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WATER QUALITY MONITORING: DEVELOPING DATA QUALITY OBJECTIVES FOR GIBRALTAR MINE

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ABSTRACT

Site or project specific data quality objectives (DQOs) describe the amount of error that is acceptable for a water quality monitoring program. Held quality control samples are used to include sample collection in the measurement of data quality. The results of analysis of the field quality control samples are compared to DQOs to evaluate if overall data quality is acceptable.

Gibraltar Mine has a water quality monitoring program for surface water, ground water and process water. The program includes the analysis of total metals, dissolved metals, anions and nutrients. Field quality control samples include field blanks, filtration blanks, and field duplicates. In this study DQOs are developed for field blanks and field duplicates. DQOs are also developed for the comparison of total and dissolved metals, which is not normally considered a component of quality control. The proposed DQOs are applied to water quality monitoring data from Gibraltar Mine. This paper discusses the development and application of DQOs for water quality monitoring at Gibraltar Mine, and presents new DQO approaches for field duplicates and comparison of total and dissolved metals.

INTRODUCTION

Gibraltar Mine has a water quality monitoring program for surface water, ground water and process water that has been ongoing for many years. In the last several years field quality control samples (field blanks and field duplicates) have been incorporated into the program. Data quality objectives were developed specifically for the Gibraltar Mine water quality monitoring program.

The purpose of data quality objectives (DQOs) for a water quality monitoring program is to "identify the maximum amount of uncertainty (or error) which can be tolerated in the data if it is to be satisfactory for its intended use" (British Columbia Field Sampling Manual, 1996 edition (permittee)). A DQO requires a target value and an acceptable range. A data point is compared to a relevant DQO and if it is within the acceptable range it "passes", and the accuracy of the data point and all associated data is deemed to be acceptable. If a data point is outside the DQO acceptable range it "fails", and the accuracy of the data point and all associated data is suspect. Generally a DQO failure should be investigated to identify (and correct) the cause of the failure. DQOs can be applied to any measurable component of a monitoring program for which a target value and acceptable range can be established, such as: blanks, duplicates, dissolved metal concentration vs. total metals concentration, reference samples and spiked samples.

Statistical system DQOs can be derived by collecting sufficient number of replicate or repeat samples of the same type and by performing the appropriate statistical calculations to determine the target (i.e. mean) and the acceptable range (i.e. confidence interval) as described by Taylor (1987). The statistical approach is useful to derive the actual system target and acceptable range to a 95% or 99% confidence interval. The DQO failure rate for a statistical system DQO is predetermined by the selection of the confidence interval. For example, with a *95%* confidence interval, one can expect a DQO failure rate of approximately 5%. It is important the data used for statistical calculations has not been rounded, or otherwise modified, or the calculations may be biased or impossible to perform.

Gibraltar Mine field quality control data from March 1999 through March 2001 has rounded data, and where the results are below the detection limit there is no data, therefore it is not possible to perform statistical calculations on the available data.

Generic system DQOs can be established biased upon the program requirements and the intended use of the data. Each DQO is defined without a direct statistical derivation. This is a practical and cost effective alternative to statistically deriving the DQOs, and it is usually the first step when defining and implementing system DQOs. Generic system DQOs are not statistically derived, therefore, it is important that they are compared against real system data to ensure the resultant DQO failure rate is acceptable.

This paper demonstrates a practical approach for establishing generic system DQOs to meet the requirements of the Gibraltar Mine water quality monitoring program. Our approach takes into account statistical limitations of the system detection limit, and uses techniques from published and unpublished documents. Gibraltar Mine field quality control data from March 1999 through March 2001 are compared to the generic DQOs, and the failure rates are summarized.

OBJECTIVE

This report outlines how generic data quality objectives (DQOs) were developed for the water quality monitoring program at Gibraltar Mine. The DQOs apply to field blanks, field duplicates and for data pairs of dissolved and total metals. The DQOs were developed from:

- the water quality monitoring goals of Gibraltar Mine,
- the requirements of the Ministry of Environment, Lands and Parks as outlined in "A Compendium of Working Water Quality Guidelines for British Columbia" (2001), and "Guidelines for Interpreting Water Quality Data" (1998),
- the capabilities of common and generally accepted lab procedures,
- the Gibraltar Mine field quality control data from March 1999 through March 2001,
- and from statistical and practical approaches used to estimate uncertainty.

The DQOs are intended to assist Gibraltar Mine in the assessment of water quality monitoring data.

FIELD BLANK DATA QUALITY OBJECTIVES

Gibraltar Mines has several water quality monitoring programs:

- Cuisson Creek: Baseline monitoring. Surface water only.
- Standard: Permit monitoring requirements. Surface, ground and process waters.
- Internal: Internal monitoring requirements. Surface, ground and process waters.

Each program has a unique list of parameters that are analyzed by different analytical methodologies, therefore, it is appropriate to establish distinct field blank DQOs for the Cuisson Creek program and the Standard and Internal programs.

Blank acceptability in the "Quality Assurance Guidelines to Supplement the Standard Effluent and Receiving Environment Quality Assurance Clause prepared by BC Environment with input from the BC Laboratory Quality Assurance Advisory Technical Subcommittee (2001) is described as follows:

> "Field blank contamination preferably should not be significantly greater in concentration nor occurrence than laboratory method blank contamination."

and,

> "Laboratory method blanks...must not exceed the detection limit reported by the laboratory for the associated samples."

The detection limit reported by laboratories accounts for test method sensitivity and for contaminants that may be introduced at the laboratory. To allow for the additional potential sources of contamination related to field sampling, we propose that, where practical, the field blank DQOs are set to twice the laboratory's reported DL for each parameter. If an applicable guideline level is near the reported DL, or if the trace concentration of a parameter is of particular concern, then the reported DL should be used as the field blank DQO. The limits should be reviewed, and revised if necessary, as field blank data is collected and assessed.

Three sets of DQOs are derived as described below. The DQOs for the Standard and Internal programs are presented as one set. For the Cuisson Creek program two field blank DQO options are presented. For one option the DQO is limited by the lowest applicable BC Water Quality Guideline, while for the other option the DQO is limited by the laboratory reported DL. For these reasons the two Cuisson Creek program field blank DQOs differ for the following parameters: antimony, arsenic, barium, boron, iron, lead, silver, thallium, titanium, uranium, and vanadium.

Field Blank DQOs: Standard + Internal Monitoring Programs

The Standard and Internal monitoring programs are grouped together for convenience of presentation. These programs are used for permit and internal monitoring requirements. There are no established guidelines for the parameters in these monitoring programs, therefore, field blank DQOs for these programs emphasize contamination control near the reported DL concentration level. The DQO for each parameter was developed as follows:

1. The DQO was set equal to twice the reported DL.

For each parameter the field blank concentration must not exceed the DQO presented in Table 4.

Field Blank DQOs: Cuisson Creek Monitoring Program, BCWO

There are no established guidelines for the Cuisson Creek monitoring program. The BCWQ field blank DQO option is only presented to demonstrate how a guideline-based field blank DQO is developed. The only consideration for this DQO are the lowest guidelines of the Ministry of Environment, Lands and Parks as outlined in "A Compendium of Working Water Quality Guidelines for British Columbia" (2001), and "Guidelines for Interpreting Water Quality Data" (1998). By emphasizing the guideline levels for a parameter, the selected DQO may be significantly larger than the reported DL for that parameter. The DQO for each parameter was set to one tenth of the lowest guideline level, unless it was close to the reported DL. The following rules outline the process used:

1. If a guideline level exists, and the reported DL is one twentieth the guideline level or less, then the DQO was set equal to one tenth of the guideline level,
2. If a guideline level exists, and the reported DL is between one fourth and one twentieth the guideline level, then the DQO was set equal to twice the reported DL,
3. If a guideline level exists, and the reported DL is between the guideline level and one fourth the guideline level, then the DQO was set equal to the reported DL,
4. If a guideline level exists, and the reported DL is greater than or equal to the guideline level, then the DQO was set equal to the reported DL,
5. If no guideline level exists the DQO was set equal to twice the reported DL.

