

DATE April 26, 2013**PROJECT No.** 1313490001-5000-5020**TO** Alexandra Hood
De Beers Canada Inc.**CC** Lisa Bridges, John Faithful and Peter Chapman**FROM** Tasha Hall**EMAIL** thall@golder.com**2012 TOTAL DISSOLVED SOLIDS RESULTS - LABORATORY CALCULATION DISCREPANCY****1.0 INTRODUCTION**

The concentration of total dissolved solids (TDS) is a measure of the amount of dissolved major ions, such as calcium and chloride, in water. Total dissolved solids concentrations can be measured (TDS_{meas}) directly by evaporating a known volume of filtered water and measuring the mass of the residue left after evaporation. Alternatively, TDS concentrations can be calculated (TDS_{calc}) from the summation of major ions in the sample (APHA 2005). In March 2013, Golder Associates Ltd. (Golder) noticed that ALS Canada Ltd. (ALS) changed their TDS_{calc} formula to a version that was no longer consistent with past practice or the Standard Method for calculating TDS as outlined in APHA (2005). The discrepancy affected samples collected as part of the Aquatic Effects Monitoring Program (AEMP) and Surveillance Network Program (SNP) in 2012. This technical memorandum provides background on TDS_{calc} (Section 2), describes the calculation discrepancy in detail (Section 3), and the follow-up actions taken to correct and prevent this from occurring in future (Section 4). The overall effect on the 2012 TDS_{calc} results from the SNP and AEMP is outlined in Section 5. Note that calculations of TDS for at least this year will be as per APHA (2005) not APHA (2012) because, in the course of this investigation, an error was discovered in the newest (22nd) edition of Standard Methods, which the Standard Methods Technical Manager has noted and indicated will be corrected in the 23rd edition of Standard Methods.

2.0 BACKGROUND ON CALCULATED TOTAL DISSOLVED SOLIDS

ALS routinely provides both TDS_{calc} and TDS_{meas} as part of their routine analysis package. Calculated TDS is used rather than measured TDS for the De Beers Canada Inc. (De Beers) Snap Lake Project to be consistent with recommendations in the Water Licence (MVLWB 2012) and for the reasons outlined in De Beers (2012a,b):

- 1) TDS_{meas} is subject to laboratory interferences that can reduce the accuracy of the measurement (Evaristo-Cordero 2011). Waters with considerable calcium, magnesium and chloride concentrations, such as those from Snap Lake, can form a hygroscopic (i.e., absorbs ambient water) residue that will continue to absorb water under normal laboratory conditions, thereby biasing the measurement high (APHA 2005; Evaristo-Cordero 2011). Unlike TDS_{meas} , TDS_{calc} implicitly assumes the analytes exist in the sample in the forms analyzed, so are not influenced by any changes that may occur when taken out of solution. Using this method is likely more accurate given the practical limitations in handling and measuring TDS.
- 2) TDS_{calc} was used in the EAR and in recent modelling updates to predict the concentration of TDS in the treated effluent. To be consistent with the EAR predictions, past practice has been to use TDS_{calc} in the reporting of monitoring results and modelling.



- 3) Forecasts of TDS concentrations in the treated effluent from the Snap Lake Mine (the Mine) must be based on TDS_{Calc} to account for the contribution of the specific ions to mass releases associated with Mine activities, such as groundwater contributions (e.g., calcium and chloride) and blasting (e.g., nitrate).

3.0 DESCRIPTION OF THE ERROR

Until the end of 2011, ALS used an equation very similar to Method 1030E in Standard Methods (SM) for TDS_{Calc} (Equation 1; APHA 2005). Equation 1 includes the major inorganic ions, measured in milligrams per litre (mg/L), which measurably contribute to TDS in Snap Lake and at the Mine. There are other dissolved inorganic ions that could also contribute to TDS, such as nitrite, strontium, and iron; however, concentrations of these parameters are very low in proportion to the major inorganic ions in water quality samples collected from the Snap Lake Mine.

In January 2012, Golder noticed that the 2012 TDS_{Calc} included nitrite, but did not include the silicate anion as per Standard Methods (APHA 2005). ALS was asked to update the formula to include the silicate anion. Nitrite continued to be included, as its contribution to the overall TDS concentration was negligible. By March 2012, ALS had added the silicate anion, but made other changes to the formula as part of their Canada-wide standardization process without notifying Golder (Section 2). The 2012 equation was inconsistent with Standard Methods and included parameters not appropriate to the TDS calculation. All of the AEMP TDS_{Calc} values received since January 2012 (i.e., January to September 2012, February 2013) and SNP TDS_{Calc} values after April 2012¹ were affected. The discrepancy was recently identified, and work has been done to notify the laboratory, correct the issue, update the database and implement preventative measures to detect any future changes in the TDS calculation method should they occur.

