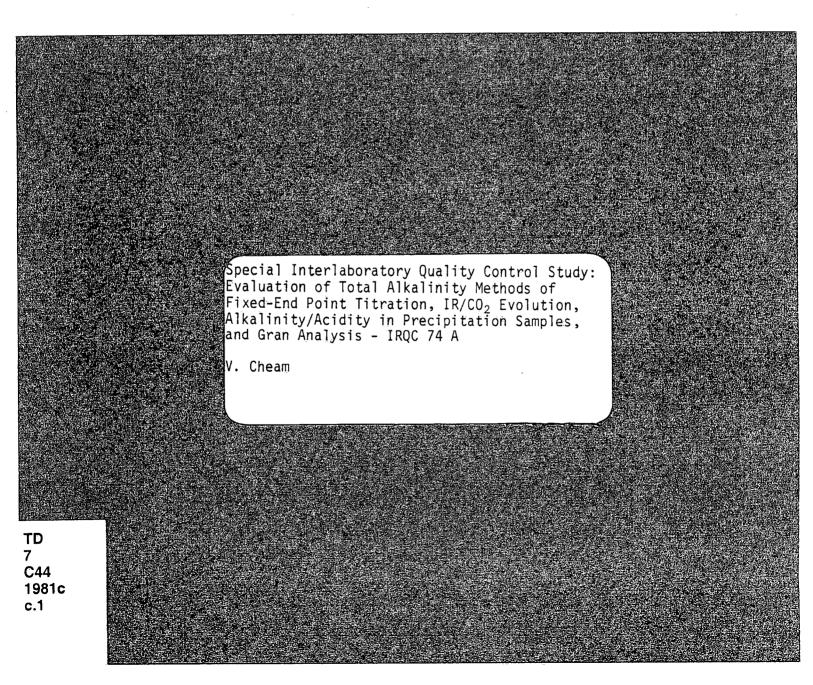
NWRI (unpublished) CHEAM, V 1981



Environment Canada Environnement Canada

National Water Research Institute Institut National de Recherche sur les Eaux



TECHNICAL REPORT - 09-AMD-T-6-81-VC

Special Interlaboratory Quality Control Study: Evaluation of Total Alkalinity Methods of Fixed-End Point Titration, IR/CO₂ Evolution, Alkalinity/Acidity in Precipitation Samples, and Gran Analysis - IRQC 74 A

V. Cheam

IWD-HQ Water Quality Branch Regional Managers

Contents

	rage
Abstract	i
Introduction	1
Experimental	3
Samples	3
In-house Stability Monitoring	3
and confirmatory analyses	
Distribution	4
Results and Discussion	4
Natural Samples with Low Levels - Beaver	5
Skin Lake, Pebbleloggitch Lake, and	
Composite Rain	
Natural Samples, Medium-Normal levels -	8
Lake Superior, Lake Superior spiked with	
borax, and Hamilton Harbor Waters	
Natural Samples, high - levels = Qu'Appelle River	10
and Wascana Creek	
Standards, Low and high levels = Solid Na ₂ CO_3 with	11
Instruction for dilution	

Summary and Conclusions	16
Appendix 1 - References	20
Appendix 2 - Distribution of the special study	21
Appendix 3 - Results of IR 60-61	24
Table 1 - Comparison of alkalinity results	25
Table 2 - Data summary (3 printouts)	26

<u>,</u>

Page

ABSTRACT

Non-comparability of WQB data were observed in the inter-regional quality control studies for total alkalinity in water. This special interlaboratory study was designed and conducted in order to shed light to this problem area.

Since alkalinity/acidity is very important in the acid rain program, precipitation samples and groundwaters are included in this study, in addition to artificial and natural waters from various locations.

The submitted data, obtained from four WQB methods, are commented on. The limitation and application of these four methods are also discussed.

INTRODUCTION

The inter-regional quality control studies No. 60-61 identified a problem area in the determination of total alkalinity. We contacted all the chemists and analysts who reported alkalinity data in order to verify the results and procedures. Mr. Merl Korchinski (Calgary) expressed concerns about their observed non-compatibility of the two analytical methos used by Water Quality Branch laboratories — the IR/CO₂ evolution, and the traditional fixed-end point titration method (NAQUADAT CODED 10106 and 10101, respectively). Subsequently, Korchinski expressed interest in a round-robin study which addresses the subject matter and offered to send some samples for the study (IR60-61 report). It was thought most appropriate to carry out a detailed study as the alkalinity intimately relates to the acidity and acid rain pollution, which is now one of the most serious threats to the environment and probably heads the list of priority pollutants in many countries.

The purpose of the study is to shed light on the non-compatibility of data and methods for total alkalinity. We took

- 1 -

the multi-sample and multi-method approach. The samples, natural and standards, covered a very wide range of analyte concentration and background composition and thus put to test the analytical methods under possibly the toughest challenge ever encountered by WQB laboratories on a one shot basis.

Several preliminary data summaries were sent to laboratories after we received data from them in October 1980, December 1980, January 1981, March 1981, and May 1981. After the study went out in August 1980, the regions were contacted on many occasions in order to recheck reported data, verify method codes, accommodate request for additional samples, and to request to reanalyze some samples.

- 2 -

EXPERIMENTAL

Samples

We considered several natural samples for the study. The criterion for selection was to use the waters from the various regions as much as possible and that they represent waters with quite a variety of composition and concentrations. Waters from very low to very high conductivity were considered so that samples related to acid rain as well as those with complex background matrices are altogether investigated under the same study.

In-House Stability Monitoring and Confirmatory Analyses

We monitored samples alkalinity for about one month to determine their stability and chose the most stable ones. Sub sampling was then made into 250 mL polyethylene bottles and confirmatory analyses made using mostly methods of fixed end point and Gran analysis; occasionally, CO₂ and a special inflextion point methods were utilized.

Distribution

The following samples were distributed to each of the six Water Quality Branch laboratories across Canada: Beaver Skin Lake water (sample 1), Lake Superior water plus borax (sample 2), Lake Superior water (sample 3), Qu'Appelle River water (sample 4), Hamilton Harbour water (sample 5), Wascana Creek water (sample 6), Pebbleloggitch Lake water (sample 7), composite rain water (sample 8), and a solid sample of ultrapure Na₂CO₃ (exactly 0.265 g). We requested storage of water samples at 4°C until analysis. Instructions were given for dissolution of solid sample.

