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Technical Assistance
HYDROLOGY PROJECT

DHV CONSULTANTS & DELFT HYDRAULICS with HALCROW, TAHAL, CES, ORG & JPS

Findings of Third Inter-Laboratory AQC Exercise (Surface Water Laboratories Level II & II+)

Conducted by
K & G BO, Central Water Commission – Hyderabad

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Foreword

Quality control and assurance is of prime concern in the generation of reliable water quality data. The Hydrology Project (HP) introduced a two-tier system of conducting 'Analytical Quality Control (AQC)' exercises amongst the laboratories developed/strengthened under the Project in 1997-98. The first one is for enhancing the precision of an individual laboratory in water quality analysis through 'Within-laboratory' AQC, and the second is for minimization of bias through 'Inter-laboratory' AQC, so that the accuracy in the data generation is maintained.

In the initial phase, the Central Pollution Control Board conducted two rounds of inter-laboratory AQC exercises amongst the HP- laboratories in December 1998 and April 2000. To have continuity, the Ministry of Water Resources has recently decided for conducting the exercise on an annual basis by the Central Water Commission (CWC)'s level II^+ laboratory at Hyderabad for the surface water laboratories, and by the Central Ground Water Board (CGWB)'s level II^+ laboratory at Bhopal for the groundwater laboratories. In this approach, the scientists/chemists of the designated laboratory of the CWC and CGWB were trained for conducting Inter-laboratory AQC on a sustainable basis and also to enable gradual withdrawal of the external support. Accordingly, the two laboratories conducted the 3rd AQC programme during September-October 2001. The HP-Consultants were also associated with the programme and provided technical assistance.

The present report is the outcome of the 3rd Inter-laboratory AQC exercises for the surface water laboratories.

The Hydrology Project expresses thanks to the scientists/chemists of the CWC's laboratory at Hyderabad for conducting the exercise and preparing the report. We would also like to thank the laboratories participating in the programme.

July 10, 2002

J. G. Grijsen
Team Leader

1 Background

Analytical Quality Control **(AQC)** is one of the main components of a Quality Assurance system, wherein the quality of analytical data being generated in any laboratory is controlled through minimising or controlling errors to achieve a target accuracy. A particular water quality study or any organised water quality monitoring programme involves the collection, comparison and interpretation of analytical data, which leads to a decision for the management and use of the water resource. The correctness of decision or action depends largely upon the accuracy of the analytical results. If the errors of the analytical results are high, the manpower, material and money spent on any monitoring programme or study would be futile and further lead to wrong decision and improper action plans. Since the success and usefulness of an information system derived from analysis results depend on the quality of input data, it is essential to ensure that adequate comparability and accuracy of analytical results are achieved.

The need for analytical quality control (AQC) in HP laboratories was first discussed in the 'Water Quality Standardisation Workshop', December 9-10 1996, Hyderabad. It was recommended that AQC exercises should be organised for the HP laboratories to achieve a target accuracy so that the results obtained from different laboratories are comparable. Consequently, the following actions were taken:

- In May 1997 and March 1998, many HP laboratories participated in the 'within-laboratory, AQC exercises organised by HP consultants. The results of the first exercise were discussed in two technical meetings, held at Bangalore and Bhopal and a report was brought out in February 1998. Results of the second exercise were reported in June 1999.
- Since the 'within-laboratory' AQC exercises evaluate only the precision of the laboratory, an 'inter-laboratory' AQC exercise was conducted in December, 1998 by the Central Pollution Control Board (CPCB) to test the bias of the laboratories. Twenty-five (25) laboratories participated in this 'inter-laboratory' AQC-1 exercise.
- In continuation of the AQC-1 exercise, AQC-2 was conducted by CPCB in April 2000 for 42 laboratories.
- As a sequel to the AQC-1 and AQC-2 exercises, AQC-3 was conducted in September-October 2001 for 37 laboratories (mostly surface water and combined surface and ground water laboratories) by the Upper Godavari Division Laboratory (level II+) of the Central Water Commission (CWC) at Hyderabad. A comparable number of groundwater laboratories also participated in the AQC-3 exercise conducted by the Central Ground Water Board's (CGWB) Regional Laboratory at Bhopal. The chemists of both these laboratories, i.e. CGWB, Bhopal and CWC, Hyderabad, were trained at CPCB, Delhi for organising such AQC exercises under the guidance of Hydrology Project (HP) Consultants.

In the *inter-laboratory AQC* programme for the surface water laboratories, the CWC laboratory at Hyderabad organised the exercise and did the statistical analysis of the data, under the guidance of Shri A.K. Mitra, Research Officer, CWC. The present report has been prepared jointly by the Chemists of the CWC laboratory and the HP-Consultants.

2 Objectives

The main objectives of an *inter-laboratory* AQC programme are:

- to assess the status of analytical facilities and capabilities of concerned laboratories.
- to identify the serious constraints (random & systematic) in the working environment of laboratories.
- to provide necessary assistance to the concerned laboratories to overcome the short comings in the analytical capabilities.
- to promote the scientific/analytical competence of the concerned laboratories to the level of excellence for better output.
- to enhance the internal and external quality control of the concerned laboratories

3 Methodology

3.1 Standard samples

The list of parameters covered under the *inter-laboratory* AQC-3 exercise is given below:

1. Conductivity (COND)
2. Total Dissolved Solids (TDS)
3. Total Hardness (TH)
4. Sodium (Na)
5. Fluoride (F)
6. Sulphate (SO_4)
7. Nitrate-N (NO_3-N)
8. Phosphate-P (PO_4-P)
9. Boron (B)

The above parameters were selected for the exercise because the procedures for their determination involve various analytical techniques, namely, potentiometric (COND), gravimetric (TDS), titrimetric (TH), absorption-spectrometric (F, NO_3-N, PO_4-P and B), nephelometric (SO_4) and emission-spectrometric (Na) and common laboratory operations, such as weighing, heating, filtering etc. These tests are routinely carried out in the HP laboratories for characterisation of surface water and groundwater. All HP laboratories are required to carry out these types of analyses. The capability of a laboratory to perform these tests satisfactorily would indicate its preparedness to carry out its assigned Hydrological Information System (HIS) functions.

Two synthetic samples, labelled as A & B, were prepared in the Upper Godavari Division's Laboratory at Hyderabad by mixing different volumes of 7 different solutions made from high quality chemicals and distilled water. The list of solutions and their strengths and the volumes used as ingredients for each sample are given in Annexure I.

The samples were distributed to all the 37 participating laboratories by Courier service to avoid any transport delay. A copy of the communication/instructions for carrying out analysis and the data reporting format are shown in Annexures II and IIa respectively. The analysis data, as received from the respective participating laboratories, are presented in Annexure III.

3.2 Reference value

The parameter concentrations in each of the samples were determined in three different ways:

- from the stoichiometric considerations;
- by the analytical procedure in the CWC-Hyderabad laboratory; and
- from the combined results of analysis of the participating laboratories (reference mean).

The estimation of the value of a parameter from the combined analysis results of the participating laboratories is performed by the software developed by HP-Consultants for this

purpose. Procedural steps for analysis of AQC data, as performed by the software, are outlined in Annexure IV.

Table 1 presented below compares the concentration of the chosen parameters in the test samples, as estimated by the organising laboratory and referred to as the theoretical value (this value is the expert choice for either the stoichiometric or the analytical procedure value) with the value calculated from the combined results of analysis of the participating laboratories (reference mean). It can be seen that there is a close agreement among the values calculated by the two methods. Therefore, the reference mean is used for further analysis.

Parameter	Sample A			Sample B		
	Theoretical value	Reference Mean value	Acceptable value	Theoretical value	Reference Mean value	Acceptable value
Conductivity (µmho/cm)	347	364	340 - 389	216	222	209 - 235
TDS (mg/L)	233	235	210 - 260	138	141	132 – 150
Total Hardness (mg $CaCO_3$/L)	58.0	63.8	55.6 - 72.1	32.0	36.5	31.3 - 41.7
Sodium (mg/L)	35.0	34.0	29.1 - 38.9	22.0	21.9	18.9 - 24.9
Fluoride (mg/L)	2.44	2.38	2.18 - 2.58	1.40	1.43	1.23 - 1.63
Sulphate (mg/L)	30.0	29.9	26.1 - 33.7	14.0	15.1	11.7 - 18.4
Nitrate-N (mg N/L)	3.74	3.45	2.45 - 4.45	2.24	2.15	1.77 - 2.54
Phosphate-P (mgP/L)	0.416	0.361	0.286 - 0.436	0.204	0.202	0.166 - 0.237
Boron (mg/L)	1.66	1.60	1.21 - 1.98	0.92	0.88	0.7 - 1.06

Table 1: Reference values and acceptable ranges for AQC Round ID: 3

3.3 Acceptable range for reported values

The acceptable limits for various parameters were arrived at using the method described in Annexure IV.

A laboratory was considered to qualify for the analysis of a parameter if both the reported analysis results for the two samples A and B were in the acceptable ranges.