Equation 1: (APHA 2005)

$$TDS_{Calc}(SM) \text{ (mg/L)} = (0.6 \times \text{Total Alkalinity as CaCO}_3) + Na^+ + Mg^+ + K^+ + Ca^{2+} + SO_4^- + Cl^- + NO_3^- + F^- + SiO_3^{2-}$$

SM = Standard Methods; Na^+ = sodium cation; Mg^+ = magnesium cation; K^+ = ion; Ca^{2+} = calcium cation; $CaCO_3$ = calcium carbonate; SO_4^- = sulphate anion; Cl^- = chloride anion; NO_3^- = nitrate anion (multiply nitrate as nitrogen by 4.427); F^- = fluoride anion; and SiO_3^{2-} = silicate anion (multiply reactive silica as SiO_2 , by 1.266).

In January 2012, ALS added the silicate anion upon request; however, other parameters, including total organic carbon (TOC), ammonium (NH_4^+), dissolved aluminum (Al^+), dissolved iron (Fe^{2+}), dissolved manganese (Mn^{2+}), dissolved copper (Cu^{2+}), and dissolved zinc (Zn^{2+}) were also added. The 2012 equation with the additional parameters (Equation 2) will be referred to as $TDS_{Calc}(Lab)$.

Equation 2: (Evaristo-Cordero 2013)

$$2012 \text{ } TDS_{Calc}(Lab) \text{ (mg/L)} = (0.6 \times \text{Total Alkalinity as CaCO}_3) + Na^+ + Mg^+ + K^+ + Ca^{2+} + SO_4^- + Cl^- + NO_3^- + NO_2^{2-} + F^- + SiO_3^{2-} + NH_4^+ + Fe^{2+} + Mn^{2+} + Al^+ + Cu^{2+} + Zn^{2+} + TOC$$

¹ ALS was asked by Golder to update their TDS_{Calc} formula to include silicate in January 2012. The revised, but erroneous, formula was not in place until April 2012. The formula was retroactively applied to all of the AEMP TDS samples collected since January 2012; however, this was not done for the SNP samples. The formula was applied only to SNP samples collected after April 2012.

ALS provided a document from Dalhousie University (Evaristo-Cordero 2013) as the source of the 2012 $TDS_{Calc(Lab)}$ equation. Golder reviewed the document and determined that it did not specify that the additional parameters need to be included in the TDS calculation. The 2012 $TDS_{Calc(Lab)}$ equation was inconsistent with Standard Methods, past practice (De Beers 2011), and specific project documentation and approval (De Beers 2005a,b; DFO 2006). The inclusion of the additional parameters, particularly TOC and ammonium, introduced potential bias in the lake data, site data, and modelling results (Section 4). For consistent and defensible data, it was determined that the discrepancy needed to be addressed and that using the $TDS_{Calc(SM)}$ was the most accurate and transparent path forward.

4.0 FOLLOW-UP ACTIONS

Shortly after the discrepancy was noticed, the actions outlined in Table 1 were implemented.

Table 1: Actions to Correct Total Dissolved Solids Calculation Discrepancy

Actions	Date Completed
Completed Actions	
ALS was notified of the TDS_{Calc} discrepancy.	March 1, 2013
ALS was asked to use the $TDS_{Calc(SM)}$ equation as outlined in Equation 1 and Standard Methods (APHA 2005) effective immediately, and not to deviate from this formula without explicit permission.	March 1, 2013
ALS agreed to re-issue all 2012 $TDS_{Calc(Lab)}$ results to De Beers,.	March 1, 2013
Dialogue occurred between ALS and the Standard Methods Technical Manager regarding the TDS equation. Through those discussions, it was discovered that the newest, 22 nd Edition, of Standard Methods (APHA 2012) contains an error. The Standard Methods Technical Manager stated they will be reverting back to the 2005 formula in the next edition (Equation 1).	March 1 to 7, 2013
De Beers was notified of the issue and agreed re-calculation was appropriate. Implications and plan forward for the WLAR were discussed.	March 8, 2013
Preliminary $TDS_{Calc(SM)}$ results from the database were provided to De Beers and Golder for review.	March 9, 2013
The 2012 erroneous $TDS_{Calc(Lab)}$ values were renamed in the database to "Total Dissolved Solids, Calculated (Lab) (mg/L)". "Total Dissolved Solids, Calculated (Standard Methods) (mg/L) was added".	March 11, 2013
ALS was directed not to calculate TDS for samples for which they do not have analytical results for all of major contributors to the ionic balance (i.e., total alkalinity, Cl, Ca, Mg, Na, K, and SO_4). If TDS is selected on the analytical request form, and at least one of those parameters is not selected, De Beers and/or Golder should be notified for clarification.	March 11, 2013
"Interim" $TDS_{Calc(SM)}$ were calculated using the De Beers environmental database. The interim $TDS_{Calc(SM)}$ was used until ALS re-issued their final revised results. This was necessary to meet deadlines for the ARD, AEMP, and WLAR reports.	March 9 to 12, 2013
ALS issued preliminary 2012 re-calculated TDS results.	March 15, 2013
Ongoing Actions	
Continued dialogue with ALS and follow-up data checks to verify the $TDS_{Calc(Lab)}$ results	Ongoing, expected completion by end of April 2013
A TDS check will be built into the database: $TDS_{Calc(SM)}$ using the database will be compared to $TDS_{Calc(Lab)}$. If values are not equal, within acceptable significant figure and rounding differences ^(a) , results will be flagged and reviewed, and the laboratory will be notified.	Ongoing, expected completion by end of May 2013