RESULTS AND DISCUSSION

The analytical methods used to determine total alkalinity by WQB laboratories were: fixed end-point titration (Code 10101), infra-red or CO₂ evolution method (Code 10106), method for precipitation samples (Code 10107) and Gran titration analysis (Code 10110). The method for determining acidity in rain smaples was also used (Code 10210).

- 4 -

As the samples in this study substantially differ from one another in types and concentration levels, it would be advantageous to group similar samples and discuss comparison of results and methods group by group. There may be four groups - natural samples with low concentration levels, natural samples with medium levels, natural samples with high levels, and standards with low and high levels.

Natural samples with low levels - Beaver Skin Lake, Pebbleloggitch Lake, and Composite Rain

÷.

The waters from Beaver Skin Lake (sample 1) and Pebbleloggitch Lake (sample 7) were supplied to us by Moncton Laboratory (Dr. Tom Pollock), whereas the composite rain sample (sample 8) by the Monitoring and Surveillance Section of Water Quality Branch, Burlington, Ontario (Mr. Lorne Perkins).

When dealing with low levels of alkalinity, or most anything else for that matter, one should expect to encounter more data scattering than with mediums or high levels. Take Beaver Skin Lake

- 5 -

sample results as a first example. Three laboratories using the fixed-end point mehod reported 2.10, 2.60, 0.05, $\langle 0.5, \langle 0.5, \text{giving an}$ average of 1.58 with a percent CV of 85.3%. Combining all the results from methods of fixed-end point, CO₂ evolution and precipitation samples, one has an average of 1.39 with 67% CV. All results, however, seem to indicate that beaver Skin Lake water, with an average pH of 5.2, and SO₄ of 3.24 ppm (all SO₄ results are comparable), is slightly alkaline.

Consider now the Pebbleloggitch Lake water (sample 7). It is a very interesting sample because of its low pH, 4.5, and its border-line classification as acidic or alkaline. Our in-house analysis, before sample distribution, indicated that the sample behaved more like distilled water as far as titration results were concerned. The Gran and fixed-end point methods indicated acidity, whereas the CO_2 and "inflection" methods indicated alkalinity.

This interlaboratory study seems to show that Pebbleloggitch Lake water is acidic. Both Calgary and Moncton reported negative

- 6 -

values for total alkalinity by fixed-end point method and Gran analysis, respectively (data summary printout). In addition, CCIW ships reported an acidity value of 2.2 by acidity method for precipitation samples (Code 10210).

Vancouver analysed the Pebbleloggitch sample for alkalinity and acidity by the mehtods for precipitation samples (Codes 10107 and 10210), and respectively reported 11.9 and 12.1 mg/L. These results contradict each other and, therefore, cannot be used to disprove or support the implications made above.

Three laboratories analyzed Pebbleloggitch Lake sample by the CO_2 method and reported an average of 4.56 ±23% which is a fair precision at this level. But this method never sees a negative value even if the test sample were acidic; also, at low analyte levels it tends to give larger responses than they actually are. Recognizing these facts, CCIW ships now use titration methods to determine low alkalinity of =5 ppm or less (Yusuf Sheik, personal communication). Another example of high result by the method is seen in the composite rain sample (see below).

- 7 -

Sulfate results agree fairly well with each other, giving an average of 5.43 ±18%.

Turning now to the composite rain sample (pH 5.9, sample 8), the methods for precipitation samples and the fixed-end point produced positive alkalinity results with an average of 1.66 pm $\pm 32\%$. These reusits are in fair agreement with each other and indicate that the water is slightly alkaline.

The CO_2 evolution method, again, gives high results with an average of 5.44 ppm, as in Pebbleloggitch Lake water, and the explanation given there may be applied here as well. All sulfate results are fairly comparable with a mean of 3.59 ±16%.

Natural Samples, Medium-Normal Levels = Lake Superior, Lake Superior Spiked with Borax, and Hamilton Harbour Waters

The waters used were Lake Superior water (sample 3), Lake Superior water spiked with some borax (sample 2), and Hamilton Harbour

- 8 -

water (sample 5). These types of waters are often tested by Water Quality Branch laboratories and expected to cause no difficulty.

The analytical results were obtained by three methods: fixed-end point titration (Code 10101), CO2 evolution method (Code 10106), and the titration method for precipitation samples (Code 10107). Even though the results seem to be comparable and indicate that the three methods are compatible, a few points of interest should be made here. Firstly, in sample 2, a small amount of borax, equivalent to 4 ppm boron, was intentionally added to the Lake Superior sample. This caused the pH to increase from 7.6 to 8.2. As boron contributes to alkalinity determination, one expects the alkalinity in sample 2 to be greater than that of sample 3 (Lake Superior waer). This was observed (45.2 ppm vs 41.9 ppm average values). Secondly, both the fixed-end point titration and the titration for precpitation samples give a difference of 4.2 ppm, whereas the CO₂ method a difference of 1.3 ppm. It is surprising that the latter difference was observed at all. Nevertheless, this small difference of 1.3 ppm indicates that the CO_2 method is not as adequate as the other methods in picking up the contribution from boron. What

- 9 -

if boron were present in a large quantity? This is certainly another weakness in the IR/CO₂ method, and will be amply illustrated later.

Sulfate results by CCIW ships are consistently lower than others.

Natural Samples, High-Levels = Qu'Appelle River and Wascana Creek

The waters from Qu'Appelle River - at Highway 11 (sample 4) and Wascana Creek - near the mouth (sample 6), were kindly sent to us from Regina, Saskatchewan through Mr. Merl Korchinski of Calgary laboratory. These waters are known to contain high concentration levels of alkalinity, sulfate, and other constituents and known to give some analytical problems to the Calgary laboratory (Korchinski, personal communication).

At this high alkalinity level and at $pH \approx 8$, the three analytical methods (fixed-end point, CO_2 , and precipitation) produced comaprable results in both samples. It appears that CALGARY laboratory does not have any difficulty with these samples and that their two methods (fixed-end point and CO_2) are compatible.

Vancouver's SO_4 results are high in both samples relative to others and are circled. CCIW ship's results on SO_4 , again, tend to be low.

Standards, Low and High Levels = Solid Na₂CO₃ with Instruction for Dilution

.

