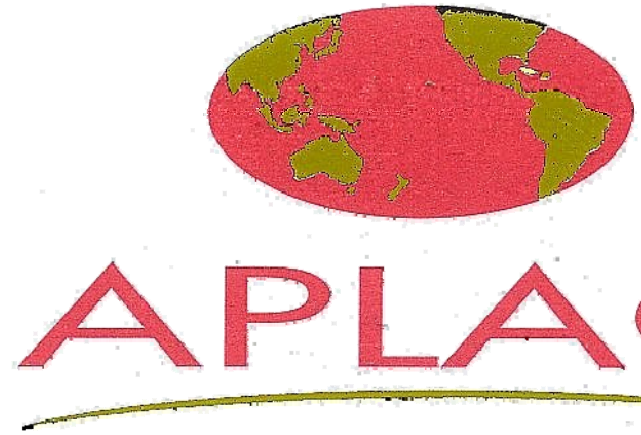


BOD, COD, NO2+NO3 & NH3 in Wastewater

Proficiency Testing Program

APLAC T062

FINAL REPORT

23 June 2009

Organized by
Standards Council of Canada
in partnership with
the Centre d'expertise en analyse environnementale du Québec (CEAEQ)

Under the Auspices of
The Asia-Pacific Laboratory Accreditation Cooperation



Standards Council of Canada
Conseil canadien des normes

Centre d'expertise
en analyse
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Québec

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CEAEQ is accredited as a proficiency testing provider (CAN-P-1593 and CAN-P-43) by the Standards Council of Canada (SCC) and is presently on the list of approved Proficiency Testing providers for SCCs Program Specific Area (PSA) Environmental Testing program. Their accreditation scope covers the Proficiency Testing measurands/matrix of this APLAC T062 Proficiency Testing Program. The CEAEQ also has extensive expertise and is an ISO/IEC 17025 accredited laboratories by the SCC since December 1999.

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Summary of Results

1. The proficiency testing (PT) programme, APLAC T062, was conducted in August and September 2008.

2. A total of 77 laboratories from 18 economies (21 accreditation bodies) participated in the program and 76 laboratories submitted their results. Of the 77 laboratories, 66 laboratories were accredited for all measurands, 6 laboratories were accredited for some of the measurands and 5 laboratories were not accredited for any of the measurands (3 of these are accredited for other measurands). The two (2) non accredited laboratory's performance was as good as the majority of the accredited laboratories.

3. The program was specifically designed to evaluate some of the most commonly used measurands for monitoring of wastewater effluents: Biochemical Demand for Oxygen (BOD_5), Chemical Demand for Oxygen (COD), Nitrites plus Nitrates (NO_2+NO_3) and Nitrogen Ammonia (NH_3). The PT program consisted of three samples for BOD_5 and three samples for COD with no preservative, NO_2+NO_3 and NH_3 preserved with sulfuric acid 0.1% in 250 mL Nalgene™ bottles. The Biochemical Demand for Oxygen (BOD_5) test was a 5 day test and the laboratories were required to seed the samples (polyseed or natural seeding) for this analysis.

4. Z-scores were used to evaluate the performance of the participants.

5. Results of this PT programme are summarized as follow:

Measurand (units)	Sample No.	Assigned value (Robust average)	Total number of reported results	No. of laboratories with satisfactory z-scores	% of laboratories with satisfactory z-scores
BOD_5 (mg O_2/*l*)	1	134	72	55	76.4%
	2	334	71	61	85.9%
	3	194	72	57	79.2%
COD (mg O_2/*l*)	1	83.1	71	47	66.2%
	2	401	71	55	77.5%
	3	716	72	55	76.4%
NH_3 (mg N/*l*)	1	5.65	73	56	76.7%
	2	4.09	71	53	74.6%
	3	15.1	72	54	75.0%
NO_2+NO_3 (mg N/*l*)	1	3.39	67	47	70.1%
	2	44.8	66	45	68.2%
	3	29.5	68	48	70.6%

1: Foreword

This report summarizes the results on the ***APLAC T062 BOD, COD, NO2+NO3 & NH3 in Wastewater Proficiency Testing Program*** for testing laboratories on behalf of the Asia Pacific Laboratory Accreditation Cooperation (APLAC). The Standards Council of Canada coordinated the program in cooperation with our collaborator, the Centre d'Expertise en Analyse Environnementale du Québec. The program covered the analysis of biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), nitrites plus nitrates (NO_2+NO_3) and ammonia (NH_3) in wastewater.

2: Introduction

2.1 Objectives for the Evaluation

Water is essential for life and it is used in various economic activities. Agriculture, fishing, industrial production, recreational activities, sanitary installation and of course consumption, all need a good source of water quality. Water pollution is a major problem for many countries and wastewater treatment is one of the solutions to reduce it. Therefore laboratory results comparable in wastewater monitoring around the world is essential.

The primary objective of this proficiency testing program specifically was to evaluate some of the most commonly used measurands for monitoring of wastewater effluents and to make sure wastewater can be tested around the world with similar results. Biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), nitrite plus nitrate (NO_2+NO_3) and ammonia (NH_3) were chosen as the tested measurands since they are the most commonly used in wastewater monitoring. The PT program consisted of three samples for BOD_5 and three samples for COD with no preservative, NO_2+NO_3 and NH_3 preserved with sulfuric acid 0.1% in 250 mL Nalgene™ bottles. The Biochemical Demand for Oxygen (BOD_5) test was a 5 day test and the laboratories were required to seed the samples (polyseed or natural seeding) for this analysis.

This program also had a secondary objective: to compare the results of this proficiency testing program with the results from laboratories that are required to participate in a regular accredited proficiency testing program. Thus, the results of this program were to be compared with the results obtained from Quebec provincial laboratories (Canada) that participated on a continual basis in the same evaluation with the same samples that were provided to the participants of this program.

Information on the analysis methods used by the participating laboratories was provided along with the results. A graphic presentation of the performance of each method is also part of this report.

2.2 Participants in the Evaluation

On the 10th April 2008, the SCC send a letter detailing the study to appropriate APLAC and IAAC Accreditation Bodies requesting that they nominate laboratories in their respective economies to participate in this study. Included in the invitation was the number of participants allowed, a description of the samples (matrix, concentration range) and measurands to be analyzed and a nomination form to be completed for each participant. It was indicated that preference will be given to the laboratories that are accredited for the test. Information provided was used to register the laboratories and assigned a unique identification for reporting PT results. The deadline for returning the nomination form was 26th May 2008.

A total of 77 laboratories from 18 economies (21 accreditation bodies) participated in the program. APLAC and IAAC member laboratory accreditation bodies were invited to participate. 76 laboratories submitted their results. The details of the participating economies, accreditation bodies and number of laboratories from that Accreditation Body are presented in Annex A.

3: Design and Implementation

3.1 Sample Preparation and Distribution

Three samples for BOD_5 and three samples for COD with no preservative, NO_2+ NO_3 and NH_3 preserved with sulphuric acid 0.1 % in 250 ml Nalgene™ bottles were prepared in large batches of 50 litres, well homogenized and dispensed to individually uniquely labelled bottles.

The 3 samples for each set had concentrations that were unique, randomly spanning the concentration ranges for each measurand within the low to high concentrations identified in the following table:

Measurand	Concentration range
BOD_5	From 50 to 500 mg O_2/l
COD	From 15 to 1000 mg O_2/l
NO_2+NO_3	From 1 to 100 mg N/l
NH_3	From 0.5 to 20 mg N/l

A different concentration level was chosen for each sample. The matrix used was an effluent from a Quebec wastewater facility. Standard solutions of the measurands were added to the matrix to obtain the desired concentrations.

Each bottle was identified with a unique serial number. The bottle serial numbers were randomly distributed to each laboratory.

3.2 Homogeneity and Stability Testing

Homogeneity was evaluated for each sample with the analysis of 10 replicates randomly selected among the bottles. All the measurands were analysed for each sample by the CEAEQ's SCC accredited laboratory. The between-samples standard deviation (S_s) was compared to the inter laboratory standard deviation (σ_{pt}). The samples were considered adequately homogeneous if

$$S_s \leq 0.3\sigma_{pt}$$

The individual test results for each sample and measurand for the homogeneity verification is found in Annex D.

The samples were stabile for months. Replicates kept at 4°C since August 2008 were analysed in February 2009 for stability verification. All the measurands were analysed for each sample by the CEAEQ's SCC accredited laboratory. The samples were considered stable if the difference between the stability results (X) with the reference value (Y) from homogeneity testing is lower than $0.3\sigma_{pt}$.

$$|X - Y| \leq 0.3\sigma_{pt}$$

The individual results for each sample and measurand from the stability verification is found in Annex D.

3.3 Samples distribution

The samples were labelled as APLAC-PT 062 – Wastewater samples 1, 2 and 3 with identification of measurands and preservative agent.

A package was prepared and labelled for each participating laboratory. Hardcopies of the "*APLAC T062 instruction letter for laboratory.doc*", "*APLAC T062 receipt of samples acknowledgement form (for laboratories).doc*", "*APLAC T062 Information on analysis method.doc*" as well as a reporting form spreadsheet customized for each laboratory (*"APLAC-01_1xxxxx.xls")* were enclosed in each individual package. Each participating laboratory was identified with a confidential unique laboratory code number.

A bulk package containing individually labelled packages for the participating laboratories was prepared for each Accreditation Body. A hardcopy of the "*APLAC T062 instruction letter for AB.doc*" and "*APLAC T062 receipt of samples acknowledgement form (for AB).doc*" was enclosed in each bulk package.

An electronic copy of all the documents and report files was also send to each Accreditation Body by email on August 14th 2008 with detailed instructions to forward the appropriate electronic documents and unique reporting spreadsheet to their participating laboratories. Refer to Annex H for these documents and forms.

The bulk package with the PT samples was send via courier to the Accreditation Bodies on August 18th 2008. Each AB was responsible to distribute the individually labelled packages to their participating laboratories and forward via email the appropriate electronic documents and unique reporting spreadsheet to their participating laboratories. Each Accreditation Body had to acknowledge via email the receipt of the samples to the Coordinator of the APLAC T062 PT program before August 28th 2008 employing the "*APLAC T062 receipt of samples acknowledgement form (for AB).doc*".

The participating laboratories had to acknowledge via email the receipt of their PT samples before September 5th 2008 to their Accreditation Body and the Coordinator of the APLAC T062 PT program employing the "*APLAC T062 receipt of samples acknowledgement form (for laboratories).doc*". The laboratories had to analyse and return their results to their Accreditation Body before October 3rd 2008 employing the customized *"APLAC-01_1xxxxx.xls"* spreadsheet along with their completed "*APLAC T062 Information on analysis method.doc*". The Accreditation Body had to report the laboratory's data (spreadsheet) and methods document to the Coordinator of the APLAC T062 PT program before October 8th 2008.

3.4 Sample results reception

Each of the participants was randomly allocated a unique confidential code number and provided their own uniquely numbered *"APLAC-01_1xxxxx.xls"* spreadsheet. All reference to the participants in this report is via the code they were allocated. The laboratories reported their results with the associated measurement uncertainty, where available. Additional information on the analysis method used for each measurand was also reported by the participants on the supplied "*APLAC T062 Information on analysis method.doc*". All results were registered in a database used for the statistical analysis.

Only one laboratory did not analyse or report results for any of the PT samples. Twelve laboratories did not send results for all the measurands included in the study and five did not provide results for all the samples but did analyse all the measurands include in the study. Overall, an average of 72 results (out of a possible 77) was registered for each sample and measurand. The results with associated uncertainty values reported by each laboratory are shown in Annex B.

4: Statistical Evaluation of Results

Proficiency testing by interlaboratory comparisons is used to determine the performance of individual laboratories for specific tests or measurements. This APLAC T062 PT program used the ISO/IEC Guide 43 and ILAC G13 protocols as well as those outlined in APLAC PT 002 ("*APLAC Testing Interlaboratory Comparison"*). All statistical methods used for the assessment of the laboratories are described in the ISO 13528:2005, *"Statistical methods for use in proficiency testing by inter laboratory comparisons"*, Geneva, Switzerland.

4.1 Determination of the assigned values and standard deviations:

The assigned value was calculated employing the consensus value from participants and is the robust average of the results reported by all participants in the round using robust statistics as determined by Algorithm A in ISO 13528. The details concerning this calculation method are described in Annex I. With this robust method the outliers have no influence on the values of the robust estimates.

The standard deviation σ_{pt} used to assess the proficiency of participants was also derived from the results reported by the participants in the round. It is the robust standard deviation reported by all participants, also calculated using the Algorithm A in ISO 13528.

4.2 Determination of the uncertainty of the assigned value

Statistically, the assigned value from any PT round has a standard uncertainty μ_x that depends on the method that is used to derive it, and also, when it is derived from tests in several laboratories, on the number of laboratories and perhaps on other factors. If the standard uncertainty μ_x of the assigned value is too large in comparison with the standard deviation for proficiency testing σ_{pt}, then there is a risk that some laboratories will receive action and warning signals because of inaccuracy in determination of the assigned value, not because of any cause within the laboratories.

When the assigned value is derived as a robust average calculated using Algorithm A, the standard uncertainty of the assigned value X is estimated as:

$$\mu x = 1{,}23 \times s^* / \sqrt{p}$$

Where s* is the robust standard deviation of the results calculated using Algorithm A.

If:

$$\mu x \leq 0.3 \sigma pt$$

Where, σ_{pt} is the standard deviation used to assess proficiency.

When the standard uncertainty of the assigned value is negligible it not need be included in the interpretation of the results of the proficiency test.

The standard uncertainty of each assigned value was estimated and compared with the standard deviation for proficiency testing. For all assigned values for every measurand, the calculated standard uncertainty was negligible and was not included in the interpretation of the results.

The expanded uncertainty (U) values for each sample reported by the laboratories are found in the tables in Annex B.

4.3 Z-score calculation

The z-scores were calculated using the assigned value and the standard deviation calculated from the results of the participants as:

$$z = |x - X| / \sigma_{pt}$$

Where σ_{pt} is the standard deviation for proficiency assessment, X is the assigned value and x the laboratory result.

The z-scores were interpreted and evaluated as follows:

(a) $|z| \leq 2$ Satisfactory
(b) $2 < |z| < 3$ Questionable
(c) $|z| \geq 3$ Unsatisfactory

The z-scores and their evaluations are found in Annex C.

Laboratories having a z-score > 3 or < -3 should thoroughly investigate their results. Also, the laboratories having a z-score in the range $2 < |z| < 3$ are encouraged to review the results.

Because of the number of participants, samples and parameters, only ordered z-scores bar-charts were done for each sample as graphic presentation of the z-score. On these charts each laboratory's z-score is shown, in order of magnitude and is marked with its code number. The ordered z-score bar charts of the results are found in Figures C.1 to C.12.

An interim report containing the participant's results and the respective z-score results was issued to participants and their Accreditation Bodies on 2nd December 2008. Participants were requested to check the correctness of their submitted data and to inform the organizers of any transcription errors on or before 15th December 2008.

A draft final report was distributed to the Accreditation Bodies for circulation to their participant laboratories on 17th April 2009 for their review and comments. They were requested to provide any comments by the 1st May 2009.

5: Technical comments and discussion

5.1 Results

A total of 77 laboratories from 18 economies (21 accreditation bodies) participated in the program and 76 laboratories submitted their results. Of the 77 laboratories, 66 laboratories were accredited for all measurands, 6 laboratories were accredited for some of the measurands and 5 laboratories were not accredited for any of the measurands (3 of these are accredited for other measurands).

The two (2) non accredited laboratory's performance was as good as the majority of the accredited laboratories. The results reported from the participants are detailed in the Tables in Annex B.

An overall summary of the results of this PT program are summarized as follow:

Measurand (units)	Sample No.	Total number of reported results	Assigned value (Robust Average)	Standard deviation for proficiency assessment (σ_{pt})	Standard uncertainty of the assigned value (μ_x)
BOD_5 (mg O_2/*l*)	1	72	134	32.0	4.71
	2	71	334	95.8	14.24
	3	72	194	41.1	6.04
COD (mg O_2/*l*)	1	71	83.1	10.6	1.655
	2	71	401	29.2	4.303
	3	72	716	36.3	5.303
NH_3 (mg N/*l*)	1	73	5.65	1.21	0.177
	2	71	4.09	0.77	0.114
	3	72	15.1	1.88	0.277
NO_2+NO_3 (mg N/*l*)	1	67	3.39	0.63	0.098
	2	66	44.8	10.4	1.602
	3	68	29.5	4.29	0.65

The z-scores of the individual participants and their evaluations are presented in the tables in Annex C and the ordered z-scores bar charts of the results are in Figures C.1 to C.12 within Annex C. The z-score performance of the participants is summarized as follows:

Measurand (units)	Sample No	Total No. Results reported	$\|z\| \leq 2$		$2 < \|z\| < 3$		$\|z\| \geq 3$	
			No.	%	No.	%	No.	%
BOD_5 (mg O_2/*l*)	1	72	55		8		9	
	2	71	61		4		6	
	3	72	57		8		7	
	Total:	**215**	**173**	**80.5%**	**20**	**9.3%**	**22**	**10.2%**
COD (mg O_2/*l*)	1	71	47		4		20	
	2	71	55		1		15	
	3	72	55		4		13	
	Total:	**214**	**157**	**73.4%**	**9**	**4.2%**	**48**	**22.4%**
NH_3 (mg N/*l*)	1	73	56		6		11	
	2	71	53		6		12	
	3	72	54		7		11	
	Total:	**216**	**163**	**75.5%**	**19**	**8.8%**	**34**	**15.7%**
NO_2+NO_3 (mg N/*l*)	1	67	47		2		18	
	2	66	45		8		13	
	3	68	48		4		16	
	Total:	**201**	**140**	**69.7%**	**14**	**7.0%**	**47**	**23.4%**
Overall Totals:		**846**	**633**	**74.8%**	**62**	**7.3%**	**151**	**17.8%**

The individual measurement uncertainty estimates provided by the participants is found in the tables in Annex B. In reviewing these reported values it became apparent that there certainly are vast differences in the estimated uncertainties reported. It would appear that some laboratories are severely underestimating uncertainty while others are overestimating these values. For the NH_3 and NO_2+NO_3 data, in particular, the majority of the reported values are unrealistically low given the low concentrations of some of the samples.

The table below summarizes the lowest and highest expanded uncertainties (U) reported by participants. Some laboratories did not report any uncertainty for their results. The last column is provided for comparison and is calculated from the calculated standard uncertainty (μ_x) of the assigned value from all reported results and is provided solely for informational purposes as a potential reference point.

Measurand	Sample No	Total No. Results reported	Assigned value (Robust Average)	Expanded Uncertainties (U) reported by participants		Estimated Expanded Uncertainty (U) of the assigned value[1]
				lowest	highest	
BOD_5 (mg O_2/*l*)	1	72	134	0.057	63	9.42
	2	71	334	0.057	172	28.48
	3	72	194	0.057	550	12.80
COD (mg O_2/*l*)	1	71	83.1	0.05	25	3.31
	2	71	401	0.05	118.68	8.61
	3	72	716	0.05	716	10.6
NH_3 (mg N/*l*)	1	73	5.65	0.000	4.88	0.354
	2	71	4.09	0.006	4.88	0.228
	3	72	15.1	0.002	4.88	0.554
NO_2+NO_3 (mg N/*l*)	1	67	3.39	0.013	7.36	0.196
	2	66	44.8	0.006	8.2	3.204
	3	68	29.5	0.012	8.7	1.30

1. For simplicity it is assumed that the standard uncertainty of the assigned value in the summary of results table above is multiplied by k=2 (i.e. approximate 95% confidence)

Because of the extreme range of the expanded uncertainty results reported, it was not possible to graph those results for each sample set. Hence, to facilitate a visual comparison of the range of reported expanded uncertainty values, the reported expanded uncertainty was transformed into a percentage of the analytical result reported by the laboratory. While this an unusual approach, these values were plotted together by measurand to illustrate the vast dispersion of the reported uncertainties (Figures H1 to H12). Some laboratories reported the expanded uncertainty as a negative value only, others with ± range, some reported expanded uncertainty as a percentage

(unacceptable but GUM results) and still others as a single value. For the same measurand the values reported ranged from 0.5% to more than 60% of the reported result. Multiple laboratories had the same value as uncertainty for each result. This leads to too small and uncertainty with higher concentration or too excessively large with smaller concentration. This can be dramatically seen in Figures H.4 to H.6 for the COD results where the means of the samples ranged from 83 mg O_2/l to 716 mg O_2/l.

It is strongly recommended that the laboratories re-evaluate their calculated uncertainties. Because of the extreme values reported it is also strongly recommended that Accreditation Bodies review their accredited laboratory's procedures for estimating uncertainty.

5.2 Adverse effects of irradiation on the sample stability

Gamma irradiation of packages at their entrance in the country is a courant practice in certain countries. When the interim results were analyzed by the participants and Accreditation Bodies in mid December 2008, one economy questioned whether stability problems were experienced from the high gamma irradiation of the PT samples entering their economy. Consistent unsatisfactory results were obtained (all results on all samples/measurands were low) for all the participant laboratories that had their PT samples undergoing irradiation before entering their economy.

To put this in perspective, this represents 4 sample sets (12 samples/set) out of a total of 77 samples sets shipped, or 5.2% of the total number of samples sent to all participants (48 samples out of 924 samples).

The usual treatment by gamma-irradiation was 50 kGy for all samples entering that economy. In cooperation with that economy, in February - March 2009, comparisons were done between sample replicates of the same APLAC T062 batch sent to the original participants and they were processed as follows:

- One complete set of samples were re-send to the economy to be irradiated and send back to be analysed by our CEAEQ reference lab in Canada;
- One complete set of samples were not irradiated and were analysed by our CEAEQ reference lab in Canada at the same time as the returned irradiated samples.

Irradiation significantly affected the concentration of all the measurands in all the samples from that economy. Our CEAEQ reference laboratory did obtain similar low results as the participant laboratories which originally reported low results on all samples and measurands. Detailed results and pictures of the samples before and after irradiation are shown in Annex E clearly indicating this adverse effect. More detailed investigation are still being conducted to see if the adverse effects of irradiation on our PT samples could be prevented in the future.

It should be stated, however, that the reported results from these irradiated samples from this economy did not affect the final data analysis for any of the assigned values and standard deviations. As indicated in 4.1, the robust statistics employed ensured that any outliers had no significant influence on the values of the robust estimates for the assigned values and standard

deviations. This was verified by removing the irradiated sample sets from the overall data set and comparing the final data obtained. Hence there was no reason to exclude the data from the final analysis of the results.

5.3 Graphic comparison of the method performances

Participating laboratories were asked to describe the analytical methods used in the APLAC T062 program using the "*APLAC T062 Information on analysis method.doc*" form. Each method described was regrouped in similar categories in order to present trends in their performance.

No statistical assessments were made regarding methods performance. Therefore, the graphical displays in Appendix F are only informational. Data are presented as percentage of laboratories obtaining satisfactory, questionable and unsatisfactory results using a particular method. Since some of the methods were used only by a small number of laboratories, no conclusion can be made on the real performance of the method (e.g. If only 3 laboratories used method X and all of them failed, we would find that, for this study, 100% of laboratories that used method X have an unsatisfactory results).

On the other hand, these graphical displays provide information on the 'popularity' of specific methods and their integration in laboratories as routine methods.

One common concern about the use of consensus means for the assigned value is when a single method dominates the population, and the possibility of the effect that a method bias can have on the mean and standard deviation and thereby on the evaluation of laboratories using a different method. There are clear differences in performance for the most frequently used methods for BOD_5 and COD. In both the BOD_5 and COD there is one method used by more than 50% of labs, and the performance is generally better in that group, as apparent in graphs F.1 and F.2.

While we did no statistical assessments on the method performances, but we did compare the assigned value with the preparation value or expected value. This preparation value is showed in the Tables C1 to C4. For most of the samples, the assigned value is close to the preparation value.

Difficulties of some laboratories in order to get a satisfying performance can be related to the choice of method but could be induced by some deficiencies in the assurance quality program and maintenance of equipment. In general, good practices like instrument calibration and maintenance, the use of reference material in real matrices (when it is possible), fortified samples and different sources of reference material in addition of the use of standards are very important.

Problems with the Biochemical Oxygen Demand (5 days) could be related to the type of seed used. Validation with other sources is very important. The electrode membrane is also a source of problems if the maintenance is inadequate. The incubation temperature should be monitored when performing the method and should comply with the requirements of the method. The sample pH should be verified and adjusted if necessary. The standard procedures recommend a pH of 7.0 ± 1.0.

Problems with the Chemical Oxygen Demand vary upon the method used. For example, closed reflux colorimetric methods used commercial kit of reagents. Verification of each lot before using them is very important. The monitoring of the distillation temperature is also critical. Distillation temperature and time are also very important with the open reflux method and should be monitored and the requirements of the method should be followed.

Finally, the acidification of the samples for the Nitrites + Nitrates analysis transforms the nitrites into nitrates. For the laboratory using a Cadmium reduction as pre treatment, they should put emphasis on the frequency of the column regeneration. Acidification could be a problem with some methods because of the pH and the presence of sulphates. Sulphates are a major interference with Chromatographic ionic method. Precautions are therefore important to eliminate the impact of the sulphates on the results.

5.4 Comparison with Quebec laboratories performance

In Canada, environmental laboratories accredited by Standard Council of Canada are required to participate twice a year in available proficiency testing programs in order to maintain their SCC accreditation. The province of Quebec has an accreditation program with the Ministère du Développement durable de l'Environnement et des Parcs concerning Quebec environmental analytical laboratories for regulation purposes. The Quebec accreditation program (PALA) complies with ISO/IEC 17025:2005, *General requirements for the competence of testing and calibration laboratories*. A Proficiency Testing program (accredited by SCC) is part of the Quebec accreditation program. Quebec laboratories must participate, twice a year, in this SCC accredited proficiency testing program to maintain their Quebec accreditation. This mandatory participation has been in place since 1990 for the measurands/matrix in this study. Thus, comparing the results obtained by the APLAC T062 participants with Quebec laboratories that continually participate in the CEAEQs SCC accredited proficiency testing program for these measurands was a secondary objective of this interlaboratory scheme.

The samples for APLAC T062 were used as PT samples in a regular Proficiency Evaluation of the Quebec PT program in September 2008. A summary of the means, standard deviations and the numbers of participants of the Quebec proficiency evaluation along with the ones of the APLAC T062 participants are found in Tables G.1 to G.3 of Annex G.

It can be clearly seen in Tables G.1 and G.3, with the exception of BOD_5 sample 2, the means are relatively close. However, the standard deviations for the Quebec laboratories are clearly much tighter and in some instances significantly tighter (ex. BOD_5 sample 2).

In the graphical representations (Figures G1 to G12), the performance of the APLAC participants are compared to Quebec laboratories (Appendix G) using the standard deviation of the APLAC T062 interlaboratory scheme. Percentage of laboratories in each category is used instead of the number of participants because the number of APLAC participants is higher than the Quebec laboratories. Each bar is the proportion of laboratory with the same z-score on the total number of participants.

Because the Quebec laboratories participate in the same program for these measurands/matrices on a continual basis it was expected that they would have better performance on these samples. Indeed, there was a clear difference in the Quebec laboratory's performance, employing the same statistical protocols as this APLAC T062 program with the exception of the COD sample 3 (Figure G6), all of the Quebec laboratories did perform very well with z-scores within -2.0 to 2.0 and exceptionally well (within -1.0 to 1.0) in 3 of the samples (NH_3 samples 1 and 3 as well as NO_2+NO_3 sample 1) (Figures G7, G9 and G10).

It should be stated that in the normal CEAEQ PT program the Quebec laboratories are evaluated employing different criteria for the expected deviation. We have added the normal CEAEQ standard deviation criteria used to calculate the z-scores for the evaluation of the Quebec laboratories into Table G3 for informational purposes. As the expected deviation may change from evaluation to evaluation, CEAEQ's criteria is based on an average of many standard deviations from many CEAEQ PT evaluations. This helps a lot the laboratories in their quality assurance program by using those criteria.

We have also included in Table G.4 the mean and standard deviation results for the 13 Canadian laboratories that participated in this APLAC T062 proficiency testing round. All of these laboratories are accredited and must also meet strict provincial regulatory requirements. It can be seen that these Canadian laboratories did significantly better than the APLAC results (Table G.1) and were very comparable to the Quebec laboratories performance (Table G.3).

6: Conclusion

In general, the laboratories participating in APLAC T062 proficiency testing program performed well. Technical factors such as lack in instruments calibration and maintenance, the absence of reference material in real matrices (when it is possible), fortified samples and different sources of reference material could explain the difficulties of some laboratories in order to get a satisfying performance. A good assurance quality program should include the use of reference material, fortified samples, etc. on a regular basis with acceptance criteria. It should also include a calibration and maintenance program of the critical equipment.

As this program demonstrates, proficiency testing is also essential to ensure an effective measurement of water quality by laboratories. This program also highlights the positive effect of a regular and close in time frame proficiency testing participation of laboratories on their analytical performances.

In addition, this program also highlighted the vast differences in the estimated measurement uncertainties reported. It would appear that some laboratories are severely underestimating uncertainty while others are overestimating these values. For the NH_3 and NO_2+NO_3 data, in particular, the majority are unrealistically low given the low concentrations of some of the samples.

Finally, the program provided some unexpected but valuable information concerning the instability of the distributed samples when they are subjected to irradiation according to the import requirements of one economy. The impact of irradiation on the PT samples was not known before the study. Further investigation will be undertaken to gain a better understand these effects.

7: Acknowledgments:

A proficiency testing study of this magnitude would not be possible without the help of a team of dedicated people. We thank all the technical staff of the reference material division of the CEAEQ for their excellent work preparing and packaging the samples. We would also like to thank the team of chemists and technicians of our reference laboratory, the CEAEQ division of industrial pollutions for their assistance in the verification of the homogeneity and stability verification and the investigation of the irradiation impact on the PT samples.

