NWRI CONTRIBUTION 87-64

UPPER GREAT LAKES CONNECTING CHANNELS INTERLABORATORY PERFORMANCE EVALUATION STUDY QM-4: MAJOR IONS IN SURFACE WATER FINAL REPORT

by

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May 1987 Revised August 1987

MANAGEMENT PERSPECTIVE

The Upper Great Lakes Connecting Channels (UGLCC) have been designated as "Areas of Concern" by the International Joint Commission. A Canada-U.S. binational study, involving the identification and assessment of the environmental impacts of toxic substances, in those In order to assist analytical areas, was initiated in 1984. laboratories, who are contributing data for the UGLCC study, to generate reliable and accurate data during the study, a Quality Management Work Group was formed and thirteen interlaboratory performance evaluation studies were implemented. This report describes the results from the interlaboratory performance evaluation study, QM-4, which fourth consisted of the analysis of 23 major ions and nutrients in surface Results were received from ten out of 13 participating water. Overall, most of the data laboratories (seven Canadian, three U.S.). received from the participants were satisfactory and comparable, except for some parameters. All participating laboratories have been provided with the appropriate feed-back.

Dr. J. Lawrence Director, Research and Applications Branch National Water Research Institute

PERSPECTIVE - GESTION

La Commission mixte internationale a désigné les voies d'eau reliant les Grands Lacs d'amont "Secteurs de préoccupation". En 1984, le Canada et les Etats-Unis ont entrepris une étude conjointe sur la détermination et l'évaluation des effets des substances toxiques sur l'environnement de ces régions. Afin d'aider les laboratoires qui participent à cette étude à fournir des données fiables et précises, on a créé un Groupe de travail sur la gestion de la qualité et procédé à 13 études interlaboratoires. Le présent rapport décrit les résultats de la quatrième évaluation comparative de la performance des laboratoires, QM-4, qui portait sur l'analyse des 23 principaux ions et éléments nutritifs dans les eaux de surface. 10 laboratoires participants sur 13 ont fait parvenir leurs résultats (sept laboratoires canadiens et trois américains). En général, presque toutes les données revues étaient valables et comparables, sauf dans certains cas. On a envoyé à tous les laboratoires participants les commentaires appropriés.

ABSTRACT

The Upper Great Lakes Connecting Channels (UGLCC) study recognizes Quality Assurance/Quality Control (QA/QC) aspects as crucial elements to the overall utility of study results. As part of the QA/QC program, 13 interlaboratory performance evaluation studies were designed and conducted by the Quality Management Work Group.

This report describes the results from the fourth interlaboratory performance evaluation study, QM-4, which consisted of the analysis of 23 major ions and nutrients in surface water. Results were received from ten out of 13 participating laboratories (seven Canadian, three U.S.). Ten of the parameters were evaluated for bias by Youden's ranking technique and results which deviated significantly from the median were flagged. The rest of the parameters were evaluated for outliers by the Grubbs and Dixon tests. The interlaboratory comparability of major ion data was satisfactory for most of the parameters. Included in this report is a summary of each laboratory's performance.

RÉSUME

L'assurance et le contrôle de la qualité (AQ/CQ) sont des éléments essentiels à l'utilité générale des résultats de l'étude sur les voies d'eau reliant les Grands Lacs d'amont. Dans le cadre du programme AQ/CQ, le groupe de travail sur la gestion de la qualité a conçu et réalisé treize évaluations comparatives de la performance des laboratoires participant à l'étude.

Le présent rapport décrit les résultats de la quatrième évaluation de performance, QM-4, soit l'analyse des 23 principaux ions et éléments nutritifs dans les eaux de surface. 10 laboratoires participants sur 13 ont fait parvenir leurs résultats (sept laboratoires canadiens et trois américains). Certains paramètres ont fait l'objet d'une évaluation des biais possibles dans les données grâce à la technique de Youden et on n'a pas tenu compte des résultats qui s'écartaient de façon significative de la médiane. De plus, tous les résultats ont été calculés en pourcentage de récupération par rapport aux valeurs théoriques. Dans certains cas, les données sur les principaux ions étaient comparables d'un laboratoire à l'autre. En général, la comptabilité entre les valeurs théoriques et les médianes des laboratoires était bonne, sauf exception. On a annexé au présent rapport un résumé de la performance de chaque laboratoire.

INTRODUCTION

The Upper Great Lakes Connecting Channels (UGLCC) have been designated as "Areas of Concern" by the International Joint Commission (IJC). To identify and deal with the environmental problems, a three year, binational study was initiated in 1984, involving Canadian and U.S. environmental and resource agencies, to study the St. Marys, St. Clair and Detroit Rivers and Lake St. Clair. The study involves identifying, quantifying and determining the environmental impacts of conventional and toxic substances from various sources.

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The UGLCC Study recognizes Quality Assurance/Quality Control (QA/QC) aspects as crucial elements to the overall utility of study results. As part of the QA/QC program, 13 interlaboratory performance evaluation (QC) studies were designed and conducted by the Quality Management Work Group. The goal of these QC studies is to assist analytical laboratories, which are producing data for the UGLCC study, to generate reliable, accurate data and to assess their overall performance during this study. A total of some 100 parameters (organic, inorganic and physical properties) in three types of matrices (water, sediment and biota), will be assessed.

This fourth interlaboratory study, QM-4, was intitiated on January 31, 1986. It involved the analysis of 23 major ions and nutrients in surface water. The original deadline for reporting results was set for April 30, 1986. However, several laboratories were late in reporting, so the study was not closed until August 8, 1986.

STUDY PROFILE

From the returned questionnaires, the following 13 laboratories affirmed that they would participate in this study: U001, U010, U014, U049, U057, U075, U077, U089, U091, U013, U063, U078, U090. By the time the study closed, the last three laboratories had not sent back any results. See the list of participants at the end of this report. Each laboratory was provided with four naturally occurring surface water samples as described in Table 1. All samples were reference waters developed by the Quality Assurance and Methods Section (QAMS) of the National Water Research Institute (NWRI). The design values of some of the parameters and the interlaboratory medians are given in Table 2. The design values are based on in-house and external analyses. The same water samples are used twice yearly in the Federal Provincial Interlaboratory Program. The design values of most of the parameters in these samples were confirmed by the interlaboratory medians of these studies (1). Some of the parameters do not have confirmed design values.

Participants were asked to analyze samples 401-404 for 23 major ions and nutrients (colour, conductivity, turbidity, boron(B), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), total Kjeldahl nitrogen (TKN), nitrite + nitrate N (NO_2 + NO_3), ammonia N (NH_3), total nitrogen (TN), fluoride (F), alkalinity - CaCO₃, acidity - CaCO₃, pH, hardness, sodium (Na), magnesium (Mg), silica - SiO₂ (Si), total phosphorus (P), sulphate (SO₄), chloride (Cl), potassium (K) and calcium (Ca)). In order to provide some indication of the precision of such analyses, these samples were sent out in blind duplicate pairs, as shown in Table 1.

RESULTS AND DISCUSSION

Analytical Methodology

All samples could be analyzed directly without dilution, using $_{\sim}$ appropriate methods and standards.

For colour, four out of six laboratories used the visual comparison method with cobalt-platinum standards, while laboratories UO89 and UO91 analyzed apparent colour spectrophotometrically.

All laboratories analyzed conductivity with a conductivity meter, except laboratory U057 which used the conductivity cell in their Dionex Ion Chromatograph. Turbidity was analyzed by all seven laboratories, by the nephelometric method.

Boron was analyzed by three laboratories, laboratories 0010 and 0057 used an inductively coupled plasma atomic emission spectrometer (ICP-AES) and laboratory 0077 used a direct current plasma atomic emission spectrometer (DCP-AES).

Dissolved organic carbon (DOC) was analyzed by four laboratories and laboratory UO14 analyzed total organic carbon (TOC). All laboratories used a total carbon analyzer. The procedure included catalytic combustion of the sample folowed by detection by a non-dispersive infrared analyzer.

Dissolved inorganic carbon (DIC) was analyzed by four laboratories. Laboratories U075 and U077 determined DIC by difference (total dissolved carbon (TDC) - DOC). U001 and U049 analyzed for DIC directly using the inorganic channel of the carbon analyzer with a non-dispersive infrared detector.

Total Kjeldahl nitrogen (TKN) was analyzed by eight laboratories. Two different methods were used, either digestion, distillation and titration by laboratories U001 and U049, or digestion and colorimetry by the rest of the laboratories.

For $(NO_3 + NO_2)N$ laboratory U057 used ion chromatography (IC) while the remaining laboratories used colorimetry azodye (five out of the seven used Cadmium reduction and the other two used hydrazine reduction).

All eight laboratories used colorimetry (automated phenate) for ammonia nitrogen (NH_3) . Only U057 reported results for total nitrogen, which were calculated by summing TKN, $(NO_3 \text{ and } NO_2)N$ results.

Three methods were used for fluoride. Four laboratories used a potentiometric method (specific ion electrode), two laboratories used ion chromatography and one laboratory used a colorimetric method (complexone).

For alkalinity, five laboratories used fixed end point titration and one laboratory used dual end point/inflection point titration. Only laboratory UO14 used a colorimetric end point (methyl orange). Only laboratories U001 and U077 analyzed the samples for acidity $(CaCO_3)$ and both used electrometric titration.

All seven laboratories which reported pH results used a pH meter.

There were two different methods used to analyze hardness. Two laboratories calculated hardness from their calcium and magnesium data and the other three laboratories used an EDTA titrimetric method.

Of seven laboratories analyzing for sodium (Na), one used automated flame photometry, two used D.C.P.-A.E.S., four used Atomic Absorption Spectrophotometry (A.A.S.)-flame.

Eight laboratories analyzed for magnesium (Mg). One used I.C.P.-A.E.S., two used D.C.P.-A.E.S. and five used A.A.S.-flame. All six laboratories analyzing for silica (SiO_2) used colorimetry (heteoropoly blue).

Total phosphorus was analyzed by six laboratories, all of which used some form of acid digestion followed by various colorimetric methods.

Sulphate was analyzed by eight laboratories of which three used colorimetry (methylthymol blue), four used ion chromatography, and one used turbidimetry (barium sulfate).

Chloride was analyzed by five laboratories colorimetrically (ferric thiocyanate), and three laboratories used ion chromatography.

Seven laboratories analyzed for potassium, one used flame photometry, four used A.A.S.-flame and two used D.C.P.-A.E.S.

Calcium was analyzed by eight laboratories. Five used A.A.S.-flame, two used D.C.P.-A.E.S. and one used I.C.P.-A.E.S.