4 Findings and discussions

4.1 Findings of AQC-3 exercise

The reported analysis results for the two samples for each parameter were compared with the respective acceptable ranges shown in Table 1. The performances of the laboratories are summarised in Table 2, and are also shown in the Youden 2-sample plots (Figures 1-9). The following observations can be made regarding the performance of the laboratories:

- Out of the 37 laboratories that participated in the AQC exercise, 35 laboratories have reported results (i.e. 2 laboratories did not send in results).
- Out of 35 laboratories responding, only 16 could provide results for all the 9 parameters.
- The decreasing order of response for various parameters is as follows: Conductivity, 100%; Sodium, 100%; Total Hardness, 97%; Sulphate, 97%; Total Dissolved Solids, 94%; Phosphate-P, 94%; Nitrate – N 88 %; Fluoride, 83%; and Boron, 66% .
- The low response may be due to the fact that fluoride is not of prime interest for surface waters. The low response for Boron is serious because Boron is an important parameter for irrigation.
- Out of the 35 laboratories that reported, 4 could not analyse any of the 9 parameters within acceptable limits. At the other extreme, 5 laboratories identified only 1 parameter correctly.
- An overall view of the performance of laboratories for each parameter can be obtained from Youden 2-sample plots. Figures 1 to 9 give the plots for the 9 parameters covered under this exercise. For each parameter, the plot shows the value for Sample A against that for sample B reported by a laboratory. Thus, there is one data point for each laboratory. The acceptable limits for the two samples are also shown on the plot as two parallel horizontal lines for the sample values plotted on the Y-axis, and two parallel vertical lines for the sample values plotted on the X-axis. In case of plots for Conductivity, Total Dissolved Solids, Total Hardness, Sulphate, and Phosphate, due to very high values reported by some of the laboratories narrowing down the acceptable range. This is causing overlapping of some of the points (please see Figures 1, 2, 3, 6, and 7). To get better resolution of the acceptable range and position of the laboratories, an additional plot is drawn for each of the above three parameters excluding the outliers, as shown in Figures 1a, 2a, 3a, 6a, and 7a.

The centre of the rectangular block created by the two sets of parallel lines is the reference value for the parameter. Results close to this point are considered to represent a high degree of accuracy.

The figure can be divided in 4 quadrants by drawing a vertical and a horizontal line through the reference value. If only random error influences the determinations, the points would be randomly distributed in all the four quadrants. This is rarely seen. The points tend to concentrate in the first (++) or the third (--) quadrant, indicating that the laboratories tend to get either high values or low values, for both the samples. This points to the dominant role of systematic error. If a point lies on a line of unit slope passing through the reference value, then the determination has only systematic error.

Lab ID	Laboratory Name	Cond	TDS	TH	Na	F	SO_4	NO_3-N	PO_4-P	B	Total Reported	Within Limit	% success of reporting
401	CWC , KGBD,	OK	OK	OK	OK	OK	OK	OK	OK	OK	9	9	100
402	CWC, LKD, Hyderabad	OK	X	X	OK	OK	X	OK	OK	X	9	5	56
405	AP Dowlaiswaram SW	X	OK	OK	OK	X	X	X	X	OK	9	4	44
407	AP Cuddapah SW (+)	X	X	X	X	X	-	X	-	-	6	0	0
410	GU GERI, Vadodara	X	X	OK	X	OK	X	X	OK	X	9	3	33
411	CWC Ahmedabad	X	X	OK	OK	X	X	OK	X	-	8	3	38
412	CWC Surat	OK	X	-	X	X	X	X	X	-	7	1	14
415	GU Rajkot SW, GERI	OK	X	X	X	-	X	X	X	-	7	1	14
416	GU Rajkot GW	OK	OK	X	X	-	OK	X	OK	-	7	4	57
418	CWC Bangalore	OK	X	OK	OK	X	X	OK	OK	OK	9	6	67
421	KA KERS, Mysore	OK	X	X	OK	OK	OK	X	X	X	9	4	44
428	CWC Cochin	OK	X	OK	OK	X	OK	-	X	X	8	4	50
435	MP Bhopal	OK	-	OK	X	X	OK	OK	X	X	8	4	50
436	MP Sagar	X	X	X	X	X	X	X	X	X	9	0	0
437	MP Jabalpur	-	-	-	-	-	-	-	-	-	0	0	0
438	MP Satna	OK	OK	OK	OK	X	X	X	X	-	8	4	50
439	MP Balaghat	X	X	OK	X	X	X	X	X	-	8	1	13
441	MP Gwalior	X	X	X	X	X	X	X	X	OK	9	1	11
442	CWC Raipur (+)	OK	-	X	X	-	X	X	X	-	6	1	17
444	MP Bilaspur	X	X	X	X	-	X	-	-	-	5	0	0
445	MP Raipur	X	X	OK	OK	X	X	OK	X	-	8	3	38
447	CWC Nagpur	OK	X	OK	OK	OK	OK	OK	OK	X	9	7	78
448	CWC Pune	X	X	OK	OK	X	OK	X	X	X	9	3	33
451	MH Nashik SW	X	X	OK	OK	X	X	OK	OK	OK	9	5	56
454	MH Pune SW	X	OK	X	OK	X	X	OK	X	OK	9	4	44
459	CWC Bhubaneshwar	OK	X	X	OK	OK	OK	OK	OK	OK	9	7	78
461	OR Bhubaneshwar	OK	OK	X	X	OK	X	X	X	X	9	3	33
462	OR Berhampur	X	X	X	X	OK	OK	X	X	X	9	2	22

Lab ID	Laboratory Name	Cond	TDS	TH	Na	F	SO_4	NO_3-N	PO_4-P	B	Total Reported	Within Limit	% success of reporting
463	OR Baripada	-	-	-	-	-	-	-	-	-	0	0	0
464	OR Sambhalpur	X	X	X	X	-	X	X	X	-	7	0	0
465	OR Bolangir	X	X	X	OK	X	X	-	X	-	7	1	14
466	TN Chennai	OK	X	OK	OK	X	OK	OK	OK	OK	9	7	78
467	CWC Coimbatore	OK	X	OK	OK	X	OK	OK	OK	OK	9	7	78
468	TN Trichi	OK	X	OK	OK	OK	OK	OK	OK	OK	9	8	89
469	TN Madurai	OK	X	X	OK	X	OK	X	X	OK	9	4	44
470	TN Pollachi	OK	X	OK	X	OK	OK	X	X	X	9	4	44
471	CWC Chennai	OK	X	X	OK	-	X	-	X	X	7	2	29
Labs reporting		35	33	34	35	29	34	31	33	23	287	122	43
No. Acceptable		20	6	17	20	10	14	13	11	11			
% success in the analysis of respective parameters		57	18	50	57	34	41	42	33	48			
Ranking in the analysis of respective parameters		1	8	2	1	6	5	4	7	3			

OK Within acceptable range

X Not in acceptable range

NR Not reporting

Note: The eligibility of a particular parameter is arrived based on the values found within acceptable range in both samples A & B.

Table 2: Evaluation of AQC-3 analysis results in comparison with the reference values

4.2 Comparison of laboratory performance in AQC-1 and AQC-2 exercise

A comparative analysis on the performance of the laboratories in the 1st, 2nd and 3rd rounds of inter-laboratory AQC exercises were made and the findings are summarised below in Table 3:

S. No.	Parameters	% of labs within limit	% of labs within limit	% of labs within limit
		AQC-3	AQC-2	AQC-1
1	Phosphate-P	33	45	46
2	Nitrate-N	42	53	48
3	Conductivity	57	58	63
4	Sulphate	41	53	41
5	TDS	18	50	33
6	Sodium	57	46	54
7	Total Hardness	50	39	44
8	Fluoride	34	39	41
9	Boron	48	37	63
	Overall Performance	42	47	48

Table 3: Percentage of laboratories found within acceptable limits

- The number of laboratories participating in the AQC and the number of parameters being analysed has increased in the 3rd round. That is a very good result. We requested 37 laboratories to analyse 9 parameters (333 analysis) and they actually performed 287, which is 86%!
- It may be noted that the comparison of the three exercises, though indicate more or less similar level of performance, may lead to false conclusions, since the rounds are not homogeneous. In HP, the number of laboratories participating in AQC has increased every round (good!). Because of these newcomers (freshly established or upgraded laboratories) the group performance for some parameters decrease as observed in case of Phosphate, Nitrate and Total Dissolved Solids!
- Comparing the performance of the laboratories participating in all the three rounds is a suitable way of analysisng performance against time. But since in third round, the laboratories were split in to two groups, i.e. 'Surface Water' and 'Groundwater', it was not possible. The new software developed for the purpose is, however, capable of doing it.