Annex A: List of participating economies

Table A.1: List of participating economies and their related accreditation bodies

Economy	Accreditation Body	No. of Labs
Australia	National Association of Testing Authorities (NATA)	4
Brazil	General Coordination for Accreditation of Inmetro (Cgcre/Inmetro)	3
Canada	Canadian Association for Environmental Analytical Laboratories (CAEAL)	4
Canada	Standards Council of Canada (SCC)	11
Chile	Instituto Nacional de Normalizacion (INN)	4
China	China National Accreditation Service for Conformity Assessment (CNAS)	4
Ecuador	Ecuadorian Accreditation Body (Organismo de Acreditación Ecuatoriano-OAE)	4
Hong Kong	Hong Kong Accreditation Service	2
India	National Accreditation Board for Testing and Calibration Laboratories. (NABL)	4
Japan	The Japan Accreditation Board for Conformity Assessment (JAB)	2
Japan	Japan Chemical Laboratory Accreditation (JCLA)	4
Malaysia	Department of Standards Malaysia (Standards Malaysia)	4
México	Entidad Mexicana de Acreditación (ema)	4
Mongolia	Mongolian Agency for Standardization and Metrology (MASM)	4
New-Zealand	International Accreditation New Zealand (IANZ)	3
Papua New Guinea	Papua New Guinea Laboratory Accreditation Scheme (PNGLAS)	2
Philippine	Philippine Accreditation Office (PAO)	4
Singapore	Singapore Accreditation Council	4
USA (Qatar)	International Accreditation Service. Inc	2
USA	American Association for Laboratory Accreditation (A2LA)	3
Viet Nam	Bureau of Accreditation (Viet Nam)	1

Annex B: Data reported by laboratories

Table B.1: Biochemical Oxygen Demand (5 days) (mg O_2/l) results reported by laboratories and their associated expanded uncertainty values (in the same units unless otherwise indicated)

# Lab	Sample 1		Sample 2		Sample 3	
	Results	Uncertainty (U)	Results	Uncertainty (U)	Results	Uncertainty (U)
101001	129.6	8.59	390	8.59	197.4	8.59
101002	44.3	3.86	247	4.13	485.3	4.89
102001	122	4	295	6	159	5
102002	112	19.3	285	48	182	29
102003	120	0.5	315	0.5	171.9	0.5
102004	111	12	303	12	143	12
103001	171	12	776	14	233	12
103002	140	21	350	52	180	27
103003	37	5.32	188	27.05	192	27.62
104001	105	9.80%	295	1.80%	154	5.50%
104002	210	7.3	610	21	310	11
105001	140	14	120	14	250	14
105002	192	22.7	234	25.6	280	32
105003	175	10	405	10	230	10
105004	175	5	378	5	225	5
106001	37	8	186	39	213	45
106002	102	1	109	1	100	1
106003	173	-	132	-	215	-
106004	147	0.07	345	0.07	194	0.07
107001	7.3	-	190	-	100	-
107002	140	-	390	-	210	-
107003	100	7.28	321	23.3	149	10.8
107004	136	21	373	28	196	21
108001	189	16	483	39	289	23
108002	140	44	389	123	193	61
108003	144	20	390	55	198	28
108004	167	20%	444	20%	226	20%
109001	154	20	438	57	220	27
109002	50	-	10	-	20	-
109003	151.71	12.49	391.45	35.51	224.02	35.51
109004	240	0.32	250	0.32	200	0.32
110001	125	25	316	60	177	33
110002	49.9	1.9	39.4	14.4	37.5	3.3
111001	120	8.78	300	17.55	150	8.78
112001	98.9	14.4	-	-	144.4	32.4
112002	156.67	4.26	437.29	11.89	227.91	6.20
112003	197	17.73	480	43.2	282	25.38
112004	149	5.51	390	14.4	211	7.8
113001	-	-	-	-	-	-
113002	123	-	334	-	171	-

113003	78	11.7	230	34.5	113	17
113004	162	-	272	-	151	-
114001	140	16	390	44	200	23
114002	156	11	430	30	212	15
115001	120.06	4.9	308.6	5.0	162.85	6.2
115002	57	3	257	13	122	6
115003	121	11.9	231.6	12.1	147.1	12.1
115004	417.9	4.9	460	5.0	480	6.0
116001	-	-	-	-	-	-
116002	-	-	-	-	-	-
116003	88	10	240	20	130	15
116004	110	43	340	134	180	71
116005	120	25	260	54	147	31
116006	154	-	405	-	225	-
116007	142	40	402	160	209	40
116008	150	18	430	51.6	230	27.6
116009	142	63	388	172	175	77
116010	124	26	347	73	208	44
116011	134	24	397	72	211	38
117001	152	16.7	423	46.3	210	23.0
117002	143	22	383	58	193	29
117003	208	37	477	85	285	550
118001	1.58	-	321	-	244	-
118002	93.4	1.0	288.5	3.0	145.5	1.6
118003	-	-	-	-	-	-
118004	215	0.057	478	0.057	242	0.059
119001	9	2.3	30	8	10	2.6
119002	9	2.2	26	6.5	14	3.5
119003	-	-	-	-	-	-
119004	13	5	37	15	16	6
120001	137	22	401	78	184	28
120002	160	3	375	7	232	4
120003	154	1.9	433	9.3	224	5.7
120004	162	10	424	27	229	15
121001	53	-	204	-	203	-
121002	141	21	375	56	206	31
121004	150	45	380	110	220	66

Table B.2: Chemical oxygen demand (COD) (mg O_2/l) results reported by laboratories and their associated expanded uncertainty values (in the same units unless otherwise indicated)

# Lab	Sample 1		Sample 2		Sample 3	
	Results	Uncertainty (U)	Results	Uncertainty (U)	Results	Uncertainty (U)
101001	76	3.5	405	11.66	732	17.26
101002	92.7	5.86	425.3	24.23	805.3	45.98
102001	256	6	646	6	341	5
102002	86	3.44	423	3.04	726	4.44
102003	78	0.5	410	0.5	730	0.5
102004	102	20	409	9	726	9
103001	75	3	373	6	674	5
103002	82	12	440	66	730	110
103003	92	10.85	420	49.56	742	87.56
104001	9	0.39%	18.6	0.38%	33.2	0.57%
104002	9	0.30	27	1.1	45	1.7
105001	370.07	12	362.96	12	676.1	12
105002	87	15	416	45	738	59
105003	85	5	400	7	730	7
105004	91	2	450	2	740	2
106001	80.5	5.6	389	27	708	49
106002	80	1	448	2	736	2
106003	502	-	389	-	669	-
106004	80	0.05	405	0.05	721	0.05
107001	6.8	-	12	-	19	-
107002	9.4	-	24	-	36	-
107003	9.78	0.65	23.2	1.54	35.1	2.32
107004	75.1	0.5	399	12	680	8.2
108001	86	8	375	25	713	46
108002	75.6	6	416	33.3	725	58
108003	80	4	400	21	720	37
108004	75	10%	402	10%	717	10%
109001	69	2	357	11	781	23
109002	85	20%	404	10%	719	10%
109003	96	6	408	6	714	6
109004	123	0.34	448	0.34	760	0.34
110001	220	25	850	85	880	90
110002	-	-	-	-	-	-
111001	79	3.04	388	10.05	676	21.07
112001	-	-	390	53	693	93
112002	178.63	0.35	489.28	0.98	799.94	1.60
112003	216.67	2.17	448.33	4.48	795	7.95
112004	89	4.05	396	18	712	32.4
113001	78	5	420	10	752	20
113002	85	-	397	-	702	-
113003	89	0.8	424	3.8	872	7.8
113004	80	-	398	-	722	-
114001	78	7.2	400	37	710	66
114002	82.5	4	396	20	687	35
115001	98.51	5.3	401.22	5.6	720.66	3.0

115002	95.9	3.8	393	15.7	719	28.8
115003	60.42	4.6	357.9	5.0	678.61	5.7
115004	38.4	5.3	28.8	4.9	748.8	10.0
116001	-	-	-	-	-	-
116002	-	-	-	-	-	-
116003	58	8	346	35	634	60
116004	-	-	-	-	-	-
116005	76	6	409	31	722	54
116006	83.1	-	394	-	710	-
116007	113	6	421	23	744	40
116008	76	7.6	370	22.2	660	39.6
116009	-	-	-	-	-	-
116010	110	20	430	70	760	120
116011	82	6	414	31	762	56
117001	93.9	2.99	-	-	718	22.8
117002	77.1	5.9	441	34	785	60
117003	82.2	4	428	21	759	716
118001	208	-	516	-	873	-
118002	80.2	1.0	386.5	5.0	721.5	8.5
118003	46.82	12.38	442.63	118.68	748.38	200.57
118004	82	2.7	482	11.1	737	10.1
119001	<10	2.1	242	51	654	138
119002	<10	<10	230	29	520	65
119003	3	1	217	43	497	99
119004	0	0	243	39	568	91
120001	94.4	2.9	401	5	714	24
120002	89	3.2	406	14.6	730	26.3
120003	81.1	0.8	399	1.5	710	0.6
120004	91	6	407	28	718	50
121001	81	-	393	-	722	-
121002	236	24	638	64	330	33
121004	83	17	410	82	720	140

Table B.3: Ammonia Nitrogen (mg N/l) results reported by laboratories and their associated expanded uncertainty values (in the same units unless otherwise indicated)

# Lab	Sample 1		Sample 2		Sample 3	
	Results	Uncertainty (U)	Results	Uncertainty (U)	Results	Uncertainty (U)
101001	12.6	1.14	4.2	1.14	16.8	1.14
101002	5.6	0.31	4.3	0.25	14.5	0.6
102001	4.9	0.4	3.5	0.3	18.2	0.7
102002	6.42	0.19	5	0.2	19.4	0.22
102003	5.88	0.4	4.36	0.4	15.5	0.4
102004	5.66	-	4.09	-	15.61	-
103001	3.35	0.18	1.75	0.18	13.05	0.18
103002	7	1	5	0.75	19	2.8
103003	5.56	0.035	4.56	0.028	15.4	0.096
104001	5.34	0.46%	4.03	0.47%	15.2	0.31%
104002	6	0.14	4	0.096	14	0.33
105001	1.8	0.2	1.2	0.2	2.6	0.2
105002	5.68	2.1	4.28	1.5	15	3.9
105003	6.28	0.5	5	0.5	19.2	0.5
105004	8.06	0.05	3.27	0.05	18	0.05
106001	5.74	0.63	4.14	0.45	15.5	1.7
106002	4.52	0.01	3.54	0.01	15.71	0.03
106003	0.9	-	0.74	-	0.61	-
106004	6.4	0.09	4.85	0.09	17.2	0.09
107001	7.2	0.015	5.4	0.015	19	0.015
107002	7.2	-	-	-	18.5	-
107003	8	0.09	5.14	0.098	20.9	0.73
107004	6.4	1.4	4.4	1.4	15.4	1.4
108001	2.3	0.303	1.8	0.237	8	1.055
108002	5.57	0.21	3.49	0.13	15.1	0.56
108003	7	0.5	5	0.4	14	1
108004	4.61	21%	3.2	21%	14	21%
109001	5.54	-	4.17	-	13.59	-
109002	4.75	10%	3.73	10%	13.78	10%
109003	5.43	0.05	4.08	0.05	15.25	0.05
109004	7.66	-	5.9	-	26	-
110001	6.62	0.53	6.22	0.5	19.1	1.5
110002	0.005	0.000	0.006	0.001	0.006	0.002
111001	2.68	0.035	2.31	0.035	6.63	0.064
112001	4.13	0.54	-	-	13.93	1.39
112002	4.33	0.029	3.46	.023	15	0.100
112003	5.5	0.22	4.5	0.18	13.6	0.54
112004	5.94	0.07	3.66	0.043	13.7	0.162
113001	5.5	0.5	4.5	0.5	18.4	0.5
113002	0.18	-	4.1	-	16	-
113003	15.3	0.3	7.9	0.2	10.3	0.2
113004	12.5	-	5.7	-	16.3	-
114001	6.2	0.49	4.5	0.36	17	1.4
114002	5.65	0.96	4.08	0.69	-	-
115001	5.59	0.16	4.18	0.19	14.4	0.31

115002	3.06	0.15	4.02	0.20	15.15	0.75
115003	5.77	0.006	3.82	0.006	14.94	0.008
115004	2.3	0.05	1.52	0.05	4	0.05
116001	7.378	0.055	5.47	0.055	20.57	0.055
116002	-	-	-	-	-	-
116003	0.239	0.025	0.46	0.04	0.226	0.023
116004	-	-	-	-	-	-
116005	5.6	0.22	4.01	0.16	14.7	0.6
116006	-	-	-	-	-	-
116007	5.75	0.29	3.85	0.19	14.7	0.75
116008	5.09	0.51	3.81	0.38	14.3	1.43
116009	5.78	1.206	4.05	0.845	14.8	3.087
116010	5	-	4.08	-	13.6	-
116011	6.1	0.24	3.85	0.15	14.78	0.58
117001	6.6	0.15	1.6	0.04	13.5	0.30
117002	6	0.39	3.88	0.25	12.4	0.8
117003	5.45	0.5	4.07	4.09	14.7	1.4
118001	3.4	4.88	2.7	4.88	8.4	4.88
118002	2.7	0.04	2.5	0.04	9	0.13
118003	-	-	-	-	-	-
118004	6.9	0.387	3.5	0.102	17	0.781
119001	8.27	2.26	8.53	2.34	15.35	4.2
119002	10	1.2	8.4	1.0	17	2.1
119003	9.45	1.9	10.19	2.04	18.7	3.74
119004	9.9	2	10.8	2.2	17.8	3.6
120001	5.68	0.22	4.82	0.12	14.87	0.44
120002	5.49	0.13	4.22	0.1	15	0.36
120003	5.72	0.08	4.56	0.08	15.6	0.1
120004	5.56	0.2	4.23	0.15	14.7	0.5
121001	5.3	-	3.9	-	14.7	-
121002	4.52	0.68	3.28	0.49	15	1.5
121004	5.2	0.52	3.9	0.39	15	1.5

Table B.4: Nitrite plus Nitrate (mg N/l) results reported by laboratories and their associated expanded uncertainty values (in the same units unless otherwise indicated)

# Lab	Sample 1		Sample 2		Sample 3	
	Results	Uncertainty (U)	Results	Uncertainty (U)	Results	Uncertainty (U)
101001	-	-	-	-	-	-
101002	3.4	0.34	38.9	2.24	25.6	1.57
102001	-	-	-	-	-	-
102002	14.6	1.15	106	2.42	131	2.44
102003	-	-	-	-	-	-
102004	2.88	0.09	41.73	1	26.64	1
103001	4.3	0.08	54.15	0.1	32.59	0.1
103002	3.1	0.46	42	6.3	28	4.2
103003	5.345	0.496	50.01	4.641	40.006	3.712
104001	3.08	0.42%	45.7	0.25%	29.7	0.26%
104002	3.2	0.046	46	0.67	30	0.44
105001	33.69	3.5	65.2	3.5	68.4	3.5
105002	3.66	1.2	55.04	8.2	32.4	6.8
105003	3.98	0.9	6.2	0.9	30.61	1.0
105004	4.01	0.3	15.3	0.3	30	0.3
106001	3.65	0.4	44.4	4.9	29.2	3.2
106002	30.85	0.5	82.43	1	86.32	1
106003	2.17	-	1.86	-	2	-
106004	45	0.1	53	0.1	33.4	0.1
107001	3	0.026	43	0.026	29	0.026
107002	3.3	-	49	-	28	-
107003	3.41	0.013	46.3	0.26	30.1	0.13
107004	3.2	0.2	46.1	1.6	28.4	1
108001	3.1	0.22	45	3.195	29	2.059
108002	3.99	0.04	22.3	0.22	23.4	0.23
108003	5	0.5	49	5	32	3
108004	3.2	11%	44.7	11%	28.8	11%
109001	3.4	-	45.23	-	26.36	-
109002	3.23	-	32.19	-	21.16	-
109003	8	0.23	88.8	0.23	75	0.23
109004	15.08	-	93.17	-	98.14	-
110001	7.84	0.78	78.8	7.9	86.6	8.7
110002	-	-	-	-	-	-
111001	2.4	0.018	34.6	2.460	25.15	0.614
112001	2.69	0.54	-	-	28.6	7
112002	8.2863	0.4143	0.9002	0.0450	77.95	3.8975
112003	3.67	0.04	36.86	0.44	26.82	0.32
112004	3.27	0.187	46.6	2.67	33.9	1.94
113001	2.9	0.3	45.9	0.5	29	0.5
113002	<0.05	-	0.33	-	0.21	-
113003	3.26	0.05	37	0.59	23.39	0.37
113004	12	-	192	-	122	-
114001	3	0.14	45	2.2	29	1.4
114002	3.28	0.52	46.8	7.49	30.5	4.88
115001	2.79	0.1	66.95	0.1	36.23	0.1
115002	0.128	0.01	1.889	0.20	1.811	0.20
115003	2.03	0.006	4.28	0.006	9.68	0.012
115004	4.280	0.05	20.902	0.05	29.701	0.05

116001	-	-	-	-	-	-
116002	-	-	-	-	-	-
116003	4.44	0.6	54	7	35	5
116004	-	-	-	-	-	-
116005	3.5	-	46.2	-	29	-
116006	-	-	-	-	-	-
116007	3.46	0.09	47	1.2	30.5	0.78
116008	3.045	0.55	43.73	4.37	28.29	2.83
116009	3.06	0.443	45.6	6.598	29.8	4.312
116010	3.83	0.27	52.2	3.6	30.9	2.2
116011	2.8	-	42.6	4.3	27.2	2.7
117001	3.1	0.26	47.5	3.92	29.5	2.44
117002	3.14	0.18	46.5	2.7	28	1.6
117003	<5		41.7	1	29.3	0.7
118001	3.6	7.36	76	7.36	36	7.36
118002	2.3	0.03	22.2	0.03	20.3	0.03
118003	-	-	-	-	-	-
118004	-	-	-	-	32.82	0.028
119001	0.13	0.044	28.8	9.75	21	7.11
119002	-	-	22	2.8	15	1.9
119003	0.09	0.02	25	5	16.7	3.34
119004	0.14	0.03	29.4	5.9	19.2	3.8
120001	7.93	0.42	71.7	3.9	76.3	4.0
120002	2.81	0.22	43.9	3.51	27.9	2.23
120003	3.27	0.03	46.9	0.5	30.1	0.3
120004	9.2	0.41	77.6	3.5	90.7	4.1
121001	3.46	-	47.2	-	32.2	-
121002	3.27	0.327	46.8	4.68	28.7	2.87
121004	3.1	0.31	46	4.6	29	2.9

Annex C: Z-scores and evaluations

Comparison of BOD results, z-scores, evaluations and ordered z-score bar charts

Table C.1: Biochemical Oxygen Demand (5 days) (mg O_2/l) results, z-score and evaluations

	Sample 1			Sample 2			Sample 3		
# Lab	Results	z-score	Evaluation	Results	z-score	Evaluation	Results	z-score	Evaluation
101001	129.6	-0.138	Satisfactory	390	0.583	Satisfactory	197.4	0.059	Satisfactory
101002	44.3	-2.803	Questionable	247	-0.906	Satisfactory	485.3	7.080	Unsatisfactory
102001	122	-0.375	Satisfactory	295	-0.406	Satisfactory	159	-0.878	Satisfactory
102002	112	-0.688	Satisfactory	285	-0.510	Satisfactory	182	-0.317	Satisfactory
102003	120	-0.438	Satisfactory	315	-0.198	Satisfactory	171.9	-0.563	Satisfactory
102004	111	-0.719	Satisfactory	303	-0.323	Satisfactory	143	-1.268	Satisfactory
103001	171	1.156	Satisfactory	776	4.604	Unsatisfactory	233	0.927	Satisfactory
103002	140	0.188	Satisfactory	350	0.167	Satisfactory	180	-0.366	Satisfactory
103003	37	-3.031	Unsatisfactory	188	-1.521	Satisfactory	192	-0.073	Satisfactory
104001	105	-0.906	Satisfactory	295	-0.406	Satisfactory	154	-1.000	Satisfactory
104002	210	2.375	Questionable	610	2.875	Questionable	310	2.805	Questionable
105001	140	0.188	Satisfactory	120	-2.229	Questionable	250	1.341	Satisfactory
105002	192	1.813	Satisfactory	234	-1.042	Satisfactory	280	2.073	Questionable
105003	175	1.281	Satisfactory	405	0.740	Satisfactory	230	0.854	Satisfactory
105004	175	1.281	Satisfactory	378	0.458	Satisfactory	225	0.732	Satisfactory
106001	37	-3.031	Unsatisfactory	186	-1.542	Satisfactory	213	0.439	Satisfactory
106002	102	-1.000	Satisfactory	109	-2.344	Questionable	100	-2.317	Questionable
106003	173	1.219	Satisfactory	132	-2.104	Questionable	215	0.488	Satisfactory
106004	147	0.406	Satisfactory	345	0.115	Satisfactory	194	-0.024	Satisfactory
107001	7.3	-3.959	Unsatisfactory	190	-1.500	Satisfactory	100	-2.317	Questionable
107002	140	0.188	Satisfactory	390	0.583	Satisfactory	210	0.366	Satisfactory
107003	100	-1.063	Satisfactory	321	-0.135	Satisfactory	149	-1.122	Satisfactory
107004	136	0.063	Satisfactory	373	0.406	Satisfactory	196	0.024	Satisfactory
108001	189	1.719	Satisfactory	483	1.552	Satisfactory	289	2.293	Questionable
108002	140	0.188	Satisfactory	389	0.573	Satisfactory	193	-0.049	Satisfactory
108003	144	0.313	Satisfactory	390	0.583	Satisfactory	198	0.073	Satisfactory
108004	167	1.031	Satisfactory	444	1.146	Satisfactory	226	0.756	Satisfactory
109001	154	0.625	Satisfactory	438	1.083	Satisfactory	220	0.610	Satisfactory
109002	50	-2.625	Questionable	10	-3.375	Unsatisfactory	20	-4.268	Unsatisfactory
109003	151.71	0.553	Satisfactory	391.45	0.598	Satisfactory	224.02	0.708	Satisfactory
109004	240	3.313	Unsatisfactory	250	-0.875	Satisfactory	200	0.122	Satisfactory
110001	125	-0.281	Satisfactory	316	-0.188	Satisfactory	177	-0.439	Satisfactory
110002	49.9	-2.628	Questionable	39.4	-3.069	Unsatisfactory	37.5	-3.841	Unsatisfactory
111001	120	-0.438	Satisfactory	300	-0.354	Satisfactory	150	-1.098	Satisfactory
112001	98.9	-1.097	Satisfactory	-	-	-	144.4	-1.234	Satisfactory
112002	156.67	0.708	Satisfactory	437.29	1.076	Satisfactory	227.91	0.803	Satisfactory
112003	197	1.969	Satisfactory	480	1.521	Satisfactory	282	2.122	Questionable
112004	149	0.469	Satisfactory	390	0.583	Satisfactory	211	0.390	Satisfactory
113001	-	-	-	-	-	-	-	-	-
113002	123	-0.344	Satisfactory	334	0.000	Satisfactory	171	-0.585	Satisfactory
113003	78	-1.750	Satisfactory	230	-1.083	Satisfactory	113	-2.000	Questionable
113004	162	0.875	Satisfactory	272	-0.646	Satisfactory	151	-1.073	Satisfactory
114001	140	0.188	Satisfactory	390	0.583	Satisfactory	200	0.122	Satisfactory

114002	156	0.688	Satisfactory	430	1.000	Satisfactory	212	0.415	Satisfactory
115001	120.06	-0.436	Satisfactory	308.6	-0.265	Satisfactory	162.85	-0.784	Satisfactory
115002	57	-2.406	Questionable	257	-0.802	Satisfactory	122	-1.780	Satisfactory
115003	121	-0.406	Satisfactory	231.6	-1.067	Satisfactory	147.1	-1.168	Satisfactory
115004	417.9	8.872	Unsatisfactory	460	1.313	Satisfactory	480	6.951	Unsatisfactory
116001	-	-	-	-	-	-	-	-	-
116002	-	-	-	-	-	-	-	-	-
116003	88	-1.438	Satisfactory	240	-0.979	Satisfactory	130	-1.585	Satisfactory
116004	110	-0.750	Satisfactory	340	0.063	Satisfactory	180	-0.366	Satisfactory
116005	120	-0.438	Satisfactory	260	-0.771	Satisfactory	147	-1.171	Satisfactory
116006	154	0.625	Satisfactory	405	0.740	Satisfactory	225	0.732	Satisfactory
116007	142	0.250	Satisfactory	402	0.708	Satisfactory	209	0.341	Satisfactory
116008	150	0.500	Satisfactory	430	1.000	Satisfactory	230	0.854	Satisfactory
116009	142	0.250	Satisfactory	388	0.563	Satisfactory	175	-0.488	Satisfactory
116010	124	-0.313	Satisfactory	347	0.135	Satisfactory	208	0.317	Satisfactory
116011	134	0.000	Satisfactory	397	0.656	Satisfactory	211	0.390	Satisfactory
117001	152	0.563	Satisfactory	423	0.927	Satisfactory	210	0.366	Satisfactory
117002	143	0.281	Satisfactory	383	0.510	Satisfactory	193	-0.049	Satisfactory
117003	208	2.313	Questionable	477	1.490	Satisfactory	285	2.195	Questionable
118001	1.58	-4.138	Unsatisfactory	321	-0.135	Satisfactory	244	1.195	Satisfactory
118002	93.4	-1.269	Satisfactory	288.5	-0.474	Satisfactory	145.5	-1.207	Satisfactory
118003	-	-	-	-	-	-	-	-	-
118004	215	2.531	Questionable	478	1.500	Satisfactory	242	1.146	Satisfactory
119001	9	-3.906	Unsatisfactory	30	-3.167	Unsatisfactory	10	-4.512	Unsatisfactory
119002	9	-3.906	Unsatisfactory	26	-3.208	Unsatisfactory	14	-4.415	Unsatisfactory
119003	-	-	-	-	-	-	-	-	-
119004	13	-3.781	Unsatisfactory	37	-3.094	Unsatisfactory	16	-4.366	Unsatisfactory
120001	137	0.094	Satisfactory	401	0.698	Satisfactory	184	-0.268	Satisfactory
120002	160	0.813	Satisfactory	375	0.427	Satisfactory	232	0.902	Satisfactory
120003	154	0.625	Satisfactory	433	1.031	Satisfactory	224	0.707	Satisfactory
120004	162	0.875	Satisfactory	424	0.938	Satisfactory	229	0.829	Satisfactory
121001	53	-2.531	Questionable	204	-1.354	Satisfactory	203	0.195	Satisfactory
121002	141	0.219	Satisfactory	375	0.427	Satisfactory	206	0.268	Satisfactory
121004	150	0.500	Satisfactory	380	0.479	Satisfactory	220	0.610	Satisfactory
Preparation value	143			393			206		
Assigned value	134			334			195		
Expected deviation	32			96			41		
Lab with results	72			71			72		
Standard uncertainty	4.71			14.24			6.04		
$0.3*\sigma_{pt}$	9.6			28.8			12.3		
$\mu \leq 0.3*\sigma_{pt}$	**YES**			**YES**			**YES**		

Note: " – " Denotes no value transmitted from the laboratory

Figure C.1: Ordered z-scores Bar Chart of results for Biochemical Oxygen Demand sample 1

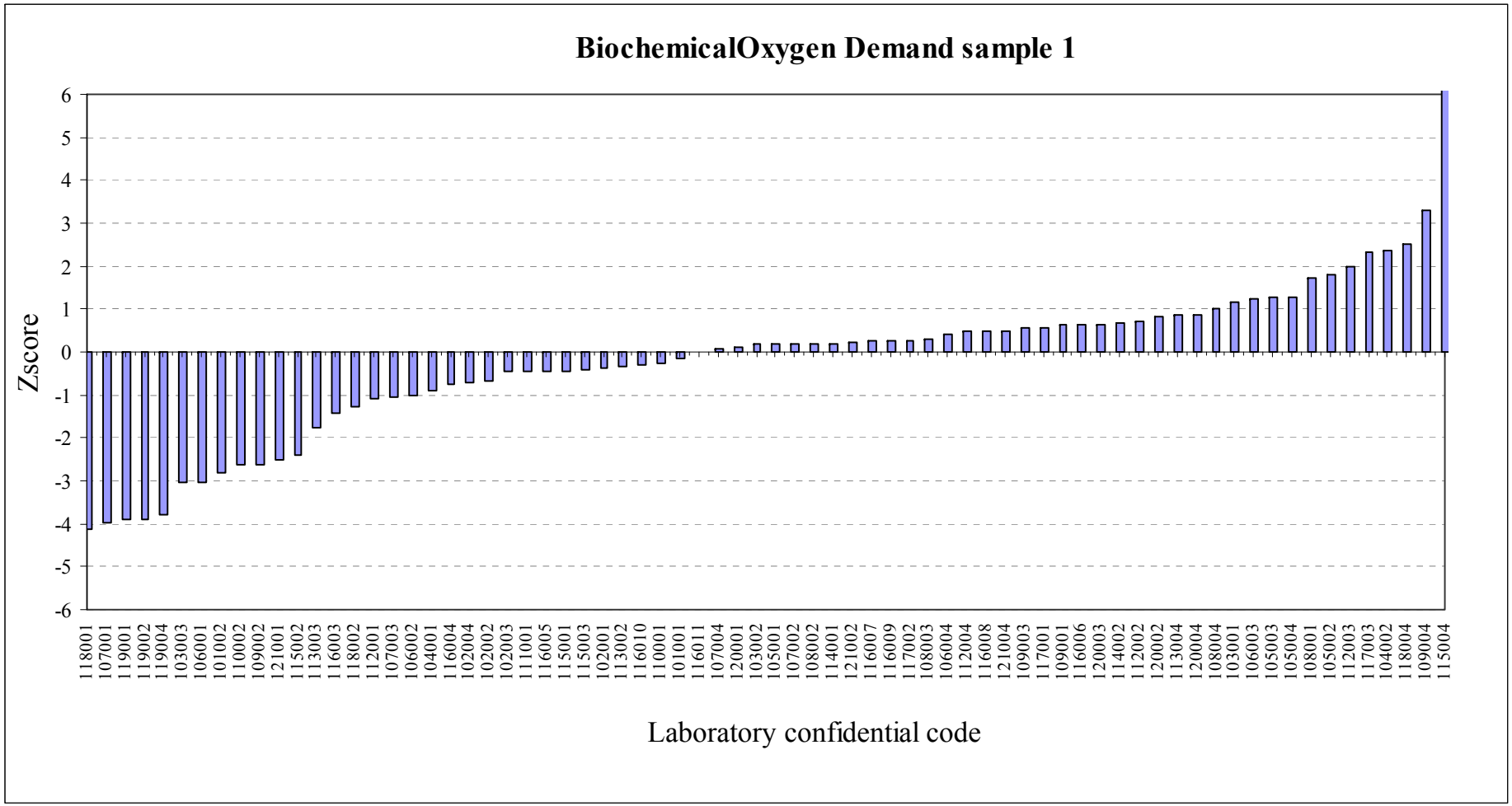


Figure C.2: Ordered z-scores Bar Chart of results for Biochemical Oxygen Demand sample 2