Data Evaluation

All raw data submitted by the participants are listed by parameter in the data summary (Appendix II). Individual laboratory results for only ten parameters (conductivity, $(NO_2 + NO_3)N$, pH, hardness, Na, Mg, SO₄, Cl, K and Ca) were evaluated by the Youden ranking technique (2) for the detection of bias, as well as a computerized flagging procedure (3). A laboratory's results are judged biased high or low, when its total rank is outside of a statistically allowable range. Results are flagged very low, low, high or very high, when they deviate significantly from the interlaboratory median. For a further explanation of the ranking and flagging procedure, see Appendix I. This statistical procedure, which semi-quantitatively evaluates data accuracy is widely used in other interlaboratory QC studies. A summary of the ranking and flagging of the data is given in Appendix II. The accuracy of results has been summarized in Table 5. In this table, the number of results reported, the sum of results flagged VH, H, L and VL, the percentages of results flagged and a statement of biased results are presented for each laboratory.

For the rest of the parameters, since the number of reporting laboratories was small, and some of the data reported were unuseable, (less than values or w codes), neither the Youden ranking technique nor the computerized flagging procedure were used to evaluate the data. This data was evaluated for outliers, by the Grubbs (4) and Dixon (5) tests. Less than values and "W" coded values were not included in these tests. Five percent significance level was used. In order to be an outlier, both of these tests had to be positive.

General Comments

Laboratories U010, U014, U089 and U091 reported their data by the originally set deadline (April 30, 1986). All laboratories, except U013, submitted their results by the second closing date (August 8, 1986). Since laboratory U013 submitted their results extremely late (October 17, 1986), well after the final data summary had been sent out, their results were not included in this report, but can be found in Appendix IV and in the lab specific comments section.

Computer printouts of the raw data were sent to all reporting laboratories for verification in July 1986. All laboratories returned their results verified, except laboratory U001, whose results were

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verified by telephone. The only changes made were from laboratory U089, for fluoride results, which they changed from <1.0 mg/L to <0.01 mg/L.

A final data summary was sent to the participating laboratories, the Quality Management Work Group, the Work Group Chairmen, and the MC and AIC Chairmen on September 15, 1986.

The overall interlaboratory performance of major ion and nutrient analysis was satisfactory for some parameters and samples. The interlaboratory relative standard deviation was less than 30% for colour (401, 402), conductivity, DOC (401), DIC (401, 402) TKN (401), $(NO_3 + NO_2)N$ (401, 402, 404), alkalinity, pH, hardness, Na (403, 404), Mg, SO₄, Cl, K and Ca. The rest of the parameters and samples had an interlaboratory relative standard deviation greater than 30%. In most cases, the difference between the interlaboratory mean and median was less than 15%. There was a greater than 15% difference between the mean and median for turbidity, DOC (402), TKN (403, 404), NH₃ (404), Si (401, 402) and P (401, 402). For the parameters with design values, the agreement between the design values and the interlaboratory medians was within 15%.

In most cases the precision of within laboratory analysis was within a relative standard deviation (RSD) of 15%. All laboratories reported detection limits for most parameters. Table 4 contains the reported detection limits.

General Comments by Parameter

Only laboratory U057 reported data for total nitrogen. Two laboratories (U001 and U077) reported data for acidity, and for the rest of the parameters the number of reporting laboratories varied from three to eight. Laboratory U010 reported results for boron only. Laboratory U014 analyzed for total organic carbon (TOC) instead of dissolved organic carbon (DOC). Laboratory U089 did not have enough sample to analyze DOC and acidity and laboratory UO91 did not have enough of sample 401 to analyze turbidity.

The following ten parameters were analyzed by the Youden ranking technique and the computerized flagging procedures: conductivity, $(NO_2 + NO_3)N$, pH, hardness, Na, Mg, SO₄, Cl, K and Ca.

For conductivity, laboratory UOO1 was biased high, laboratory UO57 had two very low flags and was biased low and laboratory UO75 had two low flags. Thirteen percent of the results submitted for conductivity were flagged.

No laboratories had biased results for $(NO_2 + NO_3)N$. Laboratory U001 had one very high flag, laboratory U057 had two very high flags and laboratories U049 and U075 had two very low flags. Overall, 22% of the results submitted for $(NO_2 + NO_3)N$ were flagged.

For pH, no laboratories had biased results. Laboratories U001 and U014 had one low flag each. Overall, only 7% of the results submitted were flagged.

For hardness, laboratory U001 had one high flag, laboratory U014 had one very high flag and was biased high, and laboratory U089 had a very low flag. Overall 15% of the results reported were flagged.

Twenty-five percent of the results reported for Na were flagged. Laboratory UO14 had one high flag, laboratory UO49 had two low flags, laboratory UO89 had two very low flags and laboratory UO77 had two very high flags and results were biased high.

For Mg, 22% of the results reported were flagged. Laboratory U049 had two high flags and results were biased high. Laboratory U075 had one low and very low flag and results were biased low, laboratory U077 had two very high flags and laboratory U089 had one low flag.

For SO₄, both laboratories UO14 and UO49 had one low flag each, laboratory UO75 had two high flags, and laboratory UO77 had a very low and a low flag. Overall 19% of the results reported were flagged.

Twenty-two percent of the results reported for Cl were flagged. Laboratories U014 and U089 had two low flags each. Laboratory U075 had two very high flags and laboratory U077 had one high flag. For K, 25% of the results reported were flagged. Laboratory U014 had three low flags, laboratory U075 had two very low flags, and laboratories U089 and U049 had one high flag each. Results for U049 were also biased high.

For Ca, 13% of the results reported were flagged. Laboratory U075 had three very low flags, one low flag and results were biased low.

The following parameters: colour (401, 402), turbidity, DOC, DIC (401, 402), TKN, NH₃ (404), F(401, 402), alkalinity, Si(401, 402) and total P (401, 402, 403) were all tested for outliers by the Grubbs and Dixon tests. Most of the data were comparable except for the following outliers which were confirmed by both of these tests: DIC (401 and 402) for laboratory U075, TKN (403 and 404) for laboratory U014 and total P (401 and 402) for laboratory U077.

For the following parameters: colour (403, 404), B, DIC (403, 404), NH₃ (401 - 403), total N, F (403, 404), acidity, Si (403, 404) and total P (404), there was no basis for comparison as there was less than three sets of useable results for each parameter. Some of these parameters were at low levels which were close to the laboratories detection limits and difficult to analyze.

Lab Specific Comments (see Appendix III for each laboratory's appraisal)

U001

This laboratory's results were overall satisfactory for the ten parameters analyzed by the flagging and Youden's ranking procedure, as only only five percent of the results were flagged. Na, Mg, SO₄, Cl, K and Ca were all satisfactory with no flags or biases. Hardness and pH were both satisfactory, except for one H flag and one L flag respectively. Although no results were flagged for conductivity, ranking indicated the results were biased high. $(NO_2 + NO_3)N$ was flagged VH on one sample.

No results were reported for B, Total N, alkalinity (403, 404) and acidity (401, 402). Less than values were reported for colour, NH_3 , DIC (403, 404), F (403, 404) and Si (403, 404).

There was no basis for comparison for colour, DIC (403, 404), NH_3 , F (403, 404), acidity (403, 404), Si (403, 404), and total P (404). Turbidity, DOC, DIC (401, 402), TKN, F (401,402), alkalinity (401, 402), Si (401, 402) and total P (401-403) were all comparable with the data set.

The precision between duplicate results was in most cases within a RSD of 15%, except for turbidity, DOC (401, 402), TKN (403, 404), $(NO_2 + NO_3)N$ (403, 404), and total P.

U010

This laboratory agreed to participate in QM-4 for B and Ca only, but results were submitted only for B. The results submitted were less than values.

U014

For the ten parameters evaluated by the flagging and Youden procedures, conductivity, $(NO_2 + NO_3)N$, Mg and Ca results were all satisfactory. SO_4 and pH were satisfactory except for one low flag each and Na was satisfactory except for one high flag. Hardness was flagged very high on one sample and ranking indicated the results were biased high. Cl was flagged low on two samples and K was flagged low on three samples. Thirteen percent of the reported results were flagged.

Colour, B, DIC, total N and acidity were not analyzed. Less than values were reported for NH_3 (402-404), alkalinity (403, 404), Si (403, 404), F, and total P (401,404). Total organic carbon (TOC) was reported instead of DOC.

There was no basis for comparison for alkalinity (403, 404), NH_3 , F, Si (403, 404) and total P (401, 404). The following parameters

were comparable with the data set: turbidity, TKN (401, 402), alkalinity (401, 402), Si (401, 402) and total P (402, 403). According to the Grubbs and Dixon tests, TKN results for samples 403 and 404 were outliers in this data set.

Precision between duplicate samples was in most cases within a RSD of 15%, except for TKN (401, 402), total P, Cl (401, 402), K (401, 402) and NH_3 (401, 402).

U049

For the ten parameters evaluated by the flagging and Youden procedures, conductivity, pH, hardness, Cl and Ca were all satisfactory with no flags or biases. SO₄ was satisfactory with one low flag. Results for $(NO_2 + NO_3)N$ (403, 404) were unuseable ("<" values) and were flagged very low. Na had two low flags. Ranking indicated that both Mg and K results were biased high, Mg had two high flags and K had one high flag. Thirteen percent of the results submitted for these ten parameters were flagged.

No results were submitted for turbidity, B, total N, alkalinity, acidity, Si and total P. Less than values were reported for colour, DOC (403, 404), DIC (403, 404) and $(NO_2 + NO_3)N$ (403, 404) and NH_3 (401).

There was no basis for comparison for colour, DOC (403, 404), DIC (403, 404), NH₃ (401, 402, 403) and F (403, 404). The following parameters were comparable with the data set: DOC (401, 402), DIC (401, 402), TKN, NH₃ (404) and F (401, 402).

The precision was within a RSD of 15%, except for DOC (401, 402), TKN and NH_3 .

U057

Six of the ten parameters evaluated by the flagging and ranking procedures were reported. Seventeen percent of these results

were flagged. Mg, SO₄, Cl, and Ca were all satisfactory. Conductivity had two very low flags and ranking indicated the results were biased low. $(NO_2 + NO_3)N$ had two very high flags.

No results were reported for pH, hardness, Na, K, total P, DOC, DIC and acidity. The latter three are not routinely analyzed by this laboratory. "W" codes were reported for colour, turbidity, B (403, 404), NH₃ (401 - 403) and Si (403, 404).

There was no basis for comparison for colour, turbidity, B, NH_3 (401 - 403), total N, F (403, 404) and Si (403, 404). The following parameters were comparable with the data set NH_3 (404), F (401, 402), TKN, alkalnity and Si (401, 402).

Precision between duplicate samples was within a RSD of 13%.

U075

Of the ten parameters evaluated by the flagging and Youden procedures, this laboratory had the highest percent flagged with 34%. Only pH, hardness and Na were satisfactory. Conductivity was flagged low on two samples; $(NO_2 + NO_3)N$ was flagged very low on two samples and results for samples 403 and 404 were unuseable (less than values). Mg was flagged low on one sample, very low on one sample and ranking indicated results were biased low. SO_4 was flagged high on two samples, C1 was flagged very high on two samples and K was flagged very low on two samples. Ca was flagged very low on three samples, low on one sample and ranking indicated results were biased low.