A carefully weighted solid sample of Na_2CO_3 (0.265 g, ultra high purity, Ultrex) was sent to each participant with instructions to:

a) dissolve the whole soid content in a 1 L volumetric
 flask using deionized distilled water, and call it
 sample 9;

 b) to pipette 40 mL of sample 9 into another flask and make up to the 1 L mark with the same deionized distilled water; and

c) analyze the background d.D.W. as sample 11.

The average background alkalinity in d.D.W. is -0.01 ppm with a C.V. of -3200% and is equated to zero in subsequent calculations.

Four methods were used - fixed-end point, CO_2 , precipitation samples method, and Gran analysis. Using known added values of 250 and 10 ppm $CaCO_3$ of alkalinity, the precision and recoveries by the method of fixed-end point, and that for precipitation samples, are excellent. The Gran analysis, used by the Moncton laboratory only, appears to give satisfactory results (this method is believed to give dependable results at all levels). On the other hand, the CO_2 evolution method is imprecise and unaccuate giving a recovery of 59% at both levels of 250 and 10 ppm (data summary printout). The IR method converts the sample inorganic content to total alkalinity by using the conversion factor of 4.166. As sodium carbonate, Na_2CO_3 , was used, the total alkalinity conversion factor is 8.333. Thus, in principle, the present IR method should show a recovery of 50% only (rather than 59%). If one applies the latter factor to the present IR data, one would obtain 293 mg CaCO₃/L and 11.8 mg CaCO₃/L in samples 9 and 10, respectively. Now the recoveries are 118%, which is an improvement, but is high. This is due, in part, to high results by Calgary (data summary printout).

Let us now return to the IR60-61 study, where a 50/50 mixture of HCO_3 -C and CO_3 -C was used to ensure stability in test samples 12, 13, and 14. There, we observed non-compatibility between the fixed-end point and IR methods, and the IR data did not agree with each other (IR60-61 report). We propose that the TIC values from the IR method (CCIW ships and Calgary) and spikes be converted to total alkalinity by the following equation:

$$\frac{\text{TIC}}{2} (4.166) + \frac{\text{TIC}}{2} (8.333) \tag{1}$$

- 13 -

The calculated results are shown in Table 1. It can be seen that the three results are now much more comparable than before.

In the above calculation of IR data, we intentionally omitted CCIW INORG results, which, for all practical purposes, agree with those in Table 1 without being subjected to recalculation by equation 1 (IR60-61, Appendix 3). This accuracy of IR data by CCIW INORG is puzzling in the light of the following points:

- a) In this special study, IR74A, their results are approximately half of theoretical values, basically agree with other IR data of ships and Calgary, and, therefore, produce low results as expected.
- b) In IR60-61, their results basically agree with theoretical values, disagree with other IR data of SHIPS and CALGARY, and unexpectedly produce accurate results.
- c) Mr. Doug Sturtevant and Mr. Rick Wells (personal communication) insist that no deviations from CO₂ evolution procedures were followed in the IR60-61 study.

- 14 -

In sample 9 of this study, the average pH of 10.5 indicates the titration region of CO_3 's. As each CO_3^{-1} species requires two hydrogen ions in total alkalinity determination, the fixed-end point method, the Gran analysis, and the method for precipitation samples, should provide accurate determinations as they are directly relevant to the volume of acid used. On the other hand, the CO_2 evolution method mainly concerns with the amount of CO_2 measured following the addition of acid. Thus, in samples where there are significant amounts of CO_3^{-1} , the CO_2 method is bound to give low results unless proper accounts are made such as those suggested above. Furthermore, as we saw earlier, the method does not pick up other alkalinity contributing consitutents such as borax (in sample 2). As it mainly reflects the sample bicarbonate content, perhaps the method should be identified as determining bicarbonate alkalinity rather than total alkalinity.

As bad as it may sound, the CO_2 evolution method is useful in determining the inorganic content. Furthermore, as most natural samples encountered by WQB laboratories have pH <8.3, and do not, in general, contain significant amounts of other species such as boron,

- 15 -

the CO_2 method should be adequate in these instances. In samples where the pH is high and where it is known that alkalinity contributing species are present in a significant quantity, titration methods should be the preferred methods to use. In the CO_3^{-} - HCO_3^{-} - H_2CO_3 titration system, a pH of 8.3 indicates predominance of HCO_3^{-} species, and that one now enters the HCO_3^{-} - H_2CO_3 equilibrium • system , and therefore, may be used as a qualitative signal for the applicability of the IR method.

SUMMARY AND CONCLUSIONS

 The six participating laboratories used four analytical methods for alkalinity, and one method for acidity in this special study:

CCIW INORG - IR method (11 samples)

MONCTON - Fixed-end point (11 samples) - Gran analysis (3 samples)

- 16 -

CCIW SHIPS - IR and precipitation sample methods (11

samples)

- acidity method 10210 (1 sample)

CALGARY - IR and fixed-end point (11 samples)

VANCOUVER - Fixed-end point (10 samples) Precipitation samples method (one sample)

LONGUEUIL - Fixed-end point (seven samples)

It is difficult to draw definitive conclusions about the four methods since they were not uniformly used by the laboratories for all ll samples. In fact, none of the methods were commonly used by all six laboratories, and some methods was used for a few samples only (see 1). Therefore, it is not meaningful to have detailed statistical treatments of the data.

2.

Some useful conclusions may, nevertheless, be made:

- The IR method should be used with reservation when dealing with low levels of alkalinity, ≈5 ppm CaCO₃ or less, as it tends to give high results. The titration methods — fixed-end point, Gran, or precipitation samples — would provide better accuracy. CCIW ships (Omar Elkei, personal communication) do away with the CO₂ method for rain samples, but titrate them using a Metrohm Titroprocesor.
- The IR method will be biased low when alkalinity contributing species such as boron and carbonate (CO3^T) are significantly present in test samples.
- A a general rule of thumb, it is not advisable to use the IR method for alkalinity determination in samples with pH <8.3. (Note: This does not imply that for test samples with pH <8.3, the IR method is always adequate. Results on alkalinity and pH in sample 2 illustrate this point).

3.

- 18 -

- In spite of the above weaknesses, the CO₂ evolution method is still applicable to most inland waters encountered by WQB laboratories.
- CALGARY, Lab does not seem to have any difficulty analysing alkalinity in complex water samples such as Wascana Creek and Qu'Appelle River waters

- Sulfate results:

- CCIW ships tend to be biased low.

- CCIW INORG's are somewhat erratic.