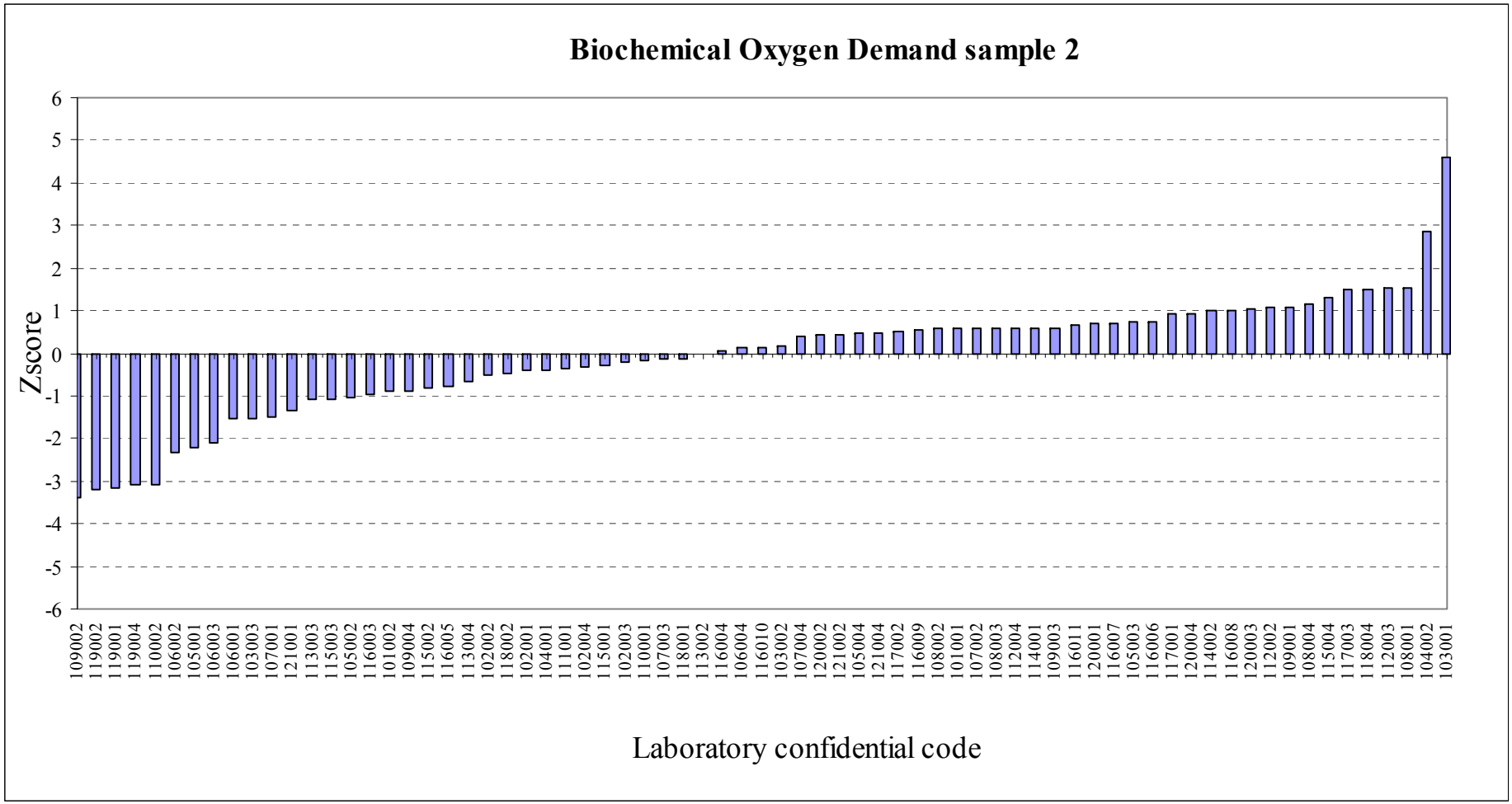
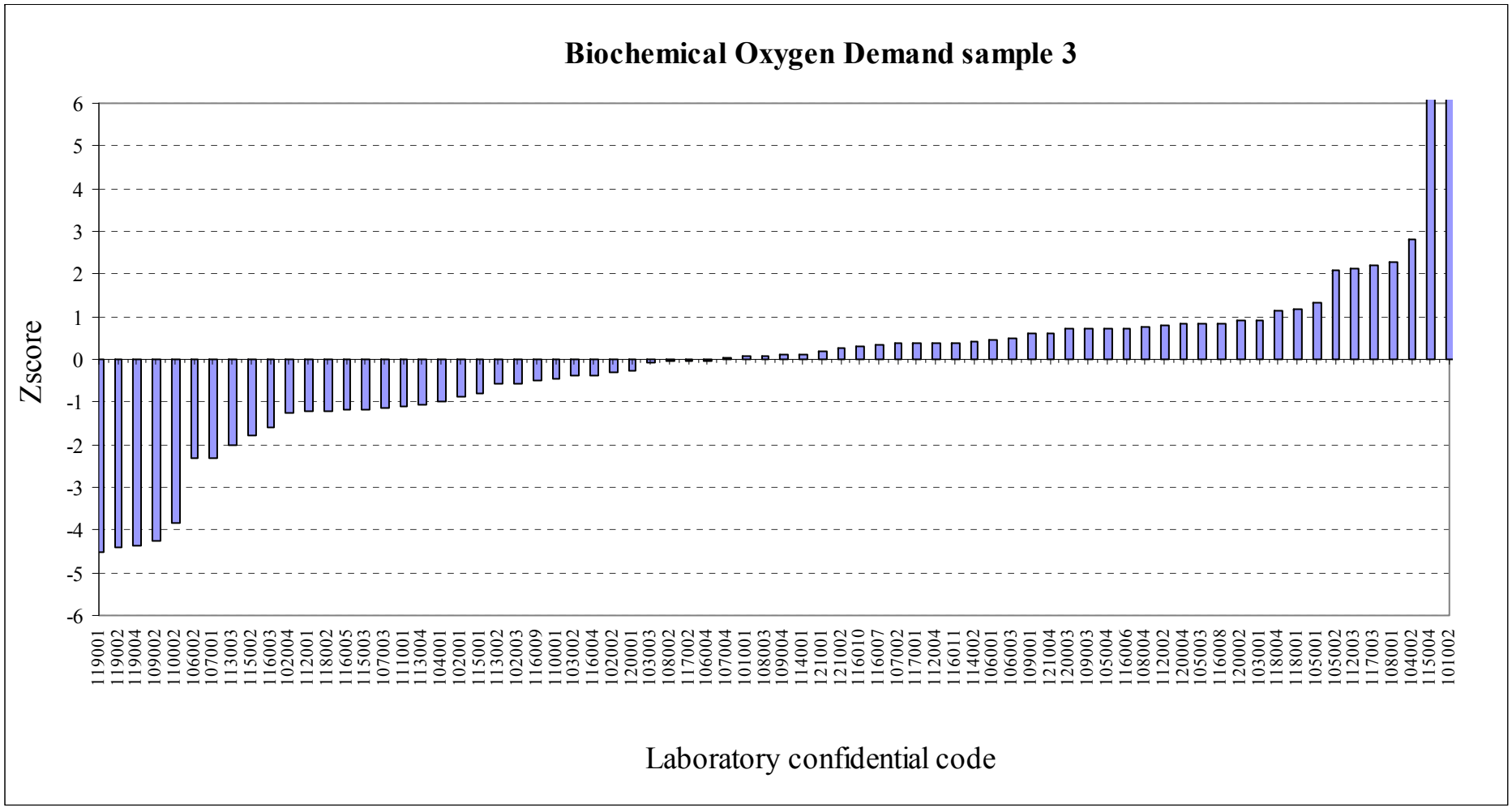


Figure C.3: Ordered z-scores Bar Chart of results for Biochemical Oxygen Demand sample 3



Comparison of COD results, z-scores, evaluations and ordered z-score bar charts

Table C.2: Chemical Oxygen Demand (mg O_2/l) results, z-score and evaluations

# Lab	Sample 1			Sample 2			Sample 3		
	Results	z-score	Evaluation	Results	z-score	Evaluation	Results	z-score	Evaluation
101001	76	-0.636	Satisfactory	405	0.103	Satisfactory	732	0.444	Satisfactory
101002	92.7	0.882	Satisfactory	425.3	0.803	Satisfactory	805.3	2.481	Questionable
102001	256	15.727	Unsatisfactory	646	8.414	Unsatisfactory	341	-10.417	Unsatisfactory
102002	86	0.273	Satisfactory	423	0.724	Satisfactory	726	0.278	Satisfactory
102003	78	-0.455	Satisfactory	410	0.276	Satisfactory	730	0.389	Satisfactory
102004	102	1.727	Satisfactory	409	0.241	Satisfactory	726	0.278	Satisfactory
103001	75	-0.727	Satisfactory	373	-1.000	Satisfactory	674	-1.167	Satisfactory
103002	82	-0.091	Satisfactory	440	1.310	Satisfactory	730	0.389	Satisfactory
103003	92	0.818	Satisfactory	420	0.621	Satisfactory	742	0.722	Satisfactory
104001	9	-6.727	Unsatisfactory	18.6	-13.221	Unsatisfactory	33.2	-18.967	Unsatisfactory
104002	9	-6.727	Unsatisfactory	27	-12.931	Unsatisfactory	45	-18.639	Unsatisfactory
105001	370.07	26.097	Unsatisfactory	362.96	-1.346	Satisfactory	676.1	-1.108	Satisfactory
105002	87	0.364	Satisfactory	416	0.483	Satisfactory	738	0.611	Satisfactory
105003	85	0.182	Satisfactory	400	-0.069	Satisfactory	730	0.389	Satisfactory
105004	91	0.727	Satisfactory	450	1.655	Satisfactory	740	0.667	Satisfactory
106001	80.5	-0.227	Satisfactory	389	-0.448	Satisfactory	708	-0.222	Satisfactory
106002	80	-0.273	Satisfactory	448	1.586	Satisfactory	736	0.556	Satisfactory
106003	502	38.091	Unsatisfactory	389	-0.448	Satisfactory	669	-1.306	Satisfactory
106004	80	-0.273	Satisfactory	405	0.103	Satisfactory	721	0.139	Satisfactory
107001	6.8	-6.927	Unsatisfactory	12	-13.448	Unsatisfactory	19	-19.361	Unsatisfactory
107002	9.4	-6.691	Unsatisfactory	24	-13.034	Unsatisfactory	36	-18.889	Unsatisfactory
107003	9.78	-6.656	Unsatisfactory	23.2	-13.062	Unsatisfactory	35.1	-18.914	Unsatisfactory
107004	75.1	-0.718	Satisfactory	399	-0.103	Satisfactory	680	-1.000	Satisfactory
108001	86	0.273	Satisfactory	375	-0.931	Satisfactory	713	-0.083	Satisfactory
108002	75.6	-0.673	Satisfactory	416	0.483	Satisfactory	725	0.250	Satisfactory
108003	80	-0.273	Satisfactory	400	-0.069	Satisfactory	720	0.111	Satisfactory
108004	75	-0.727	Satisfactory	402	0.000	Satisfactory	717	0.028	Satisfactory
109001	69	-1.273	Satisfactory	357	-1.552	Satisfactory	781	1.806	Satisfactory
109002	85	0.182	Satisfactory	404	0.069	Satisfactory	719	0.083	Satisfactory
109003	96	1.182	Satisfactory	408	0.207	Satisfactory	714	-0.056	Satisfactory
109004	123	3.636	Unsatisfactory	448	1.586	Satisfactory	760	1.222	Satisfactory
110001	220	12.455	Unsatisfactory	850	15.448	Unsatisfactory	880	4.556	Unsatisfactory
110002	-	-	-	-	-	-	-	-	-
111001	79	-0.364	Satisfactory	388	-0.483	Satisfactory	676	-1.111	Satisfactory
112001	-	-	-	390	-0.414	Satisfactory	693	-0.639	Satisfactory
112002	178.63	8.694	Unsatisfactory	489.28	3.010	Unsatisfactory	799.94	2.332	Questionable
112003	216.67	12.152	Unsatisfactory	448.33	1.598	Satisfactory	795	2.194	Questionable
112004	89	0.545	Satisfactory	396	-0.207	Satisfactory	712	-0.111	Satisfactory
113001	78	-0.455	Satisfactory	420	0.621	Satisfactory	752	1.000	Satisfactory
113002	85	0.182	Satisfactory	397	-0.172	Satisfactory	702	-0.389	Satisfactory
113003	89	0.545	Satisfactory	424	0.759	Satisfactory	872	4.333	Unsatisfactory
113004	80	-0.273	Satisfactory	398	-0.138	Satisfactory	722	0.167	Satisfactory
114001	78	-0.455	Satisfactory	400	-0.069	Satisfactory	710	-0.167	Satisfactory
114002	82.5	-0.045	Satisfactory	396	-0.207	Satisfactory	687	-0.806	Satisfactory
115001	98.51	1.410	Satisfactory	401.22	-0.027	Satisfactory	720.66	0.129	Satisfactory
115002	95.9	1.173	Satisfactory	393	-0.310	Satisfactory	719	0.083	Satisfactory

115003	60.42	-2.053	Questionable	357.9	-1.521	Satisfactory	678.61	-1.039	Satisfactory
115004	38.4	-4.055	Unsatisfactory	28.8	-12.869	Unsatisfactory	748.8	0.911	Satisfactory
116001	-	-	-	-	-	-	-	-	-
116002	-	-	-	-	-	-	-	-	-
116003	58	-2.273	Questionable	346	-1.931	Satisfactory	634	-2.278	Questionable
116004	-	-	-	-	-	-	-	-	-
116005	76	-0.636	Satisfactory	409	0.241	Satisfactory	722	0.167	Satisfactory
116006	83.1	0.009	Satisfactory	394	-0.276	Satisfactory	710	-0.167	Satisfactory
116007	113	2.727	Questionable	421	0.655	Satisfactory	744	0.778	Satisfactory
116008	76	-0.636	Satisfactory	370	-1.103	Satisfactory	660	-1.556	Satisfactory
116009	-	-	-	-	-	-	-	-	-
116010	110	2.455	Questionable	430	0.966	Satisfactory	760	1.222	Satisfactory
116011	82	-0.091	Satisfactory	414	0.414	Satisfactory	762	1.278	Satisfactory
117001	93.9	0.991	Satisfactory	-	-	-	718	0.056	Satisfactory
117002	77.1	-0.536	Satisfactory	441	1.345	Satisfactory	785	1.917	Satisfactory
117003	82.2	-0.073	Satisfactory	428	0.897	Satisfactory	759	1.194	Satisfactory
118001	208	11.364	Unsatisfactory	516	3.931	Unsatisfactory	873	4.361	Unsatisfactory
118002	80.2	-0.255	Satisfactory	386.5	-0.534	Satisfactory	721.5	0.153	Satisfactory
118003	46.82	-3.289	Unsatisfactory	442.63	1.401	Satisfactory	748.38	0.899	Satisfactory
118004	82	-0.091	Satisfactory	482	2.759	Questionable	737	0.583	Satisfactory
119001	<10	-	Unsatisfactory	242	-5.517	Unsatisfactory	654	-1.722	Satisfactory
119002	<10	-	Unsatisfactory	230	-5.931	Unsatisfactory	520	-5.444	Unsatisfactory
119003	3	-7.273	Unsatisfactory	217	-6.379	Unsatisfactory	497	-6.083	Unsatisfactory
119004	0	-7.545	Unsatisfactory	243	-5.483	Unsatisfactory	568	-4.111	Unsatisfactory
120001	94.4	1.036	Satisfactory	401	-0.034	Satisfactory	714	-0.056	Satisfactory
120002	89	0.545	Satisfactory	406	0.138	Satisfactory	730	0.389	Satisfactory
120003	81.1	-0.173	Satisfactory	399	-0.103	Satisfactory	710	-0.167	Satisfactory
120004	91	0.727	Satisfactory	407	0.172	Satisfactory	718	0.056	Satisfactory
121001	81	-0.182	Satisfactory	393	-0.310	Satisfactory	722	0.167	Satisfactory
121002	236	13.909	Unsatisfactory	638	8.138	Unsatisfactory	330	-10.722	Unsatisfactory
121004	83	-0.636	Satisfactory	410	0.276	Satisfactory	720	0.111	Satisfactory
Preparation value	85			402			719		
Assigned value	83			402			716		
Expected deviation	11			29			36		
Lab with results	71			71			72		
Standard uncertainty	1.655			4.302			5.303		
$0.3*\sigma_{pt}$	3.3			8.7			10.8		
$\mu \leq 0.3*\sigma_{pt}$	**YES**			**YES**			**YES**		

Note: " – " Denotes no value transmitted from the laboratory

Figure C.4: Ordered z-scores Bar Chart of results for Chemical Oxygen Demand sample 1

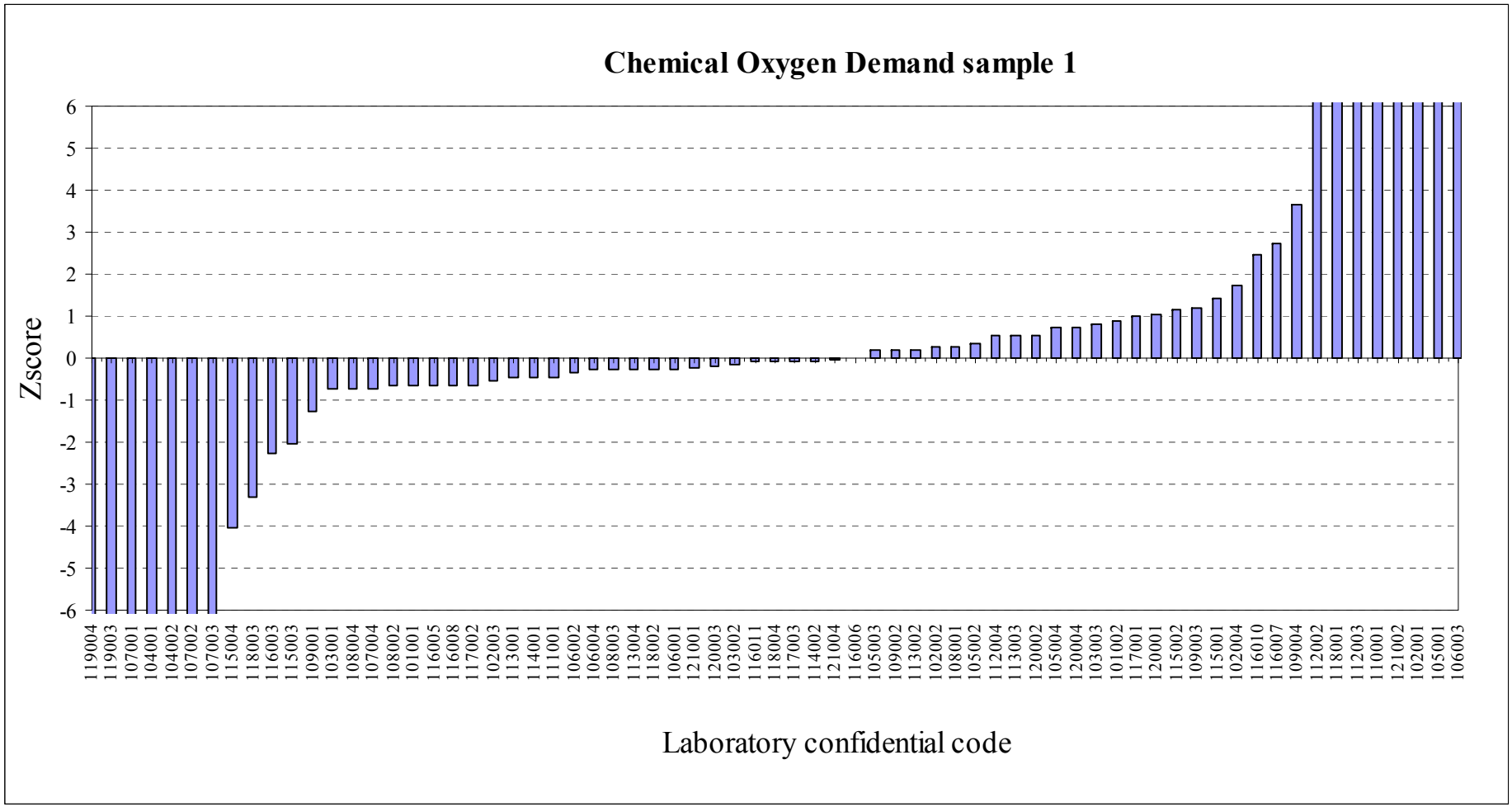


Figure C.5: Ordered z-scores Bar Chart of results for Chemical Oxygen Demand sample 2

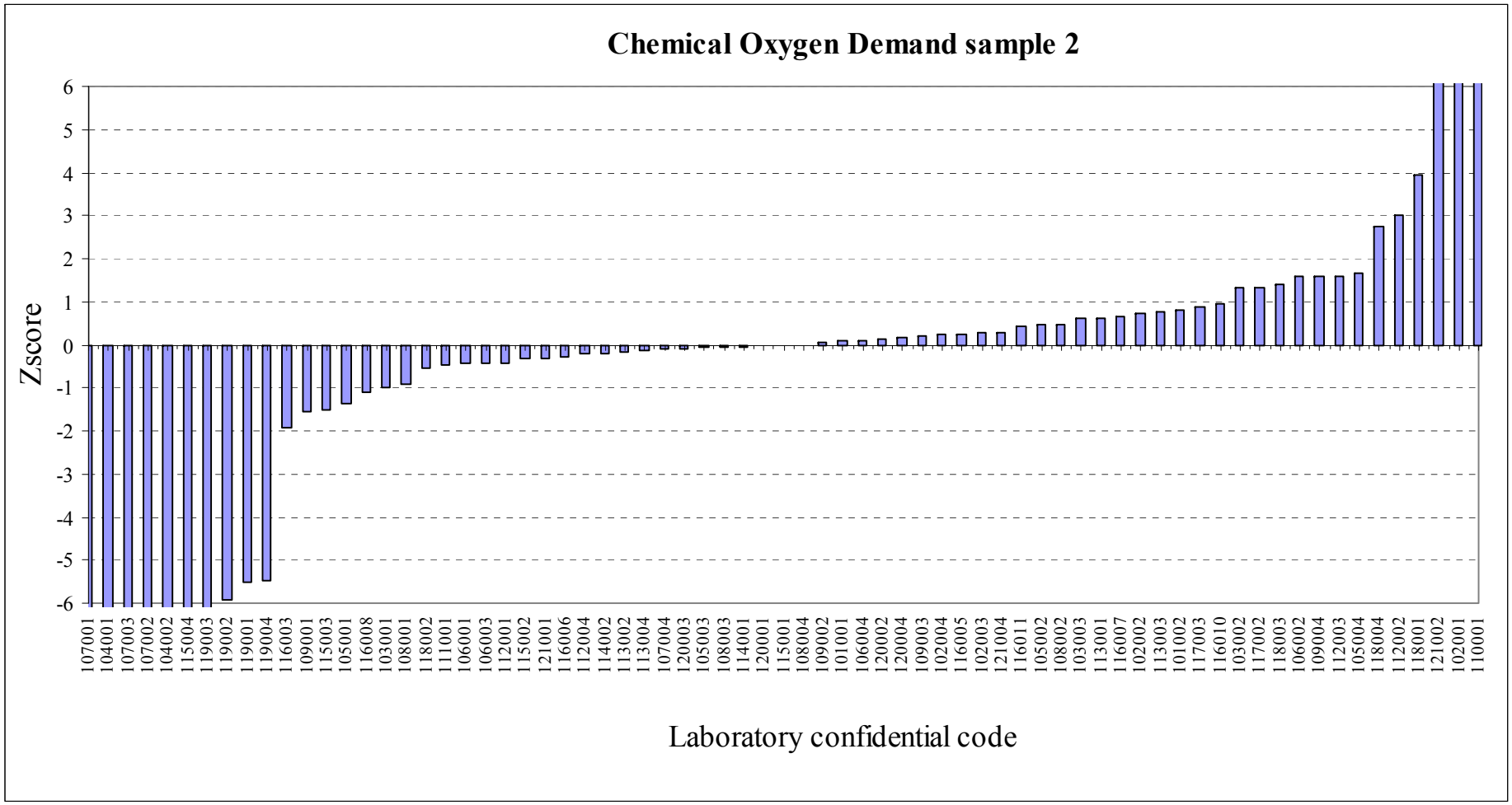
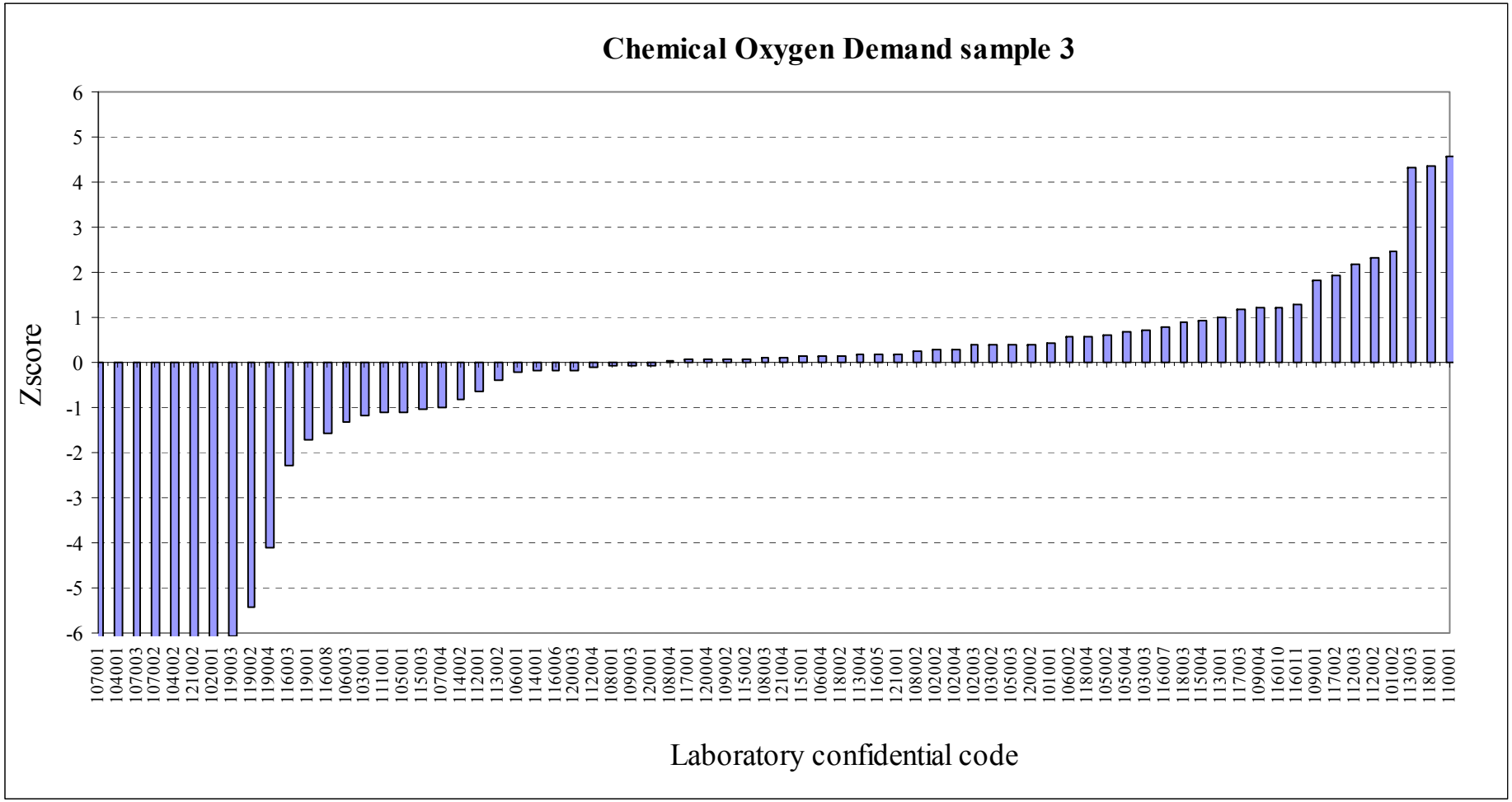


Figure C.6: Ordered z-scores Bar Chart of results for Chemical Oxygen Demand sample 3



Comparison of Ammonia results, z-scores, evaluations and ordered z-score bar charts

Table C.3: Ammonia Nitrogen (mg N/l) results, z-score and evaluations

# Lab	Sample 1			Sample 2			Sample 3		
	Results	z-score	Evaluation	Results	z-score	Evaluation	Results	z-score	Evaluation
101001	12.6	5.744	Unsatisfactory	4.2	0.142	Satisfactory	16.8	0.904	Satisfactory
101002	5.6	-0.041	Satisfactory	4.3	0.272	Satisfactory	14.5	-0.319	Satisfactory
102001	4.9	-0.620	Satisfactory	3.5	-0.764	Satisfactory	18.2	1.649	Satisfactory
102002	6.42	0.636	Satisfactory	5	1.179	Satisfactory	19.4	2.287	Questionable
102003	5.88	0.190	Satisfactory	4.36	0.350	Satisfactory	15.5	0.213	Satisfactory
102004	5.66	0.008	Satisfactory	4.09	0.000	Satisfactory	15.61	0.271	Satisfactory
103001	3.35	-1.901	Satisfactory	1.75	-3.031	Unsatisfactory	13.05	-1.090	Satisfactory
103002	7	1.116	Satisfactory	5	1.179	Satisfactory	19	2.074	Questionable
103003	5.56	-0.074	Satisfactory	4.56	0.609	Satisfactory	15.4	0.160	Satisfactory
104001	5.34	-0.256	Satisfactory	4.03	-0.078	Satisfactory	15.2	0.053	Satisfactory
104002	6	0.289	Satisfactory	4	-0.117	Satisfactory	14	-0.585	Satisfactory
105001	1.8	-3.182	Unsatisfactory	1.2	-3.744	Unsatisfactory	2.6	-6.649	Unsatisfactory
105002	5.68	0.025	Satisfactory	4.28	0.246	Satisfactory	15	-0.053	Satisfactory
105003	6.28	0.521	Satisfactory	5	1.179	Satisfactory	19.2	2.181	Questionable
105004	8.06	1.992	Satisfactory	3.27	-1.062	Satisfactory	18	1.543	Satisfactory
106001	5.74	0.074	Satisfactory	4.14	0.065	Satisfactory	15.5	0.213	Satisfactory
106002	4.52	-0.934	Satisfactory	3.54	-0.712	Satisfactory	15.71	0.324	Satisfactory
106003	0.9	-3.926	Unsatisfactory	0.74	-4.339	Unsatisfactory	0.61	-7.707	Unsatisfactory
106004	6.4	0.620	Satisfactory	4.85	0.984	Satisfactory	17.2	1.117	Satisfactory
107001	7.2	1.281	Satisfactory	5.4	1.697	Satisfactory	19	2.074	Questionable
107002	7.2	1.281	Satisfactory	-	-	-	18.5	1.809	Satisfactory
107003	8	1.942	Satisfactory	5.14	1.360	Satisfactory	20.9	3.085	Unsatisfactory
107004	6.4	0.620	Satisfactory	4.4	0.402	Satisfactory	15.4	0.160	Satisfactory
108001	2.3	-2.769	Questionable	1.8	-2.966	Questionable	8	-3.777	Unsatisfactory
108002	5.57	-0.066	Satisfactory	3.49	-0.777	Satisfactory	15.1	0.000	Satisfactory
108003	7	1.116	Satisfactory	5	1.179	Satisfactory	14	-0.585	Satisfactory
108004	4.61	-0.860	Satisfactory	3.2	-1.153	Satisfactory	14	-0.585	Satisfactory
109001	5.54	-0.091	Satisfactory	4.17	0.104	Satisfactory	13.59	-0.803	Satisfactory
109002	4.75	-0.744	Satisfactory	3.73	-0.466	Satisfactory	13.78	-0.702	Satisfactory
109003	5.43	-0.182	Satisfactory	4.08	-0.013	Satisfactory	15.25	0.080	Satisfactory
109004	7.66	1.661	Satisfactory	5.9	2.345	Questionable	26	5.798	Unsatisfactory
110001	6.62	0.802	Satisfactory	6.22	2.759	Questionable	19.1	2.128	Questionable
110002	0.005	-4.665	Unsatisfactory	0.006	-5.290	Unsatisfactory	0.006	-8.029	Unsatisfactory
111001	2.68	-2.455	Questionable	2.31	-2.306	Questionable	6.63	-4.505	Unsatisfactory
112001	4.13	-1.256	Satisfactory	-	-	-	13.93	-0.622	Satisfactory
112002	4.33	-1.091	Satisfactory	3.46	-0.816	Satisfactory	15	-0.053	Satisfactory
112003	5.5	-0.124	Satisfactory	4.5	0.531	Satisfactory	13.6	-0.798	Satisfactory
112004	5.94	0.240	Satisfactory	3.66	-0.557	Satisfactory	13.7	-0.745	Satisfactory
113001	5.5	-0.124	Satisfactory	4.5	0.531	Satisfactory	18.4	1.755	Satisfactory
113002	0.18	-4.521	Unsatisfactory	4.1	0.013	Satisfactory	16	0.479	Satisfactory
113003	15.3	7.975	Unsatisfactory	7.9	4.935	Unsatisfactory	10.3	-2.553	Questionable
113004	12.5	5.661	Unsatisfactory	5.7	2.085	Questionable	16.3	0.638	Satisfactory
114001	6.2	0.455	Satisfactory	4.5	0.531	Satisfactory	17	1.011	Satisfactory
114002	5.65	0.000	Satisfactory	4.08	-0.013	Satisfactory	-	-	-
115001	5.59	-0.050	Satisfactory	4.18	0.117	Satisfactory	14.4	-0.372	Satisfactory
115002	3.06	-2.140	Questionable	4.02	-0.091	Satisfactory	15.15	0.027	Satisfactory