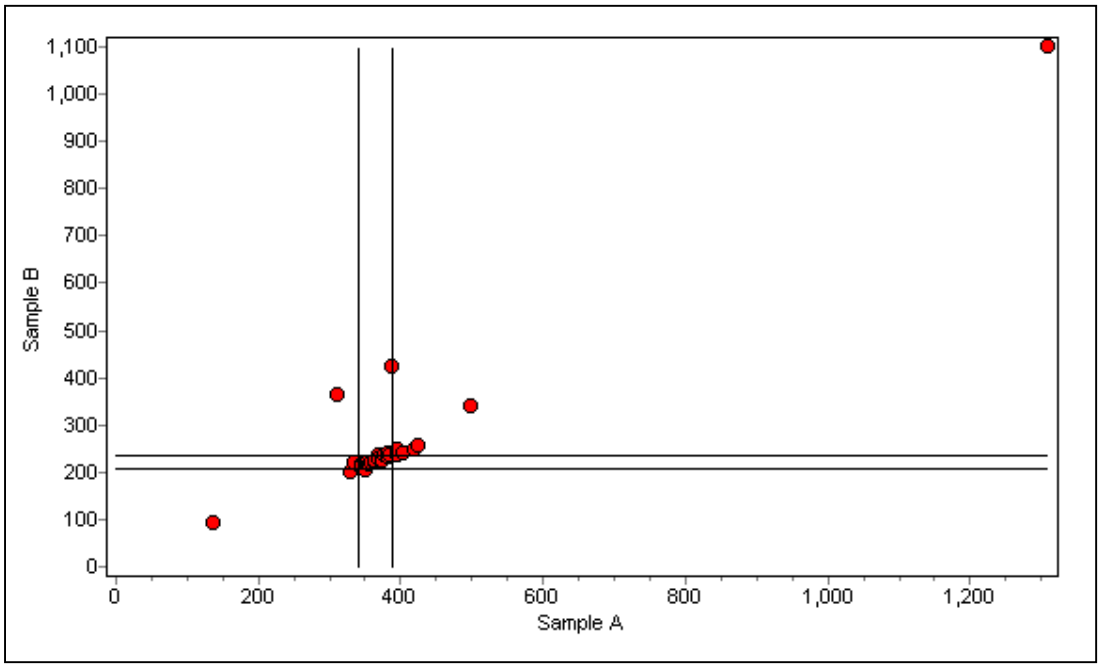

Figure 1: ***Performance of laboratories for conductivity – Youden2: sample plot AQC Round ID: 3 (all laboratories)***

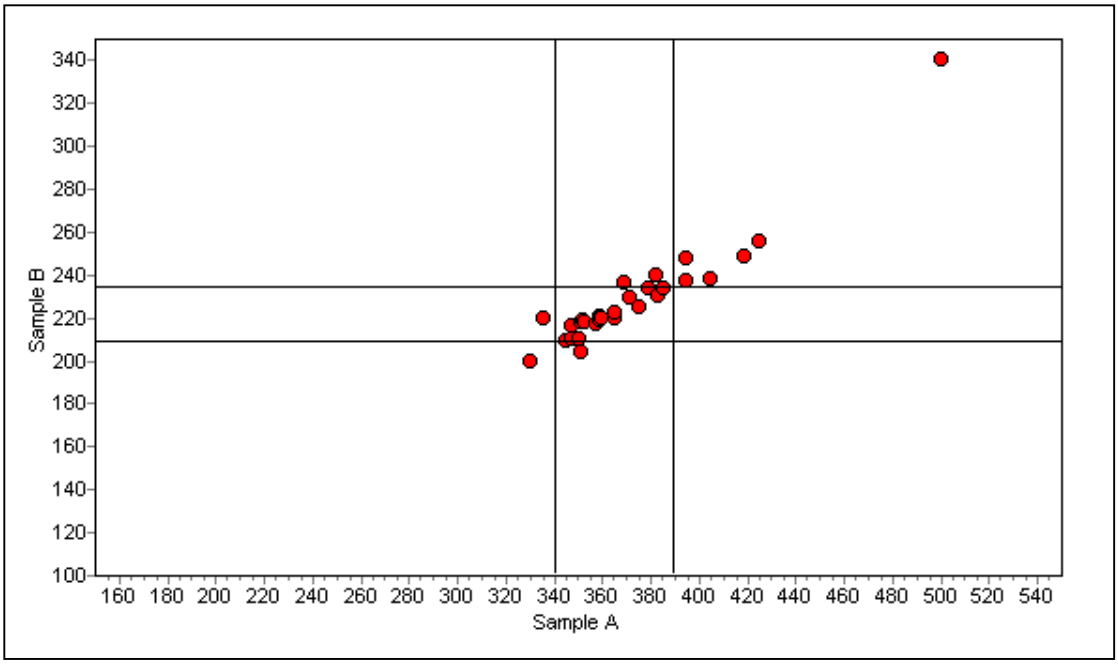

Figure 1a: ***Performance of laboratories for Conductivity-Youden 2-sample plot AQC Round ID: 3 (all laboratories)***

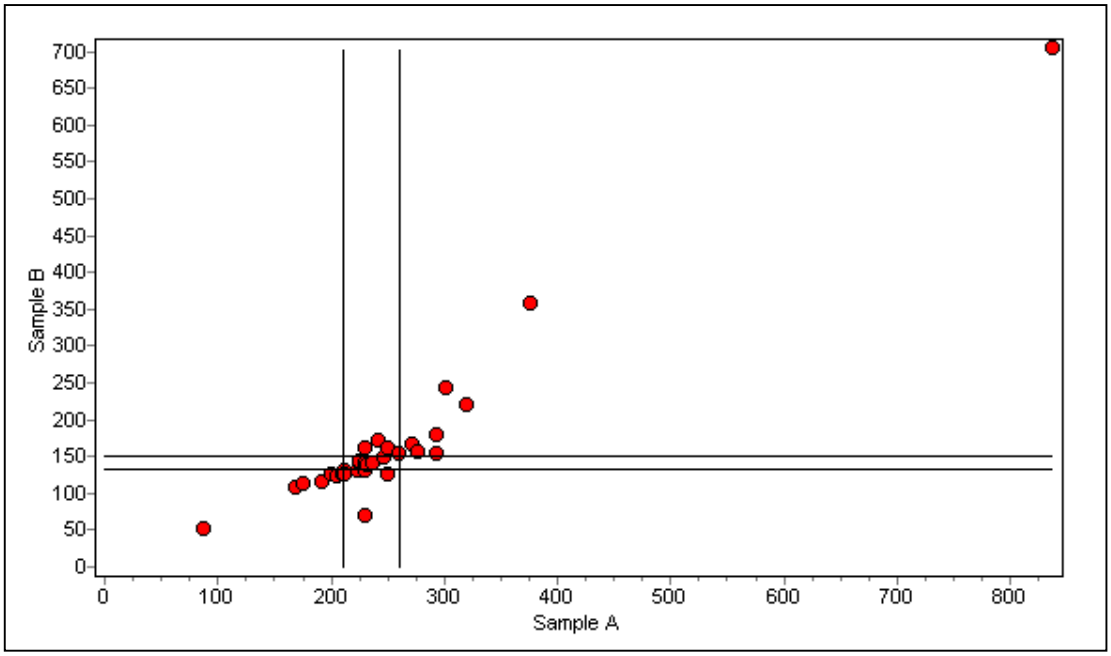

Figure 2: ***Performance of laboratories for Dissolved Solids-Youden 2-sample plot AQC Round ID: 3 (all laboratories)***

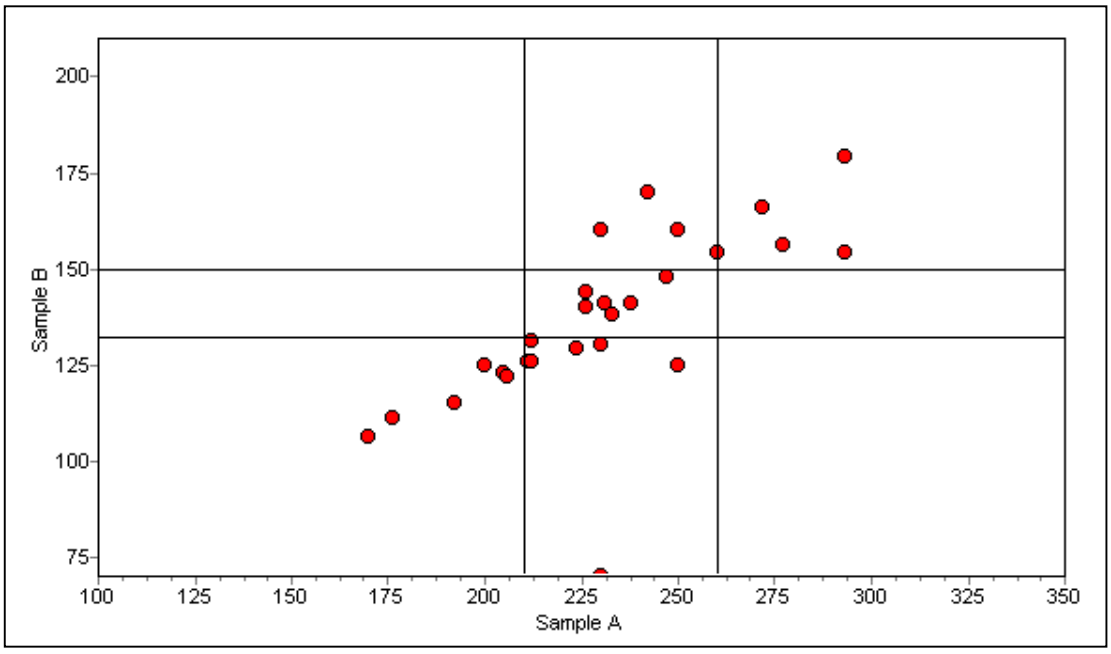

Figure 2a: ***Performance of laboratories for Dissolved Solids-Youden 2-sample plot AQC Round ID: 3 (excluding outliers)***