(a) Preliminary results from ALS indicate that their values differ from those provided by the database due to the number of significant figures reported. These differences are minor and are currently being discussed and aligned.

ARD = Acid/Alkaline Rock Drainage; WLAR = Water Licence Annual Report; TDS = total dissolved solids; Cl = chloride; Ca = calcium; Mg = magnesium; Na = sodium; K = potassium; SO_4 = sulphate; ALS = ALS Canada Ltd., TBD = to be determined.

5.0 EFFECT ON 2012 TOTAL DISSOLVED SOLIDS RESULTS

The 2012 TDS_{Calc}(SM) values were re-calculated in the database using (Equation 1; APHA 2005) and compared to the TDS_{Calc}(Lab) values provided by ALS (calculated using Equation 2). Due to extra parameters in the TDS_{Calc}(Lab), the vast majority of the 2012 TDS_{Calc}(Lab) values were biased high for both the SNP and AEMP data. Specifically, 84% of samples collected and stored in the De Beers database in 2012 had higher TDS_{Calc}(Lab) than TDS_{Calc}(SM). The remaining 16% of samples were predominantly SNP samples collected prior to April 2012, before the silicate anion was included in the ALS calculation. TDS_{Calc}(Lab) values were, on average, 8% and 6% higher for those samples collected as part of the SNP and AEMP, respectively. Samples with higher TDS concentrations tended to have lower relative percent differences (RPD) when comparing TDS concentrations calculated by ALS and Standard Methods for reasons described below. That is, the higher the TDS concentration, the less the calculation error impacted the result. For example, the same change of 0.1 mg/L yields different RPDs depending on whether the original concentration was 1 mg/L or 100 mg/L. The RPD is 9.5% in the first case of 1 mg/L and 0.1% in the case of 100 mg/L. The RPD was calculated as:

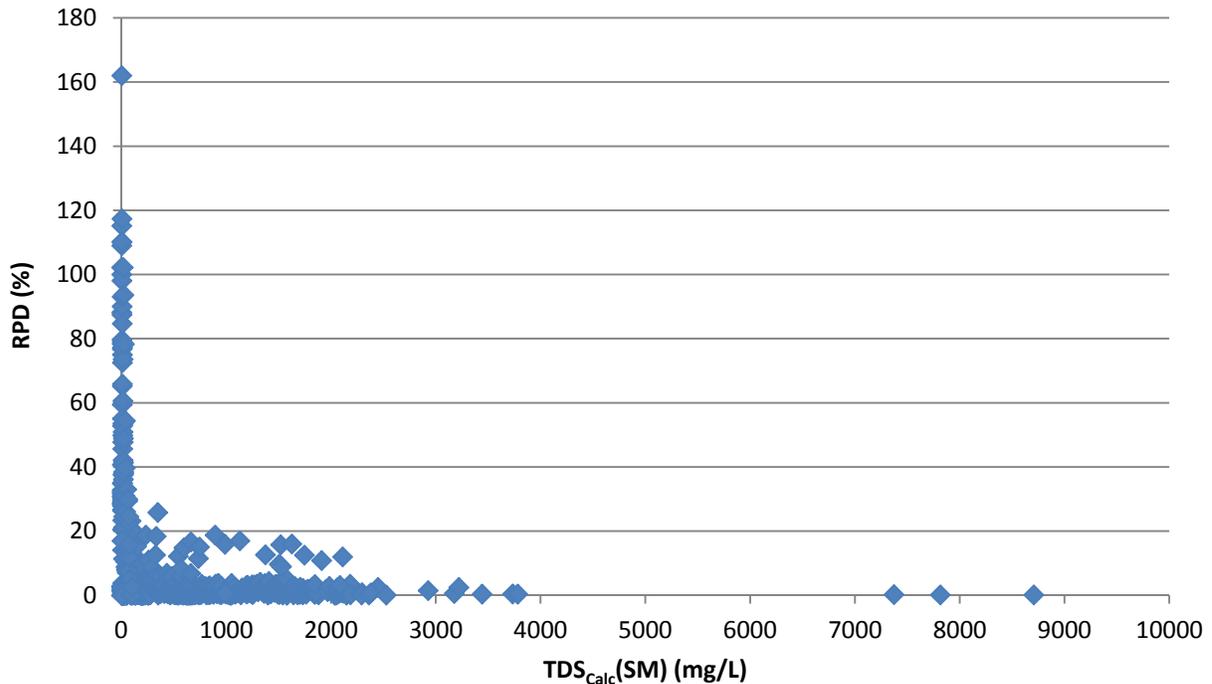
$$\text{Relative Percent Difference} = \frac{|(\text{TDS}_{\text{CalcLab}}) - (\text{TDS}_{\text{CalcSM}})|}{((\text{TDS}_{\text{CalcLab}}) + (\text{TDS}_{\text{CalcSM}})) \div 2} \times 100 \quad \text{[Equation 3]}$$