No results were reported for colour, B, total N, F, acidity and Si. Less than values were reported for TKN, $(NO_2 + NO_3)N$ (403, 404), NH₃ and total P.

There was no basis for comparison for DIC (403, 404), TKN, NH_3 , and total P. The following parameters were comparable with the data set, turbidity, DOC and alkalinity. According to the Grubbs and Dixon tests, DIC results for sample 401 and 402 were outliers in this data set.

Precision was within a RSD of 15%, except for DOC and DIC (403, 404).

<u>U077</u>

For the ten parameters analyzed by the flagging and Youden procedures, 17% of the results were flagged. Conductivity, $(NO_2 + NO_3)N$, pH, K, Ca were all satisfactory, and Cl was satisfactory, except for one high flag. Na had two very high flags and ranking indicated the results were biased high. Mg was flagged very high on two samples, SO₄ was flagged very low on one sample and low on one sample.

No results were reported for hardness, total N and total P (sample 403 had been spilled). Less than values were reported for B, TKN, NH_3 , F, alkalinity (403, 404), acidity and Si (403, 404).

There was no basis for comparison for colour (403, 404), B, DIC (403, 404), NH₃, F, alkalinity (403, 404), acidity, Si (403, 404) and total P (404). The following parameters were comparable with the data set: colour (401, 402), turbidity, DOC, DIC (401, 402), alkalinity (401, 402), and Si (401, 402). According to the Grubbs and Dixon tests, total P data for samples 401 and 402 were outliers in this data set.

Precision between duplicate samples was within a RSD of 10%, except for turbidity (403, 404).

U089

For the ten parameters evaluated by the flagging and Youden's ranking procedure, conductivity, $(NO_2 + NO_3)N$, pH, SO₄ and Ca were all satisfactory. Mg and K were satisfactory except for one low and high flag respectively. Hardness had one very low flag, Na had two very low flags and Cl had two low flags. Thirteen percent of the results submitted for these ten parameters were flagged and no parameters were biased.

DOC and acidity were not analyzed as the laboratory ran out of sample. DIC, B and total N were not routinely analyzed by this laboratory. Less than values were reported for colour (403, 404) and F. W codes were reported for NH₃, Si (403, 404), TKN (403) and total P (404). (See appendix I for an explanation of these codes).

There was no basis for comparison for colour (403, 404), TKN (403), NH₃, F, Si (403, 404) and total P (404). The following parameters were comparable with the data set: colour (401, 402), turbidity, TKN (401, 402, 404), alkalinity, Si (401, 402) and total P (401 - 403).

The precision between duplicate samples was within a RSD of 15% except for turbidity, TKN (403, 404), and total P (401, 402).

U091

For the nine parameters evaluated by the flagging and Youden's procedures all were satisfactory with no flags or biases.

Hardness, B, DOC, DIC, total N and acidity were not analyzed. There was insufficient sample to analyze turbidity (401). Less than values were reported for colour (403, 404), F, Si (403, 404), and total P (402, 403, 404).

There was no basis for comparison for colour (403, 404), NH_3 (401-403), F, Si (403, 404) and total P (402-404). The following parameters were comparable with the data set, colour (401, 402), turbidity (402 - 404), TKN, NH_3 (404), alkalinity, Si (401, 402) and total P (401).

The precision between duplicate samples was within a RSD of 10%, except for turbidity (403, 404) and total P (401, 402).

U013 - see Appendix IV

This laboratory submitted results well after the closing deadline (October 17, 1986). Results were submitted for only six parameters. Less than values were reported for NH_3 , Si (401, 402) and total P (402).

There was no basis for comparison for NH_3 , Si and total P (402). The following parameters were comparable with the data set hardness, Cl (403, 404), and $(NO_2 + NO_3)N$. According to the Grubbs and Dixon tests, data for samples 401, 403, 404 for total P and samples 401 and 402 for Cl were outliers.

The precision between duplicate samples was within a RSD of 5% except for $(NO_2 + NO_3)N$ (401, 402) and total P (401, 402). The data for this laboratory can be found in Appendix IV along with corrections to data submitted in December 1986.

COMMENTS

Overall, for the ten parameters evaluated by the Youden and flagging procedures (conductivity, $(NO_2 + NO_3)N$, pH, hardness, Na, Mg, SO₄, Cl, K and Ca, most of the data was satisfactory. There was no basis for comparison for B, total N, acidity, colour (403, 404), DIC (403, 404), NH₃ (401 - 403), F (403, 404), Si (403, 404) and total P (404). Most of the results for turbidity, DOC, TKN, alkalinity, color (401, 402), DIC (401, 402), NH₃ (404), F (401, 402), Si (401, 402) and total P (401 - 403) were comparable with some outliers by the Grubbs and Dixon tests.

ACKNOWLEDGEMENTS

The authors sincerely thank all paticipants for their cooperation, Dr. H.B. Lee, W. Li and E. Kokotich for their assistance.

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National Water Quality Laboratory, Burlington, Ontario

Ontario Ministry of Environment, London, Ontario

Ontario Ministry of Environment, Inorganic Trace Contaminants, Waters Unit, Rexdale, Ontario

Ontario Ministry of Environment, Thunder Bay, Ontario

- Raytheon Service Corporation (U.S. Environmental Protection Agency -Large Lakes Research Station) Grosse Ile, Michigan
- US Geological Survey National Water Quality Laboratory, Arvada, Colorado
- Waste Water Technology Centre (Conservation and Protection), Burlington, Ontario

The following laboratories were sent samples but did not submit any results:

Mann Testing Laboratories Ltd., Mississauga, Ontario - Volunteer Laboratory

US Army Corps of Engineers - Environmental Analysis Branch, Detroit, Michigan

Zenon Environmental Inc., Burlington, Ontario

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Samples Distributed for Analysis in QM-4

Sample	Description
. 401	CM-ION-91 (LAKE SUPERIOR)
402	Same as 401
403	CM-ION-92 (Synthetic)
404	Same as 403

TABLE 2

	Dender	Interlab	. Median	Destan	Interlab	. Median
Parameter	Design Value	401	402	Design Value	403	404
Colour (Hazen Unit)		4.5	4.5		5.0	5.0
Conductivity (µ Siemens/cm)	93.9	<u>9</u> 3.8	94.2	443	443	442
Turbidity (JTU/NTU)		0.17	0.14		0.14	0.13
Boron		0.006	0.005		0	0
DOC		2.05	1.80		0.47	0.40
DIC	9.77	9.80	9.90 -		0.25	0.29
TKN		0.115	0.095		0.060	0.058
$(NO_2 + NO_3) N$	0.30	0.30	0.30	0.032	0.035	0.032
Ámmonia N		0.006	0.015		0.020	0.010
Total N		0.460	0.450		0.100	0.110
Fluoride		0.040	0.040		0.085	0.085
Alkalinity (CaCO ₃)	41.1	42.4	42.0		2,00	2.00
Acidity (CaCO ₃)		0	0		1,60	1.40
рН	7.69	7.66	7.66	5.48	5.60	5.50
Hardness	44.4	42.0	44.0	148	142	143
Sodium	1.29	1.30	1.30	19.1	19.1	19.2
Magnesium	2.74	2.77	2.75	9.38	9.23	9.23
Silica (SiO ₂)	2.38	2.40	2.40		0	Q
Total P		0.003	0.003		0.001	0.010
Sulphate	3.32	3.20	3.24	37.1	36.8	37.4
Chloride	1.25	1.29	1.29	105	103	106
Potassium	0.488	0.500	0.500	0.884	0.900	0.900
Calcium	12.5	13.2	13.1	42.4	42.1	42.0

Design Values and Interlaboratory Medians for Major Ions (All values are in mg/L unless stated)

		-			•	· · ·			
Lab No.	LOON	UOIO	\$10 0	600	1057	U075	U077	089	1600
Parameter									
Colour	Yisual Comparison			Visual Comparison	Visual Comparison Co/Pt. stds.		Visual Comparison Apparent Co/Pt. stds. Spectroph metric	colour oto-	Apparent colour Spectrophoto- metric
Conductivity	Conductivity Conductivity Meter (Wheatstone Bridge)		Conductivity Meter Conductivit (Wheatstone (Wheatstone Bridge) Bridge)	Conductivity Meter (Wheatstone Bridge)	ty Meter flow through e Conductivity Cell from Dionex 1.C.	Conductivity Neter	Conductivity Condu Meter (Wheatstone Meter Bridge)	Conduct 1 v 1 ty Meter	Conductivity Neter
Turbidity	Nephelometric (turbidimeter)		Nephelometric (turbidimeter)		Nephel onetric	Nephelometric (Hach turbidi- meter)	Mephelometric (Hach turbidi- meter)	Nephelometric	Nephelometric
Boron		I.C.PA.E.S (direct aspiration)			I.C.P A.E.S. (direct aspira- tion)		D.C.P A.E.S.		
30	Carbon analyzer - catalytic oxidation - IR		Total organic carbon - catalytic com- bustion - IR	Total organic carbon auto analyzer - catalytic combustion - IR		Autoanalyzer - total combus- tion - nondispersive IR	Carbon amalyzer - oxidation - nondispersive IR		
DIC	Carbon analyzer - IR			Carbon auto analyzer - IR		by difference TDC - DOC	 no acidifica- tion by difference TDC-DOC 		
TKA	 acid steam dis- tillation titration 		 semi automated block digestor (acid) colorimetric 	 acid digestion (Nessler) distillation titration 	 acid digestion colorimetric (automated phenate) 	 digestion colorimetric (automated phenate) 	- acid digestion - colorimetric	 block diges- tion colorimetric (automated phenate- hypochlorite 	-block diges- tion - colorimetric (automated phenate- hypochlorite

TABLE 3 Analytical Methodology for Major lons

.

TABLE 3 (continued)

.