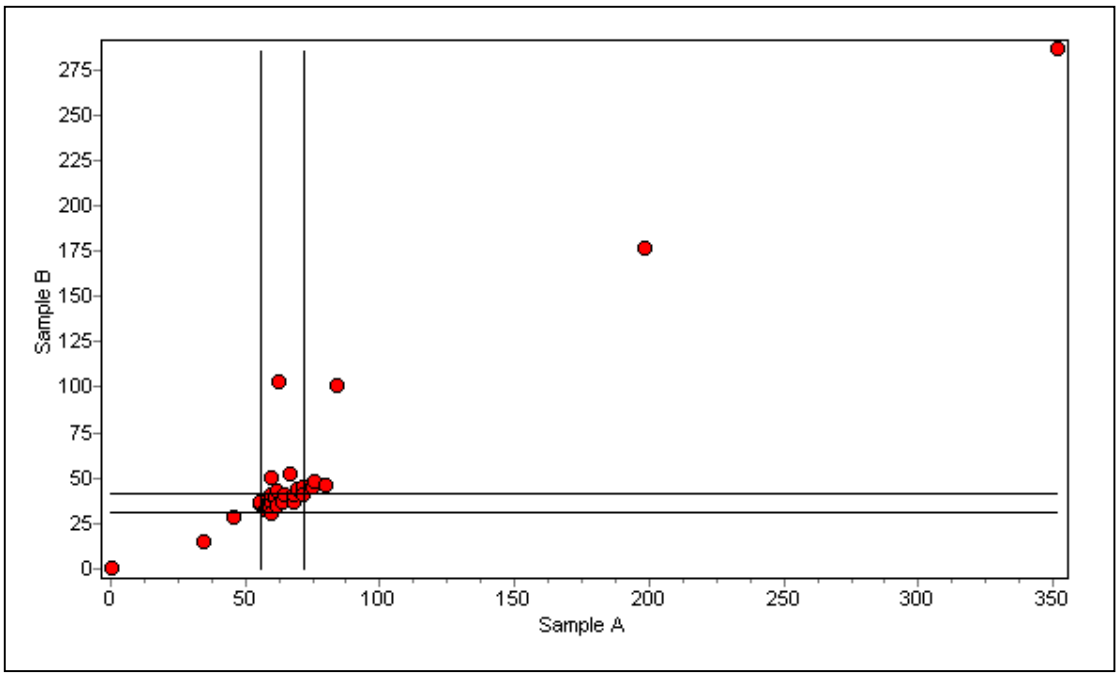

Figure 3: ***Performance of laboratories for Total Hardness-Youden 2-sample plot AQC Round ID: 3 (all laboratories)***

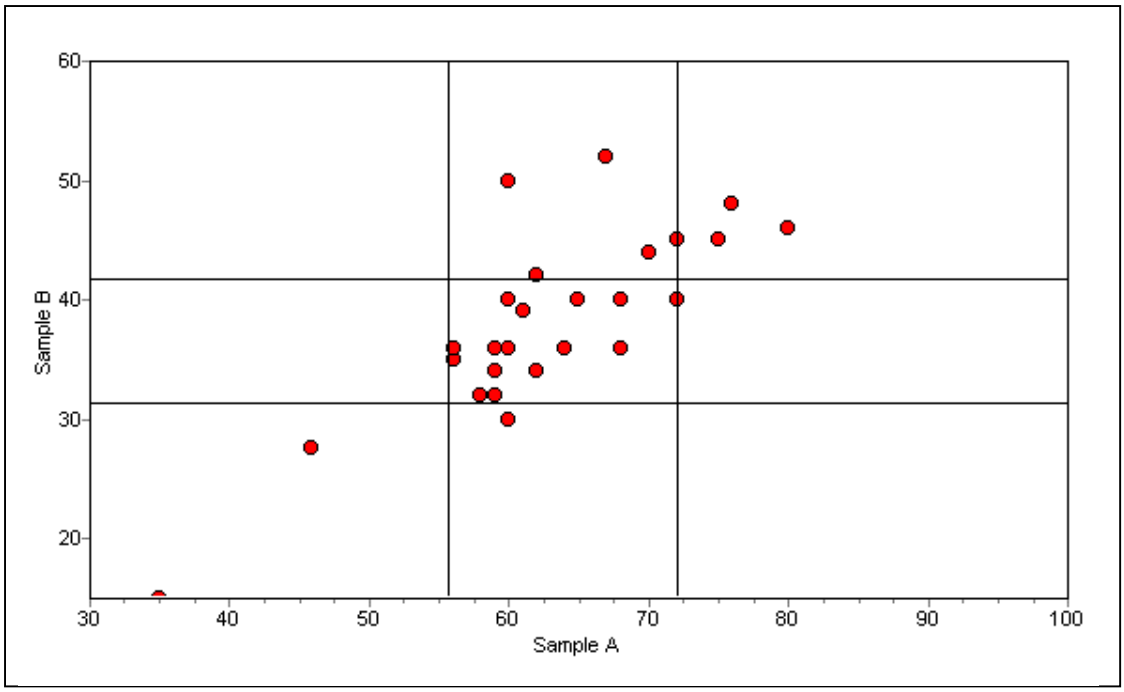

Figure 3a: ***Performance of laboratories for Total Hardness-Youden 2-sample plot AQC Round ID: 3 (excluding outliers)***

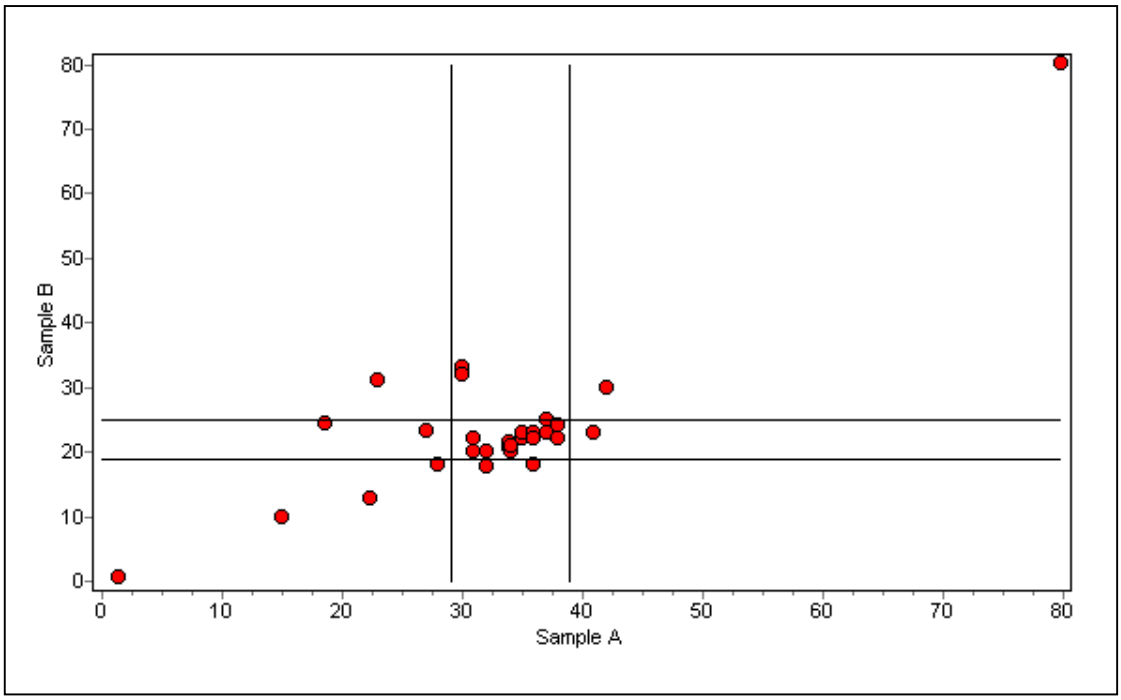

Figure 4: ***Performance of laboratories for sodium-Youden 2-sample plot AQC Round ID: 3***