115003	5.77	0.099	Satisfactory	3.82	-0.350	Satisfactory	14.94	-0.085	Satisfactory
115004	2.3	-2.769	Questionable	1.52	-3.329	Unsatisfactory	4	-5.904	Unsatisfactory
116001	7.378	1.428	Satisfactory	5.47	1.788	Satisfactory	20.57	2.910	Questionable
116002	-	-	-	-	-	-	-	-	-
116003	0.239	-4.472	Unsatisfactory	0.46	-4.702	Unsatisfactory	0.226	-7.912	Unsatisfactory
116004	-	-	-	-	-	-	-	-	-
116005	5.6	-0.041	Satisfactory	4.01	-0.104	Satisfactory	14.7	-0.213	Satisfactory
116006	-	-	-	-	-	-	-	-	-
116007	5.75	0.083	Satisfactory	3.85	-0.311	Satisfactory	14.7	-0.213	Satisfactory
116008	5.09	-0.463	Satisfactory	3.81	-0.363	Satisfactory	14.3	-0.426	Satisfactory
116009	5.78	0.107	Satisfactory	4.05	-0.052	Satisfactory	14.8	-0.160	Satisfactory
116010	5	-0.537	Satisfactory	4.08	-0.013	Satisfactory	13.6	-0.798	Satisfactory
116011	6.1	0.372	Satisfactory	3.85	-0.311	Satisfactory	14.78	-0.170	Satisfactory
117001	6.6	0.785	Satisfactory	1.6	-3.225	Unsatisfactory	13.5	-0.851	Satisfactory
117002	6	0.289	Satisfactory	3.88	-0.272	Satisfactory	12.4	-1.436	Satisfactory
117003	5.45	-0.165	Satisfactory	4.07	-0.026	Satisfactory	14.7	-0.213	Satisfactory
118001	3.4	-1.860	Satisfactory	2.7	-1.801	Satisfactory	8.4	-3.564	Unsatisfactory
118002	2.7	-2.438	Questionable	2.5	-2.060	Questionable	9	-3.245	Unsatisfactory
118003	-	-	-	-	-	-	-	-	-
118004	6.9	1.033	Satisfactory	3.5	-0.764	Satisfactory	17	1.011	Satisfactory
119001	8.27	2.165	Questionable	8.53	5.751	Unsatisfactory	15.35	0.133	Satisfactory
119002	10	3.595	Unsatisfactory	8.4	5.583	Unsatisfactory	17	1.011	Satisfactory
119003	9.45	3.140	Unsatisfactory	10.19	7.902	Unsatisfactory	18.7	1.915	Satisfactory
119004	9.9	3.512	Unsatisfactory	10.8	8.692	Unsatisfactory	17.8	1.436	Satisfactory
120001	5.68	0.025	Satisfactory	4.82	0.946	Satisfactory	14.87	-0.122	Satisfactory
120002	5.49	-0.132	Satisfactory	4.22	0.168	Satisfactory	15	-0.053	Satisfactory
120003	5.72	0.058	Satisfactory	4.56	0.609	Satisfactory	15.6	0.266	Satisfactory
120004	5.56	-0.074	Satisfactory	4.23	0.181	Satisfactory	14.7	-0.213	Satisfactory
121001	5.3	-0.289	Satisfactory	3.9	-0.246	Satisfactory	14.7	-0.213	Satisfactory
121002	4.52	-0.934	Satisfactory	3.28	-1.049	Satisfactory	15	-0.053	Satisfactory
121004	5.2	-0.372	Satisfactory	3.9	-0.246	Satisfactory	15	-0.053	Satisfactory
Preparation value	5.35			3.92			14.5		
Assigned value	5.65			4.09			15.11		
Expected deviation	1.21			0.77			1.88		
Lab with results	73			71			72		
Standard uncertainty	0.177			0.114			0.277		
$0.3^* \sigma_{pt}$	0.363			0.231			0.564		
$\mu \leq 0.3^* \sigma_{pt}$	**YES**			**YES**			**YES**		

Note: " – " Denotes no value transmitted from the laboratory

Figure C.7: Ordered z-scores Bar Chart of results for Ammonia Nitrogen sample 1

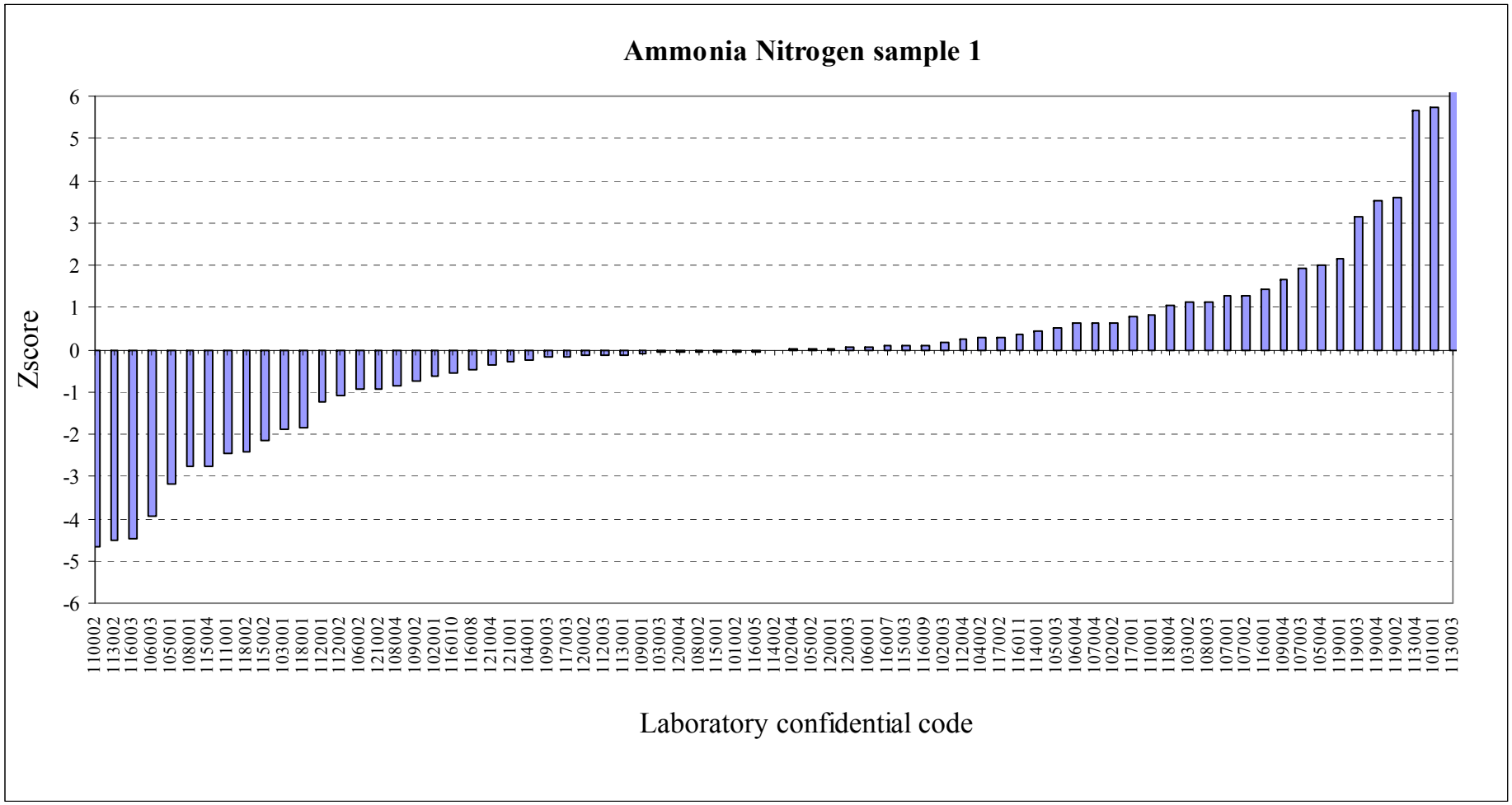


Figure C.8: Ordered z-scores Bar Chart of results for Ammonia Nitrogen sample 2

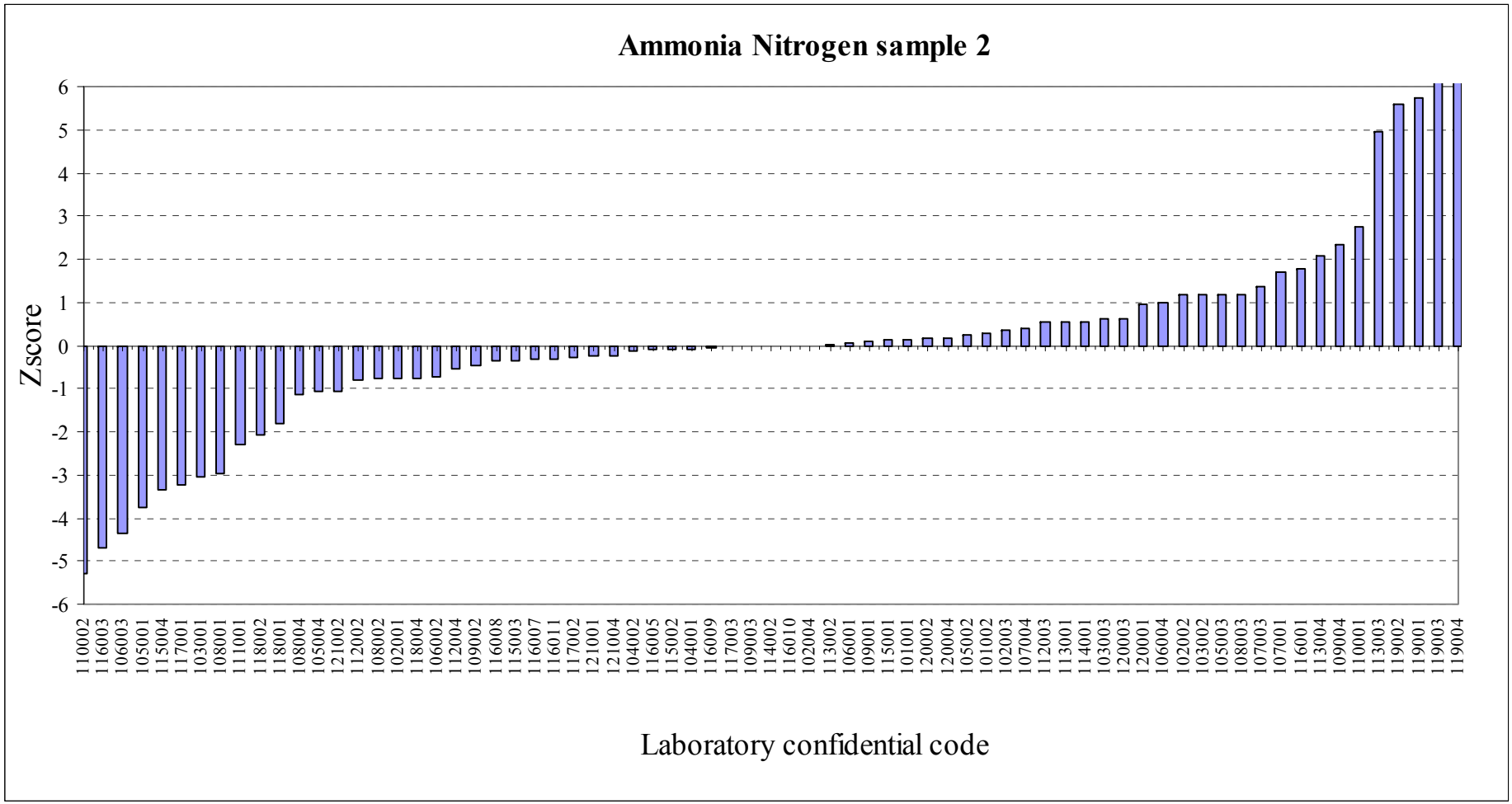
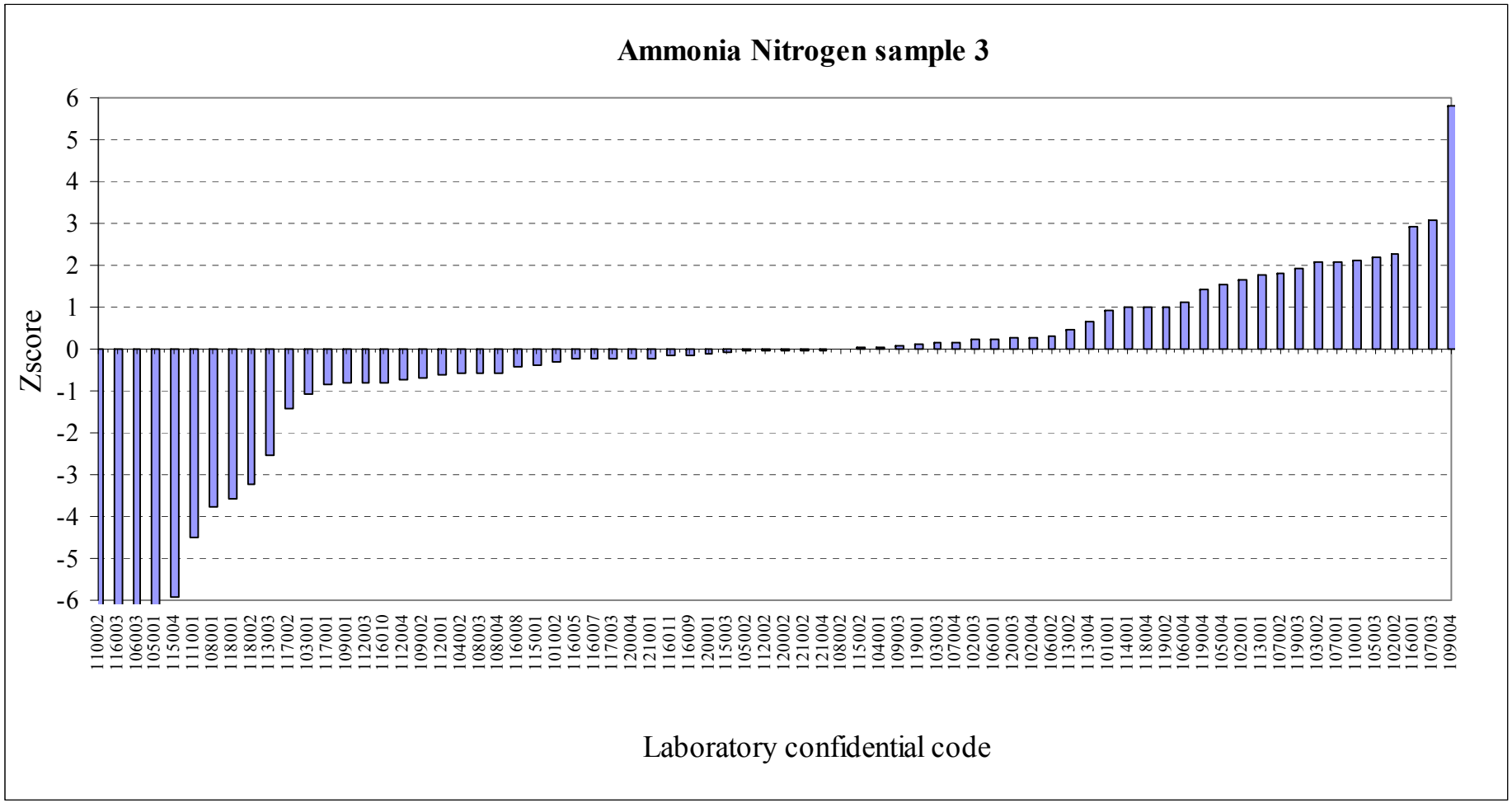


Figure C.9: Ordered z-scores Bar Chart of results for Ammonia Nitrogen sample 3



Comparison of Nitrite plus Nitrate results, z-scores, evaluations and ordered z-score bar charts

Table C.4: Nitrite plus Nitrate (mg N/l) results, z-scores and evaluations

# Lab	Sample 1			Sample 2			Sample 3		
	Results	z-score	Evaluation	Results	z-score	Evaluation	Results	z-score	Evaluation
101001	-	-	-	-	-	-	-	-	-
101002	3.4	0.000	Satisfactory	38.9	-0.577	Satisfactory	25.6	-0.932	Satisfactory
102001	-	-	-	-	-	-	-	-	-
102002	14.6	17.778	Unsatisfactory	106	5.875	Unsatisfactory	131	23.636	Unsatisfactory
102003	-	-	-	-	-	-	-	-	-
102004	2.88	-0.825	Satisfactory	41.73	-0.305	Satisfactory	26.64	-0.690	Satisfactory
103001	4.3	1.429	Satisfactory	54.15	0.889	Satisfactory	32.59	0.697	Satisfactory
103002	3.1	-0.476	Satisfactory	42	-0.279	Satisfactory	28	-0.373	Satisfactory
103003	5.345	3.087	Unsatisfactory	50.01	0.491	Satisfactory	40.006	2.426	Questionable
104001	3.08	-0.508	Satisfactory	45.7	0.077	Satisfactory	29.7	0.023	Satisfactory
104002	3.2	-0.317	Satisfactory	46	0.106	Satisfactory	30	0.093	Satisfactory
105001	33.69	48.079	Unsatisfactory	65.2	1.952	Satisfactory	68.4	9.044	Unsatisfactory
105002	3.66	0.413	Satisfactory	55.04	0.975	Satisfactory	32.4	0.653	Satisfactory
105003	3.98	0.921	Satisfactory	6.2	-3.721	Unsatisfactory	30.61	0.235	Satisfactory
105004	4.01	0.968	Satisfactory	15.3	-2.846	Questionable	30	0.093	Satisfactory
106001	3.65	0.397	Satisfactory	44.4	-0.048	Satisfactory	29.2	-0.093	Satisfactory
106002	30.85	43.571	Unsatisfactory	82.43	3.609	Unsatisfactory	86.32	13.221	Unsatisfactory
106003	2.17	-1.952	Satisfactory	1.86	-4.138	Unsatisfactory	2	-6.434	Unsatisfactory
106004	45	66.032	Unsatisfactory	53	0.779	Satisfactory	33.4	0.886	Satisfactory
107001	3	-0.635	Satisfactory	43	-0.183	Satisfactory	29	-0.140	Satisfactory
107002	3.3	-0.159	Satisfactory	49	0.394	Satisfactory	28	-0.373	Satisfactory
107003	3.41	0.016	Satisfactory	46.3	0.135	Satisfactory	30.1	0.117	Satisfactory
107004	3.2	-0.317	Satisfactory	46.1	0.115	Satisfactory	28.4	-0.280	Satisfactory
108001	3.1	-0.476	Satisfactory	45	0.010	Satisfactory	29	-0.140	Satisfactory
108002	3.99	0.937	Satisfactory	22.3	-2.173	Questionable	23.4	-1.445	Satisfactory
108003	5	2.540	Questionable	49	0.394	Satisfactory	32	0.559	Satisfactory
108004	3.2	-0.317	Satisfactory	44.7	-0.019	Satisfactory	28.8	-0.186	Satisfactory
109001	3.4	0.000	Satisfactory	45.23	0.032	Satisfactory	26.36	-0.755	Satisfactory
109002	3.23	-0.270	Satisfactory	32.19	-1.222	Satisfactory	21.16	-1.967	Satisfactory
109003	8	7.302	Unsatisfactory	88.8	4.221	Unsatisfactory	75	10.583	Unsatisfactory
109004	15.08	18.540	Unsatisfactory	93.17	4.641	Unsatisfactory	98.14	15.977	Unsatisfactory
110001	7.84	7.048	Unsatisfactory	78.8	3.260	Unsatisfactory	86.6	13.287	Unsatisfactory
110002	-	-	-	-	-	-	-	-	-
111001	2.4	-1.587	Satisfactory	34.6	-0.990	Satisfactory	25.15	-1.037	Satisfactory
112001	2.69	-1.127	Satisfactory	-	-	-	28.6	-0.233	Satisfactory
112002	8.2863	7.756	Unsatisfactory	0.9002	-4.231	Unsatisfactory	77.95	11.270	Unsatisfactory
112003	3.67	0.429	Satisfactory	36.86	-0.773	Satisfactory	26.82	-0.648	Satisfactory
112004	3.27	-0.206	Satisfactory	46.6	0.163	Satisfactory	33.9	1.002	Satisfactory
113001	2.9	-0.794	Satisfactory	45.9	0.096	Satisfactory	29	-0.140	Satisfactory
113002	<0.05	-	-	0.33	-4.286	Unsatisfactory	0.21	-6.851	Unsatisfactory
113003	3.26	-0.222	Satisfactory	37	-0.760	Satisfactory	23.39	-1.448	Satisfactory
113004	12	13.651	Unsatisfactory	192	14.144	Unsatisfactory	122	21.538	Unsatisfactory
114001	3	-0.635	Satisfactory	45	0.010	Satisfactory	29	-0.140	Satisfactory
114002	3.28	-0.190	Satisfactory	46.8	0.183	Satisfactory	30.5	0.210	Satisfactory
115001	2.79	-0.968	Satisfactory	66.95	2.120	Questionable	36.23	1.545	Satisfactory
115002	0.128	-5.194	Unsatisfactory	1.889	-4.136	Unsatisfactory	1.811	-6.478	Unsatisfactory

115003	2.03	-2.175	Questionable	4.28	-3.906	Unsatisfactory	9.68	-4.643	Unsatisfactory
115004	4.280	1.397	Satisfactory	20.902	-2.307	Questionable	29.701	0.024	Satisfactory
116001	-	-	-	-	-	-	-	-	-
116002	-	-	-	-	-	-	-	-	-
116003	4.44	1.651	Satisfactory	54	0.875	Satisfactory	35	1.259	Satisfactory
116004	-	-	-	-	-	-	-	-	-
116005	3.5	0.159	Satisfactory	46.2	0.125	Satisfactory	29	-0.140	Satisfactory
116006	-	-	-	-	-	-	-	-	-
116007	3.46	0.095	Satisfactory	47	0.202	Satisfactory	30.5	0.210	Satisfactory
116008	3.045	-0.563	Satisfactory	43.73	-0.113	Satisfactory	28.29	-0.305	Satisfactory
116009	3.06	-0.540	Satisfactory	45.6	0.067	Satisfactory	29.8	0.047	Satisfactory
116010	3.83	0.683	Satisfactory	52.2	0.702	Satisfactory	30.9	0.303	Satisfactory
116011	2.8	-0.952	Satisfactory	42.6	-0.221	Satisfactory	27.2	-0.559	Satisfactory
117001	3.1	-0.476	Satisfactory	47.5	0.250	Satisfactory	29.5	-0.023	Satisfactory
117002	3.14	-0.413	Satisfactory	46.5	0.154	Satisfactory	28	-0.373	Satisfactory
117003	<5	-	Satisfactory	41.7	-0.308	Satisfactory	29.3	-0.070	Satisfactory
118001	3.6	0.317	Satisfactory	76	2.990	Questionable	36	1.492	Satisfactory
118002	2.3	-1.746	Satisfactory	22.2	-2.183	Questionable	20.3	-2.168	Questionable
118003	-	-	-	-	-	-	-	-	-
118004	-	-	-	-	-	-	32.82	0.751	Satisfactory
119001	0.13	-5.190	Unsatisfactory	28.8	-1.548	Satisfactory	21	-2.005	Questionable
119002	<0.005	-	Unsatisfactory	22	-2.202	Questionable	15	-3.403	Unsatisfactory
119003	0.09	-5.254	Unsatisfactory	25	-1.913	Satisfactory	16.7	-3.007	Unsatisfactory
119004	0.14	-5.175	Unsatisfactory	29.4	-1.490	Satisfactory	19.2	-2.424	Questionable
120001	7.93	7.190	Unsatisfactory	71.7	2.577	Questionable	76.3	10.886	Unsatisfactory
120002	2.81	-0.937	Satisfactory	43.9	-0.096	Satisfactory	27.9	-0.396	Satisfactory
120003	3.27	-0.206	Satisfactory	46.9	0.192	Satisfactory	30.1	0.117	Satisfactory
120004	9.2	9.206	Unsatisfactory	77.6	3.144	Unsatisfactory	90.7	14.242	Unsatisfactory
121001	3.46	0.095	Satisfactory	47.2	0.221	Satisfactory	32.2	0.606	Satisfactory
121002	3.27	-0.206	Satisfactory	46.8	0.183	Satisfactory	28.7	-0.210	Satisfactory
121004	3.1	-0.476	Satisfactory	46	0.106	Satisfactory	29	-0.140	Satisfactory
Preparation value	3.04			45.8			29.5		
Assigned value	3.40			44.85			29.55		
Expected deviation	0.63			10.41			4.29		
Lab with results	67			66			68		
Standard uncertainty	0.098			1.602			0.65		
$0.3*\sigma_{pt}$	0.189			3.123			1.287		
$\mu \leq 0.3*\sigma_{pt}$	**YES**			**YES**			**YES**		

Note: " – " Denotes no value transmitted from the laboratory

Figure C.10: Ordered z-scores Bar Chart of results for Nitrite plus Nitrate sample 1

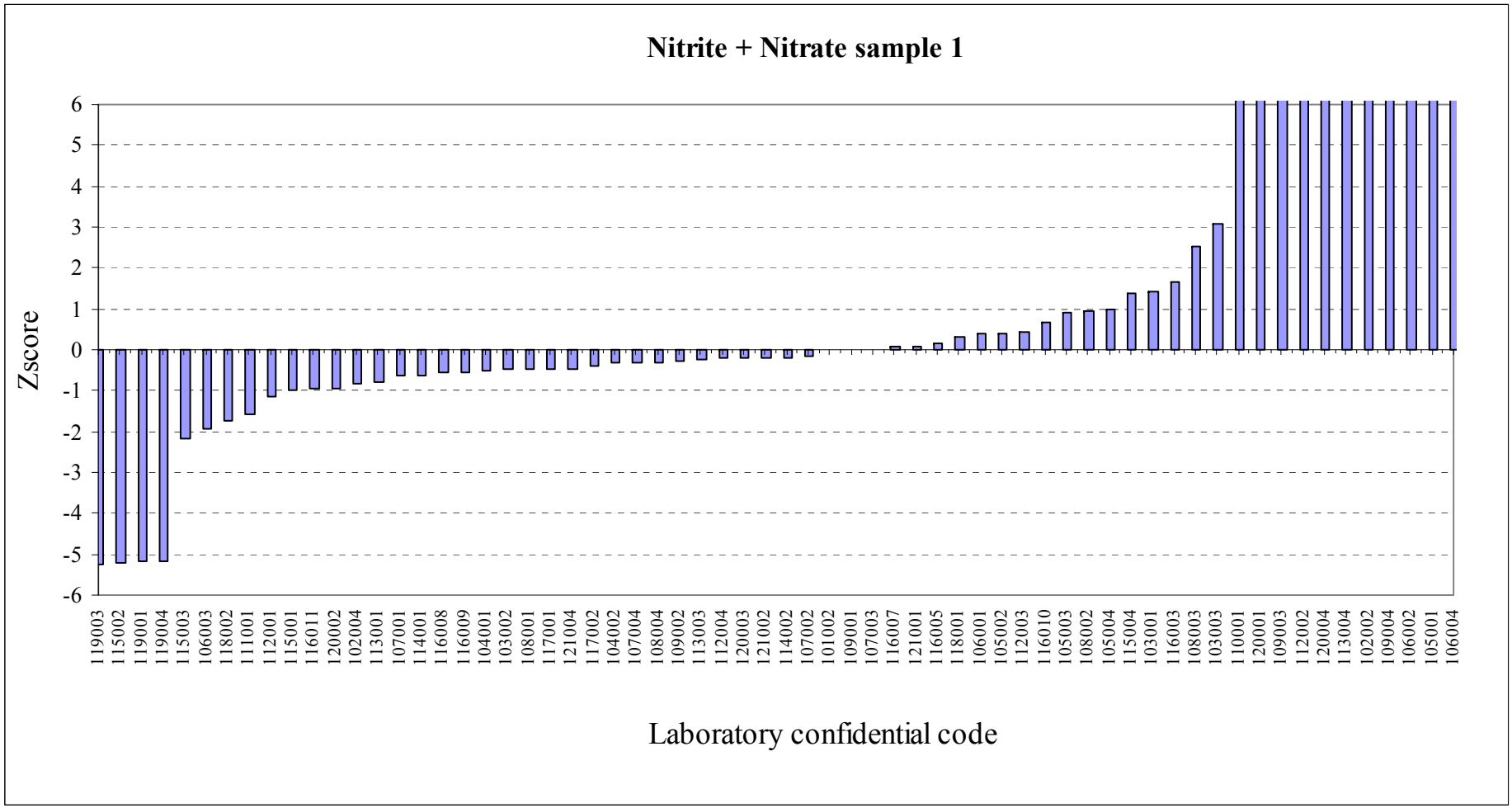


Figure C.11: Ordered z-scores Bar Chart of results for Nitrite plus Nitrate sample 2