APPENDIX 1

REFERENCES

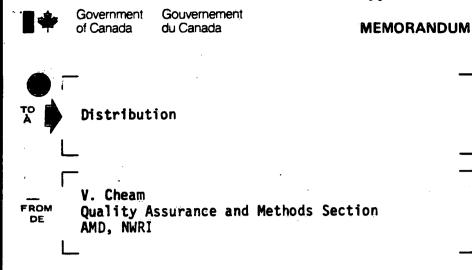
Analytical Methods Manual, 1979. Inland Waters Directorate, Water Quality Branch, Ottawa, Ontario, Canada.

Cheam, V., May 1980. Summary report on IRQC studies Nos. 60 & 61 -Specification studies on anions, nutrients, alkalinity and mercury methods. Confidential distribution to Headquarter, Ottawa and managers and analysts of all six regional Water Quality Branch laboratories.

Freiser, H. and Q. Fernando, 1963. "Ionic equilibria in analytical chemistry", John Wiley & Sons, New York.

Laitinen, H.A. 1960. "Chemical Analysis", McGraw-Hill, Toronto.

- 21 -	
Appendix	2



NOTE	DE	SER	VI	CE
------	----	-----	----	----

V.CHEAM/NWRI/4645 jb

SECURITY - CLASSIFICATION - DE S	ÊCURITÉ
OUR FILE/NOTRE RÉFÉRENCE	
YOUR FILE/VOTRE REFERENCE	<u> </u>
DATE	
18 August 1	980

SUBJECT Special Study on alkalinity

Enclosed are eight (8) water samples and one (1) solid sample for the above study. Please send results in by the week of September 15, 1980.

The water samples are in 250 ML polyethylene bottles, unpreserved, and should be stored in a 4°C room before analysis. They represent a good variety of waters with a wide range of alkalinity from the various regions.

The solid sample in the small Pyrex container should be dissolved in one (1) litre volumetric flask using deionized distilled water. Label this 1 L solution as sample 9.

Pipette an aliquot of 40 ML of sample 9 and transfer it into another one (1) litre volumetric flask and make up to the mark with deionized distilled water. Now call this solution sample 10. Sample 11 is the distilled water.

Please analyse samples 9 and 10 in duplicate. Samples 4, 6 and 9 may take more titration time than the others to reach the end points as their alkalinity values are high, around 200-400 PPM. On the other hand, samples 1, 7, and 8, having low buffer capacity, should require shorter titration time. We caution, however, that these latter samples could be the most difficult ones with respect to accurate and precise determination of alkalinity or acidity. We therefore request that samples 1, 7 and 8 be analyzed in duplicate as 9 and 10.

We are suggesting also that the analysts use as many methods as they can to determine alkalinity. Reporting negative values of alkalinity by titration method is welcome. As can be seen in the enclosed data sheet, we are also requesting analyses of SO₄, B, pH and Alkalinity/acidity, whose analytical results could shed some light on problem samples which might be encountered.

Vaght Chem

V. Cheam Enclosure



DISTRIBUTION:

Head, Analytical Services Section Pacific Region Water Quality Branch

Head, Analytical Services Section Ontario Region Water Quality Branch

Head, Analytical Services Section Quebec Region Water Quality Laboratory

Head, Analytical Services Section Atlantic Region Water Quality Branch

Head, Analytical Services Section Western Region Water Quality Laboratory

c.c: Chief, Laboratory Operations Division Water Quality Branch, Ottawa

Head, Quality Assurance and Methods Section Analytical Methods Division, NWRI CCIW, Burlington



DATA SHEET

for Special Study on ALKALINITY

CONSTITUENT,	NAQUADAT		SAMPLES												
PPM	CODE	1+	2	3	4	5	6	7+	8+	9+	10+	11			
T. ALKALINITY (as CaCO ₃)	10101 10106 *					- -									
SULFATE										1		- 23			
BORON			..	++								1			
Initial pH (pH units)			<u></u>				·								
ALKALINITY/ ACIDITY	10107 10210														

⁺Duplicate determintions.

*Any new method used for determination of T. Alkalinity is welcome, including the new semi-automated titration system. Please briefly describe the principle of the method if it is new.



