	. 073
SAMPLING POINT B	.215	.058	.044
	.152	.054	.011
	.184	.055	.029
	.210	.055	.032
	.311	.057	.088
	.157	.055	.021
Mean	.205	.056	.038
95% CONFIDENCE LEVEL	.114	.004	.053
SAMPLING POINT C	.247	.052	.072
	.180	.052	.027
	.136	.051	.012
	.200	.053	.033
	.194	.053	.035
	.218	.055	.038
Mean	.196	.053	.036
95% CONFIDENCE LEVEL	.073	.002	.039

This decrease, however, is not significantly different when considering the 95% confidence level as confirmed by a one-way analysis of variance.

The results from the Kootenay Lake Loading Study at the Fraser Narrows station (Table 3) show a gradient across the transection. Total nitrogen concentration has a mean of 0.259 mg/l at sampling point A nearest the south bank and decreases to 0.197 mg/l at point C near the north bank. The mean for total nitrogen concentration in the investigation for samples taken near point C is 0.133 mg/l. The means at this location are different for the two studies; however, the samples for the investigation were collected closer to the north bank than the samples for the Kootenay Loading Study. There was almost a four-hour time lapse between samplings for these two studies which may have a bearing upon the results. Considering the total nitrogen concentrations of both studies at all sampling points, the means of all replicate samples confirm a gradient of decreasing concentration across the outflow from the lake from south to north. This is evident for the date of sampling but may vary at other times.

The nitrate plus nitrite results for the loading study are close to those for the investigation showing only a slight gradient. The ammonia results, however, vary greatly between the two studies with the higher values found in the later sampling for the loading study. The difference in the ammonia results between samples taken for the two studies near or at point C on the transection may be because the samples for the investigation were collected closer to shore. The

loading study samples were all collected from a boat in water having a higher velocity and more turbulance than the water for the investigation.

Although the samples were not filtered before the analyses for this investigation, it is believed that filtering, even with a .22 micron filter to remove all bacteria, would not have altered the results. Tests on samples from the Okanagan (unpublished data) comparing filtered and non-filtered samples show statistically that the means between the filtered and non-filtered samples are the same. Filtering, however, does tend to lessen the chance of obtaining outliers when using six replicate samples.

CONCLUSION

The general trend of the results from the investigation over a period of six days indicate that there is no significant difference between the samples at the 95% confidence level. This is indicated by the results obtained from repeat analyses of the same sample as well as samples previously unopened. This suggests that modifications to the present methods of field sampling and laboratory analysis are not warranted.

It should be explained that this conclusion applies only to a set of samples collected from a specific location and for a certain time and date. Concentrations of nitrogen from other locations and on different dates which show means and 95% confidence levels much higher or lower than those observed for this investigation, may show trends of changing nitrogen concentrations which differ from the results obtained for this investigation.

The difference in time between sampling and analysis for different sets of samples may be due to the occasional storage of samples before being sent to the laboratory, time in transit, and samples waiting to be analyzed at the laboratory during periods of increased workload. As a result of this investigation, it appears that nitrogen samples from Kootenay Lake may be stored for up to six days before analysis without significantly altering their concentrations provided that the samples are kept at 2° C. Nothing can be said at this time about nitrogen concentrations in samples which are analyzed more than six days after collection.

ACKNOWLEDGEMENTS

The contribution from Dr. Gordon Kan of the Analytical Division of the Water Quality Branch in analyzing the samples over this six day investigation is much appreciated. Assistance from Mr. James Taylor and other members of the Water Quality Branch in planning, sampling, data analysis, interpretation and report preparation is gratefully acknowledged.

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