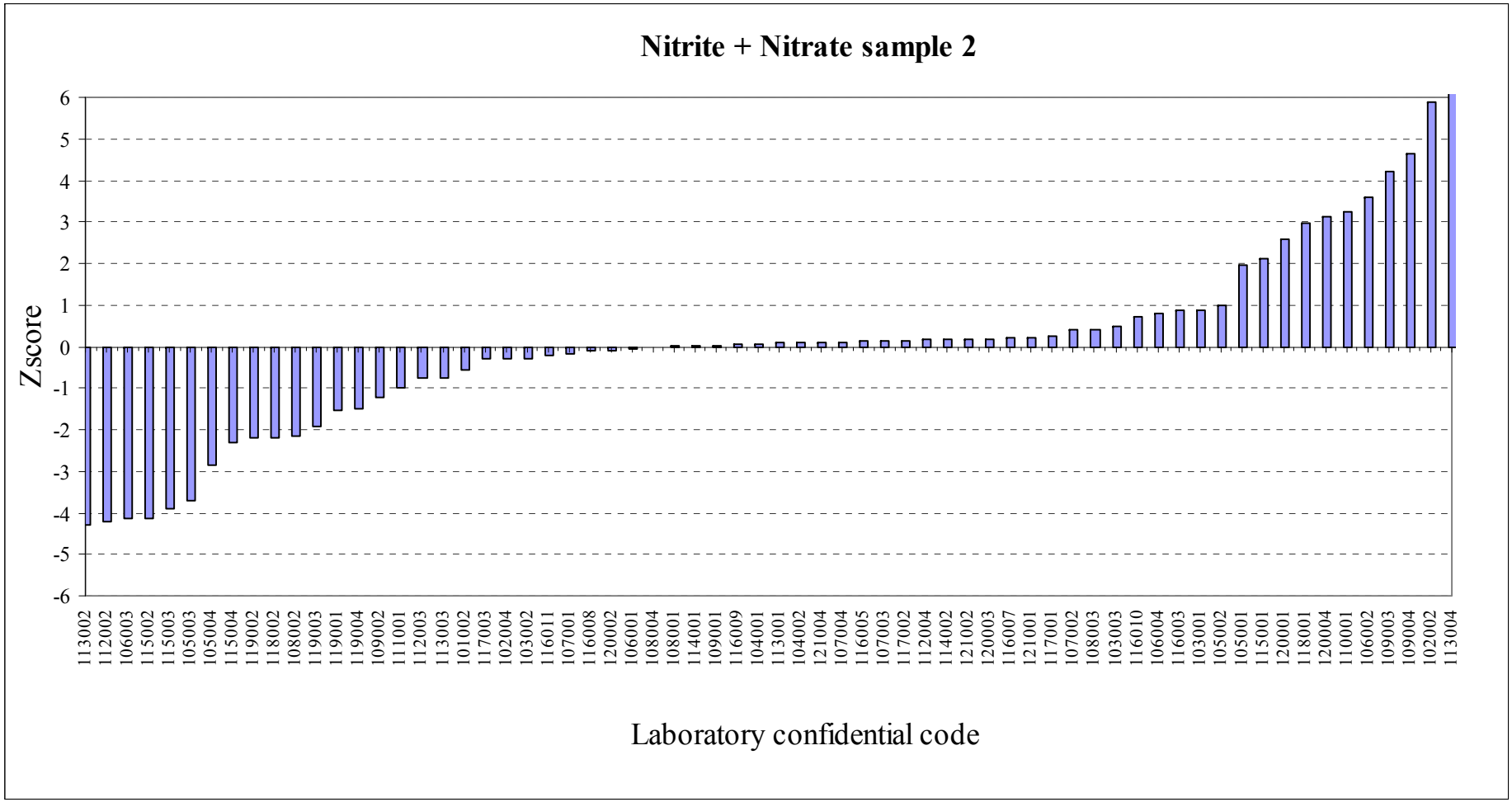
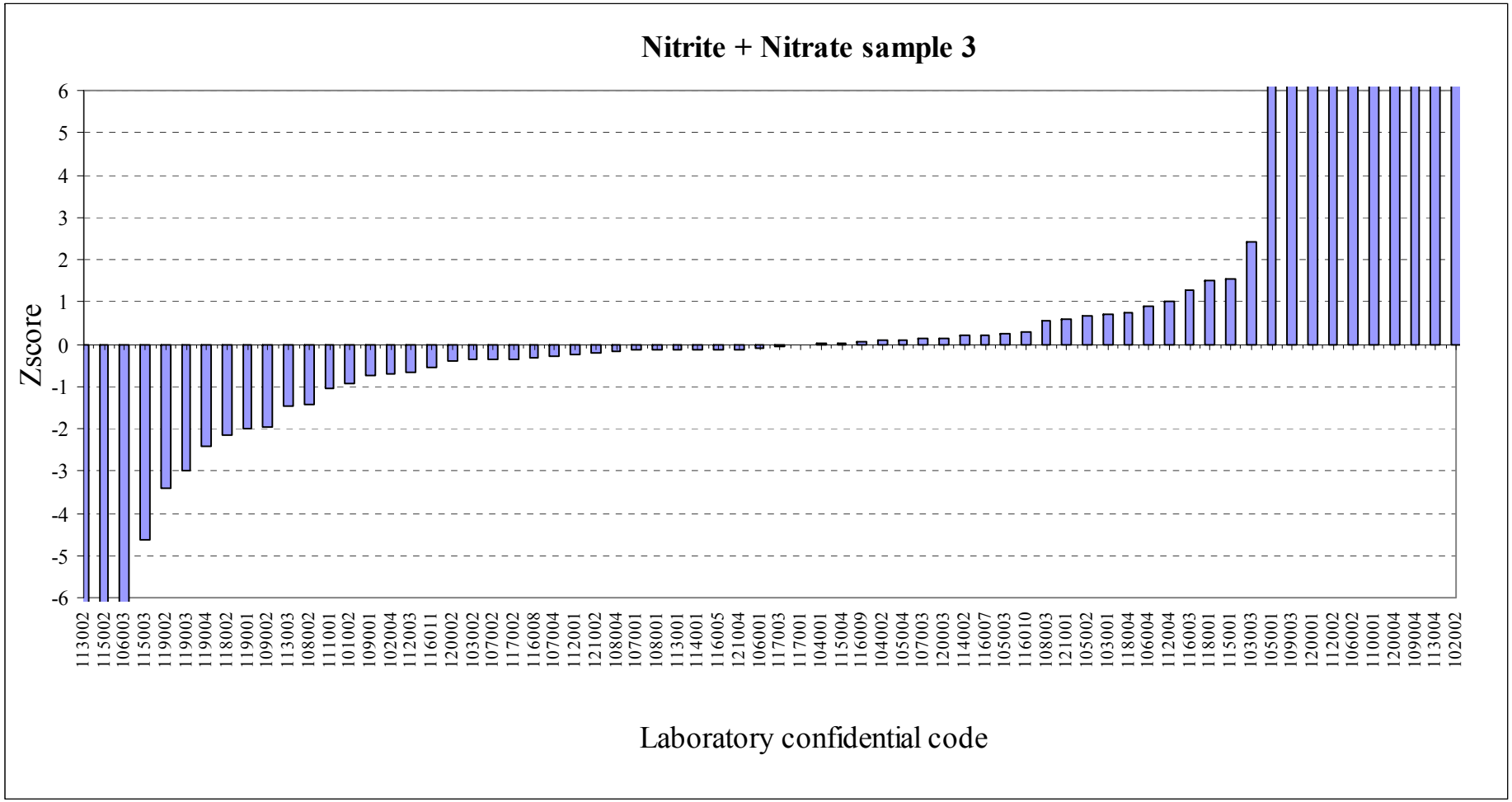


Figure C.12: Ordered z-scores Bar Chart of results for Nitrite plus Nitrate sample 3



Annex D: Homogeneity and stability verification results

Table D.1: Individual result of the replicates for homogeneity testing

Measurand	BOD_5 (mg O_2/*l*)			COD (mg O_2/*l*)			NH_3 (mg N/*l*)			NO_2+NO_3 (mg N/*l*)		
Sample no.	1	2	3	1	2	3	1	2	3	1	2	3
Analytical result	150	420	220	80	400	700	4.8	3.7	14	3.2	45	29
	150	420	220	84	400	720	4.9	3.7	14	3.2	45	29
	150	420	220	84	400	720	4.9	3.7	14	3.3	45	30
	160	420	220	85	400	720	4.9	3.8	14	3.3	46	30
	160	430	220	86	400	720	4.9	3.8	14	3.3	46	30
	160	430	220	86	400	730	4.9	3.8	15	3.3	46	30
	160	430	220	86	410	730	4.9	3.8	15	3.3	46	30
	160	430	220	87	410	730	5.0	3.8	15	3.3	46	30
	160	430	220	87	410	730	5.0	3.9	15	3.3	47	30
	160	430	220	91	410	730	5.0	4.1	15	3.3	47	31
Mean (X)	157	426	220	85.6	404	723	4.92	3.81	14.5	3.28	45.9	29.9
Between samples Standard deviation S_s	4.8	5.2	0.0	2.8	5.2	9.5	0.1	0.1	0.5	0.0	0.7	0.6
Median	160	430	220	86.0	400	725	4.90	3.80	14.5	3.30	46	30
Number of results	10	10	10	10	10	10	10	10	10	10	10	10

Table D.2: Standard deviation σ_{pt} for homogeneity testing

Assigned value	134	334	195	83	402	716	5.65	4.09	15.1	3.4	44.9	29.6
Standard deviation σ_{pt}	32	96	41	11	29	36	1.21	0.77	1.88	0.63	10.41	4.29
0.3*σ_{pt}	9.6	28.8	12.3	3.3	8.7	10.8	0.36	0.23	0.56	0.19	3.12	1.29
Between samples Standard deviation S_s	4.8	5.2	0.0	2.8	5.2	9.5	0.1	0.1	0.5	0.0	0.7	0.6
$S_s \leq 0.3*\sigma_{pt}$	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Table D.3: Stability verification

Stability results (Y)	150	400	210	84	410	720	5.2	3.7	15	3.2	47	30
Homogeneity Mean (X)	157	426	220	85.6	404	723	4.92	3.81	14.5	3.28	45.9	29.9
|X-Y|	7	26	10	1.6	6	3	0.28	0.11	0.5	0.08	1.1	0.1
0.3*σ_{pt}	9.6	28.8	12.3	3.3	8.7	10.8	0.36	0.23	0.56	0.19	3.12	1.29
|X-Y| ≤0.3 * σ_{pt}	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Annex E: Adverse effects of irradiation

Table E.1: *Adverse effects of irradiation on Biochemical Oxygen Demand*

# Lab	Sample 1			Sample 2			Sample 3		
	Results	z-score	Evaluation	Results	z-score	Evaluation	Results	z-score	Evaluation
Control	150	0.50	Satisfactory	400	0.69	Satisfactory	210	0.37	Satisfactory
Irradiated	10	-3.87	Unsatisfactory	47	-2.99	Questionable	15	-4.39	Unsatisfactory
Assigned value	134			334			195		
Expected deviation	32			96			41		

Table E.2: Adverse effects of irradiation on Chemical Oxygen Demand

# Lab	Sample 1			Sample 2			Sample 3		
	Results	z-score	Evaluation	Results	z-score	Evaluation	Results	z-score	Evaluation
Control	84	0.091	Satisfactory	410	0.28	Satisfactory	720	0.11	Satisfactory
Irradiated	6	-7.00	Unsatisfactory	260	-4.90	Unsatisfactory	590	-3.50	Unsatisfactory
Assigned value	83			402			716		
Expected deviation	11			29			36		

Table E.3: Adverse effects of irradiation on Ammonia Nitrogen

# Lab	Sample 1			Sample 2			Sample 3		
	Results	z-score	Evaluation	Results	z-score	Evaluation	Results	z-score	Evaluation
Control	5.2	-0.37	Satisfactory	3.7	-0.51	Satisfactory	15	-0.06	Satisfactory
Irradiated	8.9	2.69	Questionable	9.8	7.42	Unsatisfactory	17	1.01	Satisfactory
Assigned value	5.65			4.09			15.11		
Expected deviation	1.21			0.77			1.88		

Table E.4: Adverse effects of irradiation on Nitrite plus Nitrate

# Lab	Sample 1			Sample 2			Sample 3		
	Results	z-score	Evaluation	Results	z-score	Evaluation	Results	z-score	Evaluation
Control	3.2	-0.32	Satisfactory	47	0.217	Satisfactory	30	0.11	Satisfactory
Irradiated	0.23	-5.03	Unsatisfactory	30	-1.43	Satisfactory	19	-2.46	Questionable
Assigned value	3.4			44.85			29.55		
Expected deviation	0.63			10.41			4.29		

Annex E.1: Pictures of the PT samples before and after of irradiation

Figure E.1: Aspect of the PT samples for BOD_5 before irradiation



Figure E.2: Aspect of the PT samples for BOD_5 after irradiation



Figure E.3: Aspect of the PT samples for COD, $N0_2$+$N0_3$ before and after irradiation



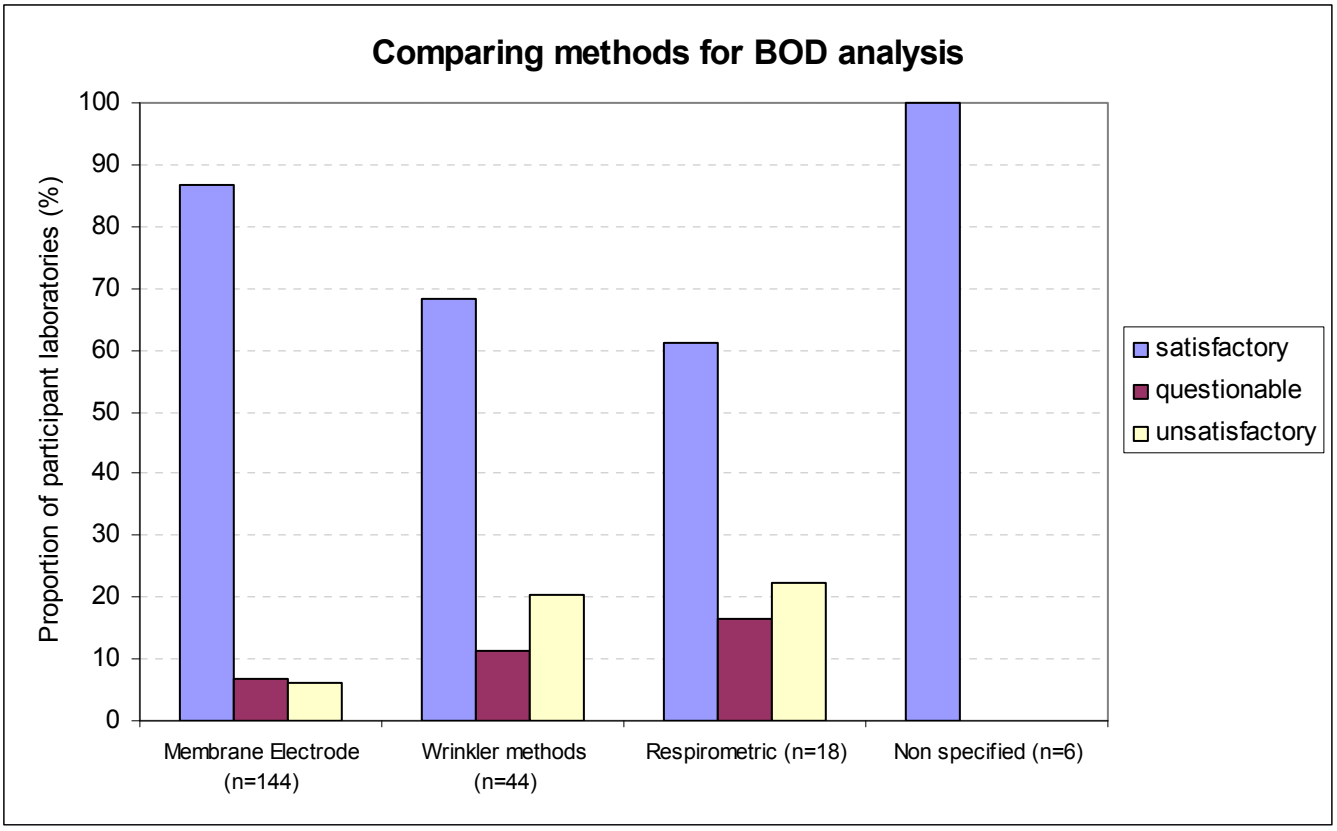
Annex F: Comparison of performance related to analytical method

These graphics represent the proportion of results obtaining a satisfactory, questionable or unsatisfactory grade for each type of methods. Therefore we considered each sample individually, which is why there is more than 77 results for each parameter.

Comparison of methods for BOD analysis

For BOD_5 analysis, the comparison is between membrane electrode, Wrinkler methods (iodometric) and the respirometric methods which include the manometric methods. The seeds used in each method were natural such as sewage effluent, sludge or others, commercial such as Polyseed, Biosystem or Bantesia or were not specified.

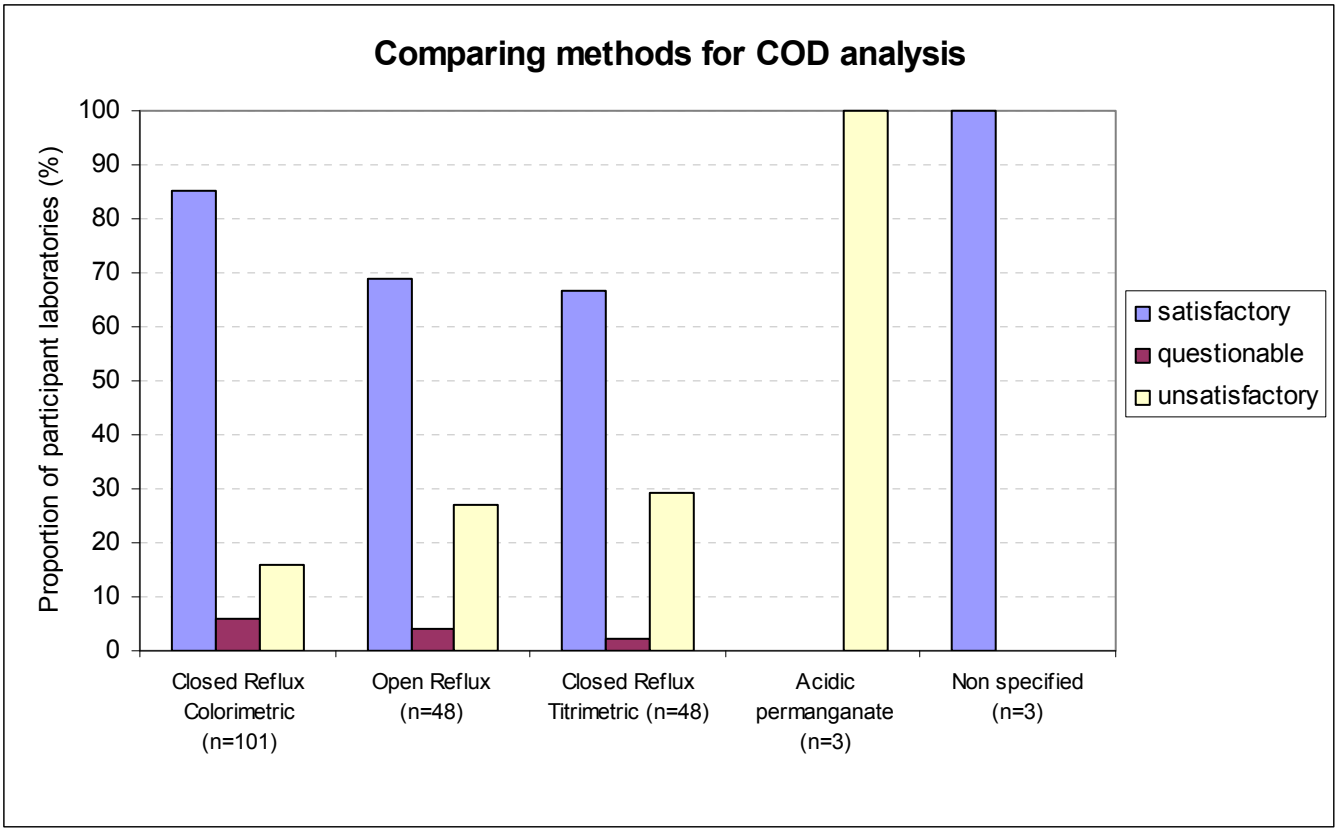
Figure F.1: Comparison of method performance for Biochemical Oxygen Demand analysis



Comparison of methods for COD analysis

For COD analysis, the methods used by the laboratories are the closed reflux colorimetric methods, the open reflux methods, the closed reflux titrimetric methods and the acidic permanganate methods.

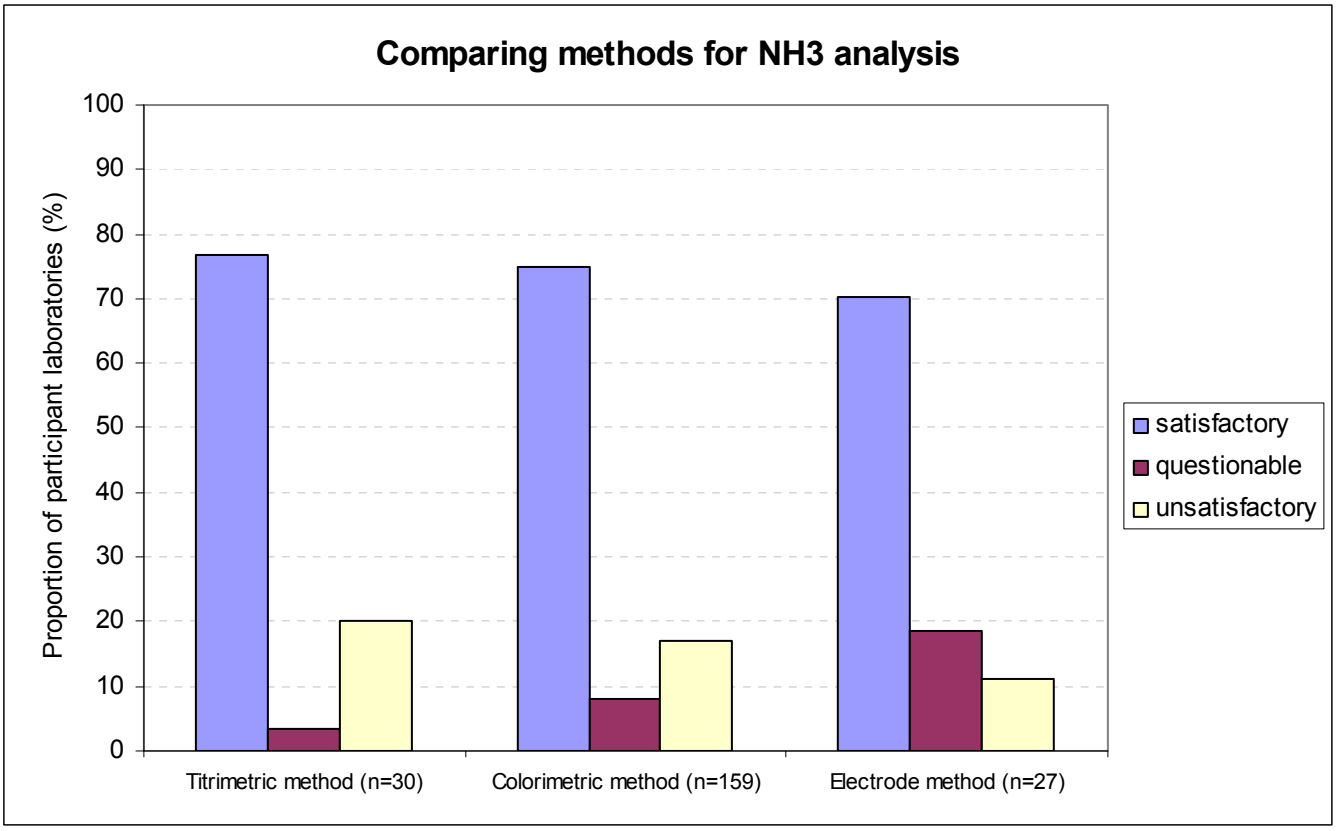
Figure F.2: Comparison of method performance for Chemical Oxygen Demand analysis



Comparison of methods for Ammonia analysis

For NH_3 analysis, the methods used by the laboratories are titrimetric methods, colorimetric methods and selective electrode methods. Distillation was mostly used with titrimetric or colorimetric methods.

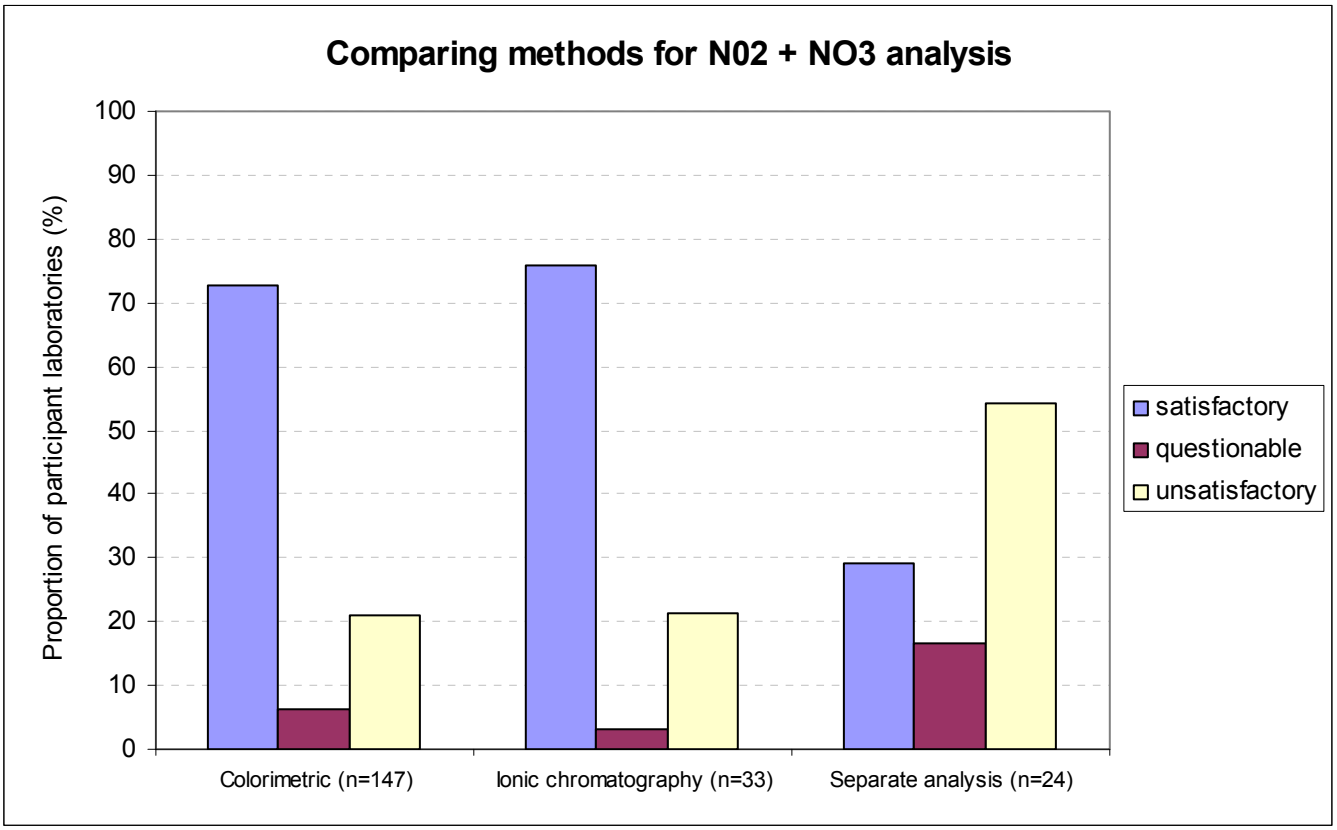
Figure F.3: Comparison of method performance for Ammonia Nitrogen analysis



Comparison of methods for Nitrite plus Nitrate analysis

For NO_2 plus NO_3 analysis, colorimetric methods including with cadmium reduction and hydrazine reduction and ionic chromatographic methods were used by the laboratories. Some of them used separate analysis methods for nitrates and nitrites and combined the results for each result.

Figure F.4: Comparison of method performance for Nitrite plus Nitrate analysis



Annex G: Comparison with results from Quebec laboratories

These tables represent the comparisons between the APLAC laboratories mean and standard deviation results; the combined APLAC laboratories plus the Quebec laboratories results; the Quebec laboratories results alone and the Canadian APLAC participant laboratories.

The graphs represent the comparisons between the APLAC laboratories z-scores and the Quebec laboratories z-score results for each of the measurands.