	APPENDIX 3	S	UNHARY		<u>·</u>			
		INTER REGIONAL Q	UALITY CONTROL P	RUGRAM				
STUDY NO. Source of S	60-61 DATE: Ample Spiked-N	01/07/79 Atural Mater Sampl				ù779		
MAJOR ANIONS NUTRIE NTS (UNPRES) HG (PRES)		N CCIM CALGARY Ships	VANGOUVER LONGE	UIL HEAN	STDEV RELA Stde	T SPIKE	860	ZREC
SAMPLE12=SPK DW		•						
86051 CARBON TOTAL IND MG/L 06051 CARBON TOTAL ING MG/L 96101 CARBON DIS ORG. MG/L	N/A 8.500 N/A N/A N/A N/A	N/A N/A N/A N/A N/A N/A	2.000 N/ 1.600 N/ 13.000 N/	A + 4.033	3.873 96.0		0.000	200.7
06101 CARBON DIS ORG. NG/L 06101 CARBON DIS ORG. MG/L 06104 DISS ORG CARBON HG/L 06104 DISS ORG CARBON HG/L 06104 DISS ORG CARBON HG/L	NZA NZA NZA NZA	NZA NZA 1.9 Z.0 NZA NZA	N/A -N/	A + 2.0	<u>5.657 33.3</u> .1 3.6		<u>0.000</u> 0.0	<u>845.8</u> 97.0
06151 DIC/COMBUST CO2 MG/L 06151 DIC/COMBUST CO2 MG/L 06152 DIC/IR DETCT CO2 MG/L 06152 DIC/IR DETCT CO2 MG/L 06152 DIC/IR DETCT CO2 MG/L 10101 TOT ALKLTY TITN MG/L 10101 TOT ALKLTY TITN MG/L	N/A N/A N/A N/A N/A N/A N/A N/A	N/A N/A N/A N/A 2.000 3.000 N/A N/A	1.600 N/	A * 1.800	•283 15•1 •707 28•3	<u>2.010</u> 2.010	<u>9.000</u>	89.6
10101 TOT ALKLTY TITN MG/L 10101 TOT ALKLTY TITN MG/L 10105 TOT ALKLTY TITN MG/L 10105 TOT ALKLTY TOZ MG/L	N/A 13.60 N/A N/A	NÍA NÍA Nía Nía 9.00 7.00	13.70 11. 12.70 10.	50 * 60 * 12.46	1.28 10.	12.56	1.73	87.2
10105 TOT ALKLIY CO2 HG/L * 10105 TOT ALKLIY CO2 HG/L * 10151 P ALKALINITY HG/L * 10151 P ALKALINITY HG/L *	11.00 N/A 12.00 N/A N/A N/A N/A N/A	N/A N/A N/A N/A N/A N/A	N/A N/ .20 0.		2.22 22.1		1.00 1 M/A	71.9
SAMPLE13=SPK DW		,	·					
06051 CARBON TOTAL INO MG/L • 06051 CARBON IOTAL INC MG/L • 06101 CARBON DIS ORG. MG/L • 06101 CARBON DIS ORG. MG/L •	N/A 32.500 N/A N/A N/A N/A N/A N/A N/A N/A	N/A N/A N/A N/A N/A N/A N/A N/A 22.0 19.0	26.000 N/ 24.000 N/ 98.000 N/ 37.000 N/	A + 27.500 A + A + 67.500		2 23.970 3 23.960	0.000 0.000	114.7 281.7
06104 DISS ORG CARBON MG/L * 06104 DISS ORG CARBON MG/L * 06151 DIC/COMBUST CO2 MG/L * 06152 DIC/COMBUST CO2 MG/L *		N/A N/A N/A N/A N/A N/A N/A N/A 25.000 23.000	26.000 N/ 29.000 N/	A + 27.500		7 23.970		69+8 114+7
06152 DIC/IR DETCI CU2 HG/L * 10101 TOT ALKLTY TITN HG/L * 10101 TOT ALKLTY TITN HG/L * 10106 TOT ALKLTY CO2 HG/L *	N/A N/A N/A 148.00 N/A N/A 145.00 N/A	N/A N/A		00 4 149.40 A 4	2.97 2.0	9 23.970	1.73	98.6
10106 TOT ALKLIY CO2 HG/L • 10151 P ALKALINITY HG/L • 10151 P ALKALINITY HG/L •	144.00 N/A N/A N/A N/A N/A	N/A N/A N/A N/A N/A N/A	N/A N/ 31.30 41. 27.90 38.	50 4	6.36 18.	<u>3 149.82</u> 2 N/A	1.00 N/A	0 • U
SAMPLE 142SPK UN			58.000 N/	/A D				
06051 CARBON TOTAL INO MG/L * 06051 CARBON TOTAL INO MG/L * 06101 CARBON DIS ORG: MG/L * 06101 CARBON DIS ORG: MG/L *	N/A 120.000 N/A N/A N/A N/A	N/A N/A N/A N/A N/A N/A	58.000 N/ 60.000 N/ 113.000 N/	A # 79.333		47.930		165.5
06101 CARBON DIS ORG. MG/L * 06104 DISS ORG CARBON MG/L *	N/A N/A N/A N/A	N/A N/A 40:.0 4:8.0	58.000 N/ I N/A N/	A 4		5 47.920	0.000	178+4 : 91+8 ;
06104 DISS ORG CARBON HG/L • 06104 DISS ORG CARBON HG/L • 06151 DIC/CONPUST CU2 HG/L • 06151 DIC/CONPUST CU2 HG/L •	NA NA NA NA NA NA	N/A N/A N/A N/A N/A N/A	N/A N/ 68.000 N/ 49.000 N/	A +	<u>5.7 12.9</u> 13.435 23.1	<u>9 47.9</u> 0 47.930	0.000	122.1
06152 DIC/IR DETCT CO2 MG/L . 06152 DIC/IR DETCT CO2 MG/L .	N/A N/A N/A N/A	50.000 48.000 N/A N/A	N/A N/	A 49.000		9 47.930	0.000	102.2
	N/A 232.00 N/A N/A	N/A N/A N/A N/A	289.00 298. 292.00 292. N/A N/	GU * 292.60	3.29 1.	1 299.60	1.73	97.1
10106 TOT ALKLTY CO2 MG/L .		185.00 H/A N/A N/A N/A N/A	N/A N/ 45.30 9.	(A + 252.33 BJ +		2 299.60	1.00	83.9
10151 P ALKALINITY HG/L .	NZA NZA	N/A N/A	69.70 10	A0 + 33.90	29.02 85.0	5 N/A	NZA	0.0

.. . - 24 -

. . .

	Sample 12	Sample 13	Sample 14
Theoretical, ppm	12.56*	149.82*	299.6*
IR method (average of SHIPS and CALGARY)	15.63	150.012	306.2
Fixed-end point titration	12.46	149.40	292.6

TABLE 1. COMPARISON OF TOTAL ALKALINITY RESULTS, ppm (IR60-61)

* An average background value of 1.55 ppm is not included.