For each parameter the field blank concentration must not exceed the DQO presented in Table 4.

Field Blank DQOs; Cuisson Creek Monitoring Program, Baseline

Again, there are no established guidelines for the Cuisson Creek monitoring program. This DQO option is designed for baseline monitoring purposes, in contrast to the Cuisson Creek BCWQ DQOs, and the primary consideration is contamination control at the reported DL concentration level. A secondary consideration are the lowest guidelines of the Ministry of Environment, Lands and Parks as outlined in "A Compendium of Working Water Quality Guidelines for British Columbia" (1998), and "Guidelines for Interpreting Water Quality Data" (1998). The DQO for each parameter was developed from one of the following rules:

1. If a guideline level exists, and the reported DL is less than one fourth of the guideline level, then the DQO was set equal to twice the reported DL.
2. If a guideline level exists, and the reported DL is between the guideline level and one fourth the guideline level, then the DQO was set equal to the reported DL,
3. If a guideline level exists, and the reported DL is greater than or equal to the guideline level, then the DQO was set equal to the reported DL,
4. If no guideline level exists the DQO was set equal to twice the reported DL.

For each parameter the field blank concentration must not exceed the DQO presented in Table 4.

Summary of Field Blank DQO Failures

All the Field Blank samples submitted to ALS Environmental between March 12, 1999 (ALS File No. K4100) and March 14, 2001 (ALS File No. M7587) were compared to the proposed DQOs. If the result for a parameter exceeded the parameter specific DQO the result is considered to have "failed". All failures are shown in Table 5, and tabulated in Table 1.

Table 1: Summary of Field Blank DQO Failures.

Parameter	Standard + Internal DQO			Cuisson Creek BCWQ DQO			Cuisson Creek Baseline DQO			Summary of all programs		
	Fail-ures	Total Number of Results	Fail-ure Rate %	Fail-ures	Total Number of Results	Fail-ure Rate %	Fail-ures	Total Number of Results	Fail-ure Rate %	Number detected	Total Number of Results	Detect Rate %
Aluminum D-Al	3	141	2.1	3	141	2.1	3	141	2.1	3	141	2.1
Aluminum T-Al	3	138	2.2	3	138	2.2	3	138	2.2	5	138	2.2
Calcium D-Ca	2	125	1.6	2	125	1.6	2	125	1.6	4	125	3.2
Copper D-Cu	7	118	5.9	0	23	0	0	23	0	17	141	12.1
Copper T-Cu	2	123	1.6	0	15	0	0	15	0	3	138	2.2
Iron D-Fe	1	125	0.8	0	125	0	1	125	0.8	4	125	3.2
Iron T-Fe	2	138	1.4	1	138	0.7	2	138	1.4	5	138	3.6
Mercury T-Hg	-	-	-	0	17	0	0	17	0	1	17	5.9
Molybdenum T-Mo	0	98	0	0	15	0	0	15	0	3	113	2.7
Zinc D-Zn	2	80	2.5	2	80	2.5	2	80	2.5	4	80	5.0
Zinc T-Zn	4	88	4.5	4	88	4.5	4	88	4.5	5	88	5.7

As shown in Table 1, only a limited number of results failed to meet the specified field blank DQOs. Of the parameters with failures, and more than 80 results, the DQO failure rates ranged from 0.7% to 5.9%. Dissolved copper, dissolved zinc and total zinc DQO failure rates are the highest, suggesting these parameters are most susceptible to contamination.

FIELD DUPLICATE DATA QUALITY OBJECTIVES

The field duplicate DQOs need to account for sampling and measurement errors associated with each result. Expressed as a percentage of the result, the measurement uncertainty increases significantly near the detection limit (Taylor, 1987), since the magnitude of the measurement uncertainty approaches the magnitude of the result. However, when the result is much larger than the detection limit the measurement uncertainty (expressed as a percentage of the result) approaches a constant value inherent in the sample collection and analysis process.

For field duplicate results relative percent difference (RPD) is used to express measurement uncertainty (Guidelines for Interpreting *Water* Quality Date, 1998), according to the following equation:

RPD = 100% * abs(result 1 - result 2) / mean(result 1, result 2)

Where:

RPD = relative percent difference

In absolute terms, the magnitude of measurement uncertainty is smallest at the method detection limit (MDL), and becomes larger as the magnitude of the result increases (Thompson and Howarth, 1978). Assuming the MDL is determined at a 95% confidence interval, the absolute amount of measurement uncertainty of a result at the MDL is equal to the magnitude of the MDL (Taylor, 1987). For the purposes of this study the reported DLs are assumed to be equal to or greater than the system MDL for each parameter.

Two options for field duplicate DQOs are presented. Each option is compared to the field duplicate data set to determine the number of replicate pair failures. In each case the allowed error at zero concentration is equal to 2 reported DLs, to account for data rounding errors and the measurement uncertainty of each result The maximum RPD is set to 15% for all parameters except turbidity, which is set to 30%. These initial limits were set to allow a realistic measurement uncertainty and they are based upon laboratory experience with duplicate samples for these tests. The allowed difference for each approach (with RPD = 15%) is shown in Figure 1. The maximum RPDs should be reviewed, and revised if necessary, as field duplicate data is collected and assessed.

For the calculations described below, note that results below the detection limit are taken to be equal to zero. To avoid rounding errors calculated values should not be rounded or truncated.

Option 1: Linear Allowed Difference Function

This is the preferred technique for establishing field duplicate DQOs. It is adapted from a paper published by Thompson and Howarth (1978). The allowed difference function described below sets an allowed error equal to 2 reported DLs when the mean concentration of duplicate results is equal to zero. As the mean concentration of duplicate results increases, the allowed error increases by the maximum RPD as described in the following function:

Allowed Difference = 2 * DL + (Maximum RPD / 100) * mean(result 1, result 2)

Where:

DL = reported detection limit.

Maximum RPD = acceptable maximum relative percent difference (between two results).

For each duplicate pair the absolute value of the difference between the results must not exceed the Allowed Difference calculated above.

Option 2; Non-continuous Allowed Difference Algorithm

This technique for establishing field duplicate DQOs is commonly used, in various forms, but is not recommended, due to the inadequate treatment of uncertainty near the 5 DL concentration range, as illustrated in Figure 1. It is taken directly from the "Quality Assurance Guidelines to Supplement the Standard Effluent and Receiving Environment Quality Assurance Clause prepared by BC Environment with input from the BC Laboratory Quality Assurance Advisory Technical Subcommittee (2001). In the table the following field duplicate guideline is presented:

> "It should *be* expected that the RPD is somewhat greater than that for laboratory duplicates. If one of a set of duplicate values [is] at or greater than five times the MDL, then RPD values >20% indicate a possible problem, and >50% indicate a definite problem..."

and for laboratory duplicates,

> "For concentrations below 5 times the MDL, the difference between the two duplicate values shall not exceed twice the reported DL value. For concentrations at or greater than 5 times the reported DL, the Relative Percent Difference (RPD) shall not exceed 20%..."