Table G.1: APLAC means, standard deviation and number of participating laboratories

APLAC laboratories												
	BOD_5 (mg O_2/*l*)			**COD** (mg O_2/*l*)			**NH_3** (mg N/*l*)			**NO_2+NO_3** (mg N/*l*)		
Number of laboratories	72	71	72	71	71	72	73	71	72	67	66	68
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Mean	134	334	194	83.1	401	716	5.65	4.09	15.1	3.39	44.8	29.5
Standard deviation	32.0	95.8	41.1	10.6	29.2	36.3	1.21	0.77	1.88	0.63	10.4	4.29

Table G.2: Combined APLAC plus Quebec mean, standard deviation and number of participating laboratories

APLAC + Quebec laboratories												
	BOD_5 (mg O_2/*l*)			**COD** (mg O_2/*l*)			**NH_3** (mg N/*l*)			**NO_2+NO_3** (mg N/*l*)		
Number of laboratories	99	98	99	100	100	101	93	91	92	77	76	78
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Mean	136	357	198	83.2	402	718	5.62	4.09	15.0	3.35	45.3	29.5
Standard deviation	24.8	70.3	32.0	9.45	23.7	30.3	0.92	0.61	1.45	0.5	6.46	3.74

Table G.3: Quebec means, standard deviation and number of participating laboratories

Quebec laboratories												
	BOD_5 (mg O_2/*l*)			**COD** (mg O_2/*l*)			**NH_3** (mg N/*l*)			**NO_2+NO_3** (mg N/*l*)		
Number of laboratories	27			29			20			10		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Mean[1]	138	392	203	83.5	403	721	5.49	4.00	14.7	3.2	46.1	29.4
Standard deviation[1]	10.4	25.1	15.7	6.38	17.5	26.9	0.50	0.29	0.92	0.09	2.66	2.04
Standard deviation CEAEQ[2]	21	60	30.9	8.3	40.2	72.5	0.55	0.388	1.45	0.32	4.72	2.96

1. This data was obtained employing the same statistical evaluation of the results as those of the T062 participants
2. This data is the "normal" evaluation criteria in the routine CEAEQ PT Program

Table G.4: Canadian APLAC laboratories means, standard deviation and number of participating laboratories

Canadian laboratories (CALA + SCC)												
	BOD_5 (mg O_2/*l*)			**COD** (mg O_2/*l*)			**NH_3** (mg N/*l*)			**NO_2+NO_3** (mg N/*l*)		
Number of laboratories	13	13	13	11	11	11	12	12	12	11	11	11
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Mean	140	383	203	80	400	721	5.49	3.81	14.36	3.52	45.9	29.5
Standard deviation	17.8	55.9	25.1	6	20.6	16.3	0.84	0.46	0.69	0.54	2.8	1.89

Comparison of BOD results from APLAC participants and Quebec laboratories

Figure G.1: Comparison of z-score from APLAC and Quebec laboratories for Biochemical Oxygen Demand sample 1

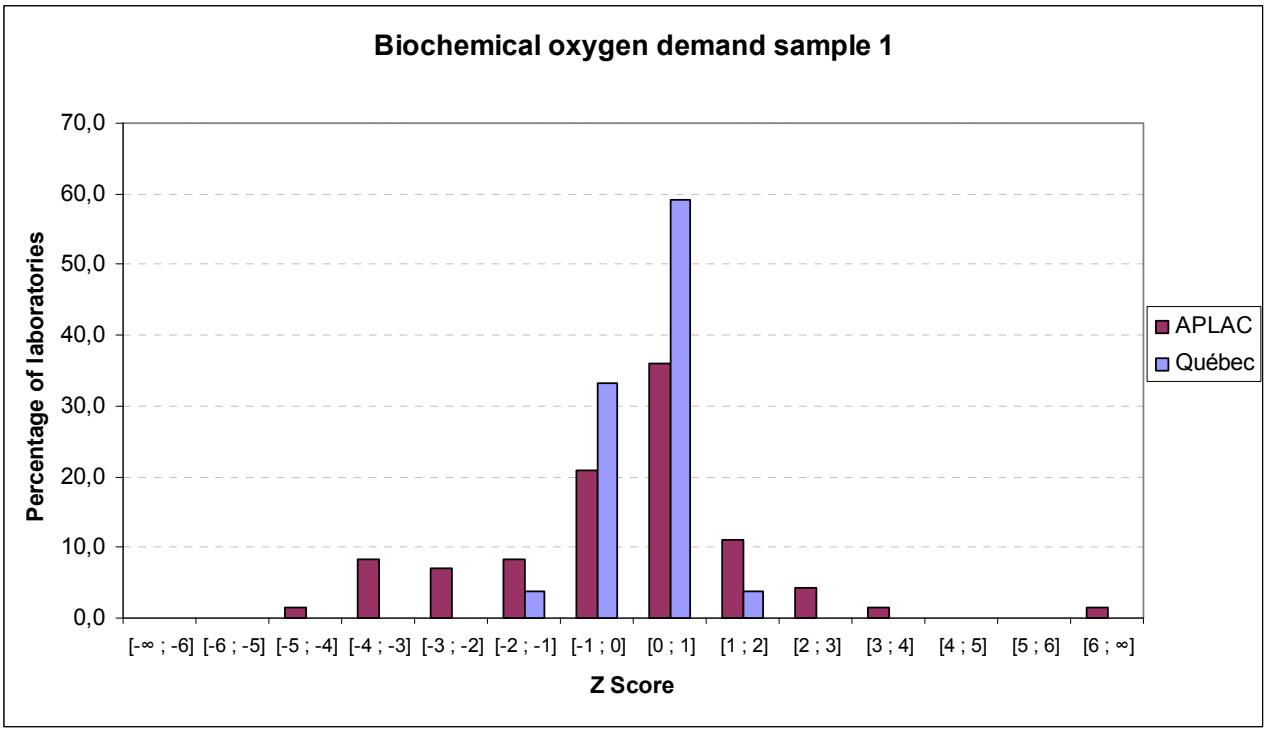


Figure G.2: Comparison of z-score from APLAC and Quebec laboratories for Biochemical Oxygen Demand sample 2

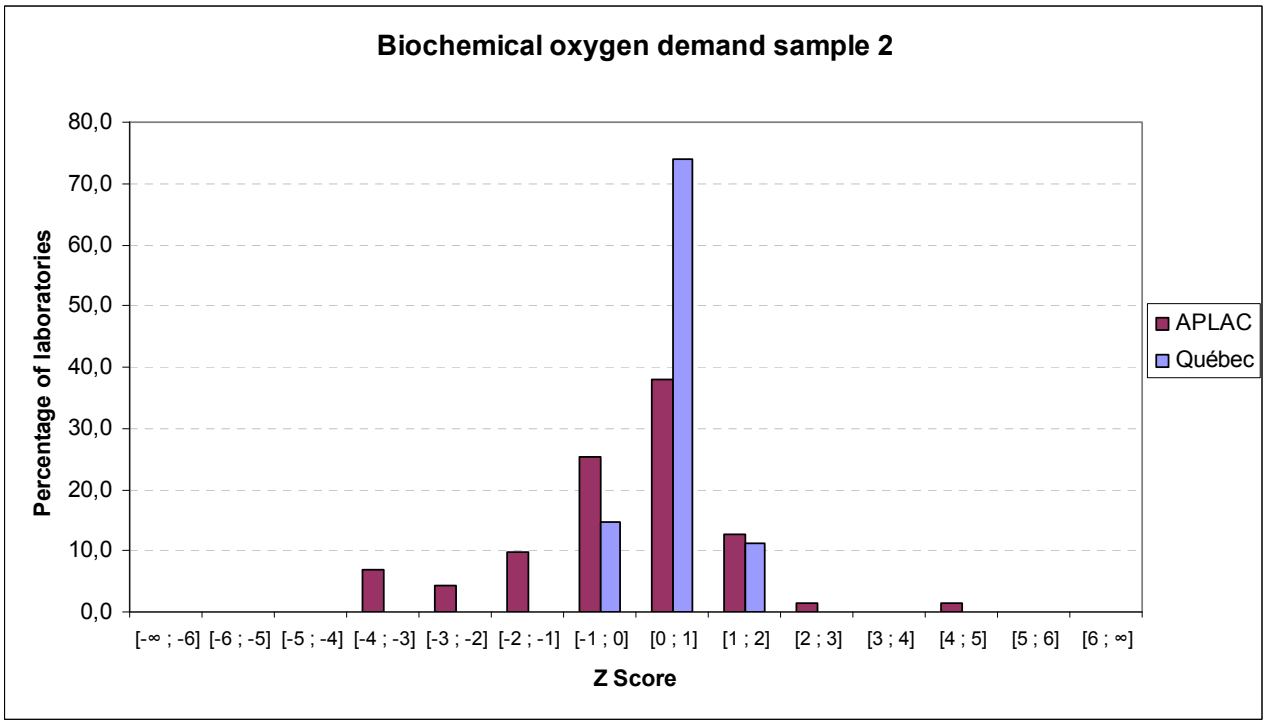
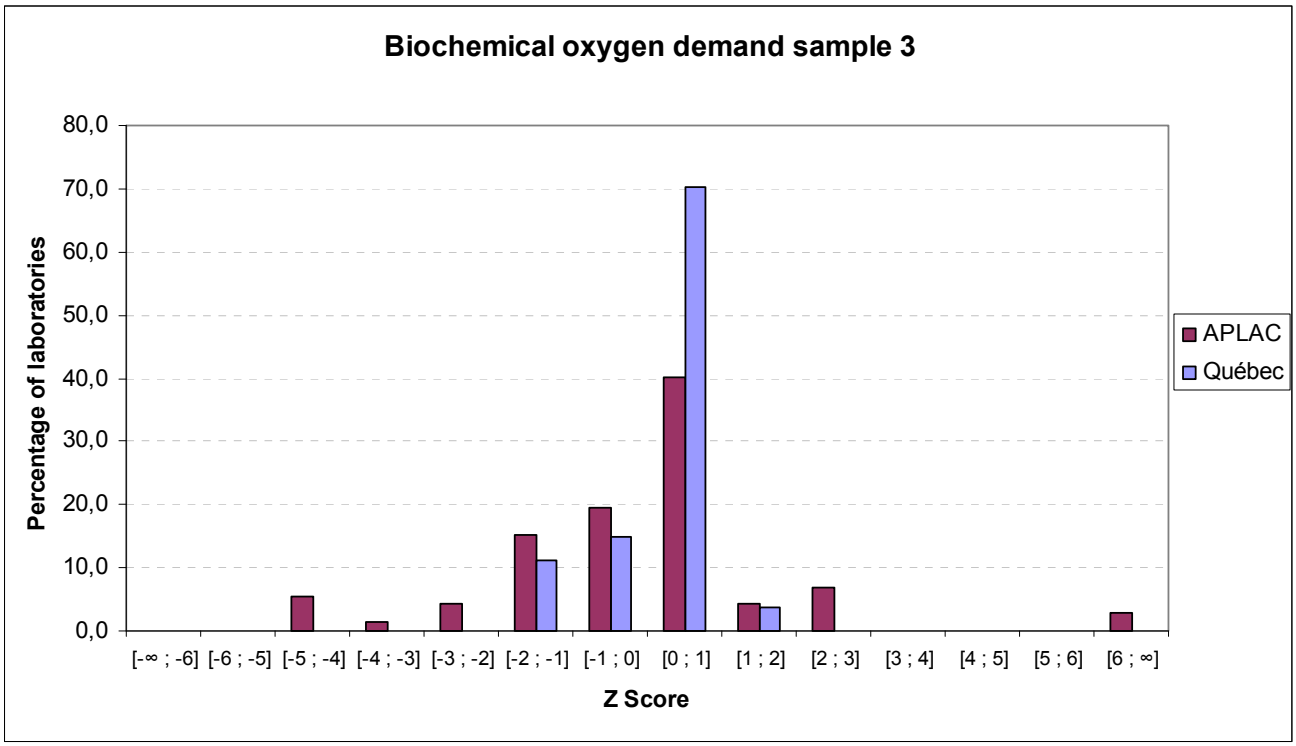


Figure G.3: Comparison of z-score from APLAC and Quebec laboratories for Biochemical Oxygen Demand sample 3



Comparison of COD results from APLAC participants and Quebec laboratories

Figure G.4: Comparison of z-score from APLAC and Quebec laboratories for Chemical Oxygen Demand sample 1

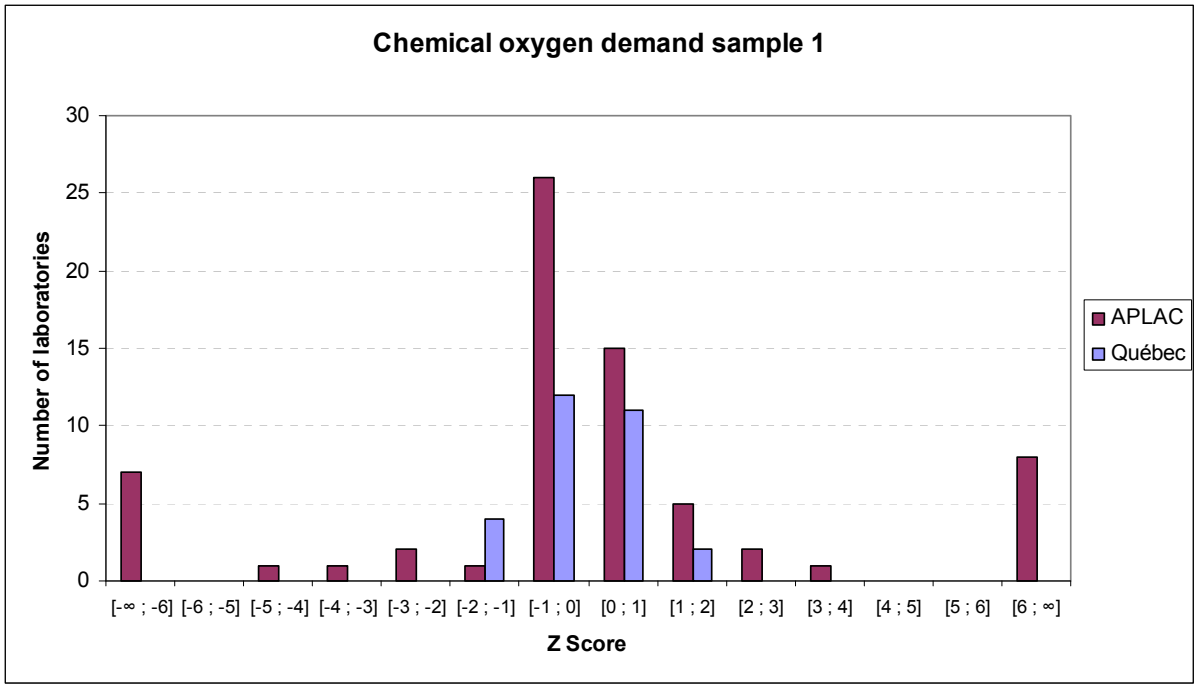


Figure G.5: Comparison of z-score from APLAC and Quebec laboratories for Chemical Oxygen Demand sample 2

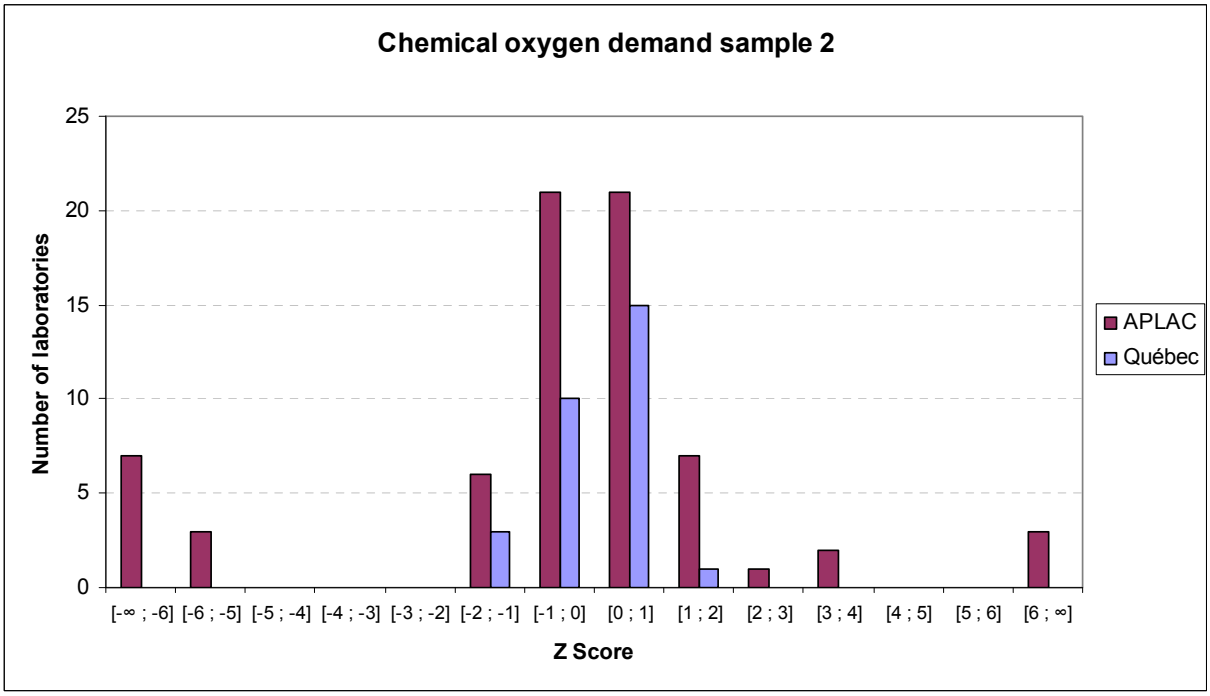
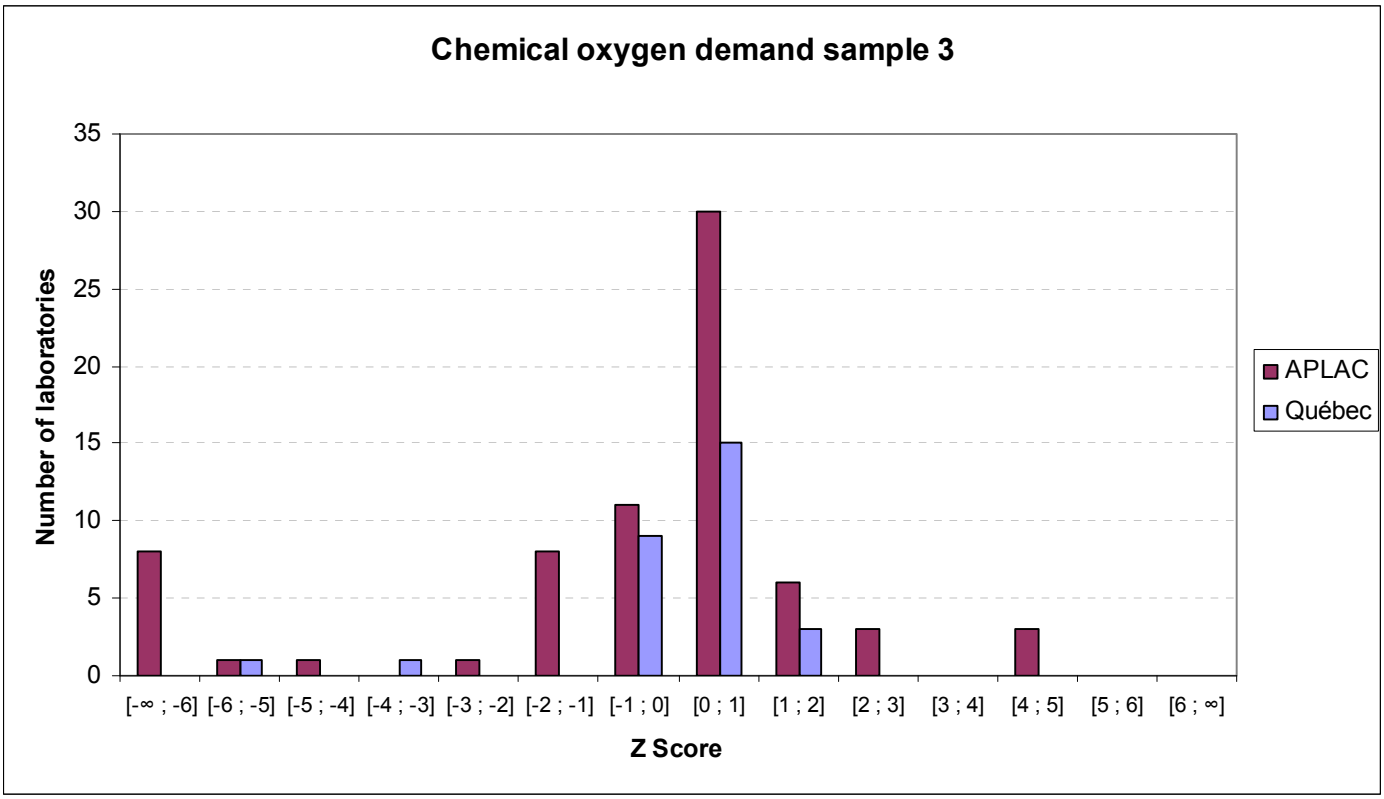


Figure G.6: Comparison of z-score from APLAC and Quebec laboratories for Chemical Oxygen Demand sample 3



Comparison of Ammonia results from APLAC participants and Quebec laboratories

Figure G.7: Comparison of z-score from APLAC and Quebec laboratories for Ammonia Nitrogen sample 1

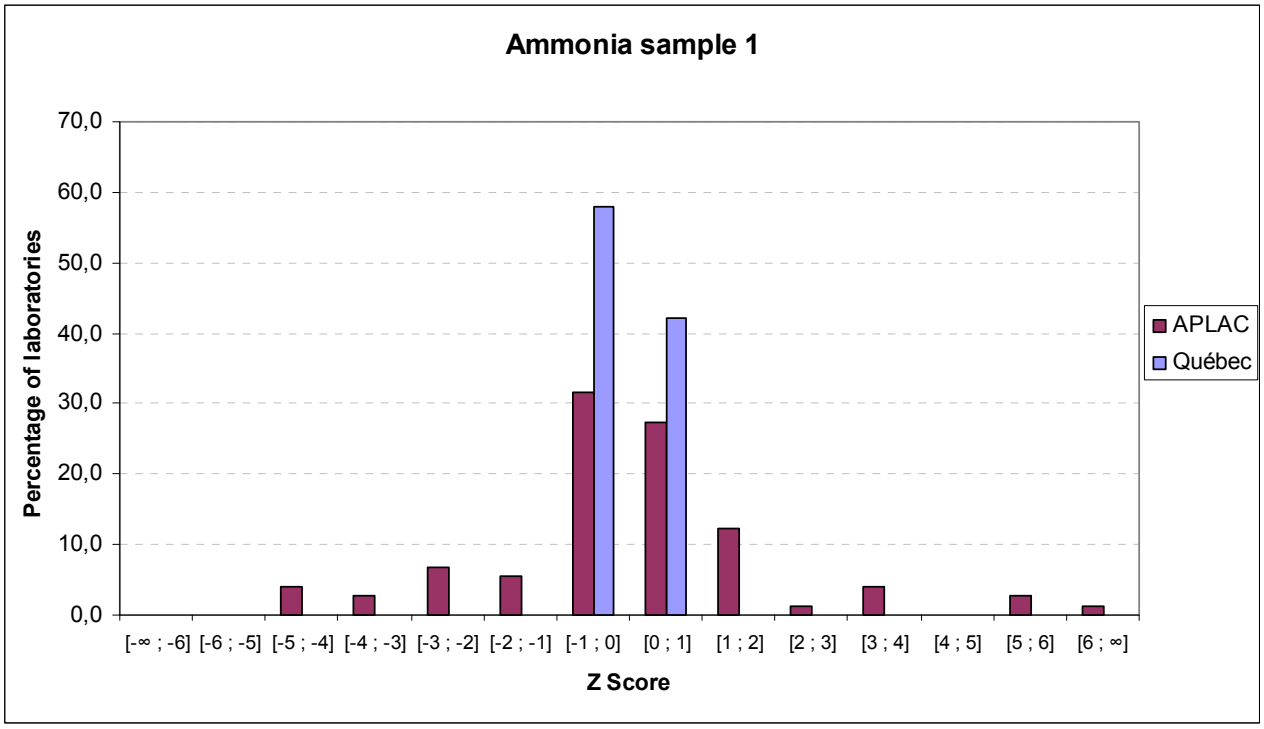


Figure G.8: Comparison of z-score from APLAC and Quebec laboratories for Ammonia Nitrogen sample 2

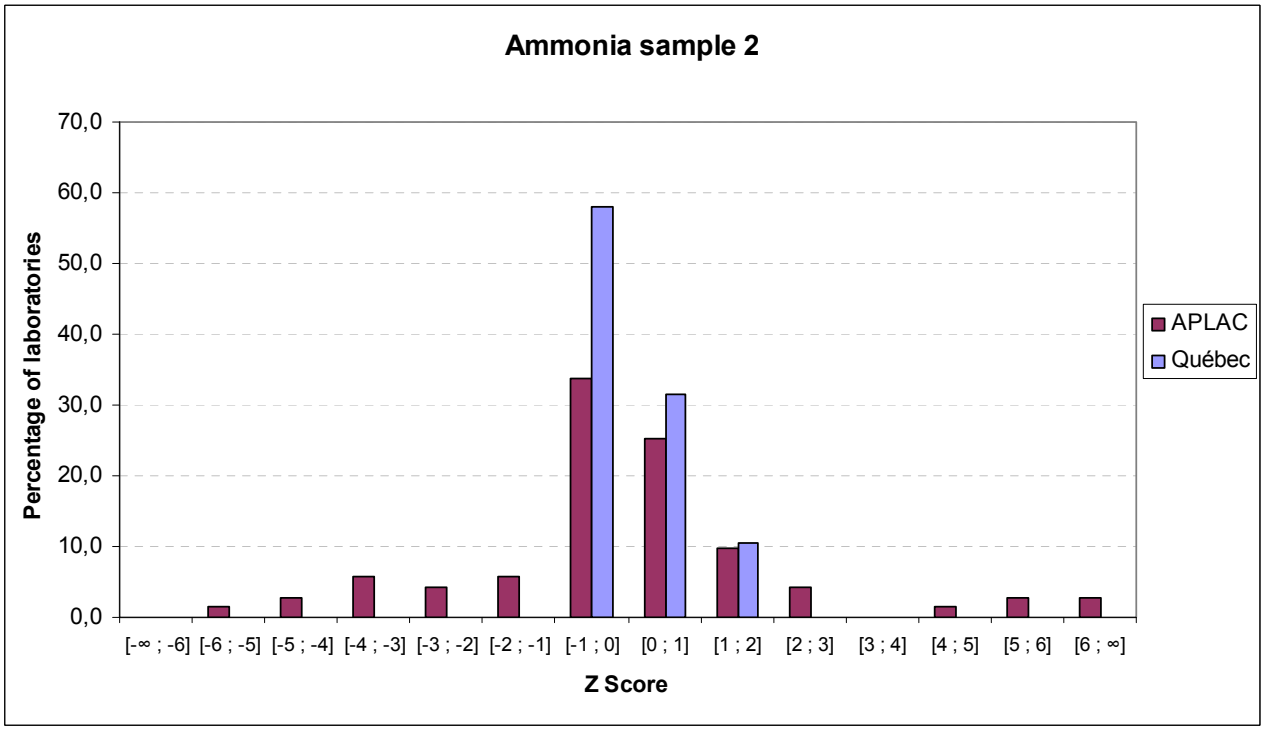
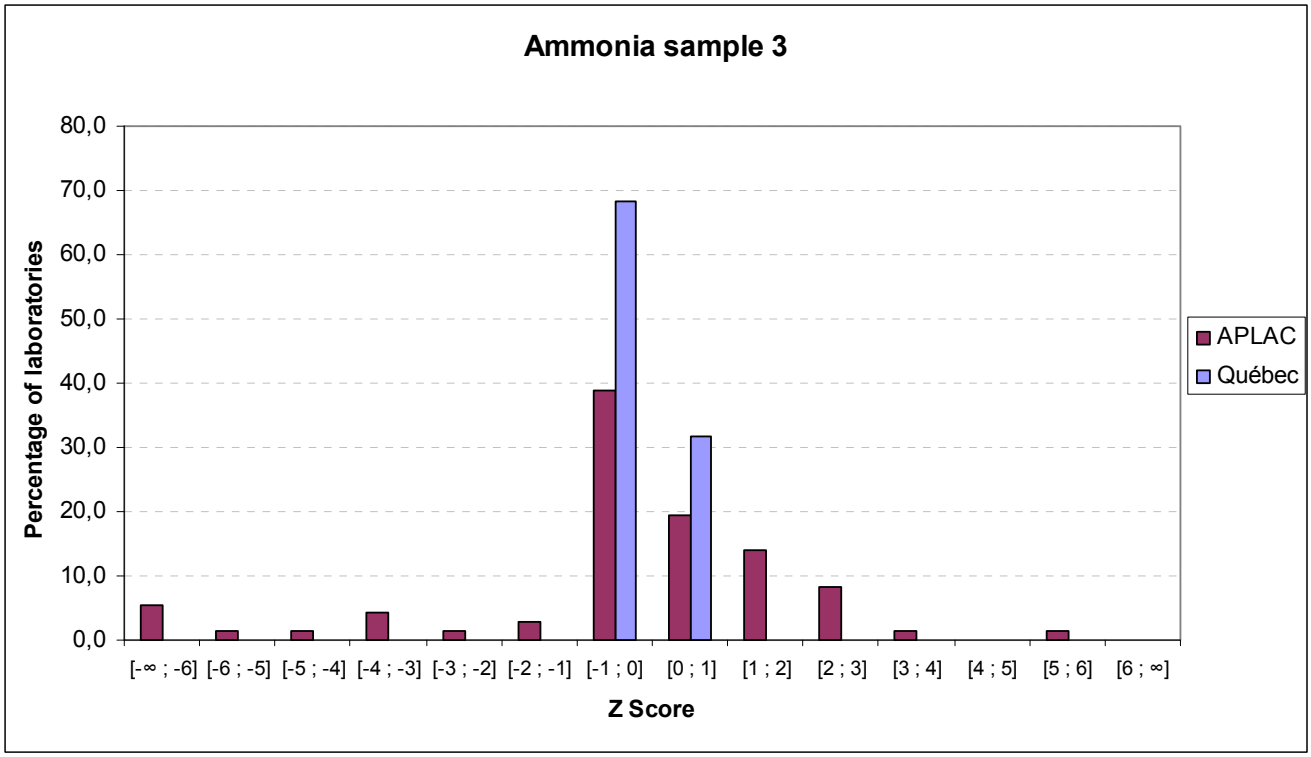


Figure G.9: Comparison of z-score from APLAC and Quebec laboratories for Ammonia Nitrogen sample 3



Comparison of Nitrite plus Nitrate results from APLAC participants and Quebec laboratories

Figure G.10: Comparison of z-score from APLAC and Quebec laboratories for Nitrite plus Nitrate sample 1

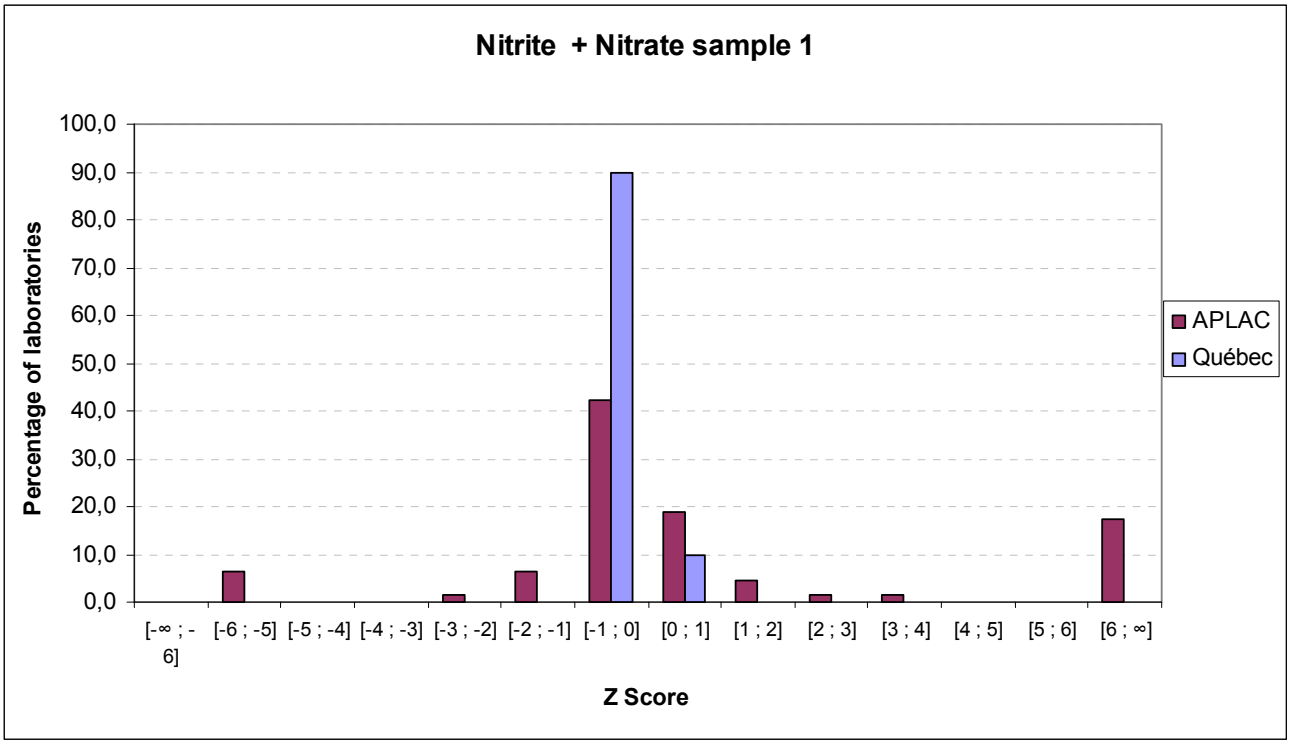


Figure G.11: Comparison of z-score from APLAC and Quebec laboratories for Nitrite plus Nitrate sample 2