Inclusion of the dissolved metals using the TDS_{Calc}(Lab) equation (Equation 2) had a negligible effect on TDS concentrations in groundwater and lake water. Dissolved metals were measured in micrograms per litre (µg/L), whereas chloride, the major contributor to TDS, was measured in the tens or hundreds of mg/L in most samples. Including TOC and the ammonium ion had a greater effect on TDS concentrations, as those parameters are typically measured on the mg/L scale. There were two noticeable effects from the addition of these two parameters:

- Ammonium and/or TOC made up a larger proportion of the calculated TDS value (as described above), so the relative percent difference (RPD) between TDS concentrations calculated by ALS and Standard Methods was typically higher at lower TDS concentrations (Figure 1). An example was for runoff samples with low TDS (e.g., 10 to 20 mg/L), and TOC concentrations of approximately 5 mg/L (e.g., SCN 2012-1028).
- Samples collected from Snap Lake on the same day may have had different TDS concentrations, solely based on the calculation method. ALS states that for the 2012 TDS calculation “*only those parameters for which analysis has been requested are included in this calculation. Absent or non-detect constituent results are assigned a zero value in the formula*”. TOC is routinely analyzed at the diffuser stations (e.g., SNP 02-20e), but not at the AEMP TDS stations (e.g., SNAP05). Therefore, on a given day, TDS concentrations at the diffuser stations would be biased high compared to the AEMP TDS stations due to the calculation method.

This TDS calculation discrepancy was discussed with the senior water quality, geochemistry, and modelling specialists within Golder. It was agreed that the bias introduced would have minimal effects on conclusions regarding lake dynamics, plume movement, underground predictions, or future in-lake estimates. However, the general consensus was to correct the values, to determine whether future assessments confirm this assumption.

Figure 1: Relationship Between Total Dissolved Solids Concentration and Relative Percent Difference



RPD = relative percent difference; % = percent TDS; mg/L = milligrams per litre; TDS = total dissolved solids.

6.0 RECOMMENDATIONS

As outlined in Table 1, the majority of the follow-up actions have been conducted to correct the issue; however, the following should be considered:

- Golder and De Beers should continue to be diligent on quality assurance and quality control (QA/QC) of laboratory-provided data. A TDS check will be built into the database, as outlined in Table 1, where TDS calculated using the database (Standard Methods) will be compared to TDS calculated by ALS. If values are not equal, within acceptable significant figure and rounding differences, results will be flagged and reviewed, and the laboratory will be notified. A similar check will be formally integrated into the AEMP QA/QC procedures and reporting.
- Finally, De Beers should consider reporting reactive silica, as SiO₂, in the monthly SNP reports. The laboratory provides this information, but it is currently not presented in the result tables. All contributing ions to TDS_{Calc} should be shown so that reviewers can easily replicate the TDS calculation.

7.0 CLOSURE

We trust that this technical memorandum provides the information you require at this time. Should you have any questions, or require further information, please contact Golder at your convenience.

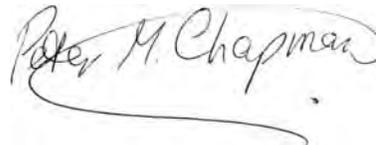
GOLDER ASSOCIATES LTD.

Report prepared by:



Tasha Hall, B.Sc.
Associate, Water Quality Specialist

Report reviewed by:



Peter M. Chapman, Principal signing for
John Faithful, B.Sc. (Hons)
Associate, Senior Water Quality Specialist



Peter M. Chapman, Ph.D.
Principal, Technical Director

TH/JF/PMC

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