The allowed difference algorithm described below sets an allowed error equal to 2 reported DLs when the concentration of both duplicate results is below 5 reported DLs, otherwise the allowed error equals the maximum RPD:

```
if (result 1 < 5 * DL and result 2 < 5 * DL)
then
        Allowed Difference = 2* DL
else
        Allowed Difference = (Maximum RPD/ 100) * mean(result 1, result 2)
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Where:

DL = reported detection limit.

Maximum RPD = acceptable maximum relative percent difference (between two results).

For each duplicate pair the absolute value of the difference between the results must not exceed the Allowed Difference calculated above.

<u>Summary of Field Duplicate DOO Failures</u>

All the field duplicate samples submitted to AJLS Environmental between March 3, 1999 (ALS File No. K3872) and January 11, 2001 (ALS File No. M5943) were compared to the proposed DQOs. If the duplicate values for a parameter exceeded the parameter specific DQO the result is considered to have "failed". All failures are shown in Table 6, and tabulated in Table 2.

Table 2: Summary of Field Duplicate DQO Failures.

Parameter	Total Number of Duplicate Pairs	Option 1 Linear Field Duplicate DQO		Option 2 Non-continuous Field Duplicate DQO	
		Failures	Failure Rate %	Failures	Failure Rate %
Aluminum D-Al	27	1	3.7	1	3.7
Aluminum T-Al	27	1	3.7	1	3.7
Calcium D-Ca	27	2	7.4	2	7.4
Chloride Cl	27	0	0	1	3.7
Copper D-Cu	27	1	3.7	2	7.4
Copper T-Cu	27	2	7.4	3	11.1
Dissolved Organic Carbon C	3	0	0	2	66.7
Dissolved Ortho Phosphate P	10	2	20	5	50.0
Total Phosphate P	4	0	0	1	25.0
Fluoride F	3	0	0	1	33.3
Hardness CaCO3	27	2	7.4	2	7.4
Iron D-Fe	27	0	0	1	3.7
Iron T-Fe	27	1	3.7	1	3.7

Table 2: Summary of Field Duplicate DQO Failures.

Parameter	Total Number of Duplicate Pairs	Option 1 Linear Field Duplicate DQO		Option 2 Non-continuous Field Duplicate DQO	
		Failures	Failure Rate %	Failures	Failure Rate %
Magnesium D-Mg	27	2	7.4	2	7.4
Molybdenum D-Mo	27	0	0	5	18.5
Molybdenum T-Mo	27	0	0	2	7.4
Nitrate Nitrogen	22	2	9.1	2	9.1
Sulphate SO4	27	0	0	1	3.7
Turbidity (NTU)	3	1	33.3	1	33.3
Zinc T-Zn	12	1	8.3	1	8.3

As shown in Table 2, the two field duplicate DQO options generally compare quite well. Option 1 DQO failure rates, for parameters with 27 duplicate pairs, ranged from 0% to 7.4%. Option 2 failure rates, for parameters with 27 duplicate pairs, ranged from 3.7% to 18.5%.

Option 1, the Linear Allowed Difference Function, should be used for field duplicate DQOs at Gibraltar Mine. Option 1 provides a realistic and defensible estimation of measurement uncertainty at all concentrations using a linear function. Option 2 DQOs are adequate but the treatment of uncertainty in the 5 DL to 10 DL range (as illustrated in Figure 1) can lead to questionable DQO failures when the duplicate results are in this concentration range. Differences in DQO failures for dissolved ortho phosphate and molybdenum, where option 2 generates more failures than option 1, illustrate the inadequacy of option 2 to address uncertainty near the 5 DL concentration range.

DISSOLVED METALS VERSUS TOTAL METALS DATA QUALITY OBJECTIVES

Total and dissolved metals are defined by how the samples are prepared. "Standard Methods for the Examination of Water and Wastewater, 20th Edition" (1998) defines total metals in water as:

> 'The concentration of metals determined in an unfiltered sample after vigorous digestion..."

Dissolved metals in water are defined as:

> "Those metals in an unacidified sample that pass through a 0.45 Jim membrane filter."

By these definitions it follows that the total metals portion of the sample should always contain a concentration of metals that equals or exceeds the dissolved metals portion of the sample. However the preceding statement does not allow for sampling and measurement error. When uncertainty of measurement of each result is considered, then it is possible for the measured total metal concentration to be less than the measured dissolved metal concentration. The data quality objective needs to allow for possible inhomogeneity of the dissolved metal portion and total metal portions, and for the analytical precision of a determination.

When the water at a monitoring location contains only dissolved metals (i.e. all metals pass through a 0.45 μm membrane filter) then all of the total metals present will be due to the dissolved metals, hi this situation the total metals sample portion and dissolved metals sample portion can be considered to behave as duplicate samples, so long as the different sample collection procedures are subject to similar errors. The rationale of measurement uncertainty for field duplicates is described in the Field Duplicate Data Quality Objectives section.

Dissolved metal versus total metal DQOs are identical to field duplicate DQOs. Only the special case where dissolved metal concentration exceeds total metal concentration is considered, and in this case the two samples are considered to behave as field duplicates. Two options for field duplicate DQOs are described in the Field Duplicate Data Quality Objectives section. Each option is compared to a data set to determine the number of failures. In each case the allowed error at zero concentration is equal to twice the reported DL. For the initial DQO the maximum RPD is set to 15%. These limits were set to allow a realistic measurement uncertainty and are based upon laboratory experience with dissolved metal and total metal analysis. The limits should be reviewed, and revised if necessary, as additional data are collected and assessed.

For the calculations, note that results below the detection limit are taken to be equal to zero. To avoid rounding errors calculated values should not be rounded or truncated. For the formulas, result 1 should be the total metal result, and result 2 should be the dissolved metal result.