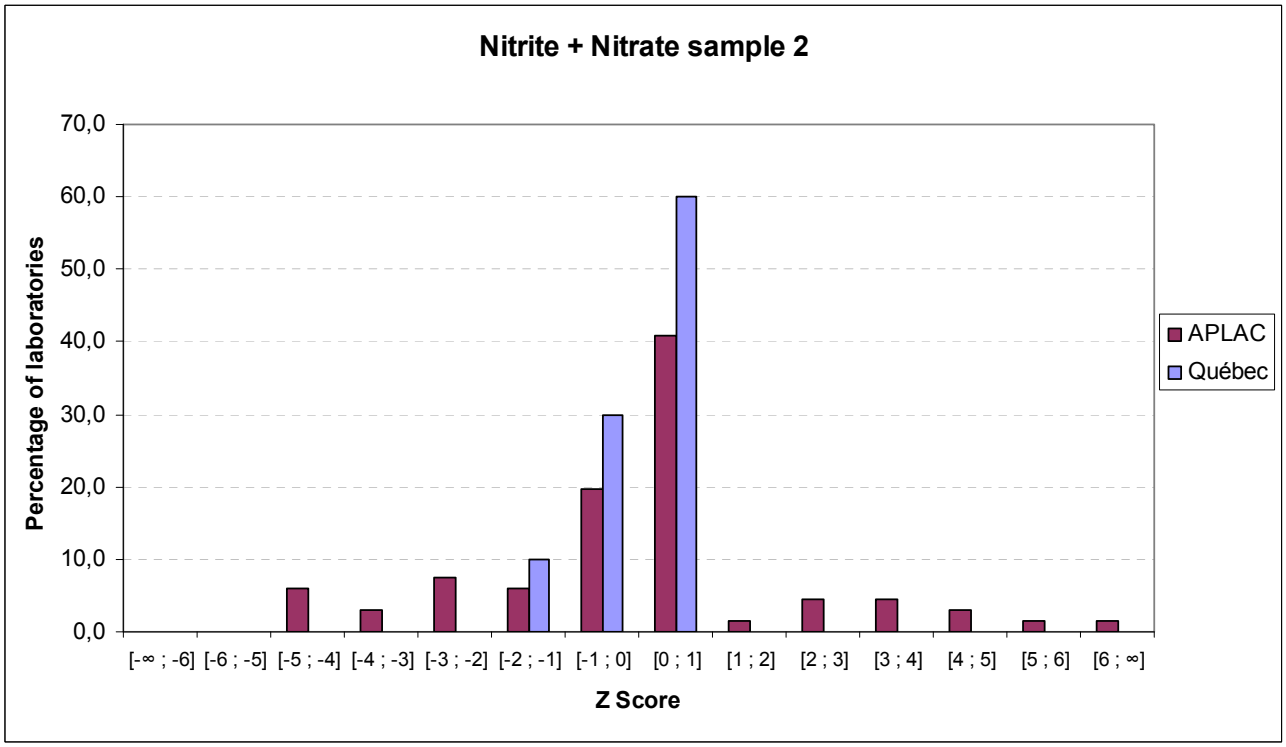
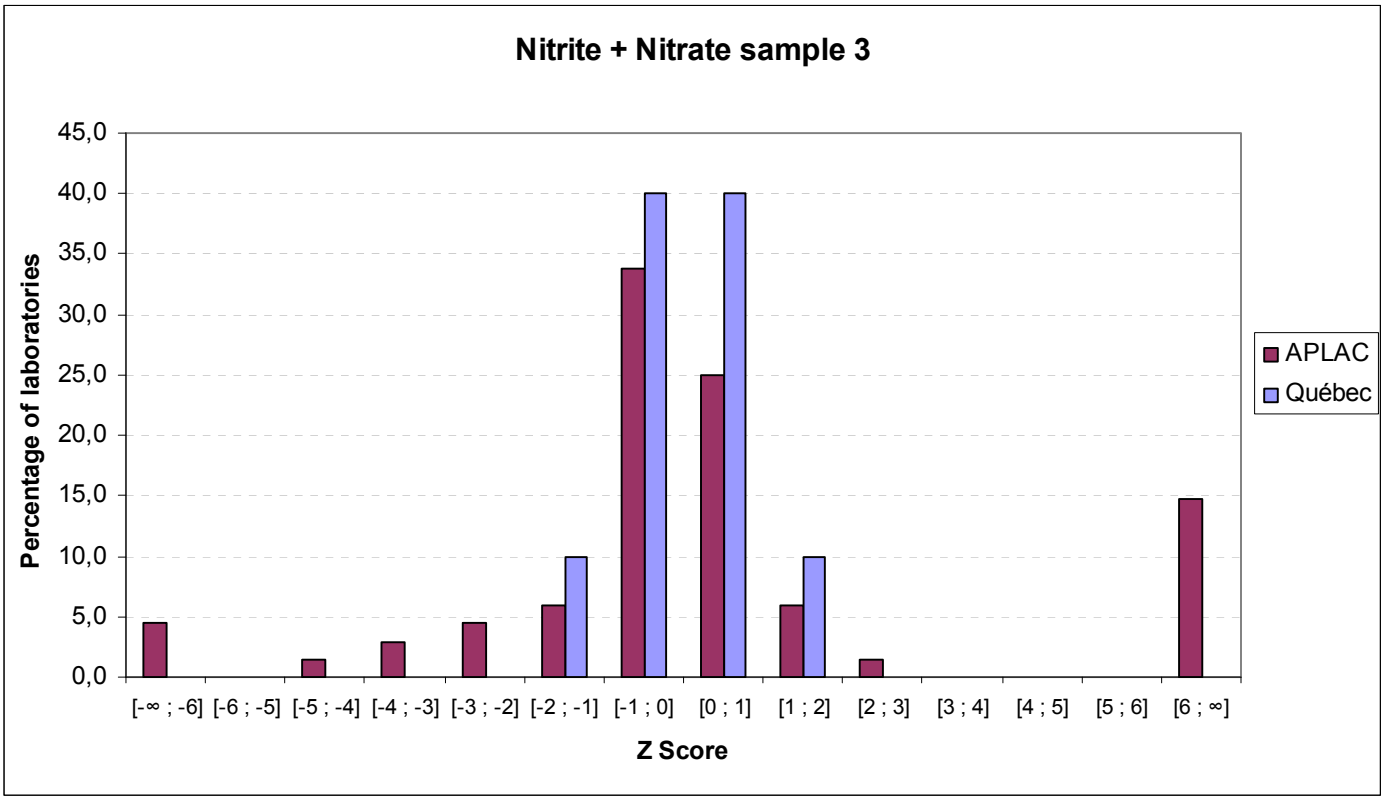


Figure G.12: Comparison of z-score from APLAC and Quebec laboratories for Nitrite plus Nitrate sample 3



Annex H: Uncertainty dispersion for each measurand

These graphics represent the uncertainty dispersions (as a % of the reported results) for each measurand.

Comparison of BOD uncertainty dispersion results

Figure H.1: Uncertainty dispersion (as a % of the reported result) for Biochemical Oxygen Demand sample 1 (Note: sample mean was 134 mg O_2/l and standard deviation was 32.0 mg O_2/l)

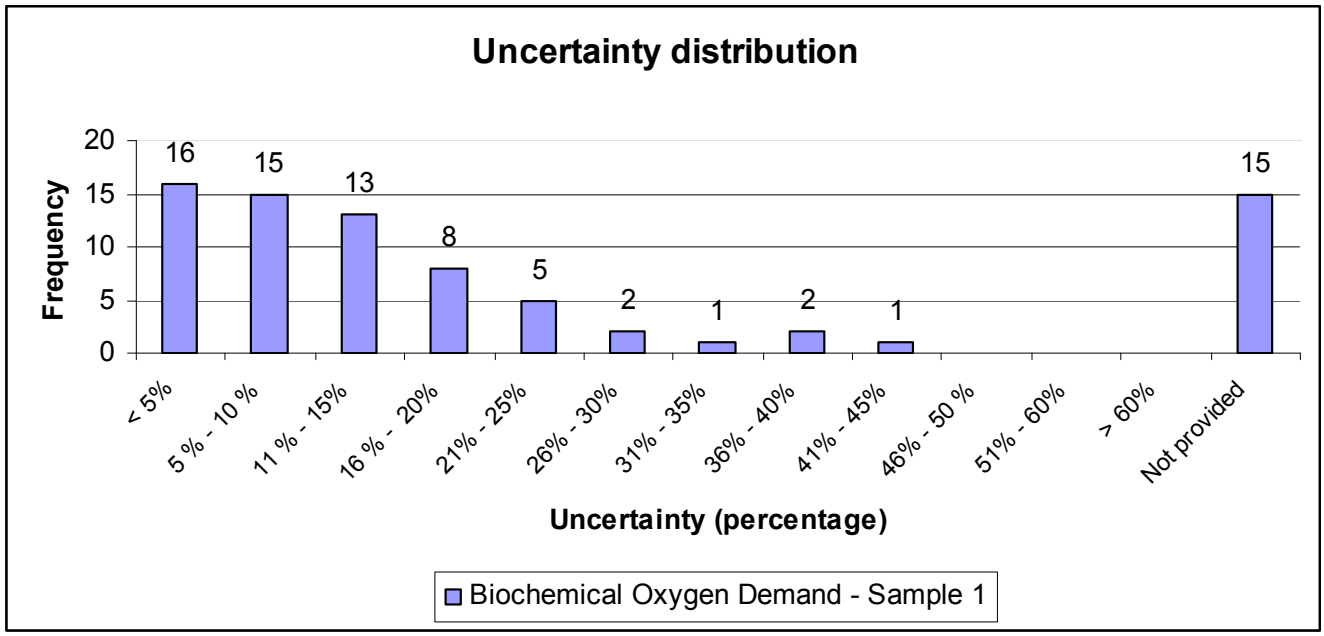


Figure H.2: Uncertainty dispersion (as a % of the reported result) for Biochemical Oxygen Demand sample 2 (Note: sample mean was 334 mg O_2/l and standard deviation was 95.8 mg O_2/l)

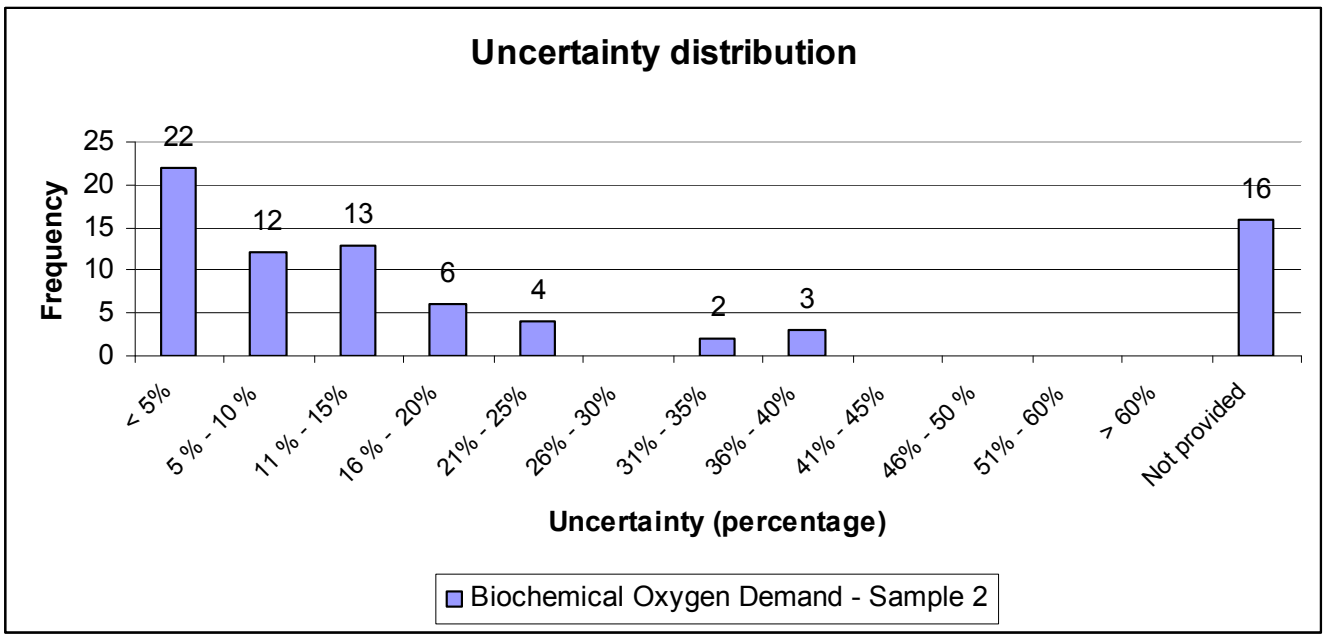
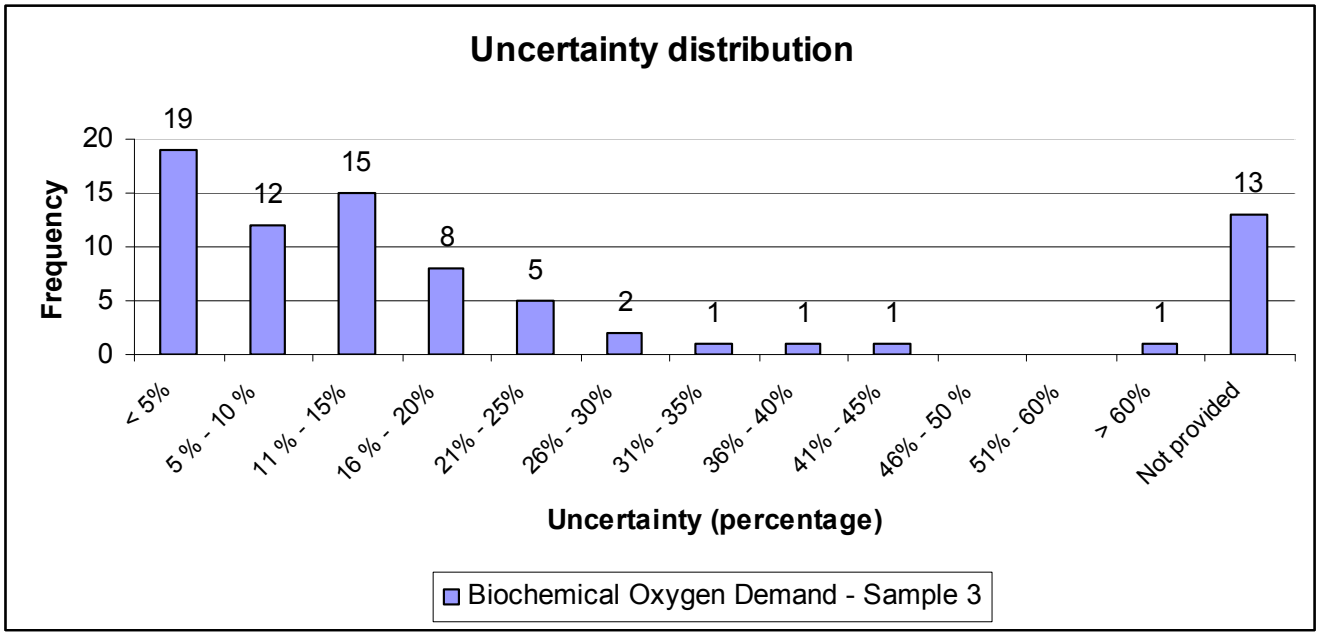


Figure H.3: Uncertainty dispersion (as a % of the reported result) for Biochemical Oxygen Demand sample 3 (Note: sample mean was 194 mg O_2/l and standard deviation was 41.1 mg O_2/l)



Comparison of COD uncertainty dispersion results

Figure H.4: Uncertainty dispersion (as a % of the reported result) for Chemical Oxygen Demand sample 1 (Note: sample mean was 83.1 mg O_2/l and standard deviation was 10.6 mg O_2/l)

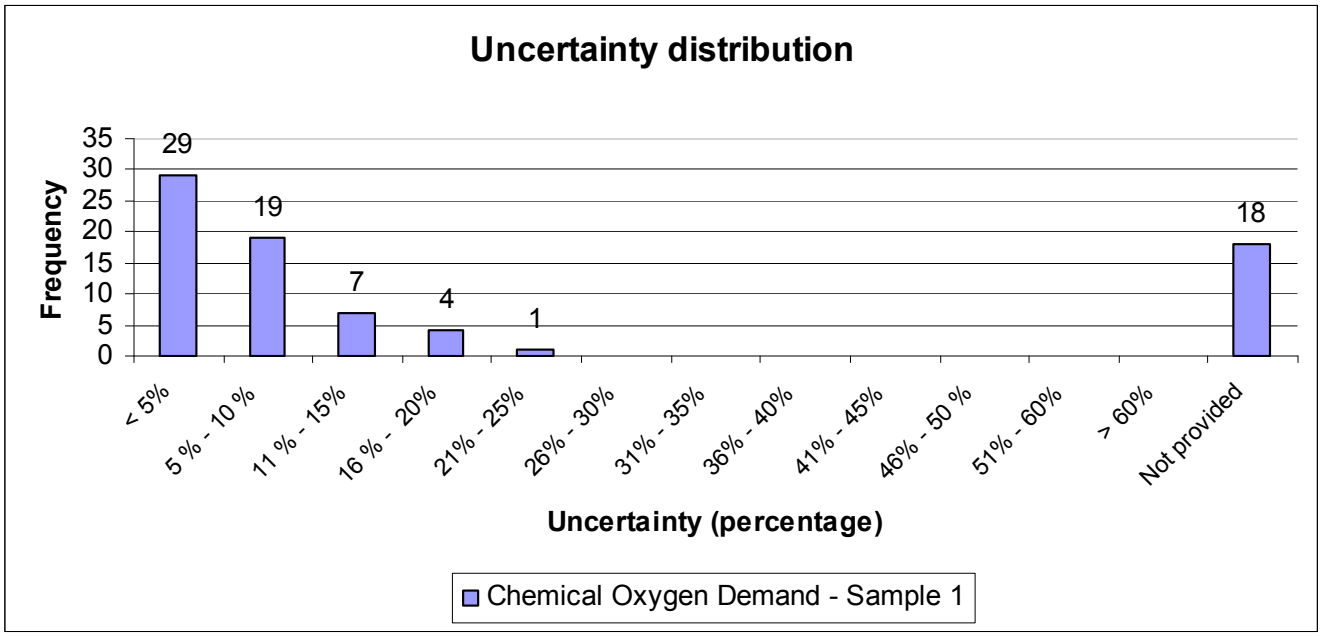


Figure H.5: Uncertainty dispersion (as a % of the reported result) for Chemical Oxygen Demand sample 2 (Note: sample mean was 401 mg O_2/l and standard deviation was 29.2 mg O_2/l)

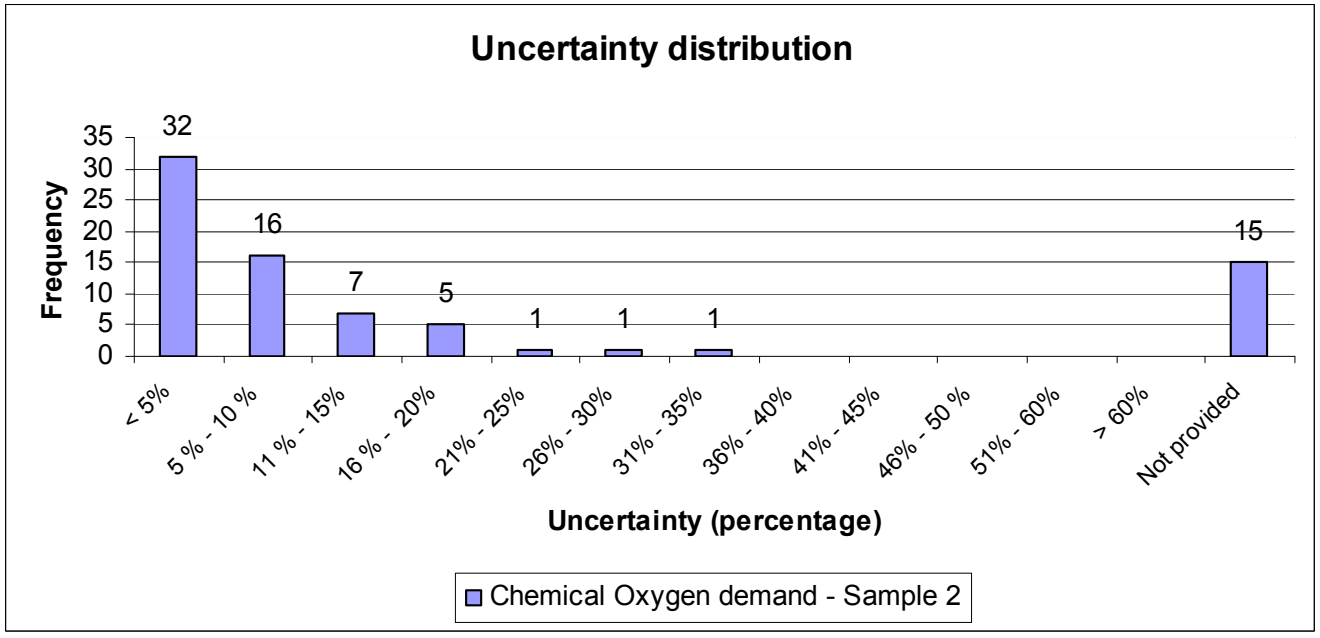
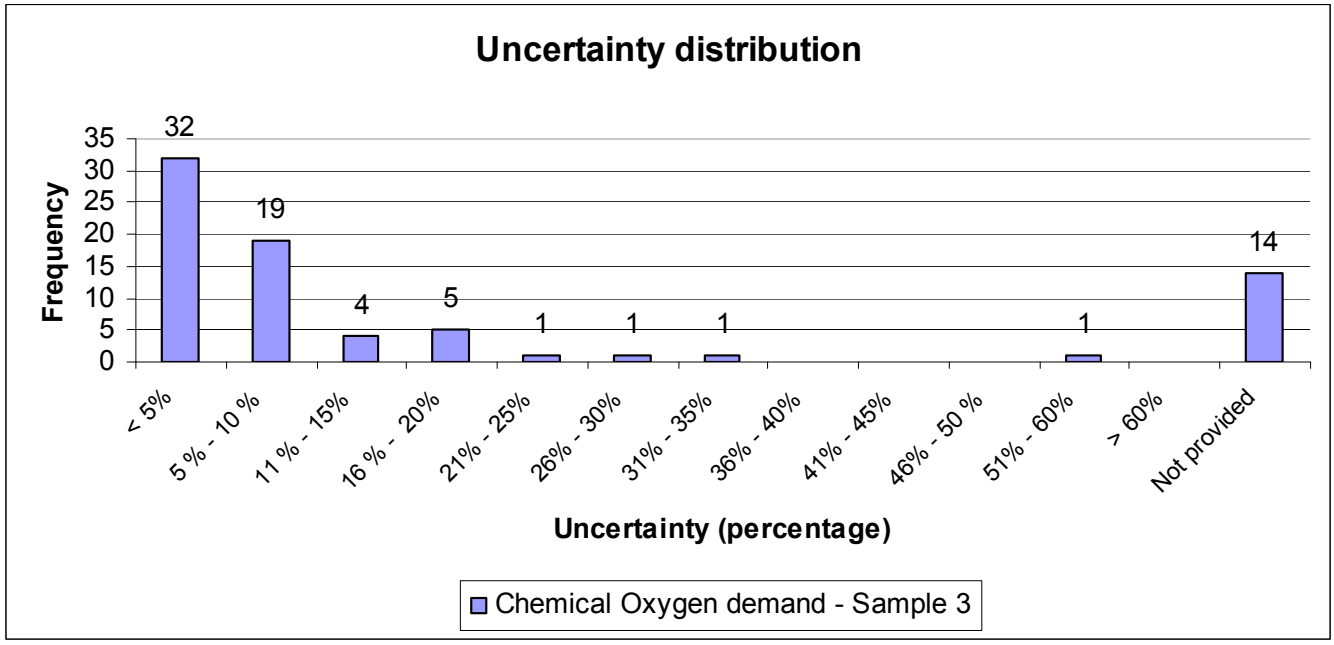


Figure H.6: Uncertainty dispersion (as a % of the reported result) for Chemical Oxygen Demand sample 3 (Note: sample mean was 716 mg O_2/l and standard deviation was 36.3 mg O_2/l)



Comparison of Ammonia uncertainty dispersion results

Figure H.7: Uncertainty dispersion (as a % of the reported result) for Ammonia Nitrogen sample 1 (Note: sample mean was 5.65 mg N/l and standard deviation was 1.21 mg N/l)

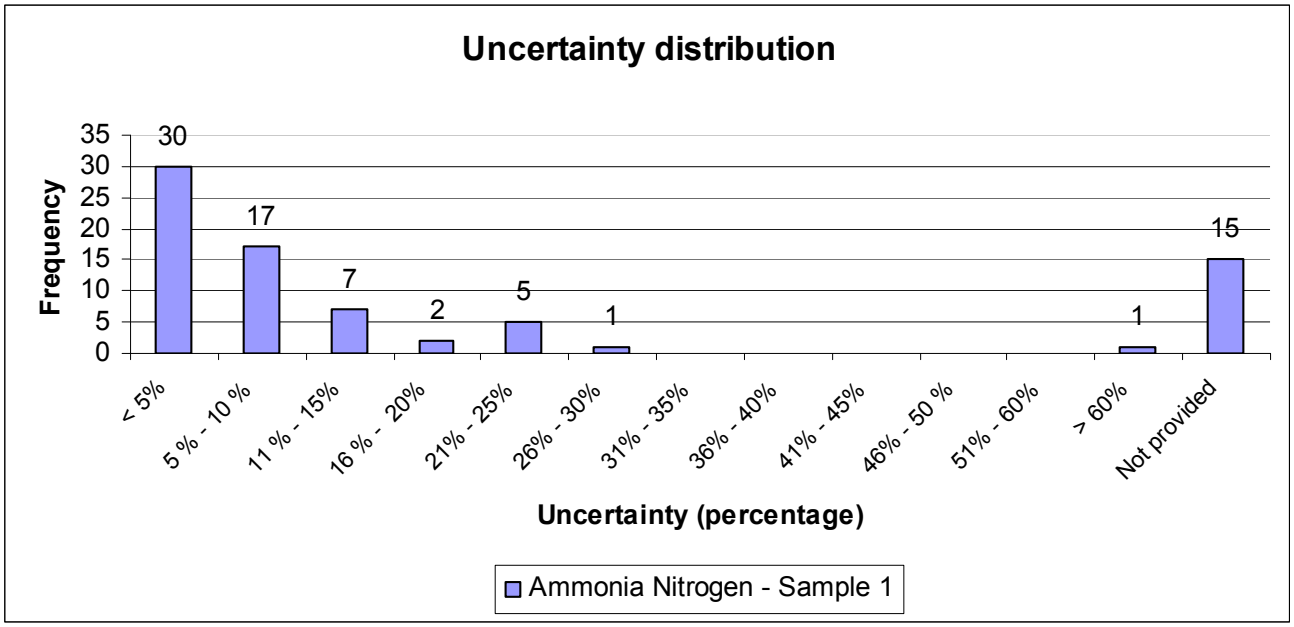


Figure H.8: Uncertainty dispersion (as a % of the reported result) for Ammonia Nitrogen sample 2 (Note: sample mean was 4.09 mg N/l and standard deviation was 0.77 mg N/l)

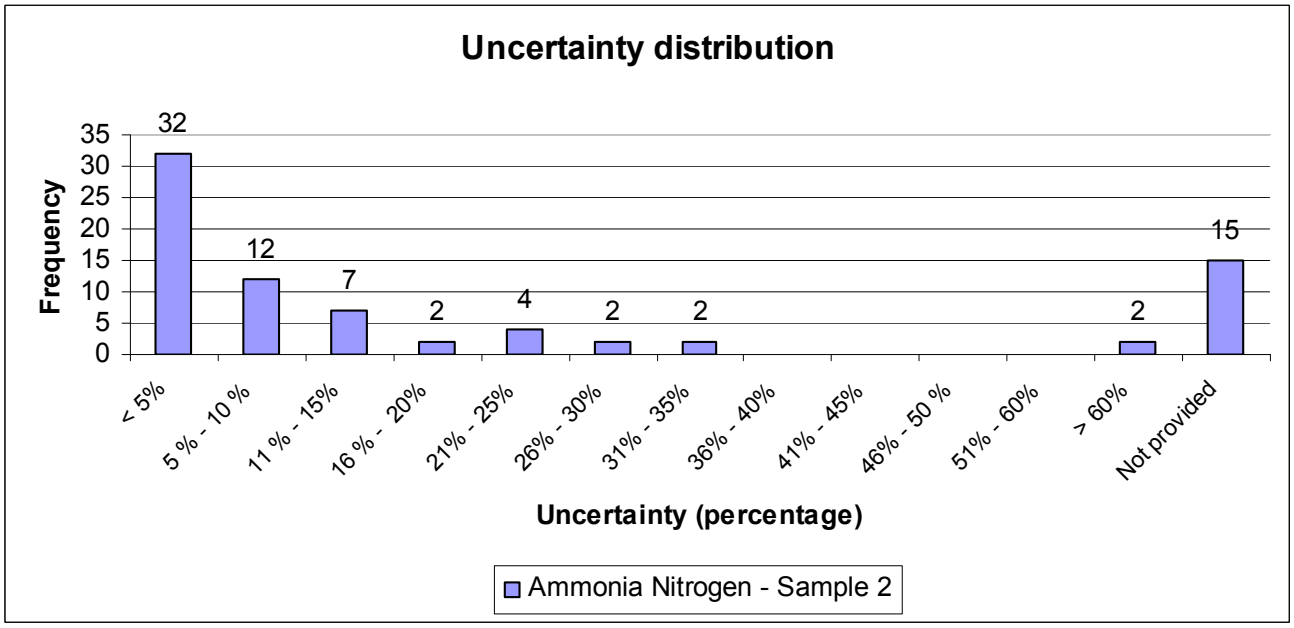
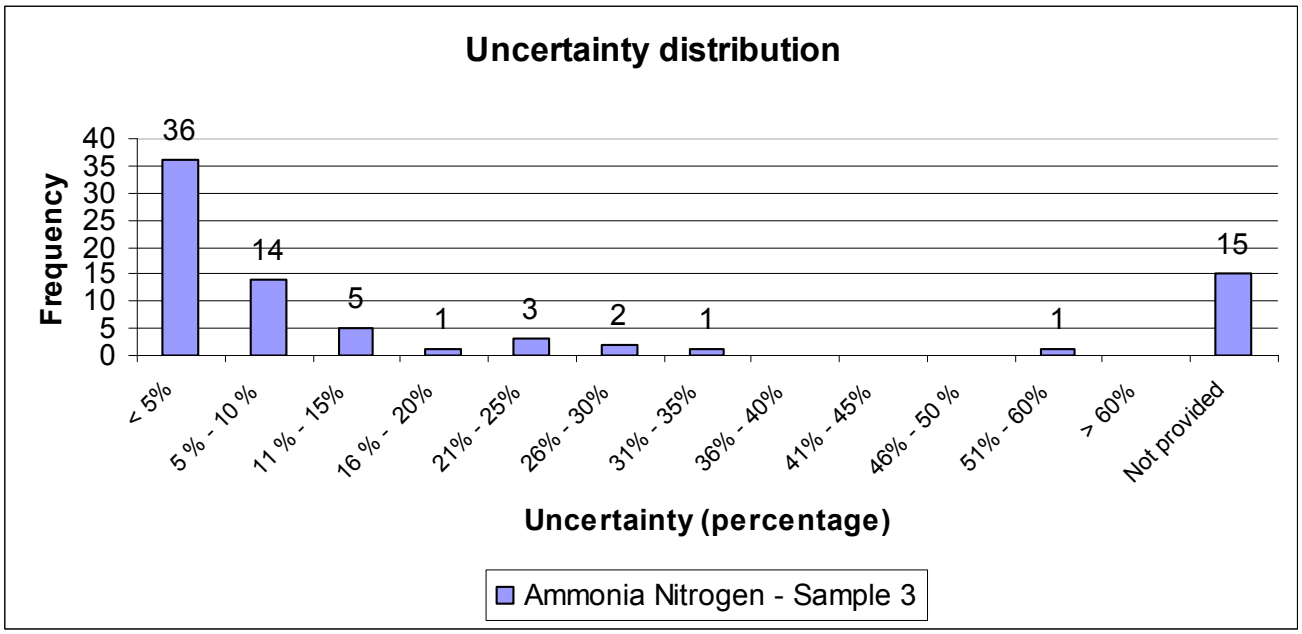