Lab No.	1001	010	014	U049		U075	100	6800	1600
(NO ₂ + NO ₃)N Automated cadmium r duction - colorim (azo dy	Automated cadmium re- duction - colorimetric (azo dye)		Automated cadmium reduction - colorimetric (azo dye)	- cadmium re- duction - colorimetric	lon Chromatography	Automated cadmium reduction - colorimetric	Automated cadmium reduction - colorimetric (diazo)	Automated hydrazine re- duction - colorimetric (azo dye)	Automated hydrazine re- duction - colorimetric (azo dye)
Aamonia N	Automated phenate - colorimetric		Automated phenate - colorimetric	phenate Automated phenate ric - colorimetric	Automated phenate - colorimetric	phenate Automated phenate Automated etric - colorimetric - colorime	phenate stric	Automated phenate- hypochlorite - colorimetric	Automated phenate- hypochlorite - colorimetric
Total N					Calculated by TKN + NO ₃ + NO ₂				
Fluoride	Automated Specific lon electrode		Automated Complexone, colorimetric	lon Chromatography	lon Chromatography		Automated Ion Selective elec- trode	Specific lon Electrode	Specific Ion Electrode
Alkalinity (CaCO ₃)	Potentio- metric titration-two end points		Automated colorimetric (methyl orange)		Titration (fixed end pt.)	Titration (manual) (fixed end pt.)	Automated titra- tion (fixed end pt.)	Potentiometric titration (fixed end pt.)	Potentiometric manual titra- tion (fixed end pt.)
Actdity (CaCO ₃)	Electrometric titration - end point 8.3						Electrometric titration-end pt. 8.3		
Hd	Electrometric (pH meter)		Electrometric (pH meter)	Electrometric (pH meter)		Electrometric (pH meter)	Electrometric (pH meter)	Electrometric (pH meter)	Electrometric (pH meter)
Hardness	Calculation from Ca and Mg data		Titrimetric - EDTA	Titrimetric EDTA		Titrimetric - EDTA (manual)		Calculation from Ca and Mg data	
Sodium	Automated Flame Photometry		A.A.S flame (direct)	D.C.P A.E.S.		D.C.P A.E.S.	A.A.S flame (direct)	Automated A.A.S flame	Automated A.A.S flame
Magnesium	Automated A.A.S flame		A.A.S flame (direct)	D.C.P A.E.S.	1.C.P A.E.S. (direct)	D.C.P A.E.S.	A.A.S flame (direct)	Automated A.A.S. Automated flame A.A.S. A.A.S f	Automated A.A.S flame

e la	
1	
1	

TABLE 3 (continued)

Lab No. Parameter	1000	010	0014	U049	no57	0075	0077	680	1600
5111ca (510 ₂)	Automated Colorimetric (Heteropoly Blue-ammonium molybdate)		Colorimetric (Heteropoly Blue molybdosilicic acid)		Colorimetric (molybdosilicic acid)		Automated Colorimetric (molybdate blue)	Automated Colorimetric (Heteropoly Blue molybdate)	Automated Colorimetric (Heteropoly molybdate)
Tota l Phosphorus	- acid diges- tion - colori- metric (Stannous chloride)		automated block digestor (acid) - colorimetric			 automated digestion colorimetric 	 acid digestion automated colorimetric (phosphomolyb- date) 	 acid digestion automated colorimetry 	 acid diges- tion automated colorimetry
Sulphate	Automated Colorimetric (methylthymol blue)		Automated Colorimetric (methylthymol blue)	lon chromato- graphy	'Ion chromato- graphy	lon chromato- graphy	Automated Turbidimetric (Barium Sulfate)	Automated Colorimetric (methylthymol blue)	Automated Ion Chromatography
Chlor 1de	Colorimetric (Ferric thiocyanate)		Colorimetric Automated (Ferric thiocyanate)	lon Chromatography	lon Chromatography	lon Chromatography	Colorimetric Automated (Ferric thiocyanate)	Colorimetric Automated (Ferric thiocyanate)	Colorimetric Automated (Ferric thiocyanate)
Potassium	Automated Flame Photometry		A.A.S flame (direct)	D.C.PA.E.S.		D.C.PA.E.S.	A.A.S flame (direct)	A.A.S flame (direct)	Automated A.A.S flame
Calctum	Automated A.A.S flame		A.A.S flame (direct)	D.C.PA.E.S.	I.C.PA.E.S. (direct)	D.C.PA.E.S	A.A.S flame (direct)	A.A.S flame (direct)	A.A.S flame

 TABLE 4

 Reported Detection Limits (All values are in mg/L unless stated)

0.10 0.03 0.01 0.01 0.05 0.03 0.1 0.01 0.005 0.01 NVR 1600 0.02 0.3 NVR NVR 0.3 0.02 NVR 0.20 0.3 0.02 0.02 0.01 0.008 0.95 0.06 NVR NVR NVR 089 NVR 1.7 2 **.** 6 0.20 0.20 0.01 0.01 0.10 0.20 0.01 0.01 0.1 0.01 0.01 1.0 0.01 0.01 U077 0.1 0°.5 5°0 NVR 0.1 O 0.1 0.05 0.05 0.1 0.15 ±0.02 1 0.1 0.1 0.1 0.1 1 0.1 **J**075 10 0**.**05 0**.**005 0.005 0.005 0.005 0.02 0.01 0.03 10.0 0.01 U057 0.1 0.2 0.2 0.1 ى 0.01 0.01 0.002 0.01 0.2 0.02 0.05 0.05 0.05 0.05 0.05 0.05 **J049** ഹ് 1 0.05 0.003 0.005 0.005 0.05 0.1 0.1 0014 0.4 0.1 5 Ч ŝ 0100 0.02 0.05 0.02 0.05 1001 0.01 0.2 NVR NVR 0.1 0.1 0.1 S Conductivity (µ Siemens/cm) [urbidity (JTU/NTU) Colour (Hazen Unit) Alkalinity (CaCO₃) Acidity (CaCO₃) Parameter $(NO_2 + NO_3)N$ Si (Si0₂) Hardness Total P Total N Boron boc DIC NH 3 TKN S04 Hd ច х Ö Ra

NVR - no value reported

TABLE 5

Summary of Results by Laboratory Based on the Flagging and Youden Procedures

(for conductivity, NO_2 + NO_3 , pH, Hardness, Na, Mg, SO₄, Cl₂, K, Ca)

(see Appendix III)

						·		
Lab Code	No. of Results Reported	Elements not Analyzed		of l agge H			% Flagged*	Comments
U001	40		1	1	1	0	5%	Conductivity - biased high
U010	0	Ca	-	-	÷	-	-	
Ü014	40	-	1	1	7	0	13%	Hardness - biased high
U049	40 (2 "<") both flagged	-	0	3	3	2	13%	Mg & K - biased high
U057	24	pH, Hardness Na, K	2	0	0	2	17%	Conductivity - biased low
U075	40 (2 "<≞)	-	2	2	4	8	34%	Mg,Ca - biased low
U077	36	Hardness	4	1	1	1	17%	Na - biased high
U089	40	-	0	1	3	3	13%	No bias
U091	36	Hardness	0	0	0	0	0%	All satisfactory
					·			

* H and L flags are counted as half of a VH and VL flag. Less than values that were flagged are included in the calculation of the % flagged.

Appen. I.1

APPENDIX I

Glossary of Terms

(1) Ranking

Ranking is a non-parametric statistical technique used for the detection of pronounced systematic error (bias) in interlaboratory According to Youden's procedure, rank 1 is given to the studies. laboratory that provided the lowest result, rank 2 to the next lowest. In case of a tie, the average rank is given to the tied laboratories. Results with a < sign are not ranked. For each parameter, the total rank of each laboratory is the sum of individual ranks on each sample. In the case of six test samples and ten laboratories, the 5% probability limits for ranking scores are 14 and 52. A laboratory with a score lower than 14 is identified as biased low. Similarly, a laboratory with a total rank higher than 52 is biased high. In both cases, their results are classified as outliers. In cases where a laboratory did not provide all the results, or some of the results were not ranked, the average rank instead of total rank was used for the determination of biased statements.

The more comparable, i.e., better, laboratories should have ranks in the middle rather than at the extreme ends. However, laboratories with middle ranks do not necessarily mean that they provide more consistent results since very high results (high ranks) and very low results (low ranks) would average out to yield a total rank close to the median. Therefore, ranking alone is not sufficient to determine the performance of a laboratory.

(2) Flagging

When the true values of constituents in test samples are unknown, individual results can be evaluated in terms of their absolute differences from the interlaboratory medians. Medians are chosen rather than means since they are not influenced by a moderate number of extreme values. By this flagging technique, all results are graded into the following three groups in the order of decreasing accuracy: (1) results with no flags, (2) results with H or L flags, and (3) results with VH or VL flags. Before evaluation is performed, three parameters, namely, Lower Limit for use of Basic Acceptable Error (LLBAE), Basic Acceptable Error (BAE), and Concentration Error Increment (CEI) are to be set. LLBAE is usually set at the lower end of the medians in the test samples. A 5-20% error at LLBAE is considered reasonable and thus this is used as BAE. For samples whose medians are at or below LLBAE, the results are evaluated according to the following formulae:

	Absolute difference between sample and median results	<u>≺</u> BAE :	acceptable
BAE <	Absolute difference between sample and median results	<u>≺</u> 1.5 x BAE:	H or L
	Absolute difference between sample and median results	> 1.5 x BAE:	VH or VL

For samples whose medians are above the LLBAE, the allowable BAE is augmented by adding an increment to the BAE. This increment is calculated by multiplying the CEI by the difference between the sample median and LLBAE values. Sample results are again evaluated by the above three formulae except that the augmented BAE is used instead of BAE.

For further discussion on this evaluation technique, please refer to the original paper by Clark.

<u>Bias:</u> A set of results is said to be biased when the <u>set</u> exhibits a tendency to be either higher or lower than some standard - the standard which has been used in the analysis of our studies thus far has been the performance of all other participating laboratories. The ranking procedure employed in testing for bias is described in W.J. Youden's paper, "Ranking Laboratories by Round-Robin Tests from <u>Precision Measurement and Calibration</u>, H.H. Ku, Editor, NBS Special Publication 300 - Volume 1, U.S. Government Printing Office, Washington, D.C., 1969. In this paper, Youden establishes the rationale for evaluating laboratories' performance by ranking results. In our use of the procedure there is about one chance in twenty of deeming a set of results biased when in fact it is not, that is, t = 0.05.

Codes

Τ:

- <u>W:</u> A "W" code is used with a reported result when no measurement was possible due to no response of the instrument to the sample. The "W" is preceded by the smallest determinative division that can be used in the units used in reporting.
 - The "T" code is used with values between the Criterion of Detection and the "W" value. The Criterion of Detection is commonly thought of by many as the limit of detection.