Summary of Dissolved Metals versus Total Metals DQO Failures

Only "qualifying" duplicate pairs, where the dissolved metal concentration exceeded the corresponding total metal concentration, for samples submitted to ALS Environmental between March 12, 1999 (ALS File No. K4100) and October 20, 2000 (ALS File No. M3531), were compared to the proposed DQOs. If the duplicate values for corresponding parameters exceeded the parameter specific DQO the result is considered to have "failed". All failures are shown in Table 7, and tabulated in Table 3.

Table 3: Summary of Dissolved Metals versus Total Metals DQO Failures.

Parameters	Number of "Qualifying" Duplicate Pairs where D > T	Option 1 Linear Dissolved > Total DQO		Option 2 Non-continuous Dissolved > Total DQO	
		Failures	Failure Rate %	Failures	Failure Rate %
Aluminum	30	7	23.3	9	30.0
Arsenic	7	0	0	2	28.6
Barium	4	0	0	1	25.0
Boron	3	1	33.3	1	33.3
Copper	69	12	17.4	22	31.9
Cobalt	8	0	0	1	12.5
Iron	30	3	10.0	6	20.0
Manganese	20	1	5.0	2	10.0
Molybdenum	156	8	5.1	25	16.0
Silver	5	2	40.0	2	40.0
Thallium	22	0	0	1	4.5
Zinc	55	4	7.3	4	7.3

As shown in Table 3, the two dissolved versus total metal DQO options generally compare quite well. Option 1 DQO failure rates, for parameters with more than 20 "qualifying" duplicate pairs, ranged from 5.0% to 23.3%. Option 2 failure rates, for parameters with more than 20 "qualifying" duplicate pairs, ranged from 7.3% to 31.9%.

The failure rates for this subset of "qualifying" duplicate pairs are less than 100%, suggesting that most occurrences where a dissolved metal concentration exceeds a total metal concentration are caused by measurement uncertainty.

Option 1, the Linear Allowed Difference Function, should be used for dissolved versus total metal DQOs at Gibraltar Mine. Option 1 provides a realistic and defensible estimation of measurement uncertainty at all concentrations using a linear function. Option 2 DQOs are adequate but the treatment of uncertainty in the 5 DL to 10 DL range (as illustrated in Figure 1) can lead to questionable DQO failures when the "qualifying" duplicate pair results are in this concentration range. Differences in DQO failures for copper and molybdenum, where option 2 generates more failures than option 1, illustrate the inadequacy of option 2 to address uncertainty near the 5 DL concentration range (as was demonstrated in the field duplicate DQO section).

SUMMARY

This report outlines generic data quality objectives (DQOs) developed for the water quality monitoring program at Gibraltar Mine. The DQOs apply to field blanks, field duplicates and dissolved metal versus total metal pairs. The DQOs are intended to assist Gibraltar Mine in the assessment of water quality monitoring data. All the proposed DQOs were applied to Gibraltar Mine data collected during 1999 through 2001 to determine if they were applicable to the Gibraltar Mine water quality monitoring program.

The proposed field blank DQOs are derived from the requirements of the Gibraltar Mine monitoring programs, the BC Water Quality Guidelines and the reported laboratory detection limit (reported DL) for each parameter. The DQOs are generally set to be twice the reported DL. Some DQOs are equal to the reported DL if the parameter is of particular concern (if the BC Water Quality Guideline is near the reported DL concentration). This level of uncertainty provides a reliable limit that is realistically achievable for the field blanks currently collected at Gibraltar Mine.

Two options for field duplicate DQOs are presented. In each case the allowed error at zero concentration is equal to 2 reported DLs. At detectable concentrations the maximum relative percent difference (RPD) is set to 15% for all parameters except turbidity which is set to 30%. These initial limits allow a realistic measurement uncertainty and they are based upon laboratory experience with duplicate samples. The Linear Allowed Difference Function DQO (Option 1) is recommended for use at Gibraltar Mine.

Two options for dissolved metal versus total metal DQOs are presented. Only the special case where dissolved metal concentration exceeds total metal concentration is considered, and in this case the two samples are considered to be field duplicates. In each case the allowed error at zero concentration is equal to 2 reported DLs. At detectable concentrations the maximum relative percent difference (RPD) is set to 15%. These initial limits allow a realistic measurement uncertainty and they are based upon laboratory experience with dissolved metal and total metal analysis. The Linear Allowed Difference Function DQO (Option 1) is recommended for use at Gibraltar Mine.

Acceptable DQO failure rate targets should be established for field blanks, field duplicates and dissolved versus total metal duplicate pairs. DQO failure rates should be routinely monitored to look for trends. Failure rates for a given population of results should remain relatively constant over time.

The proposed DQOs are useful to identify when there may be a significant error in the sample collection and analysis process. This is demonstrated by the DQO failures that were identified with field blanks, field duplicates and dissolved versus total metal duplicate pairs in the data sets that were studied. DQO failures should be investigated and documented (with the source of the failure identified, if possible) and any associated sample data should be reviewed and qualified, as described in "Guidelines for Interpreting Water Quality Data" (1998). The DQOs, and DQO failures, should be regularly reviewed (Le. annually), and based upon the data collected, and any new requirements of the monitoring programs, the DQOs and DQO failure rate targets should! be adjusted as appropriate.

REFERENCES

1. Laboratory and Systems Management, Environmental Protection Department, Ministry of Environment, Lands and Parks, Province of British Columbia, 1996, "British Columbia Field Sampling Manual, 1996 edition (permittee)", pp. 19.