Figure H.9: Uncertainty dispersion (as a % of the reported result) for Ammonia Nitrogen sample 3 (Note: sample mean was 15.1 mg N/l and standard deviation was 1.88 mg N/l)



Comparison of Nitrite plus Nitrate uncertainty dispersion results

Figure H.10: Uncertainty dispersion (as a % of the reported result) for Nitrite plus Nitrate sample 1 (Note: sample mean was 3.39 mg N/l and standard deviation was 0.63 mg N/l)

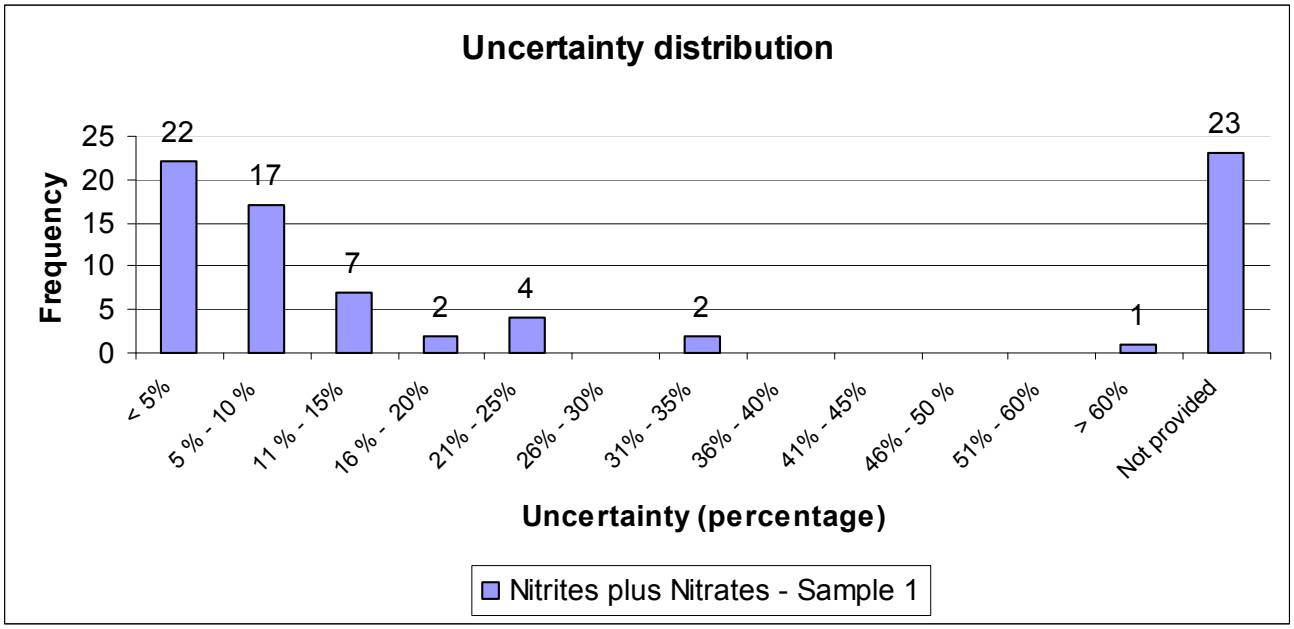


Figure H.11: Uncertainty dispersion (as a % of the reported result) for Nitrite plus Nitrate sample 2 (Note: sample mean was 44.8 mg N/l and standard deviation was 10.4 mg N/l)

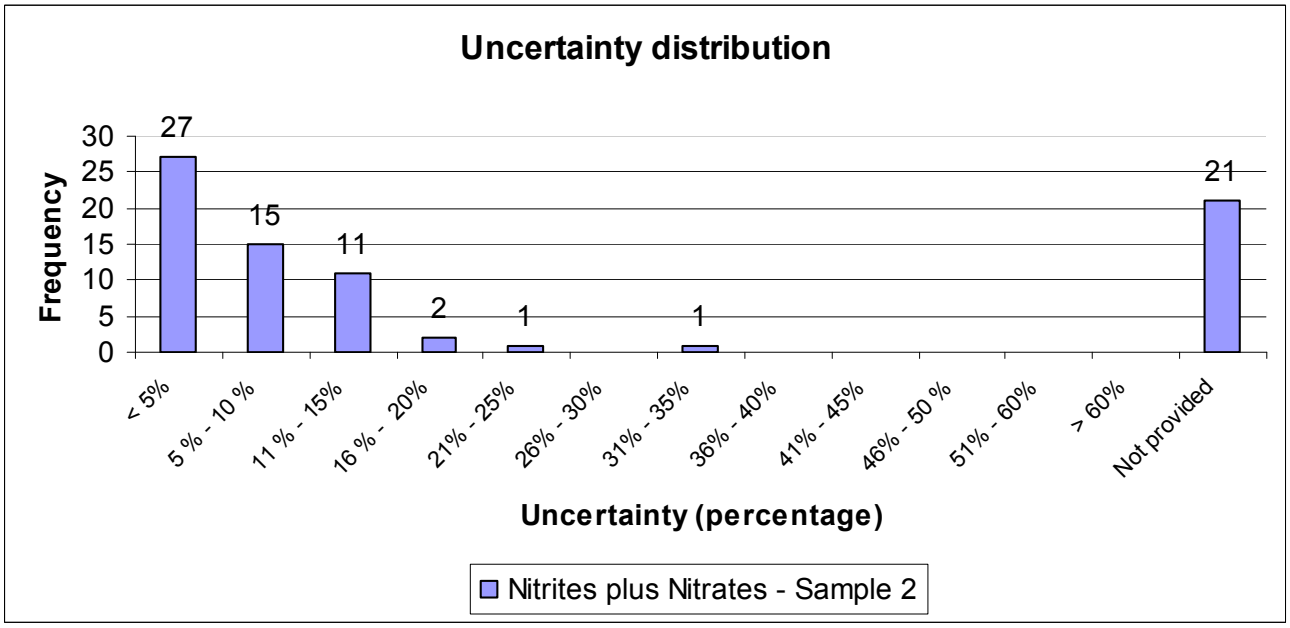
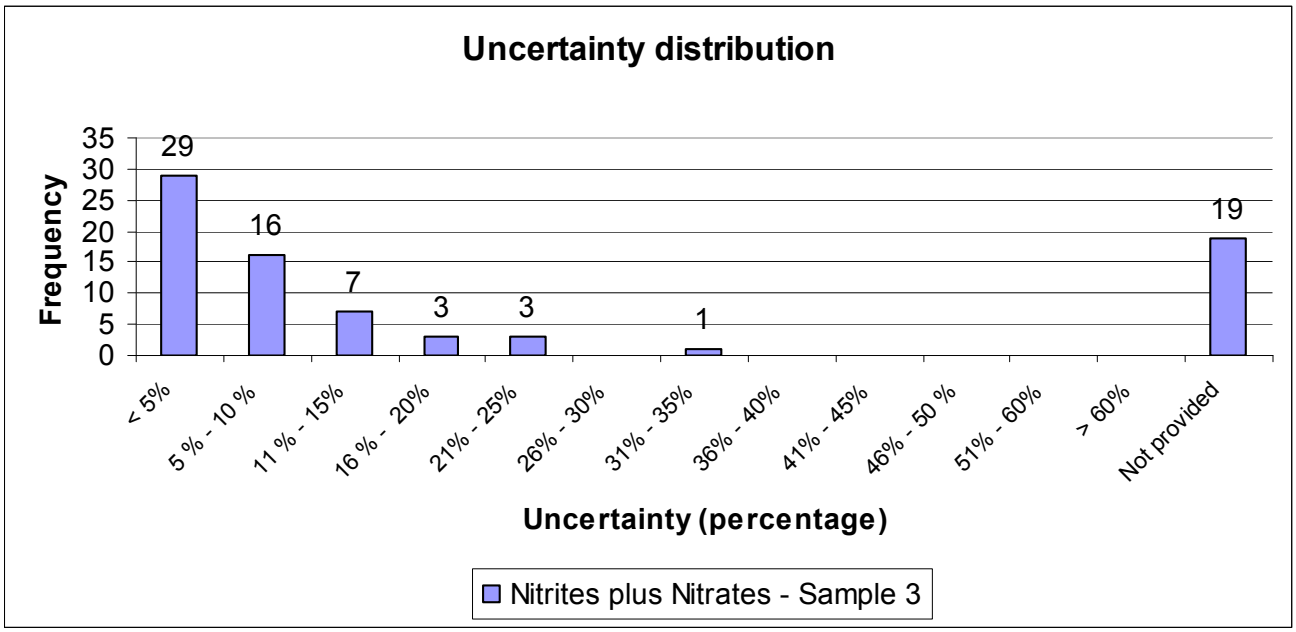


Figure H.12: Uncertainty dispersion (as a % of the reported result) for Nitrite plus Nitrate sample 3 (Note: sample mean was 29.5 mg N/l and standard deviation was 4.29 mg N/l)



Annex I: Program Documents and Forms

Annex I.1: Result Reporting Spreadsheet

("APLAC-01_1xxxxx.xls")

Standards Council of Canada
Conseil canadien des normes

Centre d'expertise en analyse environnementale Québec

APLAC T062 Wastewater Proficiency testing Program

Laboratory code: XXXX

Test	Unit	APLAC#1	Uncertainty#1	APLAC#2	Uncertainty#2	APLAC#3	Uncertainty#3	Method
BOD (5 days)	mg O2 / l							
COD	mg O2 / l							
Ammonia	mg N / l							
Nitrate & nitrite	mg N / l							

Comments:

Supervisor name (Please print):

Supervisor signature:

Report date:

Annex I.2: Instructions to Accreditation Bodies (APLAC)

("APLAC T062 instruction letter for AB (APLAC).doc")

Standards Council of Canada
Conseil canadien des normes

Centre d'expertise en analyse environnementale Québec

14 August 2008

Dear APLAC Colleagues.

Re: APLAC T062 BOD, COD, NO2+NO3 & NH3 in Wastewater Proficiency Testing Program

Instructions to Accreditation Bodies

This **APLAC T062 BOD, COD, NO2+NO3 & NH3 in Wastewater Proficiency Testing Program** is coordinated by Standards Council of Canada in partnership with our collaborator, the Le *Centre d'expertise en analyse environnementale du Québec (CEAEQ).* This APLAC T062 PT program is specifically designed to evaluate the performance of participating laboratories for some of the most commonly used parameters for monitoring of wastewater effluents: Biochemical Demand for Oxygen (BOD),Chemical Demand for Oxygen (COD), Nitrites plus Nitrates (NO2+NO3) and Nitrogen ammonia (NH3).

To ensure that results from this program can be analysed properly, participating accreditation bodies are asked to adhere carefully to the following instructions.

1. SAMPLES

Your accreditation body (AB) should receive the PT samples and instruction information (hard copy) from our collaborator, the Le *Centre d'expertise en analyse environnementale du Québec (CEAEQ)* shortly. The samples will be shipped on the 18th August. The bulk sample package you will receive contains individually labelled packages for your participating laboratories. Each of those packages consists of three samples for BOD with no preservative and three samples for COD. NO2+NO3 and NH3 preserved with sulfuric acid 0.1% in 250 mL Nalgene™ bottles.

Upon receipt of the bulk package, your AB should carefully check the individual mailing packages containing the samples and shall promptly acknowledge this to the SCC Coordinator by emailing the completed attached document "*APLAC T062 receipt of samples acknowledgement form (for AB).doc*" to aplact62@telus.net by the 28th August 2008. New samples will be re-sent by SCC/CEAEQ for any damaged sample boxes.

2. SAMPLE DISTRIBUTION

The mailing boxes are addressed to each participating laboratory and contain the samples as well as a hard copy of the instructions and the results sheet. Please do not open these packages. The confidential lab code number is identified on the hard copy of the customized laboratory reporting form labelled *"APLAC-01_1xxxxx.xls"* enclosed with each participating laboratory's samples. Your participating accreditation body will be informed of the confidential laboratory code numbers for your participating laboratories in a separate email. (A list of will be included in the bulk package).

Your AB should promptly distribute (within one week) the individual mailing boxes containing the samples, together with an electronic copy of the attached files: 1) "*APLAC T062 instruction letter for laboratory.doc*", 2) "*APLAC T062 receipt of samples acknowledgement form (for laboratories).doc*", 3) the specific *"APLAC-01_1xxxxx.xls*" and 4) "*APLAC T062 Information on analysis method.doc"* to your respective participating laboratories. The samples shall be stored in a secure environment at room temperature (around 20°C) before dispatch. There is no need to open the packaging.

Please remind your respective participating laboratories to carefully check the samples upon receipt and promptly acknowledge this to the SCC Coordinator (with a cc to you) by emailing the completed "*APLAC T062 receipt of samples acknowledgement form (for laboratories).doc*" to aplact62@telus.net by the 5th September 2008. New sample(s) will be re-sent by SCC/CEAEQ for any damaged samples.

3. TESTS TO BE PERFORMED

Each laboratory package contains the samples and a hard copy of the documents *"APLAC T062 instruction letter for Laboratory.doc*", *"APLAC-01_1xxxxx.xls*" and "*APLAC T062 Information on analysis method.doc"*. These documents outline the tests to be performed and the instructions for preparing and analysing the samples and how to report the results.

4. RESULTS and DOCUMENTS TO BE SUBMITTED

Your AB shall inform your respective participating laboratories to complete their customized electronic report forms "*APLAC-01_1xxxxx.xls*" (which contains their confidential lab code number) and "*APLAC T062 Information on analysis method.doc"* once their results are obtained and **submit this completed customized electronic form to your AB** on or before 3rd October 2008. Your AB is required to ensure that the above information has been supplied by your laboratories and is complete.

No later than 8th October 2008, your AB is required to forward these completed electronic results spreadsheet forms and any supporting documentation to the SCC Coordinator by email to aplact62@telus.net.

Notes: 1. Unless there are very special circumstances, all results submitted after the deadline shall be rejected by the organizers.
2. To avoid poor transmission quality, results by fax are not accepted.

5. GENERAL ENQUIRIES

Thank you in advance for your cooperation. We look forward to receiving the results from your laboratories participate in this program. If you have any queries or suggestions, please do not hesitate to contact me.

Yours Sincerely,



Dr. Robert J. Audette.
SCC Coordinator, APLAC T062 PT Program
Convener, TG Labs Proficiency Testing Working Group
Standards Council of Canada
270 Albert Street, Suite 200
Ottawa Ontario K1P 6N7 CANADA
Phone: 780-458-0295
E-mail: aplact62@telus.net

Attached: "*APLAC T062 receipt of samples acknowledgement form (for AB).doc*"
"*APLAC T062 instruction letter for laboratory.doc*"
"*APLAC T062 receipt of samples acknowledgement form (for laboratories).doc*"
"*APLAC T062 Information on analysis method.doc*"

Annex I.3: Instructions to Accreditation Bodies (IAAC)

(*"APLAC T062 instruction letter for AB (IAAC).doc"*)

Standards Council of Canada
Conseil canadien des normes

Centre d'expertise en analyse environnementale Québec

14 August 2008

Dear IAAC Colleagues.

Re: APLAC T062 BOD, COD, NO2+NO3 & NH3 in Wastewater Proficiency Testing Program

Instructions to Accreditation Bodies

This **APLAC T062 BOD, COD, NO2+NO3 & NH3 in Wastewater Proficiency Testing Program** is coordinated by Standards Council of Canada in partnership with our collaborator, the Le *Centre d'expertise en analyse environnementale du Québec (CEAEQ).* This APLAC T062 PT program is specifically designed to evaluate the performance of participating laboratories for some of the most commonly used parameters for monitoring of wastewater effluents: Biochemical Demand for Oxygen (BOD), Chemical Demand for Oxygen (COD), Nitrites plus Nitrates (NO2+NO3) and Nitrogen ammonia (NH3).

To ensure that results from this program can be analysed properly, participating accreditation bodies are asked to adhere carefully to the following instructions.

6. SAMPLES

Your accreditation body (AB) should receive the PT samples and instruction information (hard copy) from our collaborator, the Le *Centre d'expertise en analyse environnementale du Québec (CEAEQ)* shortly. The samples will be shipped on the 18th August. The bulk sample package you will receive contains individually labelled packages for your participating laboratories. Each of those packages consists of three samples for BOD with no preservative and three samples for COD. NO2+NO3 and NH3 preserved with sulfuric acid 0.1% in 250 mL Nalgene™ bottles.

Upon receipt of the bulk package, your AB should carefully check the individual mailing packages containing the samples and shall promptly acknowledge this to the SCC Coordinator by emailing the completed attached document "*APLAC T062 receipt of samples acknowledgement form (for AB).doc*" to aplact62@telus.net by the 28th August 2008. New samples will be re-sent by SCC/CEAEQ for any damaged sample boxes.

7. SAMPLE DISTRIBUTION

The mailing boxes are addressed to each participating laboratory and contain the samples as well as a hard copy of the instructions and the results sheet. Please do not open these packages. The confidential lab code number is identified on the hard copy of the customized laboratory reporting

form labelled *"APLAC-01_1xxxxx.xls"* enclosed with each participating laboratory's samples. Your participating accreditation body will be informed of the confidential laboratory code numbers for your participating laboratories in a separate email. (A list of will be included in the bulk package).

Your AB should promptly distribute (within one week) the individual mailing boxes containing the samples, together with an electronic copy of the files: 1) "*APLAC T062 instruction letter for laboratory.doc*", 2) "*APLAC T062 receipt of samples acknowledgement form (for laboratories).doc*", 3) the specific customized *"APLAC-01_1xxxxx.xls*" and 4) "*APLAC T062 Information on analysis method.doc"* to your respective participating laboratories. The samples shall be stored in a secure environment at room temperature (around 20°C) before dispatch. There is no need to open the packaging.

Please remind your respective participating laboratories to carefully check the samples upon receipt and promptly acknowledge this to the SCC Coordinator (with a cc to you) by emailing the completed "*APLAC T062 receipt of samples acknowledgement form (for laboratories).doc*" to aplact62@telus.net by the 5th September 2008. New sample(s) will be re-sent by SCC/CEAEQ for any damaged samples.

8. TESTS TO BE PERFORMED

Each laboratory package contains the samples and a hard copy of the documents *"APLAC T062 instruction letter for Laboratory.doc*", *"APLAC-01_1xxxxx.xls*" and "*APLAC T062 Information on analysis method.doc"*. These documents outline the tests to be performed and the instructions for preparing and analysing the samples and how to report the results.

9. RESULTS and DOCUMENTS TO BE SUBMITTED

Your AB shall inform your respective participating laboratories to complete their customized electronic report forms "*APLAC-01_1xxxxx.xls*" (which contains their confidential lab code number - **It is very important to keep the exact file name**) and "*APLAC T062 Information on analysis method.doc"* once their results are obtained and **submit this completed customized electronic form to your AB** (along with the completed "*APLAC T062 Information on analysis method.doc*" file) on or before 3rd October 2008. Your AB is required to ensure that the above information has been supplied by your laboratories and is complete.

No later than 8th October 2008, your AB is required to forward these completed electronic results spreadsheet forms and any supporting documentation to the SCC Coordinator by email to aplact62@telus.net.

Notes: 1. Unless there are very special circumstances, all results submitted after the deadline shall be rejected by the organizers.
2. To avoid poor transmission quality, results by fax are not accepted.

10. GENERAL ENQUIRIES

Thank you in advance for your cooperation. We look forward to receiving the results from your laboratories participate in this program. If you have any queries or suggestions, please do not hesitate to contact me.

Yours Sincerely,



Dr. Robert J. Audette.
SCC Coordinator, APLAC T062 PT Program
Convener, TG Labs Proficiency Testing Working Group
Standards Council of Canada
270 Albert Street, Suite 200
Ottawa Ontario K1P 6N7 CANADA
Phone: 780-458-0295
E-mail: aplact62@telus.net

Attached: "*APLAC T062 receipt of samples acknowledgement form (for AB).doc*"
"*APLAC T062 instruction letter for laboratory.doc*"
"*APLAC T062 receipt of samples acknowledgement form (for laboratories).doc*"
"*APLAC T062 Information on analysis method.doc*"

Annex I.4: Instructions to Participating Laboratories

("*APLAC T062 instruction letter for laboratory.doc*")

Standards Council of Canada
Conseil canadien des normes

Centre d'expertise en analyse environnementale Québec

14 August 2008

Dear Participating Laboratory.

Re: APLAC T062 BOD, COD, NO2+NO3 & NH3 in Wastewater Proficiency Testing Program

Instructions to Participating Laboratories

This **APLAC T062 BOD, COD, NO2+NO3 & NH3 in Wastewater Proficiency Testing Program** is coordinated by Standards Council of Canada in partnership with our collaborator, the Le *Centre d'expertise en analyse environnementale du Québec (CEAEQ).* This APLAC T062 PT program is specifically designed to evaluate the performance of participating laboratories for some of the most commonly used parameters for monitoring of wastewater effluents: Biochemical Demand for Oxygen (BOD), Chemical Demand for Oxygen (COD), Nitrites plus Nitrates (NO2+NO3) and Nitrogen ammonia (NH3).

To ensure that results from this program can be analysed properly, participating laboratories are asked to adhere carefully to the following instructions.

11. SAMPLES

a) Your accreditation body (AB) has forwarded these PT samples and instruction information (hard copy) from our collaborator, the Le *Centre d'expertise en analyse environnementale du Québec (CEAEQ)*. The sample package you received contains individually labelled samples for your laboratory. This package consists of three samples for BOD with no preservative and three samples for COD. NO2+NO3 and NH3 preserved with sulfuric acid 0.1% in 250 mL Nalgene™ bottles.

Each set of three bottles were sealed in a leak-proof plastic sleeve and placed in a standard packing carton, an absorbent paper and Styrofoam. The matrix is composed of effluent water from a wastewater treatment facilities to which parameters required have been added. The 3 samples for each set have concentrations that are unique, randomly spanning the concentration ranges for each parameter within the low to high concentrations identified in the following table.

Parameter	Concentration range
BOD	From 50 to 500 mg O_2 /L
COD	From 15 to 1000 mg O_2 /L
NO_2+NO_3	From 1 to 100 mg N /L
NH_3	From 0.5 to 20 mg N /L

b) Your confidential laboratory code number is identified on the hard copy of your customized laboratory reporting form *"APLAC-01_1xxxxx.xls"* enclosed with your laboratory's samples.

c) Your AB should have also forwarded to you electronic copies of the files: 1) "*APLAC T062 instruction letter for laboratory.doc*", 2) "*APLAC T062 receipt of samples acknowledgement form (for laboratories).doc*", 3) your customized *"APLAC-01_1xxxxx.xls"* reporting form and 4) "*APLAC T062 Information on analysis method.doc"*.

d) Upon receipt of your package, you should check the package and carefully inspect the samples for any physical damages.

e) You shall promptly acknowledge the receipt of the samples to the SCC Coordinator (with a cc to your AB) by emailing the completed document "*APLAC T062 receipt of samples acknowledgement form (for laboratories).doc*" to aplact62@telus.net by the 5th September 2008. New samples will be re-sent by SCC/CEAEQ for any damaged samples.

f) The samples shall be stored in a secure environment at room temperature (around 20°C) before use. **Do not open the bottles until the analysis**. The analysis should be done **within a week** after the opening.

12. SAMPLE ANALYSIS

a) Participating laboratories are required to determine the concentration of Biochemical Demand for Oxygen (BOD mg O_2/L), Chemical Demand for Oxygen (COD mg O_2 /L), Nitrites plus Nitrates (NO2+NO3 mg N/L) and Nitrogen ammonia (NH3 mg N/L) in the samples.

b) The Biochemical Demand for Oxygen (BOD) test is a 5 days test and the laboratories shall seed the samples (Polyseed or natural seeding) for this analysis.

c) Participating laboratories should use their accredited test methods (or if not accredited their normal test methods) which are normally used to test their customer samples. Please record the exact method used on your customized results spreadsheet *"APLAC-01_1xxxxx.xls"*.

13. RESULTS and DOCUMENTS TO BE SUBMITTED

a) Report all the results for the appropriate parameter on your customized electronic spreadsheet *"APLAC-01_1xxxxx.xls"*. **It is very important to keep the exact file name. Do not change it.** It will make unusable the file for data compilation.

b) Estimate and report the expanded uncertainty (± mg O_2/L or mg N/L as appropriate) for individual analyte.

c) Fill in the information whether this is an accredited test method in the section method of the form.

d) Fill in the information of your performed analytical method for each parameter of the "*APLAC T062 Information on analysis method.doc*.

e) Submit your results electronically via **this completed customized electronic form to your AB** (along with the completed "*APLAC T062 Information on analysis method.doc*" file) on or before 3rd October 2008.

Notes: 1. Unless there are very special circumstances, all results submitted after the deadline shall be rejected by the organizers.
2. To avoid poor transmission quality, results by fax are not accepted.

14. GENERAL ENQUIRIES

Thank you in advance for your cooperation. We look forward to receiving the results from your laboratory from your AB. If you have any queries or suggestions, please do not hesitate to contact me (with a cc to your AB contact).

Yours Sincerely,



Dr. Robert J. Audette.
SCC Coordinator, APLAC T062 PT Program
Convener, TG Labs Proficiency Testing Working Group
Standards Council of Canada
270 Albert Street, Suite 200
Ottawa Ontario K1P 6N7 CANADA
Phone: 780-458-0295
E-mail: aplact62@telus.net

Annex I.5: Receipt of Samples Acknowledgement Form for Accreditation Bodies

"*APLAC T062 receipt of samples acknowledgement form (for AB).doc*")

E-mail to: Dr. Robert J. Audette
Convener, SCC PT Working Group
E-mail: aplact62@telus.net
Phone: **+1-780-458-0295**

Standards Council of Canada
Conseil canadien des normes

Centre d'expertise en analyse environnementale Québec

APLAC T062 BOD, COD, NO2+NO3 & NH3 in Wastewater Proficiency Testing Program

Receipt of Samples Acknowledgement Form for Accreditation Bodies

In order to monitor the progress of this APLAC T062 Proficiency Testing Program, we kindly ask you, once you have received the bulk package containing the individual packages of samples for your registered laboratories and confirmed the status of these packages to please complete this Receipt of Samples Acknowledgement Form and email this form to the contact above **by no later than 28th August 2008.**

Thank you in advance for your cooperation.

Date of receipt of samples:	
Accreditation Body Name:	
Contact Name:	
Organization:	
Shipping Address:	
Country:	
Phone No.:	
Fax No.:	
E-mail address of contact:	

We acknowledge the receipt of _____(#) boxes containing the samples for our registered laboratories for the APLAC T062 Proficiency Testing Program.

The sample packages to the individual laboratories are found to be* __ damaged / __ intact and should be __ suitable / ___ not suitable for laboratory testing. They have been forwarded to the laboratories: __.

Remarks:

- Number of samples
* - Check (√) as appropriate

Annex I.6: Receipt of Samples Acknowledgement Form for Participating Laboratories

("*APLAC T062 receipt of samples acknowledgement form (for laboratories).doc*")

E-mail to: Dr. Robert J. Audette
Convener, SCC PT Working Group
E-mail: aplact62@telus.net
Phone: **+1-780-458-0295**

Standards Council of Canada
Conseil canadien des normes

Centre d'expertise en analyse environnementale Québec

APLAC T062 BOD, COD, NO2+NO3 & NH3 in Wastewater Proficiency Testing Program

Receipt of Samples Acknowledgement Form for Participating Laboratories

In order to monitor the progress of this APLAC T062 Proficiency Testing Program, we kindly ask you, once you have received the package containing the samples for your registered laboratories and confirmed the status of this package and the samples, to please complete this Receipt of Samples Acknowledgement Form and email this form to the contact above **by no later than 5th September 2008.**

Thank you in advance for your cooperation.

Nominated Laboratory:

Date of receipt of samples:	
Accreditation Body Name:	
Lab Name:	
Lab Contact Person:	
Confidential Lab Code No.:	
Shipping Address:	
Country:	
Phone No.:	
E-mail address of contact:	

We acknowledge the receipt of the box containing the samples for our registered laboratory for the APLAC T062 Proficiency Testing Program.

The sample package and samples were found to be * __ damaged / __ intact and should be __ suitable / ___ not suitable for laboratory testing.

Remarks:

* - Check (√) as appropriate

Annex I.7: Information on Analysis Method

("*APLAC T062 Information on analysis method.doc*")

Standards Council of Canada
Conseil canadien des normes

Centre d'expertise en analyse environnementale Québec

Information on analysis method

APLAC T062 BOD, COD, NO2+NO3 & NH3 in Wastewater Proficiency Testing Program

LABORATORY NAME :	

LABORATORY CODE NUMBER :	

BOD (analysis date) _____ YY _____ MM _____ DD	
1. Type of seeding used :	
2. Incubation condition (T°C) :	
3. Method used for the oxygen determination • Iodometric method • Membrane electrode method • Alternative method (please specify)	

COD (analysis date) _____ YY _____ MM _____ DD	
Type of method used • Closed reflux colorimetric method • Closed reflux titrimetric method • Open reflux method • Alternative method (please specify)	

NO2+NO3 (analysis date) _____ **YY** _____ **MM** _____ **DD**	
Type of method used : • Cadmium reduction • Hydrazine reduction • Alternative method (please specify)	

NH3 (analysis date) _____ **YY** _____ **MM** _____ **DD**	
Distillation (yes or no) Type of method used: • Titrimetric method • Colorimetric method • Selective electrode method • Alternative method (please specify)	

COMMENTS : _____

_____

_____

_____

_____

_____

_____

Supervisor name : **DATE :**

Annex J: Robust analysis: Algorithm A

From ISO 13528: 2005, "Statistical methods for use in proficiency testing by inter laboratory comparisons", Geneva, Switzerland, Annex C

This algorithm yields robust values of the average and standard deviation of the data to which it is applied.

Denote the p items of data, sorted into increasing order, by:

$$x_1.\ x_2.\ldots.\ x_i.\ldots.\ x_p$$

Denote the robust average and robust standard deviation of these data by x^* and s*.

Calculate initial values for x^* and s* as:

x^* = median of x_i $\quad (i = 1, 2.\ \ldots.\ p)$

s* = 1.483 median of $|x_i - x^*|$ $\quad (i = 1, 2.\ \ldots.\ p)$

Update the values of x^* and s* as follows. Calculate:

$$\Phi = 1.5 s^*$$

For each x_i $(i = 1, 2\ldots\ \mathrm{p})$, calculate:

$$x_i^* = \begin{cases} x_i - \Phi & \text{if } x_i < x^* - \Phi \\ x_i + \Phi & \text{if } x_i > x^* + \Phi \\ x_i & \text{otherwise} \end{cases}$$

Calculate the new values of x* and s* from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134 \sqrt{\sum \left(x_i^* - x^*\right)^2 / (p-1)}$$

where the summation is over i.

The robust estimates x^* and s* may be derived by an iterative calculation, i.e. by updating the values of x^* and s* several times, until the process converges. Convergence may be assured when there is no change from one iteration to the next in the third significant figure of the robust standard deviation and of the equivalent figure in the robust average.