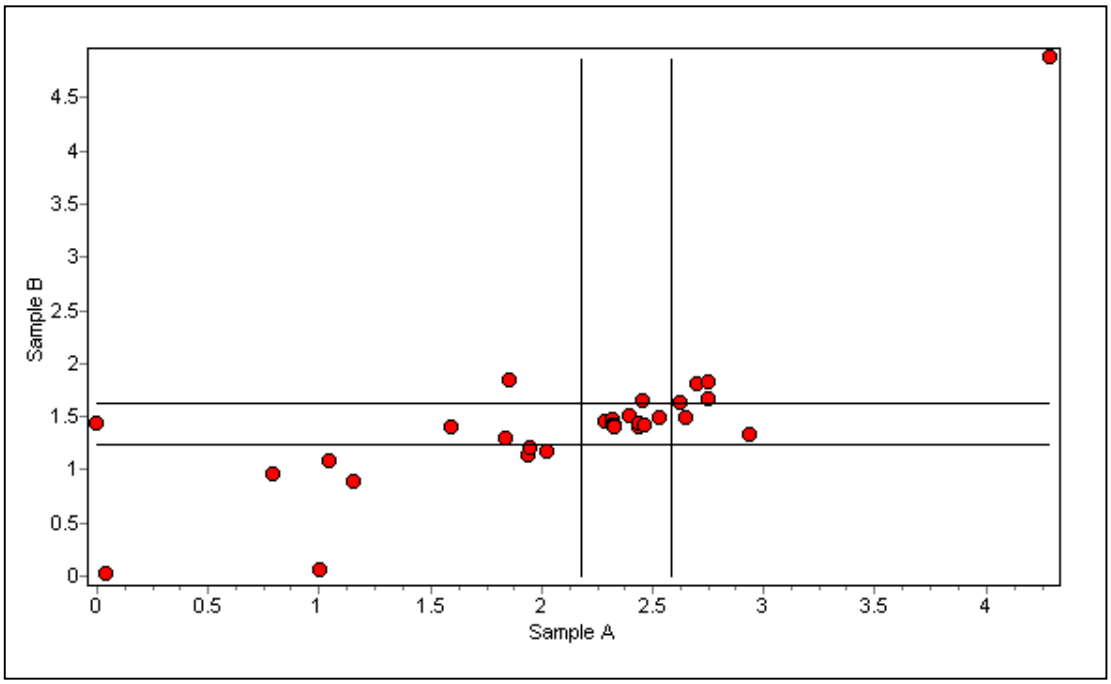

Figure 5: ***Performance of laboratories for Fluoride-Youden 2-sample plot AQC Round ID: 3***

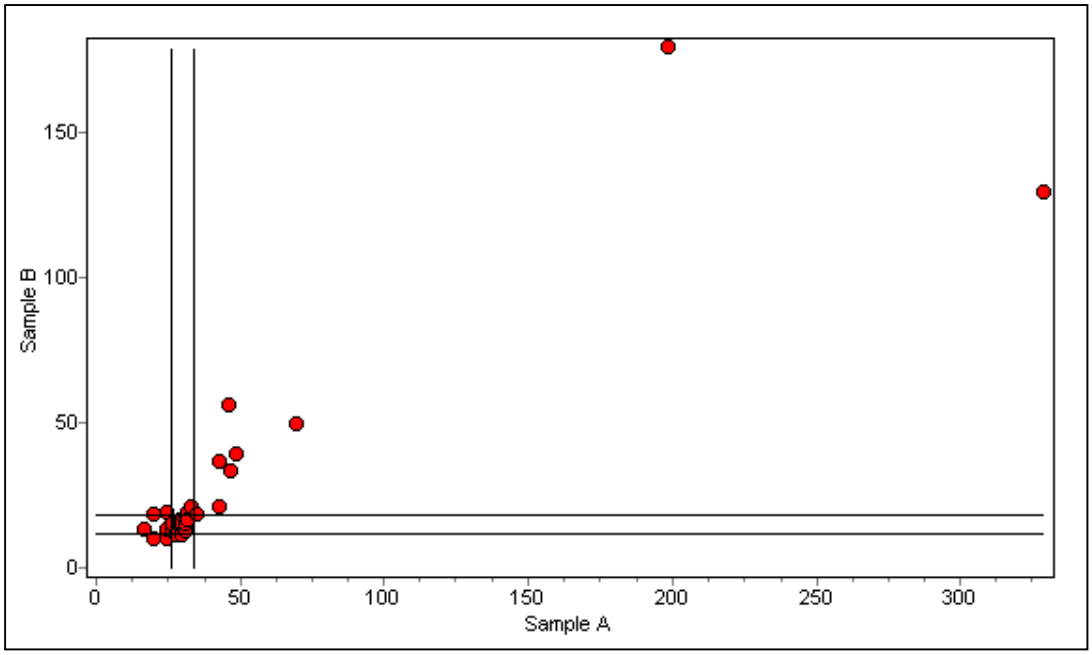

Figure 6: Performance of laboratories for Sulphate-Youden 2-sample plot AQC Round ID: 3 (all laboratories)

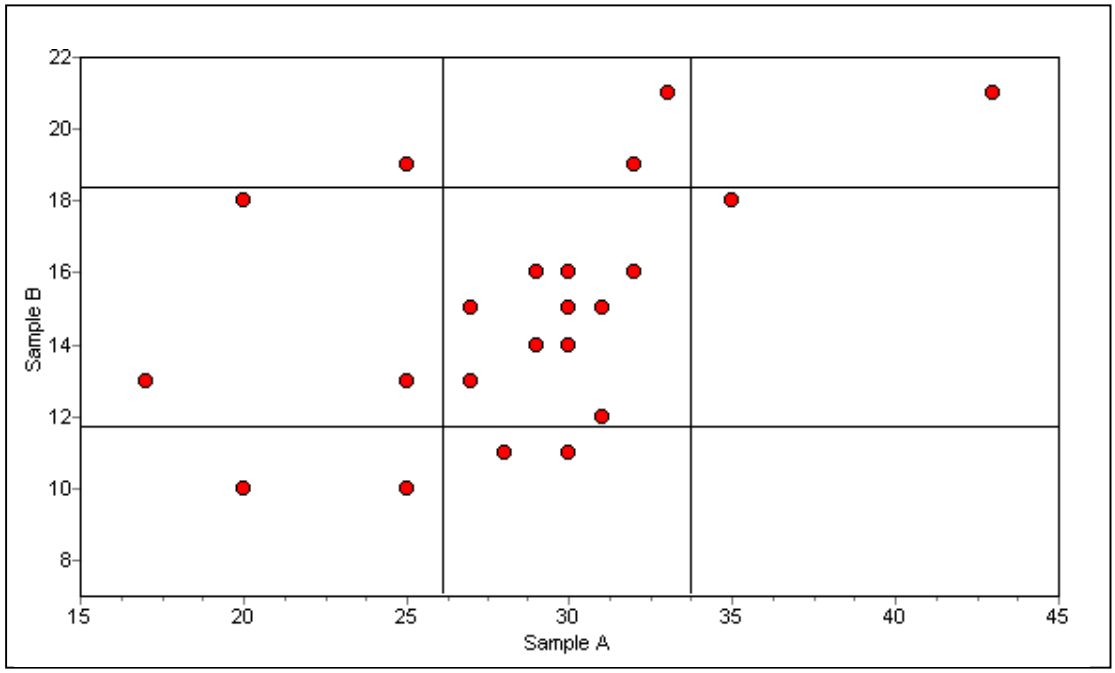

Figure 6a: Performance of laboratories for Sulphate-Youden 2-sample plot AQC Round ID: 3 (excluding defaulters)

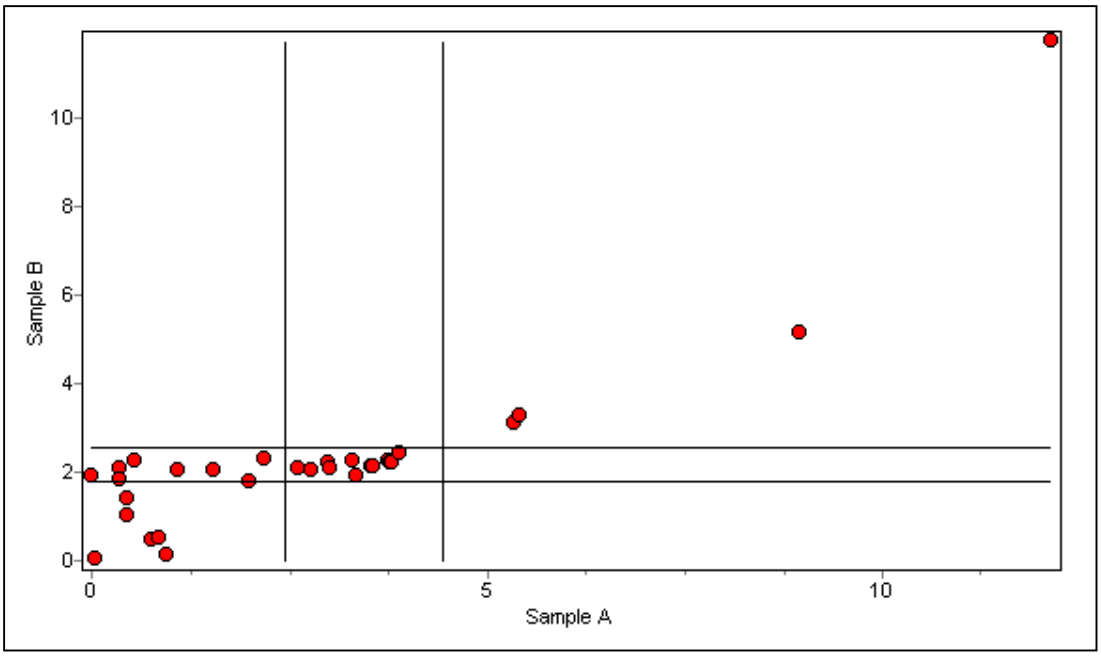

Figure 7: Performance of laboratories for Nitrate-N-Youden 2-sample plot AQC Round ID: 3