2. Water Management Branch, Environment and Resource Management Department, Ministry Of Environment, Lands and Parks, Province of British Columbia, 2001, "A Compendium of Working Water Quality Guidelines for British Columbia", 1998 edition (updated April 24, 2001).

3. Ministry of Environment, Lands and Parks, Land Data BC, Geographic Data BC, for the Land Use Task Force Resources Inventory Committee, 1998, "Guidelines for Interpreting Water Quality Data", section 2 and 5.

4. BC Laboratory Quality Assurance Advisory Technical Subcommittee of the BC Laboratory Quality Assurance Advisory Committee (BCLQAAC) for BC Environment, 2001, "Quality Assurance Guidelines to Supplement the Standard Effluent and Receiving Environment Quality Assurance Clause", unpublished.

5. Taylor, J.K., 1987, "Quality Assurance of Chemical Measurements", Lewis Publishers Inc., Chelsea, Michigan, *pp.* 10,18 to 28,77 to 83, 125.

6. Thompson, M. and Howarth, RJ., 1978, "A New Approach to the Estimation of Analytical Precision", J. Geochem. Explor., 9, pp 23 to 30.

7. American Public Health Association, 1998, "Standard Methods for the Examination of Water and Wastewater, 20th Edition", United Book Press, Inc., pp 3-1.

Table 4: Summary of Proposed DQOs and RPDs

Note: Field Blank DQO and Reported DL units are expressed as milligrams per litre, except where noted otherwise.

Parameter	Field Blank DQO		Field Blank DQO		Field Blank DQO		Field Duplicate Maximum RPDs	D > T Metals Maximum RPDs
	Cuisson Creek BCWQ		Cuisson Creek Baseline		Standard + Internal			
	Cuisson creek program, applicable DQO when compared against the lowest applicable BCWQ Guideline		Cuisson creek program, applicable DQO for baseline studies (using the lowest BCWQ Guideline to select parameters of particular concern)		standard package, nutrient 1 package, nutrient 2 package, low level zinc, applicable DQO for water monitoring		recommended to be used with field duplicate DQOs	recommended to be used with field duplicate DQOs when dissolved > total metal
	DQO	*Reported DL*	DQO	*Reported DL*	DQO	*Reported DL*		
Field Tests								
Field Conductivity (umhos/cm)	2	*1*	2	*1*	2	*1*	15%	
Field pH							15%	
Field Temperature (celcius)							15%	
Physical Tests								
Conductivity (umhos/cm)	2	*2*	2	*2*			15%	
Total Dissolved Solids	20	*10*	20	*10*			15%	
Hardness CaCO3	1	*0.5*	1	*0.5*	1	*0.5*	15%	
pH							15%	
Total Suspended Solids (NFR)	6	*3*	6	*3*			15%	
Turbidity (NTU)	0.2	*0.1*	0.2	*0.1*			**30%**	
Dissolved Anions								
Alkalinity-Total CaCO3	2	*1*	2	*1*			15%	
Chloride Cl	1	*0.5*	1	*0.5*	1	*0.5*	15%	
Fluoride F	0.04	*0.02*	0.04	*0.02*			15%	
Sulphate SO4	2	*1*	2	*1*	2	*1*	15%	
Nutrients								
Ammonia Nitrogen N	0.01	*0.005*	0.01	*0.005*	0.01	*0.005*	15%	
Total Kjeldahl Nitrogen N	0.1	*0.05*	0.1	*0.05*	0.1	*0.05*	15%	
Nitrate Nitrogen N	0.01	*0.005*	0.01	*0.005*	0.01	*0.005*	15%	
Nitrite Nitrogen N	0.002	*0.001*	0.002	*0.001*	0.002	*0.001*	15%	
Dissolved ortho-Phosphate P	0.002	*0.001*	0.002	*0.001*	0.002	*0.001*	15%	
Total Dissolved Phosphate P	0.004	*0.002*	0.004	*0.002*	0.004	*0.002*	15%	
Total Phosphate P	0.004	*0.002*	0.004	*0.002*	0.004	*0.002*	15%	
Total Metals								
Aluminum T-Al	0.01	*0.005*	0.01	*0.005*	0.01	*0.005*	15%	15%
Antimony T-Sb	0.002	*0.0001*	0.0002	*0.0001*			15%	15%
Arsenic T-As	0.0005	*0.0001*	0.0002	*0.0001*			15%	15%
Barium T-Ba	0.1	*0.01*	0.02	*0.01*			15%	15%
Beryllium T-Be	0.001	*0.0005*	0.001	*0.0005*			15%	15%
Boron T-B	0.05	*0.001*	0.002	*0.001*			15%	15%
Cadmium T-Cd	0.00005	*0.00005*	0.00005	*0.00005*			15%	15%
Calcium T-Ca	0.1	*0.05*	0.1	*0.05*			15%	15%
Chromium T-Cr	0.0005	*0.0005*	0.0005	*0.0005*			15%	15%
Cobalt T-Co	0.0002	*0.0001*	0.0002	*0.0001*			15%	15%

Table 4: Summary of Proposed DQOs and RPDs

Note: Field Blank DQO and Reported DL units are expressed as milligrams per litre, except where noted otherwise.

Parameter	**Field Blank DQO**		**Field Blank DQO**		**Field Blank DQO**		**Field Duplicate Maximum RPDs**	**D > T Metals Maximum RPDs**
	Cuisson Creek BCWQ		**Cuisson Creek Baseline**		**Standard + Internal**			
	Cuisson creek program, applicable DQO when compared against the lowest applicable BCWQ Guideline		Cuisson creek program, applicable DQO for baseline studies (using the lowest BCWQ Guideline to select parameters of particular concern)		standard package, nutrient 1 package, nutrient 2 package, low level zinc, applicable DQO for water monitoring		recommended to be used with field duplicate DQOs	recommended to be used with field duplicate DQOs when dissolved > total metal
	DQO	*Reported DL*	**DQO**	*Reported DL*	**DQO**	*Reported DL*		
Copper T-Cu	0.0002	*0.0001*	0.0002	*0.0001*	0.001	*0.001*	15%	15%
Iron T-Fe	0.03	*0.01*	0.02	*0.01*	0.02	*0.01*	15%	15%
Lead T-Pb	0.0003	*0.00005*	0.0001	*0.00005*			15%	15%
Magnesium T-Mg	0.2	*0.1*	0.2	*0.1*			15%	15%
Manganese T-Mn	0.01	*0.005*	0.01	*0.005*			15%	15%
Mercury T-Hg	0.00001	*0.00001*	0.00001	*0.00001*			15%	15%
Molybdenum T-Mo	0.001	*0.00005*	0.0001	*0.00005*	0.002	*0.001*	15%	15%
Nickel T-Ni	0.002	*0.001*	0.002	*0.001*			15%	15%
Phosphorus T-P	0.3	*0.3*	0.3	*0.3*			15%	15%
Potassium T-K	4	*2*	4	*2*			15%	15%
Selenium T-Se	0.0005	*0.0005*	0.0005	*0.0005*			15%	15%
Silver T-Ag	0.00002	*0.00001*	0.00002	*0.00001*			15%	15%
Sodium T-Na	4	*2*	4	*2*			15%	15%
Thallium T-Tl	0.0001	*0.00005*	0.0001	*0.00005*			15%	15%
Titanium T-Ti	0.02	*0.01*	0.02	*0.01*			15%	15%
Uranium T-U	0.03	*0.0001*	0.0002	*0.0001*			15%	15%
Vanadium T-V	0.01	*0.001*	0.002	*0.001*			15%	15%
Zinc T-Zn	0.002	*0.001*	0.002	*0.001*	0.002	*0.001*	15%	15%
Dissolved Metals							15%	15%
Aluminum D-Al	0.01	*0.005*	0.01	*0.005*	0.01	*0.005*	15%	15%
Antimony D-Sb	0.002	*0.0001*	0.0002	*0.0001*			15%	15%
Arsenic D-As	0.0005	*0.0001*	0.0002	*0.0001*			15%	15%
Barium D-Ba	0.1	*0.01*	0.02	*0.01*			15%	15%
Beryllium D-Be	0.001	*0.0005*	0.001	*0.0005*			15%	15%