NA:	not analyzed
NRA:	not routinely analyzed
N or ND:	not detected
NAPP:	not applicable
Н:	high
VH:	very high
L:	low
VL:	very low
LŤV:	less than value (<)

APPENDIX II

UGLCC INTERLABORATORY PERFORMANCE EVALUATION STUDY

QM-4 Major Ions in Surface Water

<u>Data Summaries</u>

DATA SUMMARY

QN4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: COLOUR

HAZEN UNIT

· · · · · · ·

				SANPLE	SAMPLE RESULTS					
LAB		401		402		403	· . ·	404		
U001 U049 U057 U077 U089 U091	K < M	55555	< < ₩	555543 555	~~~	5 • 5 • 5 • 1 • 0	~~.	5. 5. 1.0 .3		
TOTAL LABS	REPORT	ING	6		6		6	6		
TOTAL LABS	USED		3		3		1	1		
MEAN		4. 2666	7	4.3333	3	5.0000	0	5.00000		
STO DEV		. 8736	9	.7637	6	0.0000	0	0.00000	,	
MEDIAN		4.5000	0	4,5000	0	5.0000	0	5.0000		



PAGE 1

QN4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: CONDUCTIVITY

AS IE HEN/CH

SAMPLE RESULTS

	401	402	403 -	404
LAB				
U 00 1 U 014 U 04 9 U 057 U 075 U 077 U 089 U 091	95.9 95. 90. 79.7 84.9 95.5 96.	96.1 90. 79.7 83.00 95.9 92.5 96.	454 • 3 4456 • 425 • 405 • 400 • 458 • 438 • 447 •	453. 448. 415. 405. 448. 437. 447.
TOTAL LABS	REPORTING 8	8	. 8	8
TOTAL LABS	USED 8	8	8	. 8
MEAN	91.06250	91.15000	433.41250	432.25000
STO DEV	6.14444	6.48933	21.12659	20.52699
MEDIAN	93.75000	94.20000	442.50000	442.00000
DESIGN VALUE	93.9	93.9	44 3	44 3

PAGE 2

DATA SUMMARY

QM4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. Parameter: Turbidity

JT U/ NTU

SAMPLE RESULTS

·		401			402		403 -		404
LAB			· ,			-			
U001 U014 U057 U075 U077 U089 U091	W	• 11 • 4 • 2 • 17 • 3 • 10		W	06 2 14 3 13 08	W	• 08 • 3 • 16 • 4 • 12 • 08	W	.05 .32 .14 .58 .11
TOTAL LABS	REPORTI	NG	7		;	7	7		7
TOTAL LABS	USED		5		(6	6	۰.	6
MEAN		. 21	600		.1850	0	.19000		.19667
STD DEV		. 13	012		.1350	2	.13130		.17236
MEDIAN		• 17 (000		•1350	0	.14000		.12500



PAGE 3

QM4 MAJOR IONS IN SURFACE MATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: BORON

MG /L

.

	SAMPLE RESULTS								
		401		402		403		404	
LAB					•				
U010 U057	<	. 02	~	•02 •005 •01	< H <	•02 •005	<	.02	
ŬŎŹŻ	<	.006 .01	<	.01	<	.01	A M A	.02 .005 .01	
TOTAL LABS	REPORT	ING 3		.3		. 3		3	
TOTAL LABS	USEO		1	:	1	0) .	0	
MEAN		.00600		.00500		0.0000		0.0000	
STD DEV		0.0000	0	0.0000) .	0.0000	1	0.0000	
MEDIAN		.0060	0	• 00 5 0 1)	0.0000	Ì	0.00000	



QM4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: DISSOLVED ORGANIC CARBON

MG/L

		SAMPLE RES	SULTS	
1. 1.	401	402	403	404
LAB		-		
U 001 U 049	1.8	1.3	• 2	• 2_
U075 U077	1.8 2.5 2.3 1.49	2.0 < 3.7 1.60	• 05 < • 9 • 47	• 45 • 4 • 43
TOTAL LABS RE	EPORTING 4	4	4	4
TOTAL LABS US	SED 4	a de	3	3
MEAN	2.02250	2.15000	• 5 2 3 3 3	• 3 4 3 3 3
STO DEV	• 46119	1.07238	.35303	• 1 250 3
MEDIAN	2.05000	1.80000	. 47000	.40000
			• •	-
U014 (TOC)	1.41	1.47	0.19	0.21





QH4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: DISSOLVED INORG. CARBON MG/L

SAMPLE RESULTS

	401	402	403	404
LAB				•
U 00 1 U 049 U 075 U 077	9.5 10.0 12.1 9.59	9.8 < 10.0 < 11.2 9.69	•5 < •05 < •1 •40	• 5 • 0 5 • 2 • 3 7
TOTAL LABS	REPORTING 4	4	4	۰. اور
TOTAL LABS	USED 4	4	2	2
MEAN	10.29750	10.17250	.25000	.28500
STD DEV	1. 22121	• 696 92	.21213	.12021
MEDIAN	9.79500	9.90000	.25000	.28500
DESIGN VALUE	9.77	9.77		



PAGE 6

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QM4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. PARAMETER'S TOTAL KJELDAHL NITROGEN

MG/L

SAMPLE RESULTS

		401		402		403		404
LAB								
U001 U014 U049 U057 U075 U077 U089 U091	< <	•136 •13 •16 •08 •29 •10	e e	• 159 • 10 • 11 • 07 • 1 • 20 • 08 • 09	K K K	• 035 • 29 • 063 • 16 • 20 • 21 • 01	۲ ۲	• 045 • 29 • 082 • 07 • 1 • 2 • 02 • 01
TOTAL LABS	REPORTI	NĢ	8		8	8	•	8
TOTAL LABS	USED		6		6	5	;	6
MEAN		. 116 (0 0	.1015	0	.09160)	.08617
STD DEV		. 0308	35	.0315	2	• 11296)	.10363
MEDIAN		• 115 (] ()	• 095 0	0	.06000		•05750

QH4 HAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. PARAMETERS (NITRATE + NITRITE) N

SAMPLE RESULTS

	401	402	403	404
LAB				
U001 U014 U049 U057 U075 U077 U089 U091	• 306 • 30 • 31 • 38 • 2 • 30 • 28 • 30	• 31 3 • 30 • 32	•047 •024 •01 < •04 •1 < •03 •02 •04	• 0 33 • 0 27 • 0 1 • 0 4 • 1 • 0 3 • 0 2 • 0 4
TOTAL LABS R	EPORTING 8	8	8	8
TOTAL LABS U	SED 8	8	6	6
MEAN	. 29700	.29913	o03350	.03167
STO DEV	· 04908	.04980	.01050	•00776
MEDIAN	.30000	.30000	.03500	.03150
DESIGN VALUE	0.30	0.30	0.032	0.032

PAGE 8

MG/L

DATA SUMMARY

the second se

MG/L

QM4 HAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: AMMONIA N

SAMPLE RESULTS

		401		402		403		404
LAB		·						х.
U001 U014	<	• 001 • 001	<	•001 •001	K	. 001	< <	.001
Ŭ049	<	• 01 • 005		°02	-	•001 •03 •005	Κ.	•001 •04
U057 U075	W	• 1	× 1	•005 •1	¥ <	i 1	<	.005 .1
Ŭ077 U089	< H	•1 •01 •005	× N	•01 •005	< ₩	•01 •005	<. W	01 005
U091		. 01		.01		.01		.01
TOTAL LABS	REPORTI	ING 8	i	ł	3	8	•	8
TOTAL LABS	USED	2		i	2	2	2	3
MEAN		.00550	ł	• 01 5 0 ()	.02000		.01867
STO DEV		.00636)	.00707	7	.01414	•	.01858
MEDIAN		.00550		•0150	נ	.02000		•01000
TOTAL LABS Mean Std dev		2 • 00550 • 00636	2 }	• 01500 • 00707	2) 7	.02000 .01414	2	8 3 • 0 186 7 • 0 185 8



QM4 MAJOR IONS IN SURFACE HATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: TOTAL NITROGEN MG/L

SANPLE RESULTS 481 402 403 404 LAB U057 . 46 **.** 45 .10 .11 TOTAL LABS REPORTING 1 . 1 1 1 TOTAL LABS USED 1 1 1 1 MEAN - 46000 .45000 .10000 .11000 STD DEV 0.00000 0.00000 0.00000 0.0000 MEDIAN .46000 .45000 .10000 .11000

DATA SUMMARY

QH4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: FLUCRIDE

HG /L

	SANPLE RESULTS							
		401		402		403	· ·	404
LAB								
U 001 U014 U049 U057	۲	03 1 04 065	<	•03 •1 •04 •060	Č	.01 .1 .01 .160	<	•01 •1 •01 •160
U077 U089	~ ~	:10	۲. ۲	:10	~ ~ ~	.10	۲ ۲	:10
<u>0091</u>	۲	• 1	<	•1	<	•1	<	•1
TOTAL LABS	REPORT	ING	7		7	. 1	7	7
TOTAL LABS	USED		3		3	1	2	2
MEAN		. 0450	0	.0433	3	.0850	. .	.08500
STD DEV		• 0 <u>1</u> 8 0:	3	.0152	8	.10607	7	.10607
MEDÍAN		. 0400	0	.0400	0	.0850	D	.08500
÷						·		

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DATA SUMMARY

QM4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: ALKALINITY (CACO3)

MG/L

SAMPLE RESULTS

	4.01	402	403	404
LAB				
U 00 1 U 014 U 057 U 075	42°4 47° 43°5 41°	43.7 42. « 43.7 39.	5. < 2.1 2.	5. 2.2 2.
U077 U089 U091	44. 41.4 41.8	43. < 40.8 T 41.6	1. < 1.2 T. 1.8	1. 1.4 1.8
TOTAL LABS R	EPORTING 7	7	7	7
TOTAL LABS U	SED 7	7	3	3
MEAN	43.01429	41.97143	1.96667	2.00000
STO DEV	2.06594	1.70168	.15275	.2000
MEDIAN	42.40000	42.00000	2.00000	2.00000
DESIGN VALUE	41.1	41.1		

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QH4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: ACIDITY (CACO3)

MG/L

			- 1 ₅ .		SAMPL	E RÉS	ULTS		
		401	L		402		403		404
LAB									
U877	<	5.		۲	5.	<	1.6	۲	1.4 5.
TOTAL LABS	REPORT	ING	2			2		2	2
TOTAL LABS	USED		0			0		1	1
MEAN		0. 00	000		0.000	0 0	1.6000	Ò	1.40000
STO DEV		0.00	000		0 • 0 0 0 (0 0	0.0000	0	0.00000
HEDIAN		0.00	000		0.0001	0 0	1.6000	0	1.40000





QN4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. Parameter: Ph

PH UNITS

SAMPLE RESULTS

	401	402	403	404
LAB				
U001 U014 U049 U075 U077 U089 U091	7.39 7.8 7.90 7.59 7.86 7.66 7.65	7.66 7.1 7.75 7.60 7.90 7.71 7.65	5.28 5.6 5.6 5.6 5.6 5.6 5.6 5.7 5.5 5.7	5.650 5.650 5.6640 5.650 5.6400 5.64000 5.64000 5.64000 5.64000000000000000000000000000000000000
TOTAL LABS REP	PORTING 7	7	7	7
TOTAL LABS USE	ED 7	7	7	7
MEAN	7.69286	7.62429	5.52143	5.51429
STO DEV	• 176 80	. 250 52	•11978	.07955
MEDIAN	7.66000	7.66000	5.60000	5.50000
DESIGN VALUE	7.69	7.69	5.48	5.48