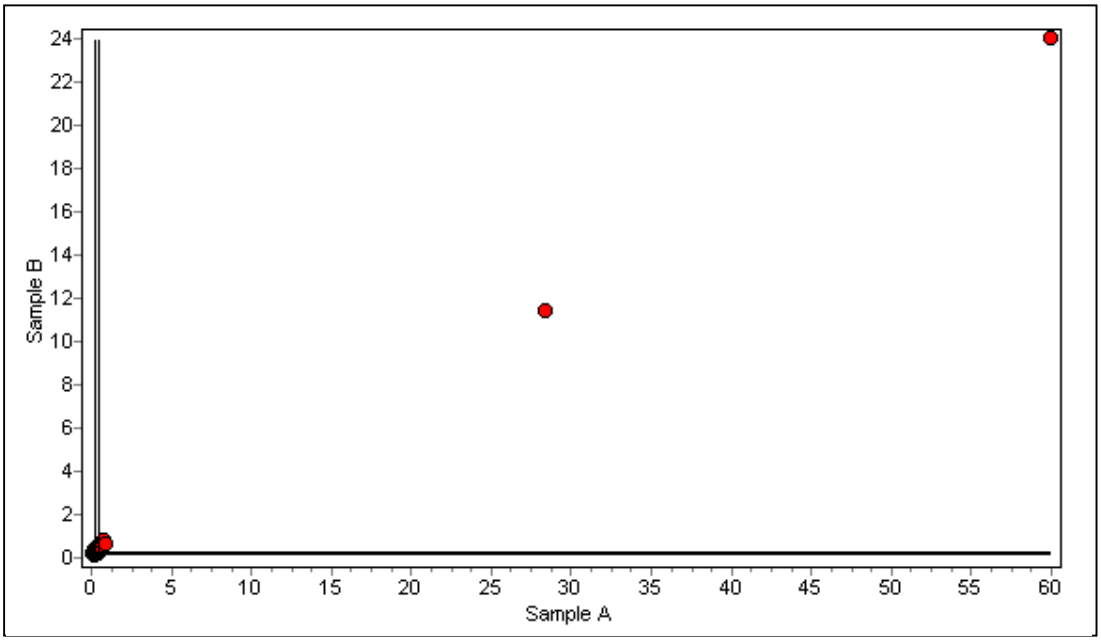

Figure 8: Performance of laboratories for Phosphate-P-Youden 2-sample plot AQC Round ID: 3 (all laboratories)

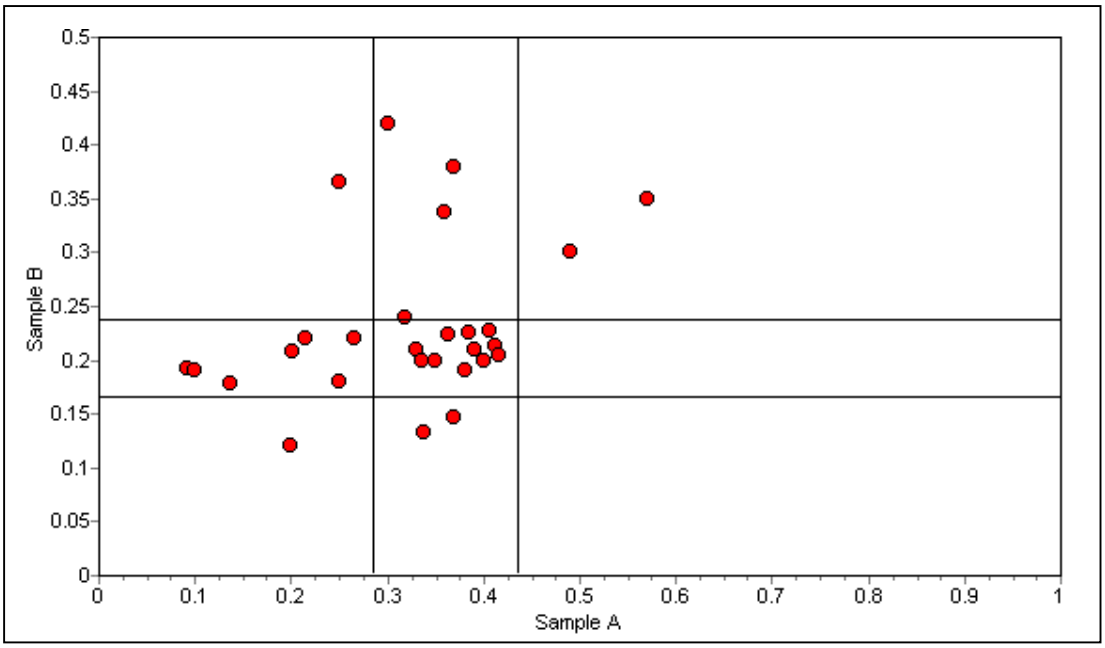

Figure 8a: Performance of laboratories for Phosphate-P-Youden 2-sample plot AQC Round ID: 3 (excluding outliers)

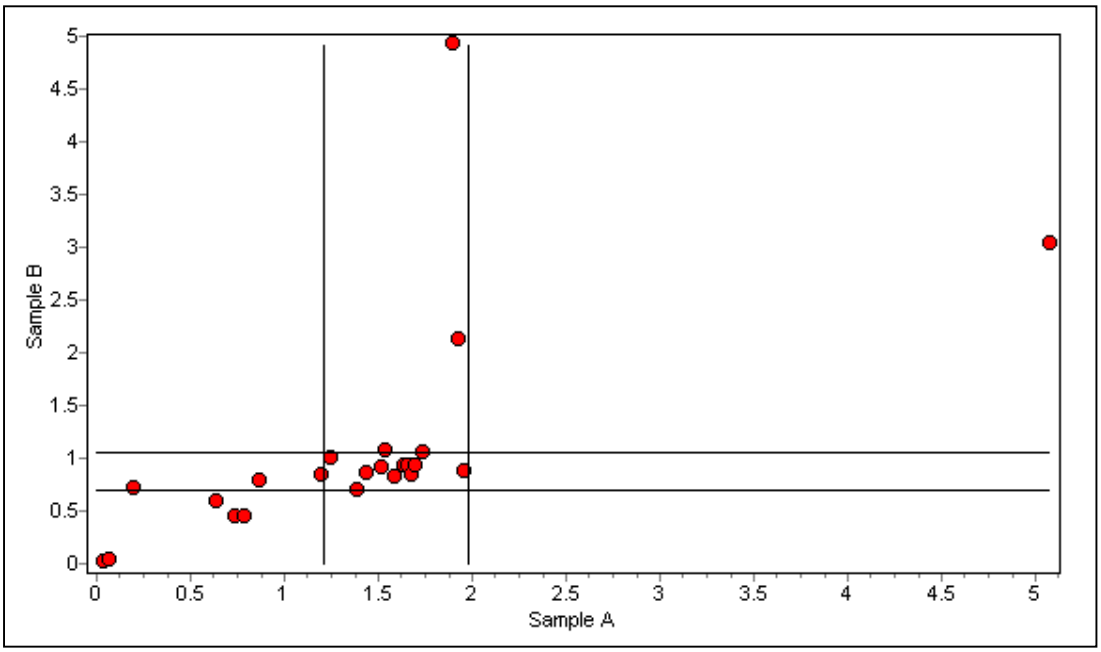

Figure 9: Performance of laboratories for Boron-Youden 2-sample plot AQC Round ID: 3

5 Conclusions and recommendations

5.1 Conclusions

- The overall performance of the 35 laboratories participating in the AQC-3 exercise was not satisfactory. Only one laboratory could analyse all 9 parameters within acceptable limits. At the other extreme, 5 laboratories identified only 1 parameter correctly, while 4 laboratories did not qualify for even a single parameter. However performance of CWC lab and some state laboratories in Tamil Nadu has improved.
- The overall performance of the AQC-3 exercise reveals that many laboratories could not report correct results for many commonly measured water quality parameters. Specifically, many laboratories had difficulty in correctly analysing nitrate-N, Total Dissolved Solids and boron.
- There was low response in the analysis of some parameters, especially boron. The reasons for this are not clear, since all laboratories should have the necessary analytical equipment and chemicals, and have received the 'Guidelines on Standard Analytical Procedures' (HP, 1999).
- Some of the errors in the reported nitrate concentrations may be caused by laboratories reporting results as NO_3 (mg/L) instead of NO_3-N (mg N/L), as requested. Some laboratories reported very low nitrate values, probably because they did not analyse in within the required timeframe.
- There is still a need for laboratories to improve the quality of their analytical procedures so that meaningful data is being produced in laboratories.