Boron D-B	0.05	*0.001*	0.002	*0.001*			15%	15%
Cadmium D-Cd	0.00005	*0.00005*	0.00005	*0.00005*			15%	15%
Calcium D-Ca	0.1	*0.05*	0.1	*0.05*	0.1	*0.05*	15%	15%
Chromium D-Cr	0.0005	*0.0005*	0.0005	*0.0005*			15%	15%
Cobalt D-Co	0.0002	*0.0001*	0.0002	*0.0001*			15%	15%
Copper D-Cu	0.0002	*0.0001*	0.0002	*0.0001*	0.002	*0.001*	15%	15%
Iron D-Fe	0.03	*0.01*	0.02	*0.01*	0.02	*0.01*	15%	15%
Lead D-Pb	0.0003	*0.0001*	0.0001	*0.0001*			15%	15%
Magnesium D-Mg	0.2	*0.1*	0.2	*0.1*	0.2	*0.1*	15%	15%
Manganese D-Mn	0.01	*0.005*	0.01	*0.005*			15%	15%
Mercury D-Hg	0.00001	*0.00001*	0.00001	*0.00001*			15%	15%
Molybdenum D-Mo	0.001	*0.00005*	0.0001	*0.00005*	0.002	*0.001*	15%	15%
Nickel D-Ni	0.002	*0.001*	0.002	*0.001*			15%	15%
Potassium D-K	4	*2*	4	*2*			15%	15%
Selenium D-Se	0.0005	*0.0005*	0.0005	*0.0005*			15%	15%
Silver D-Ag	0.00002	*0.00001*	0.00002	*0.00001*			15%	15%
Sodium D-Na	4	*2*	4	*2*			15%	15%

Table 4: Summary of Proposed DQOs and RPDs

Note: Field Blank DQO and Reported DL units are expressed as milligrams per litre, except where noted otherwise.

Parameter	Field Blank DQO		Field Blank DQO		Field Blank DQO		Field Duplicate Maximum RPDs	D > T Metals Maximum RPDs
	Cuisson Creek BCWQ		Cuisson Creek Baseline		Standard + Internal			
	Cuisson creek program, applicable DQO when compared against the lowest applicable BCWQ Guideline		Cuisson creek program, applicable DQO for baseline studies (using the lowest BCWQ Guideline to select parameters of particular concern)		standard package, nutrient 1 package, nutrient 2 package, low level zinc, applicable DQO for water monitoring		recommended to be used with field duplicate DQOs	recommended to be used with field duplicate DQOs when dissolved > total metal
	DQO	*Reported DL*	DQO	*Reported DL*	DQO	*Reported DL*		
Thallium D-Tl	0.0001	*0.00005*	0.0001	*0.00005*			15%	15%
Titanium D-Ti	0.02	*0.01*	0.02	*0.01*			15%	15%
Uranium D-U	0.03	*0.0001*	0.0002	*0.0001*			15%	15%
Vanadium D-V	0.01	*0.001*	0.002	*0.001*			15%	15%
Zinc D-Zn	0.002	*0.001*	0.002	*0.001*	0.002	*0.001*	15%	15%
Organic Parameters								
Dissolved Organic Carbon C	1	*0.5*	1	*0.5*			15%	

Table 5: Field Blank DQO Failures.

Note: This table presents a subset of the field blank data. Only parameters that were detected in a field blank sample are presented. In the case of copper, the reported DL for some field blank samples was above the Cuisson Creek DQOs, therefore these results were not compared to the Cuisson Creek DQOs.

WO	ID	Analyte	Reported DL (mg/L)	Result (mg/L)	Cuisson Creek DQO, BCWQ	Cuisson Creek DQO, BCWQ, Result Status	Cuisson Creek DQO, Baseline	Cuisson Creek DQO, Baseline, Result Status	Standard + Internal DQO	Standard + Internal DQO, Result Status
K6388	1	Aluminum D-Al	0.005	0.021	0.01	fail	0.01	fail	0.01	fail
L6019	7	Aluminum D-Al	0.005	0.017	0.01	fail	0.01	fail	0.01	fail
M1999	7	Aluminum D-Al	0.005	0.012	0.01	fail	0.01	fail	0.01	fail
M2947	6	Aluminum T-Al	0.005	0.025	0.01	fail	0.01	fail	0.01	fail
M3685	7	Aluminum T-Al	0.005	0.021	0.01	fail	0.01	fail	0.01	fail
K6388	1	Aluminum T-Al	0.005	0.012	0.01	fail	0.01	fail	0.01	fail
L9342	7	Aluminum T-Al	0.005	0.006	0.01	pass	0.01	pass	0.01	pass
K7518	1	Aluminum T-Al	0.005	0.005	0.01	pass	0.01	pass	0.01	pass
M1999	7	Calcium D-Ca	0.05	0.147	0.1	fail	0.1	fail	0.1	fail
K7435	7	Calcium D-Ca	0.05	0.106	0.1	fail	0.1	fail	0.1	fail
M1605	1	Calcium D-Ca	0.05	0.088	0.1	pass	0.1	pass	0.1	pass
L2827	1	Calcium D-Ca	0.05	0.07	0.1	pass	0.1	pass	0.1	pass
K6388	1	Copper D-Cu	0.01	0.02	0.0002	-	0.0002	-	0.001	fail
K7435	7	Copper D-Cu	0.001	0.007	0.0002	-	0.0002	-	0.001	fail
K6297	1	Copper D-Cu	0.001	0.006	0.0002	-	0.0002	-	0.001	fail
K8240	1	Copper D-Cu	0.001	0.003	0.0002	-	0.0002	-	0.001	fail
L1312	1	Copper D-Cu	0.001	0.003	0.0002	-	0.0002	-	0.001	fail
M1999	7	Copper D-Cu	0.001	0.003	0.0002	-	0.0002	-	0.001	fail
K9789	1	Copper D-Cu	0.001	0.002	0.0002	-	0.0002	-	0.001	fail
K4849	1	Copper D-Cu	0.001	0.001	0.0002	-	0.0002	-	0.001	pass
K8910	1	Copper D-Cu	0.001	0.001	0.0002	-	0.0002	-	0.001	pass

Table 5: Field Blank DQO Failures.

Note: This table presents a subset of the field blank data. Only parameters that were detected in a field blank sample are presented. In the case of copper, the reported DL for some field blank samples was above the Cuisson Creek DQOs, therefore these results were not compared to the Cuisson Creek DQOs.

WO	ID	Analyte	Reported DL (mg/L)	Result (mg/L)	Cuisson Creek DQO, BCWQ	Cuisson Creek DQO, BCWQ, Result Status	Cuisson Creek DQO, Baseline	Cuisson Creek DQO, Baseline, Result Status	Standard + Internal DQO	Standard + Internal DQO, Result Status
L4315	1	Copper D-Cu	0.001	0.001	0.0002	-	0.0002	-	0.001	pass
M2623	1	Copper D-Cu	0.001	0.001	0.0002	-	0.0002	-	0.001	pass
K9677	1a	Copper D-Cu	0.0001	0.0002	0.0002	pass	0.0002	pass	0.001	pass
K8240	1a	Copper D-Cu	0.0001	0.0001	0.0002	pass	0.0002	pass	0.001	pass
K8358	1a	Copper D-Cu	0.0001	0.0001	0.0002	pass	0.0002	pass	0.001	pass
K8557	1a	Copper D-Cu	0.0001	0.0001	0.0002	pass	0.0002	pass	0.001	pass
K9577	1a	Copper D-Cu	0.0001	0.0001	0.0002	pass	0.0002	pass	0.001	pass
L1745	1a	Copper D-Cu	0.0001	0.0001	0.0002	pass	0.0002	pass	0.001	pass
L3865r	2	Copper T-Cu	0.001	0.002	0.0002	-	0.0002	-	0.001	fail
L3865	2	Copper T-Cu	0.001	0.002	0.0002	-	0.0002	-	0.001	fail
L6295	5	Copper T-Cu	0.0001	0.0002	0.0002	pass	0.0002	pass	0.001	pass
L6253	2	Iron D-Fe	0.01	0.03	0.03	pass	0.02	fail	0.02	fail
M1999	7	Iron D-Fe	0.01	0.02	0.03	pass	0.02	pass	0.02	pass
K6388	1	Iron D-Fe	0.01	0.01	0.03	pass	0.02	pass	0.02	pass
L1412	1	Iron D-Fe	0.01	0.01	0.03	pass	0.02	pass	0.02	pass
M1834	3	Iron T-Fe	0.01	0.04	0.03	fail	0.02	fail	0.02	fail
M2947	6	Iron T-Fe	0.01	0.03	0.03	pass	0.02	fail	0.02	fail
M2103	5	Iron T-Fe	0.01	0.02	0.03	pass	0.02	pass	0.02	pass
M3276	3	Iron T-Fe	0.01	0.02	0.03	pass	0.02	pass	0.02	pass
M3198	12	Iron T-Fe	0.01	0.01	0.03	pass	0.02	pass	0.02	pass
M2892	6	Mercury T-Hg	0.00001	0.00001	0.0001	pass	0.0001	pass	0.0001	pass
L6295	5	Molybdenum T-Mo	0.00005	0.00006	0.0001	pass	0.0001	pass	0.002	pass