			TABL	E 2		MMARY					<u> </u>	-••	
					IONAL Q	UALITY CON	FOL PROG	RAM				•.	
	STUDY NG.	74A	DATE: 15	/09/80			 C	 DATE DIST	RIBUTE	D 2000	380		
	SOURCE OF	SANPLE	VARIDUS SO			SAMPLES-SY	ITHETIC SI	AMPLES		· · · · · · · · · ·			
SPECIAL STUDY/A NITY (UNPESD SM	LKALI PLESI	CCIW INORG	MONCTON	CCIW Ships	CALGARY	VANCOUVER	LONGEUIL	* MEAN	STDEV	RELAT	SPIKE	860	%RE
SAMPLE1=BEAVER	SKIN LAKE H	ATER											
19105 B UISVU CU	CTATT MG7L	• N/A	.107L 2.10	N/A N/A	N74	N/A .50L	N/A N/A	0.000	0.000	0.0	NZA	WZA	0.9
0101 TOT ALKLTY 0106 TOT ALKLTY 0106 TOT ALKLTY	TITN MG/L GO2 MG/L	N/A 1-20 1-10	2.60 N/A	N/A 2.00 2.00	N/A N/A	.50L N/A	N/A A	1.58	1.35	\sim	N/A	N/A	0.0
0107 ALKLTY PPTN 0190 t Alklty Mi	TITN MG/ X MET MG/	■ 1.03 ■ N/A ■ 1.20 ■ 1.20 ■ 1.00	N/A N/A 2.10 2.60	2.00 2.00 2.00	N/A N/A .05 N/A	N/A N/A •50L •50L	N/A N/A N/A N/A	1.55	• 5 3	33.9	N/A N/A	N/A N/A	0 • 0
0190 T ALKLIY MI 0190 T ALKLIY MI 0301 PH	UNITS	* 5.390 J	N/A 5.2001	5.2000		N/A 5.2500	NZA	1.39	.2000	G	N/A N/A	N/A	U
6304 SULPHATE DI 6306 SULPHATE FI 6390 SULPHATE FI	SS MG/L LT MG/L	N/A 3.13 3.13	3 • 30 N/A 3 • 30	N/A N/A 3.55N	N/A N/A N/A	N/A 3.00 3.00	N/A 4	3.30 3.05 3.24	0.00 07 -24	2.3	N/A N/A N/A	N/A N/A N/A	0.
SAMPLE 2=L SUPE	RIOR WATER +	BORAX				-							
9105 8 01570 CO 0101 TOT ALKLTY 0101 TOT ALKLTY	TITN MG/L TITN MG/L TITN MG/L	• N/A • N/A • N/A	44.40 48.20	N/A N/A N/A	47.00 46.00	0 N/A 45.50 N/A	43.10 N/A	1.500	1.62	4.0	4.000 N/A	N/A	<u>.0.</u> 0.
106 TOT ALKLTY	CO2 MG/L TITN MG/L	43.00 N/A	N/A N/A	46.00	43.00 N/A	N/A N/A	N/A N/A	44.00		3.9 	N/A N/A	N/A N/A	<u> </u>
0190 T ALKLTY MI 0190 T Alklty Mi 0190 T Alklty Mi 0190 T Alklty Mi	K MET MG/L K MET MG/L	• 43.0] • N/A • N/A	44.40 48.20 N/A	46.00 46.00 N/A	47.00 46.00 43.00	45.50 N/A N/A	43.10 N/A N/A	45.22	1.79	4 • B	N/A	N/A	0.
6304 SULPHATE DI	SS MG/L	• 8.200J • N/A	N/A 3.50	8.2000 N/A	N/A N/A	8.4000 N/A	8.1000 N/A	3.50	0.00	1.9	N/A	N/A	
5306 SULPHATE FI 5390 SULPHATE SO	MAL MG/L	: :::	N/A 3.50	2.90N	4.00	3.00	N/A N/A	4.10 3.74	1.15	28.1 26.1	N/A N/A	N/A	0.
SAMPLESEL SUPER			4.0.01			AL 4.6	Niza z		0 000		N / A	N/A	Π.
105 8 DISVD CON 101 TOT ALRETY 101 TOT ALKLTY	TITN MG/L	• N/A • N/A	<u>•100L</u> 44•57 43•60	<u> </u>		N/A 41.20 N/A	N/A 37.60	• • <u>030</u> • • 1• • 8	<u>0.000</u> 2.42	<u> </u>	N/A N/A	N/A	0.
106 TOT ALKLTY 1107 ALKLTY PPTN	COZ MG/L TITN MG/_	42.0J	N/A N/A	45.00	41.00 N/A	N/A N/A	N/A N/A	42.67	2.08	4.9 0.0	N/A N/A	N/A N/A	0
190 T ALKLIY MI 190 T ALKLIY MI 190 T ALKLIY MI	C MET MG/L	+ 42.01 + N/A + N/A	44.57 43.63 N/A	45.00 42.00 N/A	41.00 41.00 41.00	41.20 N/A N/A	37.60 N/A N/A	- - - 41.89	2.13	5.1	N/A	NZA	0.
301 PH 304 SULPHATE UIS 306 SULPHATE FIL	UNTES	* 7.7000 NZA	7.6000	7.6000 N/A	N/A N/A	7.6000 N/A	N/A 4	41.89 7.6200 4.00	2.13 .0447 	0.0	N/A N/A	N/A N/A	0.0
390 SULPHATE SO	T MG/L MAT MG/L	■ 4 • 3 0 ■ 4 • 3 0	N∕A 4.000	2.90N	3.00 3.00	3.00 3.00	N/A N/A	3.43 3.44	• 75	21.9 19.1	N/A N/A	N/A N/A	0.0
SAMPLE 4=QUAPPEL			100								N / A	N / A	
105 B DISVO COU 161 Tot Alkety 101 Tot Alkety	TITN MG/L	N/A N/A	.300 <u>177.03</u> 184.0]	N/A N/A N/A	.220 176.00	177.00 N/A	178.40 N/A	· 260	- 197	21.0	N/A 	N/A	. 0.
106 TOT ALKLTY	CO2 MG/L	* (193.00)	N/A N/A	190.00 177.00	1.60.00	N/A N/A	NZA 4	• 187.67 • 177.00	6.81 0.00	1.8 3.6 0.0	N/A N/A	N/A N/A	0
107 ALKLTY PPTN 190 T ALKLTY M11 190 T ALKLTY M13 190 T ALKLTY P13 301 PH		* 193.00 * N/A * 7.7003	177.00	190.00 177.00 7.9000	176.00 1800 N/A	177.00 NZA 7.9000	178.40 N/A 8.100J	181.38 7.9000	5.25 .1633	3.5	N/A N/A	N/A N/A	0.
304 SULPHATE DIS 306 SULPHATE ETI 390 SULPHATE SC	SS MG/L	• N/A • 22G.01	N/A 265.00 N/A	224.00 224.00	A/A	7.9000 N/A 280.00 (280.00)	N/A 4	265.00 242.50 247.00	27.49	0.0	N/A N/A	N/A N/A	0.
5390 SULPHATE SO	•	* (220.33)	265.01		246.90	280.00	NZA	- 247.00	25.85	10.5	N/A	NZA	υ.
		ESS	<u>THAN</u> ANAL							<u> </u>			-
	N/A =	NOT											
	N =	NO C	ODE	GIVE	N	. —							

٠

- 26 -

SUMMARY-

INTER REGIONAL QUALITY CONTROL PROGRAM

.