DATA SUMMARY

QN4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. Parameter: Hardness

SAMPLE RESULTS

	401	402	403	404
LAB				
U001 U014 U049 U075 U089	44.3 47. 41.2 42.0 41.	44°2 46° 43°2 44°0 40°	141 • 8 146 • 142 • 142 • 142 •	142.8 143. 146. 140. 142.
TOTAL LASS	REPORTING 5	5	5	5
TOTAL LABS	USED 5	5	. 5	5
MEAN	43.10000	43.48000	143,16000	142.76000
STD DEV	2.54362	2.19818	1.82428	2.1 €51 8
MEDIAN	42.00000	44.00000	142.00000	142.80000
DESIGN VALUE	44.4	44.4	148	148

PAGE 15

MG /L

1

QM4 MAJOR IONS IN SURFACE HATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: SODIUM

NG /L

SAMPLE RESULTS

	401	402	403	404
LAB				
U001 U014	1.3	1.3	19.2	19.3
U049 U075	1.0	1.1 1.19	17.8	19•2 16•9 18•3
Ŭ077 U089	1.24 3.03	3. <u>0</u> 3		20.
ŬŎŸÍ	1.3	•7 1•3	18.5 19.2	18.5 19.3
TOTAL LABS	REPORTING 7	7	7	7
TOTAL LABS	USED 7	7	7	7
MEAN	1.45286	1.43143	18.88571	18.78571
STO DEV	. 74977	.74095	•71747	1.00404
MEDIAN	1.30000	1.30000	19.10000	19.20000
DESIGN VALUE	1.29	1.29	19.1	19.1

DATA SUMMARY

QH4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. Parameter: Magnesium

MG/L

SAMPLE RESULTS

	401	402	403 -	404
LAB				
U001 U014 U049 U057 U075 U077 U089 U089	2.7 2.9 2.91 2.84 2.44 4.0 2.6 2.70	2 • 6 2 • 8 2 • 97 2 • 83 2 • 33 4 • 0 2 • 4 2 • 70	9.2 9.6 10.3 9.46 8.655 9.0 9.2 9.26	9.25 9.52 9.52 9.52 9.6 9.0 9.0 9.0 9.0 9.0
TOTAL LABS	REPORTING 8	8	8	8
TOTAL LABS	USED 8	8	8	8
MEAN	2. 88625	2.82875	9.33375	9.29500
STD DEV	. 47716	•52018	• 48412	.53001
MEDIAN	2.77000	2.75000	9.23000	9.23000
DESIGN VALUE	2.74	2.74	9.38	9.38

QH4 MAJOR IONS IN SURFACE WATER

PRINTOUT	PREPARED #	86/11/20.	
PARANETER	SILICA	(SI02)	

MG/L

.

		SAMPLE R	ESULTS	
	401	402	403	404
LAB				
U 801 U 014	2.4	2.4	< . 02 •	< .02 < .02
Ŭ 057 U 077	2.5	2.4	W .1	< .02 W .1
Ü089 U091	1.16	2.5	< .1 W .02 < .01	< .02 W .1 < .1 W .02 < .01
UUJI	1. 17	1.14	< •0 <u>1</u>	< .01
TOTAL LABS REPO	DRTING 6	6	6	6
TOTAL LABS USED	6	6	0	0
MEAN	2.00000	2.00000	0.00000	0.00000
STD DEV	.65958	.65958	0.0000	0.0000
MEDIAN	2.40000	2.40000	0.00000	0.00000
DESIGN VALUE	2.38	2.38		
		2.00		•

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QM4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: TOTAL PHOSPHORUS MG/L

SAMPLE RESULTS

		401	·	402		403		404
LAB					•			· .
U 001 U014 U075 U077 U089 U089	K	.0035 .001 .1 .014 .002 .003	< T <	0028 002 1 015 001 001	< T <	.0009 .001 .1 .001 .001	~ ~ .	.0006 .001 .1 .019 .001 .001
TOTAL LABS	REPORTI	NG 6)	· 6	5	6	•	6
TOTAL LABS	USED	40	•	. 3	5	2	1	2
MEAN		. 00563	5	.00660)	.00095	ì	.00980
STD DEV		.00562	2	.00729)	.00007	•	.01301
MEDIAN		• 00 325	i	.00280)	.00095	;	.00980
						a ser se		

QM4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: SULPHATE

SAMPLE RESULTS

	401	402	403	404
LAB				
U 00 1 U 014 U 049 U 057 U 075 U 077 U 089 U 081	3.1 3.2 3.1 3.34 3.34 3.2 3.3 3.5 2.95	3.3 2.7 3.0 3.17 3.3 3.4 3.5 3.05	35.3 37.9 36. 40.1 42. 31. 36.0 37.55	37.6 37.2 32. 41.2 42. 32. 36.5 37.70
TOTAL LABS	REPORTING 8	8	8	8
TOTAL LABS	USED 8	8	. 8	8
MEAN	3. 21125	3.17750	36.98125	37.02500
STD DEV	• 16949	.25617	3.30821	3.66011
MEDIAN	3.20000	3.23500	36.77500	37.40000
DESIGN VALUE	3.32	3.32	37.1	37.1

PAGE 20

MG /L

QM4 MAJOR IONS IN SURFACE WATER

PRINTOUT PREPARED: 86/11/20. Parameter: Chloride

MG /L

SAMPLE RESULTS

•	401	402	403	404
LAB				
U001 U014 U057 U057 U075 U077 U089 U091	1.27 1.4 1.23 1.33 1.3 1.4 1.0 1.2	1 • 28 1 • 0 1 • 21 1 • 32 1 • 4 1 • 3 1 • 0 1 • 3	103.1 94. 94. 103. 163. 114. 105. 100.	103.4 91. 105. 106. 161. 115. 105. 110.
TOTAL LABS	REPORTING 8	8	8	8
TOTAL LABS	USED 8	8	8	8
MEAN	1.26625	1.22625	109.51250	112.05000
STD DEV	• 12961	•14899	22.54110	20.91800
MEDIAN	1.28500	1.29000	103.05000	105.50000
DESIGN VALUE	1.25	1.25	105	105

QN4 MAJOR IONS IN SURFACE HATER

PRINTOUT PREPARED: 86/11/20. PARAMETER: POTASSIUM MG/L

SAMPLE RESULTS

	401	402	403	404
LAB				
U 001 U 014	• 49 • 5 • 56	• 50 • 4	•91 •8	.91 .8_
Ŭ 049 U 075	• 56 • 34 • 5	• 57 • 37	•99	•97 •88 •9
U 077 U 089 U 091	• 5 • 60 • 51	• 5 • 50 • 51	9 85 94	•9 •85 •93
0021	• 7L	• 7 4	• 7 *	• 7 3
TOTAL LABS	REPORTING 7	7	7	7
TOTAL LABS	USED 7	7	7	7
MEAN	.50000	.47857	.89857	•89143
STO DEV	. 08 1 0 3	.06914	.06094	05521
MEDIAN	• 50000	.50000	.90000	.9000
DESIGN VALUE	0.488	0.488	0.884	0.884

.

DATA SUMMARY

PRINTOUT PREPARED: 86/11/20. Parameter: Calcium

MG /L

SAMPLE RESULTS

	401	402	403	404
LAB	•			
U 00 1 U 014 U 049 U 057 U 075 U 077 U 089 U 091	13.3 14.3 12.7 13.4 10.2 14. 12.0 13.1	13.4 13.8 12.9 13.2 10.0 13. 12.0 13.2	4123 423 455 455 455 455 455 455 455 45	42.0 41.6 43.4 5 36.3 40. 42.0 42.2
TOTAL LABS	REPORTING 8	8	8	8
TOTAL LABS	USED 8	. 8	8	8
MEAN	12.87500	12.68750	41.22500	41.50000
STD DEV	1.29587	1.20171	2.74838	2.47560
MEDIAN	13.20000	13.10000	42.05000	42.00000
DESIGN VALUE	12.5	12.5	42.4	42.4