M1814	7	Molybdenum T-Mo	0.00005	0.00006	0.0001	pass	0.0001	pass	0.002	pass
L6612	7	Molybdenum T-Mo	0.00005	0.00005	0.0001	pass	0.0001	pass	0.002	pass
M1863	7	Zinc D-Zn	0.005	0.007	0.002	fail	0.002	fail	0.002	fail
M1605	1	Zinc D-Zn	0.001	0.005	0.002	fail	0.002	fail	0.002	fail
L6019	7	Zinc D-Zn	0.001	0.002	0.002	pass	0.002	pass	0.002	pass
K6622	1a	Zinc D-Zn	0.001	0.001	0.002	pass	0.002	pass	0.002	pass
K7518	1	Zinc T-Zn	0.001	0.015	0.002	fail	0.002	fail	0.002	fail
K4849	1	Zinc T-Zn	0.001	0.006	0.002	fail	0.002	fail	0.002	fail
K5125	14	Zinc T-Zn	0.001	0.004	0.002	fail	0.002	fail	0.002	fail
K4970	10	Zinc T-Zn	0.001	0.003	0.002	fail	0.002	fail	0.002	fail
M2103	5	Zinc T-Zn	0.001	0.001	0.002	pass	0.002	pass	0.002	pass

Table 6: Field Duplicate DQO Failures.

Note: This table presents a subset of the field duplicate data. Only parameters that failed one or both of the DQO options are presented. Results below the detection limit are taken to be zero. For DQO option 2 "fail-DL" means the duplicate results failed due to the allowed difference exceeding the twice the reported DL, whereas "fail-RPD" means the duplicate results failed due to the RPD exceeding the maximun allowed RPD.

WO	Analyte	Sample 1 ID	Sample 1 Result (mg/L)	Sample 2 ID	Sample 2 Result (mg/L)	Reported DL (mg/L)	RPD	Option 1 Allowed Difference	DQO Option 1 status	DQO Option : status
K6974	Aluminum D-Al	7	0	2	0.011	0.005	200.0%	0.010825	fail	fail-DL
L2270	Aluminum T-Al	10	0.032	5	0.077	0.005	82.6%	0.018175	fail	fail-RPD
K3872	Ammonia Nitrogen N	3	0.082	2	0.098	0.005	17.8%	0.0235	pass	fail-RPD
L4315	Calcium D-Ca	5	440	3	352	0.05	22.2%	59.5	fail	fail-RPD
K6974	Calcium D-Ca	7	242	2	288	0.05	17.4%	39.85	fail	fail-RPD
L6795	Calcium T-Ca	1	19.2	12	16.5	0.05	15.1%	2.7775	pass	fail-RPD

Table 6: Field Duplicate DQO Failures.

Note: This table presents a subset of the field duplicate data. Only parameters that failed one or both of the DQO options are presented. Results below the detection limit are taken to be zero. For DQO option 2 "fail-DL" means the duplicate results failed due to the allowed difference exceeding the twice the reported DL, whereas "fail-RPD" means the duplicate results failed due to the RPD exceeding the maximu allowed RPD.

WO	Analyte	Sample 1 ID	Sample 1 Result (mg/L)	Sample 2 ID	Sample 2 Result (mg/L)	Reported DL (mg/L)	RPD	Option 1 Allowed Difference	DQO Option 1 status	DQO Option status
M5819	Chloride Cl	3	5	7	6.3	0.5	23.0%	1.8475	pass	fail-RPI
L4315	Copper D-Cu	5	1.08	3	0.79	0.01	31.0%	0.16025	fail	fail-RPI
K6974	Copper D-Cu	7	0.2	2	0.24	0.01	18.2%	0.053	pass	fail-RPI
K4849	Copper T-Cu	8	0.026	9	0.010	0.001	88.9%	0.0047	fail	fail-RPI
L4315	Copper T-Cu	5	1.14	3	0.89	0.01	24.6%	0.17225	fail	fail-RPI
L2270	Copper T-Cu	10	0.005	5	0.004	0.001	22.2%	0.002675	pass	fail-RP
L6455	Dissolved Organic Carbon C	4	8.8	3	7	0.5	22.8%	2.185	pass	fail-RP
L6795	Dissolved Organic Carbon C	1	15.4	12	18	0.5	15.6%	3.505	pass	fail-RP
L6795	Dissolved ortho-Phosphate P	1	0	12	0.003	0.001	200.0%	0.002225	fail	fail-DL
L6723	Dissolved ortho-Phosphate P	6	0.004	3	0.007	0.001	54.5%	0.002825	fail	fail-RP
L1412	Dissolved ortho-Phosphate P	3	0.005	2	0.004	0.001	22.2%	0.002675	pass	fail-RP
M5819	Dissolved ortho-Phosphate P	3	0.005	7	0.004	0.001	22.2%	0.002675	pass	fail-RP
L4501	Dissolved ortho-Phosphate P	8	0.007	12	0.006	0.001	15.4%	0.002975	pass	fail-RP
L3794	Fluoride F	5	0.12	8	0.1	0.02	18.2%	0.0565	pass	fail-RP
L4315	Hardness CaCO3	5	1400	3	1080	0.05	25.8%	186.1	fail	fail-RP
K6974	Hardness CaCO3	7	719	2	853	0.05	17.0%	118	fail	fail-RP
M1833	Iron D-Fe	4	0.07	8	0.06	0.01	15.4%	0.02975	pass	fail-RP
M5286	Iron T-Fe	1	0.18	11	0.11	0.01	48.3%	0.04175	fail	fail-RP
L4315	Magnesium D-Mg	5	73.9	3	48.8	0.1	40.9%	9.4025	fail	fail-RP
K6974	Magnesium D-Mg	7	27.8	2	32.6	0.1	15.9%	4.73	fail	fail-RP
M5286	Molybdenum D-Mo	1	0.005	11	0.004	0.001	22.2%	0.002675	pass	fail-RP
M5819	Molybdenum D-Mo	3	0.005	7	0.004	0.001	22.2%	0.002675	pass	fail-RP
M1833	Molybdenum D-Mo	4	0.006	8	0.005	0.001	18.2%	0.002825	pass	fail-RF
K6974	Molybdenum D-Mo	7	0.34	2	0.4	0.03	16.2%	0.1155	pass	fail-RF
L6984	Molybdenum D-Mo	1	0.007	6	0.006	0.001	15.4%	0.002975	pass	fail-RF
M5819	Molybdenum T-Mo	3	0.005	7	0.004	0.001	22.2%	0.002675	pass	fail-RF
M1833	Molybdenum T-Mo	4	0.006	8	0.005	0.001	18.2%	0.002825	pass	fail-RF
K6974	Nitrate Nitrogen N	7	6.95	2	5.69	0.005	19.9%	0.958	fail	fail-RF
K4849	Nitrate Nitrogen N	8	0.945	9	0.786	0.005	18.4%	0.139825	fail	fail-RF
L2270	Sulphate SO4	10	107	5	92	1	15.1%	16.925	pass	fail-RF
L6795	Total Phosphate P	1	0.025	12	0.02	0.002	22.2%	0.007375	pass	fail-RF
L6795	Turbidity (NTU)	1	1.2	12	2	0.1	50.0%	0.68	fail	fail-RF
L4315	Zinc T-Zn	5	2.96	3	2.52	0.005	16.1%	0.421	fail	fail-RF

Table 7: Dissolved Metal > Total Metal DQO Failures.

Note: This table presents a subset of the dissolved metals > total metal duplicate pairs. Only parameters that failed one or both of the DQO options are presented. Results below the detection limit are taken to be zero. For DQO option 2 "fail-DL" means the duplicate pair results failed due to the allowed difference exceeding the twice the reported DL, whereas "fail-RPD" means the duplicate pair results failed due to the RPD exceeding the maximum allowed RPD.

WO	Sample ID	Analyte	D result (mg/L)	T result (mg/L)	Reported DL (mg/L)	RPD	Option 1 Allowed Difference	DQO option 1 status	DQO Option 2 status
L6019	7	Aluminum D-Al	0.017	0	0.005	200.0%	0.011275	fail	fail-DL
K8910	2	Aluminum D-Al	0.022	0.007	0.005	103.4%	0.012175	fail	fail-DL
K8240	10	Aluminum D-Al	0.019	0.006	0.005	104.0%	0.011875	fail	fail-DL
M1999	7	Aluminum D-Al	0.012	0	0.005	200.0%	0.0109	fail	fail-DL
L8627	1	Aluminum D-Al	0.028	0	0.005	200.0%	0.0121	fail	fail-RPD
L8627	4	Aluminum D-Al	0.049	0.022	0.005	76.1%	0.015325	fail	fail-RPD
K6523	2	Aluminum D-Al	0.04	0.027	0.005	38.8%	0.015025	pass	fail-RPD
K7435	8	Aluminum D-Al	0.063	0.043	0.005	37.7%	0.01795	fail	fail-RPD