27

STUDY NO. 744 DATE: 15/09/80 Source of Sample Various Sources and Solio Samples-Synthetic Samples

SPECIAL STUDY/ALKALI NITY (UNPESD SMPLES)	CCIW Inorg	MONCTON	201-2	CALGARY	VANCOUVER	LONGEUIL	MEAN	STDEV	RELAT	SPIKE	BGO	XREC
SAMPLES=HAMILTON HARBOR WATE												
10101 TOT ALKLTY TITN MG/L 10101 TOT ALKLTY TITN MG/L 10101 TOT ALKLTY TITN MG/L 10106 TOT ALKLTY CO2 MG/L	N/A N/A 94.00	97.00 102.00	N/A N/A N/A	96.00 N/4	96.20 N/A N/A	95.50 * N/A * N/A *	• 100 97 • 34 97 • 67	2.66 4.73	2.7		N/A N/A	0.0
10100 ALKLTY PTN TITN MG/L 10190 T ALKLTY MIX MET MG/L 10190 T ALKLTY MIX MET MG/L	94.00 N/A 94.00	N/A 97.00 102.00	103.00 96.10 103.00 96.10	96.00 N/A 96.00 95.00	N/A 96.20 N/A	95.50 * N/A *		3.03	0.0	- 11/2 N/A		0.0
10301 PH UNITS 16304 SULPHETE DISS HG/L 16306 SULPHATE FILT MG/L	8.000J N/A 67.00		7.9000 52.00 52.00	N/A 53.00	8.0000 N/A 62.00	8.1000 * N/A *	0.000 70.00 61.00	.0816 0.00 6.30	3.1 1.0 10.5	N/A N/A N/A	N/A N/A N/A	0.0
16390 SULPHATE SO4 MMT MG/L • Sampleg=mascang creek water	67.0]	70.00	52.00	63.00	62.00	N/A #	62.80	6.83	10.9	N/A	N/A	0.0
05105 A DISVD COLRMIY MG/L 10101 IOT ALKLIY IIIN MG/L 10101 IOT ALKLIY IIIN MG/L	N/A N/A	.600 207.00 209.00	N/A N/A	201.70 N/4	N/A 203.00	N/A * 201.70 *	•490 - 204 • 14	.156	31.7	N/A N/A	N/A	0:.0
10106 TOT ALKLTY CO2 MG/L • 10107 ALKLTY PPTN TITN MG/L • 10190 I ALKLTY MIX MET MG/L •	200.00 N/A 200.00	N/A N/A 207.09	210.00 265.00 210.00	205.00 N/A 201.00	N/A N/A 203.90	N/A + N/A + 201.70 +		5.00 0.00		NZA NZA	N/A N/A	00
10301 PH UNITS UNITS 16304 SULPHATE DISS MG/L 16306 SULPHATE FILT MG/L	7.9001 N/A 395.00	208.00 8.1000 400.00 N/A	209.00 8.0000 N/A 372-00	205.00 N/A N/A 413.00	8.1000 N/A 445.00	8.2000 * N/A * N/A *	204.92 8.0600 400.00 406.25	9.59 .1140 0.00 30.80		N/A N/A N/A N/A	N/A N/A N/A	0.0 0.0 0.0
SAMPLE7=PEOBLELOGGITCH LAKE	399.00	400°000	<u></u>	413.00	445.00	N/A *	405.00			N/ A	₩ / Α	
05105 015V0 Colrmty Hg/L * 10101 TOT ALKLTY TITN MG/L * 10101 TOT ALKLTY TITN MG/L * 10101 TOT ALKLTY TITN MG/L * 10106 TOT ALKLTY TITN MG/L *	N/A N/A N/A 4.53	•50L N/A N/A	N/A N/A N/A 5.50	• 140 - • 20 - • 60 3 • 00	N/A N/A N/A N/A	N/A * N/A * N/A *	• 140	0.000 .28(-70.7	N/A N/A	N/A N/A	0.0
10106 TOT ALKLTY COZ HG/C • 10107 Alklty PPTN TITN MG/L • 10110 T Alklty Gran TN MG/L • 10110 T Alklty Gran TN MG/L •	4.37 N/A N/A N/A	N/A 60 60	9.90 N/A N/A N/A N/A	N/A N/A N/A N/A	11.90 N/A	N/A * N/A * N/A *	4.56 11.90 60		- 22.7 0.0 0.0	N/A N/A		0.0
10190 T ALKLTY MIX MIT HG/L 10190 T ALKLTY FIX MET HG/L 10190 T ALKLTY MIX MET MG/L 10210 ACIDITY PPTN TTN MG/L	4.30 4.31 N/A N/A	67 67 60 N/A	5.50 5.50 N/A 2.200	60 60 3.00 N/A	(11.30) (12.10D	N/A # N/A # N/A # N/A #	3.27		122.3	N/A N/A	N/A N/A	0.0
10301 PH 16304 SULPHATE DISS MG/L • 16306 SULPHATE FILT MG/L • 16390 SULPHATE SO4 M4T MG/L •	4.6007 N/A 6.80 6.31	4.5059 4.50 N/A 4.59	-4:5000 N/A N/A N/A N/A	N/A N/A 5.00 5.00	N/A 5.40 5.40	4.2000 + N/A + N/A + N/A +	7.150 4.400 4.50 5.73 5.43	•1917 J•00 •95 •99	3.4 0.0 16.5 18.2	N/A N/A N/A N/A	N/A N/A N/A N/A	
SAMPLES=RAIN WATER												
05105 8 DISVO COLRMTY MG/L .	N/A	.100L	N/A	.020L	N/A	N/A #	0.000	0.00.0	0.0	N/A	N/A	0.0
10101 TOT ALKLTY TITN HG/L + 10101 TOT ALKLTY TITN MG/L + 10106 TOT ALKLTY CO2 HG/L +	N/4 5.2J	2.41 N/A	N/A N/A 7.00	1.00 1.80 3.00	1.50 1.00 N/A	N/A #	1.57	. 53	33.9	N/A	N/A	0.0
10166 TUT ALKLTY ČČŽ MG/L * 10107 ALKLTY PPTN TITN MG/L *	<u> </u>	N/A	7.00	N/A N/A	N/A N/A	N/A +	5.44	1.66	30.6	0.00 N/A	0.00 N/A	0.0
10190 T ALKLTY MIX MET MG/_ * 10190 T ALKLTY MIX MET MG/L * 10190 T ALKLTY MIX MET MG/L *	5.2) 5.0) N/A	1.79 2.41 N/A	7.00 7.00 2.20	1 • 0.0 1 • 80 3 • 00	1.50 1.00 N/A	N/A # N/A #	3.23	2.23	68.0	NZA	NZA	0.0
16301 PH 16304 SULPHATE CISS MG/L * 16306 SULPHATE FILT MG/L * 16390 SULPHATE SO4 MMT MG/L *	5.9303 N/A 3.79 3.79	5.9000 3.30 N/A 3.30	9.930L N/A N/A N/A	N/A 3.00 3.00	6.1000 N/A 4.35 4.35	9.9000 N/A * N/A * N/A *	9.6600 3.30 3.68 3.59	·2191 U.UU •68 •58	0.0 18.3 16.3	N/A N/A N/A	N/A N/A N/A	