Flagging and Youden's Ranking Procedures

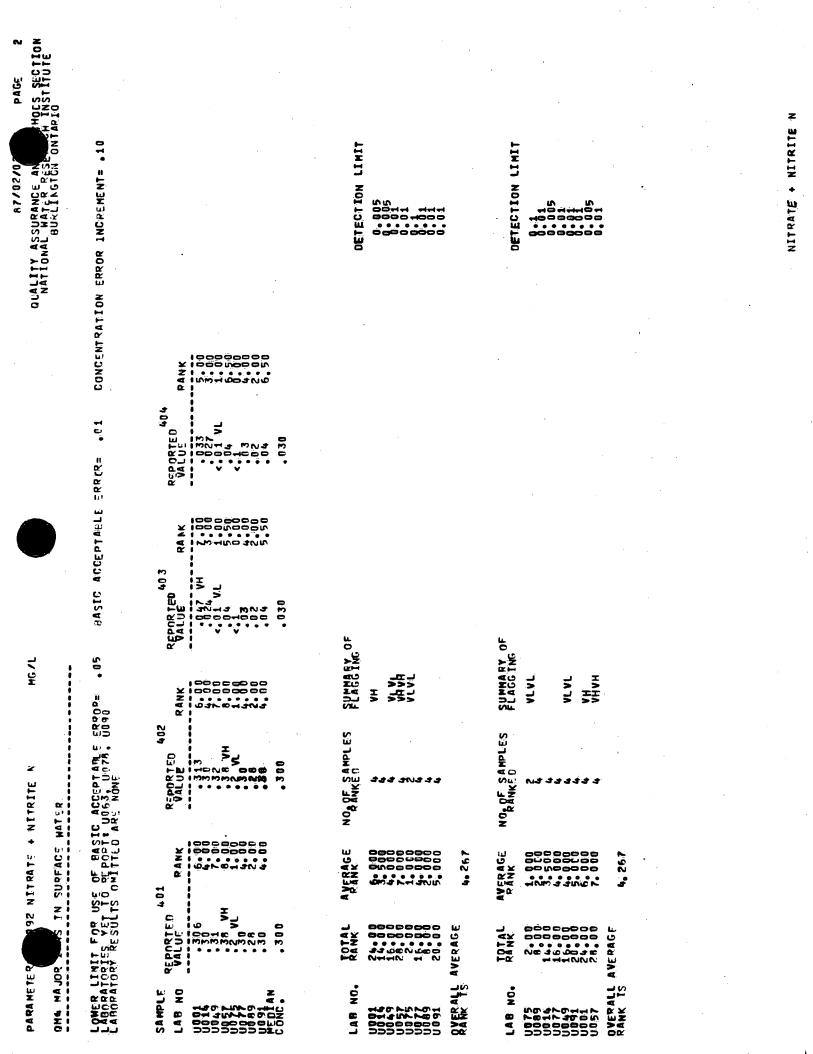
QM-4

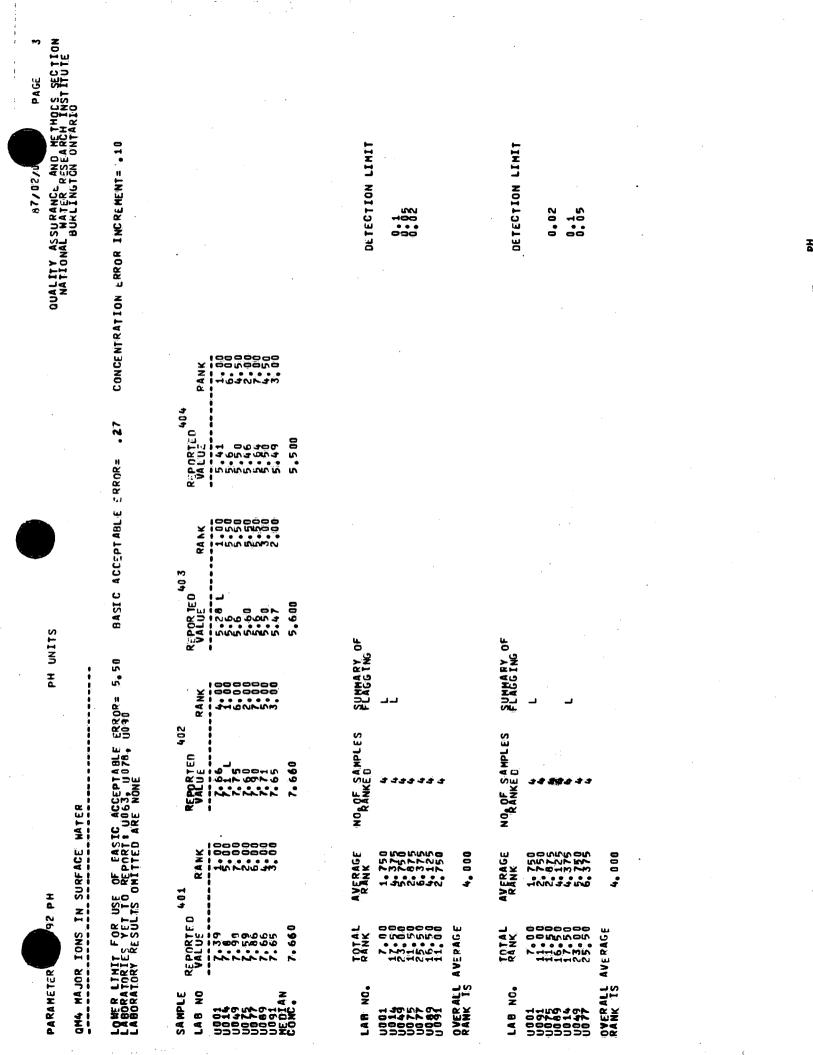
for

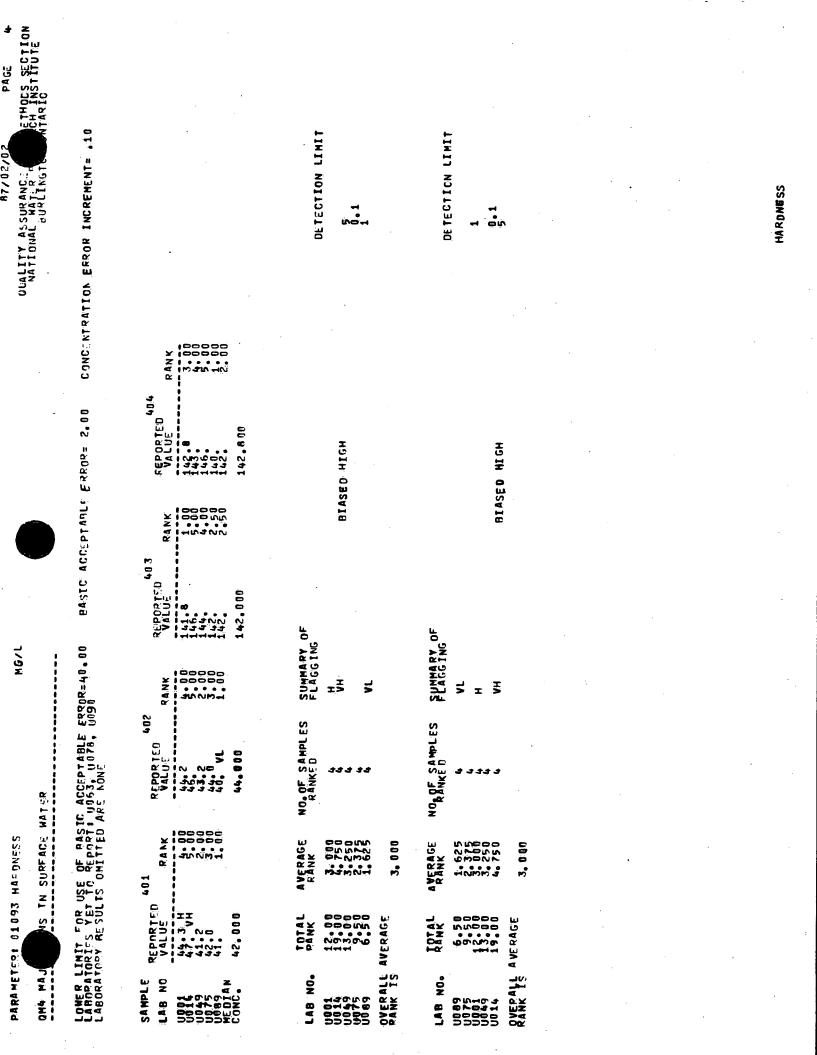
Conductivity, $(NO_3 + NO_2)N$, pH, Hardness, Na, Mg, SO₄, Cl, K and Ca

PAGE 1 ETHODS SECTION CH INSTITUTE					
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SODIUM

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	FRROP≈ 1.°25 U0:90		FSC MM FSC MM FSC FSC FSC FSC FSC FSC FSC FSC FSC FSC	FLAGGING LL LL LL LL LL LL LL LL LL LL LL LL LL
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I S	ATT FOR RTES VET RV RESUL	R R R R R R R R R R R R R R	A A A A A A A A A A A A A A	A A A A A A A A A A A A A A
PARAMETE	LOWER LI LABORATOR LABORATOR	CMCUCUCUCU CMCUCUCUCU CMCUCUCUCU CMCUCUCUCU	CUCUCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	NC NC NC NC NC NC NC NC NC NC

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• 50 IN SURFACE WATER QN4 HAJD

MG /L

PARANETERS 19091 POTASSIUM

CONCENTRATION ERROR INCREMENT= .01

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CALGIUM

APPENDIX III

UGLCC INTERLABORATORY PERFORMANCE EVALUATION STUDY

QM-4 Major Ions in Surface Water

Laboratory Appraisals

<pre>Status of Data (Refer to Appendix II - Date Files) 1a) No flags, no bias in the data set. b) No bias, only 1 minor flag (H or L). 2. No data or results reported by laboratory. 3. Data reported on less than half of the samples, no results flagged. 4. Same as Item 3, but some results are flagged. 5. No results are flagged but data set identified as hiased high or low</pre>	• • • • • •	<pre>Statement Produced in Appraisal (Appendix III) la) Satisfactory b) Satisfactory except for low/high flag on sample 2. No results reported. 3. Insufficient data to assess bias. 4. Flagged on sample and flagged on sample. Insufficient data to assess bias. 5. Although no results are flagged ranking indicates results are biased high/low.</pre>
No flags, no bias in the data set. No bias, only 1 minor flag (H or L). No data or results reported by laboratory. Data reported on less than half of the samples, no results flagged. Same as Item 3, but some results are flagged. No results are flagged but data set identified biased high or low.		for low/high flag on assess bias. e and flagged ient data to assess bias are flagged ranking e biased high/low.
No data or results reported by laboratory. Data reported on less than half of the samples, no results flagged. Same as Item 3, but some results are flagged. No results are flagged but data set identified		assess bias. eand flagged ient data to assess bias are flagged ranking e biased high/low.
Nata reported on less than half of the samples, no results flagged. Same as Item 3, but some results are flagged. No results are flagged but data set identified hiased hich or low		ufficient data to assess bias. ugged on sample , and flagged sample. Insufficient data to assess bias chough no results are flagged ranking licates results are biased high/low.
Same as Item 3, but some results are flagged. No results are flagged but data set identified		ugged on sample , and flagged sample. Insufficient data to assess bias though no results are flagged ranking licates results are biased high/low.
No results are flagged but data set identified		Although no results are flagged ranking indicates results are biased high/low.
6. Some results are flagged, the data set is discerned as biased.		Flagged on sample , ; Flagged on sample , Ranking indicates results are biased.
	7.	Flagged on sample and flagged on samples .
8. No bias statement but two or three results are flagged. One is very high, the other is very low.	œ	Flagged very high on sampleand very low on sample These results are slightly erratic.
9. No bias statement but two or more results are flagged very high and two or more results are flagged very low.	.	Flagged very high on samples and flagged very low on samples These results are erratic.
10. Results are ranked, the data set is not biased but one result is flagged very high or very low.	. 10.	Flagged on sample . This extreme result suggests the measurement process is out of control.
11. Less than values	1,1.	Unuseable values.