Table 7: Dissolved Metal > Total Metal DQO Failures.

Note: This table presents a subset of the dissolved metals > total metal duplicate pairs. Only parameters that failed one or both of the DQO options are presented. Results below the detection limit are taken to be zero. For DQO option 2 "fail-DL" means the duplicate pair results failed due to the allowed difference exceeding the twice the reported DL, whereas "fail-RPD" means the duplicate pair results failed due to the RPD exceeding the maximum allowed RPD.

WO	Sample ID	Analyte	D result (mg/L)	T result (mg/L)	Reported DL (mg/L)	RPD	Option 1 Allowed Difference	DQO option 1 status	DQO Option 2 status
K5788	7	Aluminum D-Al	0.027	0.021	0.005	25.0%	0.0136	pass	fail-RPD
M6641	7	Arsenic D-As	0.0005	0.0004	0.0001	22.2%	0.000268	pass	fail-RPD
M5779	8	Arsenic D-As	0.0005	0.0004	0.0001	22.2%	0.000268	pass	fail-RPD
L9944	1	Barium D-Ba	0.037	0.03	0.001	20.9%	0.007025	pass	fail-RPD
M5779	7	Boron D-B	0.005	0.002	0.001	85.7%	0.002525	fail	fail-RPD
K5788	9	Cobalt D-Co	0.05	0.04	0.01	22.2%	0.02675	pass	fail-RPD
M1999	7	Copper D-Cu	0.003	0	0.001	200.0%	0.002225	fail	fail-DL
L1312	1	Copper D-Cu	0.003	0	0.001	200.0%	0.002225	fail	fail-DL
K8240	1	Copper D-Cu	0.003	0	0.001	200.0%	0.002225	fail	fail-DL
K6388	1	Copper D-Cu	0.02	0	0.001	200.0%	0.0035	fail	fail-RPD
K7435	7	Copper D-Cu	0.007	0	0.001	200.0%	0.002525	fail	fail-RPD
K6297	1	Copper D-Cu	0.006	0	0.001	200.0%	0.00245	fail	fail-RPD
K6974	4	Copper D-Cu	0.005	0.001	0.001	133.3%	0.00245	fail	fail-RPD
M7469	8	Copper D-Cu	0.0011	0.0004	0.0001	93.3%	0.000313	fail	fail-RPD
M3685	5	Copper D-Cu	0.007	0.003	0.001	80.0%	0.00275	fail	fail-RPD
L8359	4	Copper D-Cu	0.014	0.008	0.001	54.5%	0.00365	fail	fail-RPD
M5779	8	Copper D-Cu	0.0029	0.0019	0.0001	41.7%	0.00056	fail	fail-RPD
L2165	19	Copper D-Cu	0.03	0.021	0.001	35.3%	0.005825	fail	fail-RPD
M1834	1	Copper D-Cu	0.005	0.004	0.001	22.2%	0.002675	pass	fail-RPD
K6974	3	Copper D-Cu	0.005	0.004	0.001	22.2%	0.002675	pass	fail-RPD
K5505	1	Copper D-Cu	0.04	0.033	0.001	19.2%	0.007475	pass	fail-RPD
M7112	3	Copper D-Cu	0.006	0.005	0.001	18.2%	0.002825	pass	fail-RPD
L9944	1	Copper D-Cu	0.012	0.01	0.001	18.2%	0.00365	pass	fail-RPD
K6297	2	Copper D-Cu	0.006	0.005	0.001	18.2%	0.002825	pass	fail-RPD
L3392	4	Copper D-Cu	0.07	0.06	0.01	15.4%	0.02975	pass	fail-RPD
L6612	5	Copper D-Cu	0.0007	0.0006	0.0001	15.4%	0.000298	pass	fail-RPD
L3951	4	Copper D-Cu	0.007	0.006	0.001	15.4%	0.002975	pass	fail-RPD
K9577	6	Copper D-Cu	0.007	0.006	0.001	15.4%	0.002975	pass	fail-RPD
L6253	2	Iron D-Fe	0.03	0	0.01	200.0%	0.02225	fail	fail-DL
K4849	3	Iron D-Fe	0.38	0	0.01	200.0%	0.0485	fail	fail-RPD
L9944	1	Iron D-Fe	1.09	0.58	0.03	61.1%	0.18525	fail	fail-RPD
L5335	6	Iron D-Fe	0.06	0.04	0.01	40.0%	0.0275	pass	fail-RPD
K8240	10	Iron D-Fe	0.06	0.04	0.01	40.0%	0.0275	pass	fail-RPD
K6523	2	Iron D-Fe	0.1	0.08	0.01	22.2%	0.0335	pass	fail-RPD
L6949	5	Manganese D-Mn	0.029	0.022	0.005	27.5%	0.013825	pass	fail-RPD
L7698	9	Manganese D-Mn	4.76	3.98	0.005	17.8%	0.6655	fail	fail-RPD
K8468	8	Molybdenum D-Mo	0.013	0.006	0.001	73.7%	0.003425	fail	fail-RPD
L9638	4	Molybdenum D-Mo	0.012	0.007	0.001	52.6%	0.003425	fail	fail-RPD
M3531	1	Molybdenum D-Mo	0.005	0.003	0.001	50.0%	0.0026	pass	fail-RPD
K7252	4	Molybdenum D-Mo	0.005	0.003	0.001	50.0%	0.0026	pass	fail-RPD
L3794	1	Molybdenum D-Mo	0.00058	0.00037	0.00005	44.2%	0.000171	fail	fail-RPD
K6523	11	Molybdenum D-Mo	0.013	0.009	0.001	36.4%	0.00365	fail	fail-RPD
K9142	9	Molybdenum D-Mo	0.024	0.017	0.001	34.1%	0.005075	fail	fail-RPD
M5779	8	Molybdenum D-Mo	0.00626	0.0046	0.00005	30.6%	0.000915	fail	fail-RPD
L1745	6	Molybdenum D-Mo	0.021	0.016	0.001	27.0%	0.004775	fail	fail-RPD
K8240	4	Molybdenum D-Mo	0.058	0.045	0.002	25.2%	0.011725	fail	fail-RPD
K4274	7	Molybdenum D-Mo	0.023	0.018	0.001	24.4%	0.005075	pass	fail-RPD
M5819	7	Molybdenum D-Mo	0.005	0.004	0.001	22.2%	0.002675	pass	fail-RPD
M3531	2	Molybdenum D-Mo	0.005	0.004	0.001	22.2%	0.002675	pass	fail-RPD
L5335	6	Molybdenum D-Mo	0.005	0.004	0.001	22.2%	0.002675	pass	fail-RPD
K6523	3	Molybdenum D-Mo	0.005	0.004	0.001	22.2%	0.002675	pass	fail-RPD
K5703	5	Molybdenum D-Mo	0.015	0.012	0.001	22.2%	0.004025	pass	fail-RPD

Table 7: Dissolved Metal > Total Metal DQO Failures.

Note: This table presents a subset of the dissolved metals > total metal duplicate pairs. Only parameters that failed one or both of the DQO options are presented. Results below the detection limit are taken to be zero. For DQO option 2 "fail-DL" means the duplicate pair results failed due to the allowed difference exceeding the twice the reported DL, whereas "fail-RPD" means the duplicate pair results failed due to the RPD exceeding the maximum allowed RPD.

WO	Sample ID	Analyte	D result (mg/L)	T result (mg/L)	Reported DL (mg/L)	RPD	Option 1 Allowed Difference	DQO option 1 status	DQO Option 2 status
M1833	1	Molybdenum D-Mo	0.006	0.005	0.001	18.2%	0.002825	pass	fail-RPD
M1679	2	Molybdenum D-Mo	0.006	0.005	0.001	18.2%	0.002825	pass	fail-RPD
L8438	1	Molybdenum D-Mo	0.006	0.005	0.001	18.2%	0.002825	pass	fail-RPD
M5605	6	Molybdenum D-Mo	0.19	0.16	0.03	17.1%	0.08625	pass	fail-RPD
L4315	8	Molybdenum D-Mo	0.013	0.011	0.001	16.7%	0.0038	pass	fail-RPD
M5286	7	Molybdenum D-Mo	0.007	0.006	0.001	15.4%	0.002975	pass	fail-RPD
L8359	4	Molybdenum D-Mo	0.007	0.006	0.001	15.4%	0.002975	pass	fail-RPD
L6984	1	Molybdenum D-Mo	0.007	0.006	0.001	15.4%	0.002975	pass	fail-RPD
K9268	8	Molybdenum D-Mo	0.007	0.006	0.001	15.4%	0.002975	pass	fail-RPD
M5779	8	Silver D-Ag	0.00003	0	0.00001	200.0%	2.23E-05	fail	fail-DL
L6795	2	Silver D-Ag	0.00005	0	0.00001	200.0%	2.38E-05	fail	fail-RPD
M6641	6	Thallium D-Tl	0.00026	0.00022	0.00005	16.7%	0.000136	pass	fail-RPD
L6795	6	Zinc D-Zn	0.003	0	0.001	200.0%	0.002225	fail	fail-DL
M4561	2	Zinc D-Zn	0.005	0	0.001	200.0%	0.002375	fail	fail-RPD
M1605	1	Zinc D-Zn	0.005	0	0.001	200.0%	0.002375	fail	fail-RPD
M1834	1	Zinc D-Zn	0.005	0.001	0.001	133.3%	0.00245	fail	fail-RPD

Figure 1: Comparison of DQO Options for Field Duplicates