5.2 Recommendations

- Since overall performance in AQC-3 has not shown improvement compared to the AQC-1 and AQC-2, it is essential to identify the problems affecting each laboratory individually and strategies are to be evolved for improvement. Laboratories, which have not qualified for a parameter should give much attention for rectifying problems associated with the concerned parameter and should discuss issues with the HP consultants where there are uncertainties.
- In many cases, improvement in performance of laboratories can be brought about by selection of better grade chemicals, glassware, and distilled water. Analytical grade reagents (e.g. AR or GR) should be used for preparing all primary standards. All the laboratories should have good distilled water generation facility to have better quality and sufficient quantity of distilled water supply. This can improve the systematic error significantly.
- All laboratories should follow standard uniform analytical methods which are described in 'Guidelines for Standard Analytical Procedures' (HP, 1999) which is available at all laboratories. This will prevent unnecessary errors, which may be caused in the calculation or reporting of results, as is suspected for some of the reported errors of nitrate.
- Internal AQC system with Shewart charts is to be introduced in all the laboratories on a regular basis, if not already introduced. Procedures for Quality Assurance and Within laboratory AQC are given in the Water Quality Training Module number 49. The use of blind samples may be considered in this context.
- It is utmost necessary to calibrate and standardise the instruments periodically to generate good analytical results. Different instruments have different requirements.
- It is suggested to have continuous and regular participation of AQC exercise for the participating laboratories in order to improve the analytical ability.

Annexure I

CENTRAL WATER COMMISSION
Upper Godavari Division Laboratory, Hyderabad
INTER-LABORATORY ANALYTICAL QUALITY CONTOL EXERCISE
FOR THE
LABORATORIES OF SURFACE WATER DEPARTMENTS
OF
CENTRAL AND STATE UNDER

HYDROLOGY PROJECT

SEPTEMBER-OCTOBER, 2001

I. Preparation of stock solutions: 9-10 September 2001

S. No.	Name of chemical	Weight in g.	Final volume
1	Magnesium Sulphate ($Mg\ SO_4.7H_2O$)	7.6910	1 litre
2	Calcium Chloride ($Ca\ Cl_2.\ H_2O$)	6.8749	1 litre
3	Sodium Flouride (NaF)	2.6504	1 litre
4	Potassium Nitrate (KNO_3)	8.8812	1 litre
5	Boric Acid (H_3BO_3)	6.6410	1 litre
6	Potassium Dihydrogen Phosphate (KH_2P0_4)	0.6593	1 litre
7	Sodium Chloride (NaCl)	11.4412	1 litre

II. Preparation of liquid sample for analysis:

SAMPLE-A

500 mL $Mg\ SO_4.7H_2O$ + 300 mL $CaCl_2.2H_2O$ + 100 mL Na F + 150 mL KNO_3 + 70 mL H_3BO_3 + 150 mL KH_2P0_4 + 350 mL NaCl → Final volume 50 litres.

SAMPLE -B

250 mL $Mg\ SO_4.7H_2O$ + 1800 mL $CaCl_2.2H_2O$ + 60 mL Na F + 90 mL KNO_3 + 40 mL H_3BO_3 + 80 mL KH_2PO_4 + 220 mL NaCl → Final volume 50 litres.

Constituents of liquid samples

Parameter	Sample-A	Sample-B
Sodium (Na), mg/L	34	22
Sulphate (SO_4) , mg/L	30	15
Fluoride (F) , mg/L	2.40	1.44
Nitrate-Nitrogen (NO_3-N) , mg/L	3.69	2.14
Boron (B) , mg/L	1.68	0.96
Phosphate-P (PO_4) , mg/L	0.450	0.240
Total Hardness (TH) , mg/L	59	32

Annexure II
Communication with the despatch of samples

CENTRAL WATER COMMISSION
UPPER GODAVARI DIVISION LABORATORY, HYDERABAD

INTER-LABORATORY ANALYTICAL QUALITY CONTOL EXERCISE
FOR THE
LABORATORIES OF SURFACE WATER DEPARTMENTS
OF
CENTRAL AND STATE UNDER

HYDROLOGY PROJECT

SEPTEMBER-OCTOBER, 2001

Please read the following instructions carefully before starting analysis of samples

Two nos. of synthetic water samples (A & B) of one lit. each labelled with lab code are provided for analysing Conductivity, Total solids, Total Hardness, Sodium, Fluoride, Sulphate, Nitrate-N, Phosphate-P and Boron.

Both labelled liquid samples (A & B) are to be analysed separately for all 9 parameters as shown below.

Important: Please report the results using the correct number of decimals, as specified in the table below.

Conductivity should be reported in whole numbers (0 decimals) e.g. 256 μmhos/cm.

Nitrate should be reported with 2 decimals, e.g. 5.17 mg N/L

S. No.	Parameter	Unit	No. of decimals to report
01	Conductivity at 25°C	μ mhos/cm	0
02	Total Dissolved Solids	mg/L	0
03	Total hardness as $CaCO_3$	mg$CaCO_3$/L	0
04	Sodium	mg/L	0
05	Fluoride as F	mg/L	2
06	Sulphate as SO_4	mg/L	0
07	Nitrate – N	mg N/L	2
08	Phosphate – P	mg P/L	3
09	Boron	mg/L	2

Note: Choose appropriate sample volume for each parameter for single run, so that analysis can be done within the provided sample volume.

ANALYTICAL METHODS:

You may choose any relevant method being followed in your laboratory for various parameters. However, the method is to be mentioned into the data format.

In case of colourimetric method, the standard graph and the factor used for calculation for sample analysis is to be submitted along with the data sheet.

Brief outline of the procedures for each analytical parameter is to be provided as Annexure along with the data sheets.

Please note the following points:

All the samples are to be analysed most preferably during 18th September 2001 to 28th September 2001 for better comparison purpose of data obtained from various laboratories.

Report the analysis result in the enclosed Data format sheet only. Kindly avoid using separate typed data sheet.

Be sure that Lab code & sample code numbers are mentioned in the Data format sheet while sending the report.

Be sure that all the units of various parameters are properly taken care of while reporting data. Especially important: Please be sure to report Nitrate in mg N/L and Phosphate in mg P/L.

Analysis report should be sent directly to the following address positively latest by 15th October 2001 positively.

Dr. A. K. Mitra,
Research Officer ,
Upper Godavari Division,
Central Water Commission,
H.No. 11-5-382/396, Red Hills,
Hyderabad – 500 004 (AP)
Phone: (040) 3391654
Fax No. (040) 3394414

Annexure IIa

CENTRAL WATER COMMISSION
UPPER GODAVARI DIVISION
WATER QUALITY LABORATORY, HYDERABAD

III AQC / WATER	SEP 2001	**LAB CODE**	

III ANALYTICAL QUALITY CONTROL (AQC/WATER) EXERCISE - SEPTEMBER 2001

FOR THE LABORATORIES OF SURFACE AND GROUND WATER DEPARTMENTS OF CENTRAL AND STATE AGENCIES UNDER "HYDROLOGY PROJECT"

01	**Name of the organisation**	
02	**Address of the laboratory with PIN code, phone and Fax**	PIN …… Phone…….. Fax……..
03	**Sample analysed by: (Name & Designation)**	1……... 2……... 3……...
04	**Date of receipt of sample**	

RESULTS

S. No.	**Parameter**	**Sample Code**		**Method adopted**	**Instrument used**	**Calibration Graph attached (yes/no)@**	**Date of analysis**
		A	**B**				
01	Conductivity at 25°C (µmho/cm)						
02	Total Dissolved Solids (mg/L)						
03	Total Hardness (mg/L)						
04	Sodium (mg/L)						
05	Fluoride (mg/L)						
06	Sulphate (mg/L)						
07	Nitrate-N (mg/L)						
08	Phosphate-P (mg/L)						
09	Boron (mg/L)						

@ A copy of the standard calibration graph, wherever applicable, is to be attached in Annexure.

Annexure III
Sample analyses data for AQC Round ID : 3 (as received from the laboratories)