Parameter	Comments
Conductivity	Although no results are flagged, ranking indicates results are biased high
$(NO_2 + NO_3) N$	Flagged VH on sample 403
рH	Satisfactory, except flagged L on sample 403
Hardness	Satisfactory, except flagged H on sample 401
Sodium	Satisfactory
Magnesium	Satisfactory
Sulphate	Satisfactory
Chloride	Satisfactory
Potassium	Satisfactory
Calcium	Satisfactory
Turbidity	Comparable with data set
DOC	Comparable with data set
TKN	Comparable with data set
Alkalinity	401,402-Comparable with data set; 403,404-no results reported
Colour	No basis for comparison (all "<" values).
DIC	401,402-comparable with data set; 403,404-no basis for comparison (2 "<" values)
Ammonia N	No basis for comparison (all "<" values)
Fluoride	401,402-comparable with data set, 403,404-no basis for comparison (2 "<" values)
Silica	401,402,-comparable with data set, 403,404-no basis for comparison (2 "<" values)
Total P	401,402,403-comparable with data set, 404-no basis for comparison
Boron	No results reported
Total N	No results reported
Acidity	403,404-no basis for comparison, 401,402-no results reported

LABORATORY APPRAISAL FOR UGLCC STUDY QM-4

Your	Labora	tory	Code is:	U010

Parameter	Comments
Conductivity	NAPP
$(NO_2 + NO_3) N$	NAPP
рН	NAPP
Hardness	NAPP
Sodium	NÄPP
Magnesium	NAPP
Sulphate	NAPP
Chloride	NAPP
Potassium	ΝΑΡΡ
Calcium	No results submitted
Turbidity	NAPP
DOC	NAPP
TKN	NAPP
Alkalinity	NAPP
Colour	ΝΑΡΡ
DIC	NAPP
Ammonia N	NAPP
Fluoride	ΝΑΡΡ
Silica	ΝΑΡΡ
Total P	ΝΑΡΡ
Boron	No basis for comparison (all "<" values)
Total N	NAPP
Acidity	NAPP

NAPP - not applicable

Parameter	Comments
Conductivity	Satisfactory
$(NO_2 + NO_3) N$	Satisfactory
рН	Satisfactory, except flagged L on sample 402
Hardness	Flagged VH on sample 401. Ranking indicates result are biased high
Sodium	Satisfactory, except flagged H on sample 401
Magnesium	Satisfactory
Sulphate	Satisfactory, except flagged L on sample 402
Chloride	Flagged L on samples 402 and 404
Potassium	Flagged L on samples 402, 403 and 404
Calcium	Satisfactory
Turbidity	Comparable with data set
DOC	No results reported. TOC was reported
TKN	401,402-comparable with data set; 403,404-outliers by Grubbs & Dixon
Alkalinity	401,402-comparable with data set, 403,404-no basis for comparison (2 "<" values)
Colour	No results reported
DIC	No results reported
Ammonia N	No basis for comparison (3"<" values)
Fluoride	No basis for comparison (all "<" values)
Silica	401,402-comparable with data set, 403,404-no basis for comparison (2 "<" values)
Total P	401,404-no basis for comparison (2 "<" values), 402,403 comparable with data set
Boron	No results reported
Total N	No results reported
Acidity	No results reported

Parameter	Comments
Conductivity	Satisfactory
$(NO_2 + NO_3) N$	Results for samples 403 and 404 are unuseable ("<" values) which were flagged VL
рН	Satisfactory
Hardness	Satisfactory
Sodium	Flagged L on samples 401 and 404
Magnesium	Flagged H on samples 403 and 404. Ranking indicates results are biased high
Sulphate	Satisfactory, except flagged L on sample 404
Chloride	Satisfactory
Potassium	Flagged H on samples 403. Ranking indicates results are biased high
Calcium	Satisfactory
Turbidity	No results reported
DOC	401,402-comparable with data set, 403,404-no basis for comparison (2 "<" values).
TKN	Comparable with data set
Alkalinity	No results reported
Colour	No basis for comparison (all "<" values)
DIC	401,402-comparable with data set; 403,404-no basis for comparison (2 "<" values)
Ammonia N	401,402,403-no basis for comparison (401-"<" value), 404-comparable with data set
Fluoride	401,402-comparable with data set, 403,404-no basis for comparison
Silica	No results reported
Total P	No results reported
Boron	No results reported
Total N	No results reported
Acidity	No results reported

Parameter	Comments
Conductivity	Flagged VL on samples 401 and 402. Ranking indicates results are biased low
$(NO_2 + NO_3) N$	Flagged VH on samples 401 and 402
pH	No results reported
Hardness	No results reported
Sodium	No results reported
Magnesium	Satisfactory
Sülphäte	Satisfactory
Chloride	Satisfactory
Potassium	No results reported
Calcium	Satisfactory
Turbidity	No basis for comparison (all "W" values reported)
DOC	No results reported
TKN	Comparable with data set
Alkalinity	Comparable with data set
Colour	No basis for comparison (all "W" values reported)
DIC	No results reported
Ammonia N	404-comparable with data set, 401,402,403-no basis for comparison ("W" values reported)
Fluoride	401,402-comparable with data set; 403,404-no basis for comparison
Silica	401,402-comparable with data set; 403,404-no basis comparison ("W" values reported)
Total P	No results reported
Boron	No basis for comparison (403,404-"W" values)
Total N	No basis for comparison
Acidity	No results reported

.

Parameter	Comments		
Conductivity	Flagged L on samples 401 and 402		
(NO ₂ + NO ₃) N	Flagged VL on samples 401 and 402. Results for samples 403 and 404 were unuseable ("<" values)		
рН	Satisfactory		
Hardness	Satisfactory		
Sodium	Satisfactory		
Magnesium	Flagged L on sample 401 and VL on sample 402. Ranking indicates results are biased low		
Sulphate	Flagged H on samples 402 and 404		
Chloride	Flagged VH on samples 403 and 404		
Potassium	Flagged VL on samples 401 and 402		
Calcium	Flagged VL on samples 401, 402, 403 and L on sample 404. Ranking indicates results are biased low		
Turbidity	Comparable with data set		
DOC	Comparable with data set		
TKN	No basis for comparison (all "<" values)		
Alkalinity	Comparable with data set		
Colour	No results reported		
DIC	401,402-outliers by Grubbs & Dixon, 403,404-no basis for comparison		
Ammonia N	No basis for comparison (all "<" values)		
Fluoride	No results reported		
Silica	No results reported		
Total P	No basis for comparison (all "<" values)		
Boron	No results reported		
Total N	No results reported		
Acidity	No results reported		

Parameter	Comments
Conductivity	Satisfactory
$(NO_2 + NO_3) N$	Satisfactory
рН	Satisfactory
Hardness	No results reported
Sodium	Flagged VH on samples 401 and 402. Ranking indicates results are biased high
Magnesium	Flagged VH on samples 401 and 402
Sulphate	Flagged VL on sample 403 and L on sample 404
Chloride	Satisfactory, except flagged H on sample 403
Potassium	Satisfactory
Calcium	Satisfactory
Turbidity	Comparable with data set
DÓC	Comparable with data set
TKN	No basis for comparison (all "<" values)
Alkalinity	401,402-comparable with data set, 403,404-no basis for comparison (2 "<" values)
Colour	401,402-comparable with data set, 403,404-no basis for comparison
DIC	401,402-comparable with data set, 403,404-no basis for comparison
Ammonia N	No basis for comparison (all "<" values)
Fluoride	No basis for comparison (all "<" values)
Silica	401,402-comparable with data set; 403,404-no basis for comparison (2 "<" values)
Total P .	401,402-outliers by Grubbs & Dixon, 403-no results 404-no basis for comparison
Boron	No basis for comparison (all "<" values)
Total N	No results reported
Acidity	No basis for comparison (all "<" values)

Parameter	Comments
Conductivity	Satisfactory
$(NO_2 + NO_3) N$	Satisfactory
рĤ	Satisfactory
Hardness	Flagged VL on sample 402
Sodium	Flagged VL on samples 401 and 402
Magnesium	Satisfactory, except flagged L on sample 402
Sulphate	Satisfactory
Chloride	Flagged L on samples 401 and 402
Potassium	Satisfactory, except flagged H on sample 401
Calcium	Satisfactory
Turbidity	Comparable with data set
DOC	No results reported
TKN	401,402,404-comparable with data set; 403-no basis for comparison ("W" value)
Alkalinity	Comparable with data set
Colour	401,402-comparable with data set; 403,404-no basis for comparison (2 "<" values)
DIC	No results reported
Ammonia N	No basis for comparison (all "W" values)
Fluoride	No basis for comparison (all "<" values)
Silica	401,402-comparable with data set, 403,404-no basis for comparison (2 "W" values)
Total P	401,402,403-comparable with data set; 404-no basis for comparison ("W" value)
Boron	No results reported
Total N	No results reported
Acidity	No results reported

Parameter	Comments	
Conductivity	Satisfactory	
$(NO_2 + NO_3) N$	Satisfactory	
рН	Satisfactory	
Hardness	No results submitted	
Sodium	Satisfactory	
Magnesium	Satisfactory	
Sulphate	Satisfactory	
Chloride	Satisfactory	
Potassium	Satisfactory	
Calcium	Satisfactory	
Turbidity	402,403,404-comparable with data set, 401-no result reported	
DOC	No results reported	
TKN	Comparable with data set	
Alkalinity	Comparable with data set	
Colour	401,402-comparable with data set; 403,404-no basis for comparison (2 "<" values)	
DIC	No results reported	
Ammonia N	401,402,403-no basis for comparison, 404-comparable with data set	
Fluoride	No basis for comparison (all "<" values)	
Silica	401,402-comparable with data set; 403,404-no basis for comparison (2 "<" values)	
Total P	401-comparable with data set, 402,403,404-no basis for comparison (3 "<" values)	
Boron	No results reported	
Total N	No results reported	
Acidity	No results reported	

Parameter	Comments
Conductivity	N.A.
$(NO_2 + NO_3) N$	Comparable with data set
рН	N.A.
Hardness	Comparable with data set
Sodium	N.A.
Magnesium	N.A.
Sulphate	N.A.
Chloride	401,402-outliers by Grubbs & Dixon; 403,404-comparable with data set
Potassium	N.A.
Calcium	N.A.
Turbidity	N.A.
DOC	N.A.
TKN	N.A.
Alkalinity	N.A.
Colour	N.A.
DIC	N.A.
Ammonia N	No basis for comparison (all "<" values)
Fluoride	N.A.
Silica	401,402-"<" values, 403,404-no basis for comparison
Total P	402-no basis for comparison ("<" value); 401,403,404-outliers by Grubbs & Dixon
Boron	N.A.
Total N	N.A.
Acidity	N.A.

NA - not analyzed

APPENDIX IV

LATE DATA SUBMITTED FOR

UGLCC INTERLABORATORY STUDY

<u>QM-4</u>

LATE DATA SUBMITTED BY LABORATORY U013

(Received on October 17, 1986)

	Sample (mg/l)				Detection
	401	402	403	404	Limit
nitrite + nitrate N	0.3	0.21	.02	.02	.01
ammonia N	<.005	<.005	<.005	<.005	.005
hardness	42	43	148	148	2
silica (SiO ₂)	<.02	<.02	2.60	2.59	.02
total phosphorus	3	<1	1	1	.5
chloride	.4	•4	102	103	Nd*

* Nd - not determined (all other parameters were Nd*)

Methodology

$(NO_2 + NO_3)N$	- colorimetry, Cu-Cd reduction (azo dye)
Ammonia N	- colorimetry, phenate
Hardness	- colorimetry, EDTA chelate
Silica	- colorimetry, molybednum blue
Total P	- colorimetry, phosphomolybdate blue
Chloride	- colorimetry; ferric thiocyanate

CHANGES TO DATA SUBMITTED BY LABORATORY U013

(Received on December 2, 1986)

	Sample (mg/l)				Criterion of
	401	402	403	404	Detection
nitrite + nitrate N	0.3	0.21	T.02	T.02	0.2
ammonia N	W	W	Ŵ	W	.0.1
hardness	42	43	148	148	30
silica (SiO ₂)	W	W	2.60	2.59	0.5
total phosphorus	T.003	W	T.001	T.001	.005
chloride	T.4	T.4	102	103	6

(all other parameters were Nd* = Not Determined)