		· · · · · · · · · · · · · · · · · · ·	201	трак у					F		
		INTER R	EGIONAL QU	LITY CON	TROL PROG	RAM		•			
STUDY NG Source g	74A DI SAMPLE VA	TES 15/09/80 LOUS SOURCES	NU SOLID SI	MPLES-ST		DATE DIST	RIBUTED	200	860		
SPECIAL STUDY/ALKALI NITY (UNPESD SMPLES)	CCIN I INORG	IONGTON CCI Shift	CALGARY S	ANCOUVER	LONGEUIL	MEAN	STDEV	RELAT	•	BGD	۲RE
SANPLE9=NA2CC3 S10											
DIVE B DISVU COLRHIY NG/L DIVI TOT ALKLIY TIIN NG/L DIVI TOT ALKLIY TIIN NG/L DIVE TOT ALKLIY CO2 NG/L DIVE TOT ALKLIY CO2 NG/L		-600 N/A 52.60 N/A 53.00 N/A N/A 136.00	248.00 268.00 268.00 268.00 175.00	250.00 250.00 250.00	247.60 N/A N/A	249.00	0.000 2.10	_	N/A 250.00	W/A 0.00	99.9
UIUF ALKLIT PPIN IIIN MG7L 0110 t Alkity gram tn mg7l	221.00		175.00 N/A N/A	N/A N/A N/A N/A	N/A N/A N/A	146.67 245.00 231.00	22.26	0.0	250.00	7.00 7.00 C.00	92.4
110 T ALKLTY GRAN TN MG/L 190 T ALKLTY MIX MIT MG/L	T N/A 2	29.00 N/A 33.00 N/A 52.00 136.00 29.00 137.00 29.00 245.00 33.00 N/A	243.00	250.00 250.00 N/A N/A	247.60 N/A N/A N/A	p p	51.47		250.00	0.00	
1301 PH UNITS 5304 SULPHATE DISS MG/L 5306 SULPHATE FILT MG/L 5390 SULPHATE SO4 MMT MG/L		1.6001 10.3000 1.001 N/A N/A N/A 1.001 N/A		10.5000 N/A N/A N/A			•1517 0•00 0•00		N/A N/A N/A N/A		
SAMPLE10=NA2CO3 STO			<u></u>		N7 B	2.600	0.00	<u> </u>		R	
DIDE DISVO COLRMIY MG/L DIDI TOT ALKLIY TIIN MG/L DIDI TOT ALKLIY TIIN MG/L DIDE TOT ALKLIY CO2 MG/L DIDE TOT ALKLIY CO2 MG/L		100L N/A 12:50 N/A 11:27 N/A N/A 5.00		N/A 9.00 9.30 N/A N/A	N/A 9.10 N/A N/A	10.16	0.000 1.28 1.01	0.0 12.6	N/A 19.90 19.90	N/A 0.00 0.00	0.0 101.0 59.2
110 ALKLTY FRAN TI'N MG/L 110 T ALKLTY GRAN TN MG/L 110 T ALKLTY GRAN TN MG/L 190 T ALKLTY MIX MET MG/L	• N/A • N/A • 4.83	N/A 10.60 9.80 N/A 9.91 N/A 12.50 5.00	H/A N/A 10-00	N/A N/A N/A 9.00	N/A N/A N/A 9,10	9.65		0.0	10.00	0.00	- 106.0 98 • 5
190 T ALKLTY MIX MET MG/L	• • • • • • • • • • • • • • • • • • •	11.20 6.00 9.80 10.60 9.90 N/4 .3009 7.2000	7.00 7.00 N/A	9.30 N/4 N/4 9.0500	N/A N/A 8.7000	8.56 8.1700	2.34 .7645	27.4	19:.00 N/A	0.90 N/A	85 · (
301 PH UNITS 304 SULPHATE LISS HG/L 306 SULPHATE FILT HG/L 390 SULPHATE SO4 MMT HG/L	• N/A • •5UL • •5JL	N/A N/A 1.0UL N/A	N/H 1.00L 1.00L	N/A N/A N/A	N/A N/A N/A		0.00 0.00 0.00	0.0 0.0 0.0	N/A N/A N/A	N/A N/A N/A	
SAMPLEIIEDIST WIER 105 8 DISVD COLRMIY MG/L	* N/A	.107L N/A	NZA	N/A	NZA	P 0.000	0.000	0.0	N/A	N/A	5 .1
105 B DISVO COLRMIY MG/L 101 IOT ALKLIY IIIN MG/L 101 IOT ALKLIY IIIN MG/L 106 TOT ALKLIY CO2 MG/L 107 ALKLY PPIN TIIN MG/L 107 ALKLY PPIN TIIN MG/L	* N/A * N/A * 1.00L * N/A	N/A 1.00	- <u>.30</u> 40 NL .25 N/A	N/A N/A N/A	N/A N/A N/A	35	.07 0.00 U.00	-20.2 0.0 0.0	N/A N/A	N/A	U • 1 0 • 1 0 • 1
190 T ALKLTY FIX PET HG/L 190 T ALKLTY FIX FET HG/L 190 T ALKLTY FIX FET HG/L 301 PH UNITS 304 SULPHATE DISS MG/L	1,13L N/A N/A 5.6501 5	•50L 1.00 •5°C •40 •7A •7A •90.00 5.700C 1.00L •7A	. 25	N/A N/A 5.3000	N/A 4	01 5.5000 0.00		- 5200 6.4	N/A N/A N/A	N/A N/A N/A	0 • 9 • 0 •
305 SULPHATE DISS MG/L 306 SULPHATE FILT HG/L 390 SULPHATE 104 MAT HG/L RESULTS FFGVD DYMOYE	• •5 L	1.07L .5a	L 1.00L	N/A N/A N/A	NZA NZA		t.UU UO	0.0	N/A N/A	N/ A N/ A	j.i J.i
		/11/30 29/13/8			01/05/81	\$					

- 28 -

 \bigcirc

े दः · · ·

.

ENVIRONMENT CANADA LIBRARY, BURLINGTON 3 9055 1016 7180 7

.

· · ·