Lab ID	EC_A	EC_B	TDS_A	TDS_B	Total HAR_A	Total HAR_B	Na_A	Na_B	F_A	F_B	SO_4_A	SO_4_B	NO_3-N_A	NO_3-N_B	o-PO_4_A	o-PO_4_B	B_A	B_B
401	347	216	233	138	58.0	32.0	35.0	22.0	2.44	1.40	30.0	14.0	3.74	2.24	0.416	0.204	1.66	0.92
402	359	221	211	126	72.0	45.0	36.0	22.0	2.40	1.50	70.0	49.0	3.80	2.20	0.385	0.225	0.04	0.02
405	369	236	231	141	64.0	36.0	36.0	22.0	1.86	1.84	35.0	18.0	0.55	2.26	0.136	0.178	1.74	1.06
407	387	423	376	356	63.0	103.0	18.6	24.3	1.16	0.89	- -		0.86	0.53	-		-	-
-																		
410	382	240	170	106	68.0	36.0	36.0	18.0	2.33	1.41	28.0	11.0	0.35	1.83	0.406	0.227	0.64	0.59
411	330	200	200	125	60.0	36.0	31.0	20.0	1.60	1.40	25.0	10.0	2.60	2.10	0.265	0.220	-	-
412	352	219	212	131	-	-	15.0	10.0	4.29	4.88	17.0	13.0	5.42	3.28	0.250	0.365	-	-
415	371	229	176	111	0.8	0.5	22.4	12.8	-	20.0	10.0	0.35	2.10	0.938	0.586	-	- -	
416	350	210	226	140	67.0	52.0	32.0	17.6	-	1.43	32.0	16.0	0.00	1.91	0.350	0.200	-	-
418	379	234	260	154	59.0	32.0	38.0	24.0	1.95	1.20	25.0	19.0	3.55	2.15	0.380	0.190	1.64	0.93
421	385	234	272	166	70.0	44.0	37.0	23.0	2.33	1.39	30.0	15.0	0.77	0.48	0.370	0.146	1.93	2.12
428	383	230	192	115	62.0	34.0	37.0	23.0	2.03	1.17	31.0	15.0	-	-	0.686	0.718	0.74	0.45
435	375			225	56.0	35.0	30.0	33.0	2.75	1.83	30.0	14.0	3.02	2.08	0.215	0.220	1.90	4.92
436	1310	1100	838	704	352.0	286.0	79.8	80.2	0.79	0.96	199.0	179.0	12.13	11.76	0.840	0.760	0.87	0.79
437	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
438	365	222	247	148	56.0	36.0	33.9	20.7	0.04	0.03	329.0	129.0	0.06	0.05	0.300	0.420	-	-
439	419	249	293	179	72.0	40.0	27.1	23.2	1.00	0.05	47.0	33.0	1.54	2.02	0.092	0.193	-	-
441	500	340	320	220	76.0	48.0	30.0	32.0	2.65	1.48	20.0	18.0	2.00	1.80	60.000	24.000	1.25	1.00
442	347	210	-	-	45.9	27.5	1.5	0.5	-	-	25.0	13.0	8.94	5.15	0.490	0.300	-	-
444	395	248	250	160	60.0	50.0	28.0	18.0	-	-	49.0	39.0	-	-	-	-	-	-
445	405	238	293	154	68.0	40.0	33.9	21.5	1.04	1.07	43.0	36.0	2.79	2.03	0.202	0.208	-	-
447	345	209	205	123	58.0	32.0	36.0	23.0	2.32	1.46	27.0	13.0	3.77	2.22	0.363	0.223	1.54	1.07
448	336	220	260	154	61.0	39.0	32.0	20.0	2.94	1.32	29.0	16.0	2.19	2.32	0.100	0.190	0.79	0.45
451	395	237	230	160	68.0	40.0	35.0	23.0	1.84	1.29	43.0	21.0	3.30	2.24	0.335	0.200	1.44	0.86
454	351	204	226	144	62.0	42.0	34.0	20.0	1.94	1.13	32.0	19.0	2.60	2.10	0.250	0.180	1.52	0.91
459	359	220	277	156	60.0	30.0	36.0	23.0	2.53	1.49	27.0	15.0	3.35	1.92	0.390	0.210	1.96	0.88
461	360	220	238	141	60.0	30.0	42.0	30.0	2.47	1.42	30.0	11.0	0.45	1.41	0.360	0.338	0.07	0.04
462	137	90	88	50	35.0	15.0	41.0	23.0	2.44	1.43	30.0	16.0	0.45	1.03	0.370	0.380	0.20	0.70
463																		
464	311	363	302	242	84.0	100.0	23.0	31.0	-	-	46.0	56.0	5.35	3.10	0.570	0.350	-	-
465	425	256	230	70	80.0	46.0	36.0	22.0	2.63	1.62	25.0	13.0	-	-	28.400	11.400	-	-
466	357	217	206	122	65.0	40.0	34.0	21.0	2.70	1.80	31.0	15.0	3.89	2.44	0.400	0.200	1.70	0.92

467	359	219	224	129	59.0	36.0	35.0	22.0	2.75	1.66	31.0	12.0	3.53	2.15	0.412	0.214	1.39	0.70
Lab ID	**EC_A**	**EC_B**	TDS_A	TDS_B	**Total HAR_A**	**Total HAR_B**	**Na_A**	**Na_B**	**F_A**	**F_B**	**SO_4_A**	**SO_4_B**	**NO_3-N_A**	**NO_3-N_B**	**o-PO_4_A**	**o-PO_4_B**	**B_A**	**B_B**
468	360	220	212	126	59.0	34.0	38.0	22.0	2.29	1.45	32.0	16.0	2.99	2.20	0.330	0.210	1.68	0.84
469	351	218	242	170	75.0	45.0	31.0	22.0	2.46	1.65	30.0	15.0	1.10	2.04	0.318	0.240	1.59	0.82
470	353	218	250	125	60.0	40.0	37.0	25.0	2.32	1.41	29.0	14.0	0.95	0.12	0.200	0.120	1.20	0.83
471	365	220	230	130	199.0	176.0	35.0	22.0	-	-	33.0	21.0	-	-	0.338	0.133	5.08	3.03
cv	43.0	60.1	45.4	66.8	76.1	98.3	34.0	49.1	37.1	53.8	127.4	126.9	93.6	86.7	374.5	338.6	70.1	95.9
N35	35	33	33	34	34	35	35	29	30	34	34	31	31	33	33	23	23	
Min	137	90	88	50	0.8	0.5	1.5	0.5	0.04	0.03	17.0	10.0	0.00	0.05	0.092	0.120	0.04	0.02
Max	1310	1100	838	704	352.0	286.0	79.8	80.2	4.29	4.88	329.0	179.0	12.13	11.76	60.000	24.000	5.08	4.92
Mean	390.69	258.71	255.15	164.12	73.96	51.71	33.24	23.34	2.15	1.44	45.88	27.18	2.79	2.30	3.03	1.33	1.42	1.08
SD(n-1)	167.95	155.37	115.88	109.62	56.27	50.83	11.29	11.47	0.80	0.77	58.46	34.49	2.61	1.99				

Annexure IV
Procedural steps for analysis of AQC data as performed by the software

Step	Procedure	Comments
1	Tabulate raw data for the laboratories (1st column Table 1 "all data")	Sorted by laboratory ID for easy reference. Displays: count, min, max, mean, stdev (for n-1 d.o.f), c.v.
For all samples (A and B) for each parameter (at present 9 numbers), the following steps are performed(*)		
2a	First Screening: remove data too far from theoretical value Tabulate remaining data (2nd column Table 1 "Xtheo")	Accept only data within a fixed predefined margin based upon the theoretical concentration value of the sample. Acceptable range: = $X_{theory} \pm 0.5 \times X_{theory}$ e.g. if the concentration measure by the organising laboratory is 40 all data outside the range of 20 - 60 will be rejected.
2b	Second Screening: statistical removal of outliers Tabulate remaining data (3rd column Table 1 "Outlier")	Procedure according to Rosner's test at a 95% confidence level. Rosner's test searches the data set for 1 up to a maximum of 10 outliers. See workbook on data analysis for documentation of Rosner's test.
2c	Calculate 95% Confidence Limit of data remaining after 2nd screening. Retain data values within LCL and UCL and tabulate (4th column Table 1 "95% CL")	Calculate upper and lower confidence limit of data remaining after 2nd screening: LCL = Mean – 1.96 $\times$ SD/$\sqrt{N}$ UCL = Mean + 1.96 $\times$ SD/$\sqrt{N}$ Retain data value (x) when: LCL $\leq$ x $\leq$ UCL
2d	Calculate accepted data range from residual data. Retain data values within LL and UL and tabulate (5th column Table 1 "Accepted")	Calculate: Reference Mean (X_{ref}) of remaining data, SD for (n-1) dof, and $SD_{(adjusted)}$) = SD*$\sqrt{2}$ Lower Limit (LL) = $X_{ref} - 3 \times SD_{(adjusted)}$ Upper Limit (UL) = $X_{ref} + 3 \times SD_{(adjusted)}$ Spread = $\pm$ 3$\times SD_{(adjusted)}$
2e	Verify if the calculated data spread is within the acceptable limits for the spread (Table B) If not acceptable, adapt the spread by correcting $SD_{(adjusted)}$	If $SD_{(adjusted)} > SD_{max}$ then: $SD_{(adjusted)} = Sd_{max}$ If $SD_{(adjusted)} < SD_{min}$ then: $SD_{(adjusted)} = Sd_{min}$ Recalculate LL and UL (from step 2d) with the updated $SD_{(adjusted)}$ and update column 5.
2f	Identify the original data values which are within the accepted range	Accept data value (x) when: Lower Limit (LL) $\leq$ x $\leq$ Upper Limit (UL)
Repeat step 2 for all other samples-parameter combinations		
3	Create Table 2	Listing of Reference mean and accepted range (LL and UL) for all parameters in both samples

4	Create Table 3	For each laboratory, identify the parameters they have correctly analysed A laboratory must report both samples (A&B) within the acceptable range for the given parameter in order to have 'correctly' analysed the parameter.
5	Create Table 4	Compare result of current AQC round with previous round(s). Compare either with the previous round or with all previous rounds.
6	Construct Youden Plots per parameter	Parameter wise plot with results of all laboratories for sample A and B together with all data together with the values for LL and UL
(*) for each sample-parameter combination (2 x 9 = 18 numbers) 5 columns are presented in Table 0. For each sample-parameter combination the 5 columns contain: (1) raw data, (2) data after first screening (3) data after statistical outlier removal, (4) residual data and (5) accepted data.		