Appendix B

SWAMP Nutrient Holding Time Study Data Review

by

Lawrence H. Keith, Ph.D.

Instant Reference Sources, Inc.
Monroe, GA

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1.0 Executive Summary

Report Content

This report addresses the goal of a requested study which is to determine if samples of any of six selected nutrients may be held longer than the currently accepted EPA holding time guidelines (see Table 1.1) with less than 10% difference in the data. Analytical data from nutrient tests were submitted for statistical evaluation and this report provides the details and summary of that evaluation.

A test consists of an analyte (for example, ammonia) and a method of preservation (for example, freezing or refrigeration). Each test was conducted using four holding times (<48 hours, 4 days, 7 days, and 28 days). In addition, these test data were provided from 6 different sampling sites.

In conducting this study the confidence intervals at the 95% confidence level of each test for four different holding times were calculated. In addition, statistical calculations of the relative standard deviations (RSD) of each test and each holding time were also calculated.

This report consists of background study assessment information plus a one page summary for each of twelve nutrient tests. In addition, Appendix A provides tables of statistical results that were used for test comparisons using six sampling sites from three different geographical areas in California. Appendix B provides an ancillary general discussion of statistical techniques used with this evaluation. Finally, the six Excel files that were provided for statistical evaluation are renamed with "-lhk" after their original names and are submitted with confidence interval and relative standard deviation calculations added to them.

Test Procedure

The currently accepted practice (from U.S. EPA) for the nutrients being analyzed in this study are listed in Table 1.1 The results for longer holding times were compared to results obtained from the initial samples analyzed in < 48 hours in all cases. Additional data with each test included the mean of seven replicate analyses for each analyte and holding time, the standard deviation, matrix spikes, and the mean of blank analysis data. This ancillary data was used for evaluating the bias, precision, and potential matrix effects with the analyses. No unusual results were found in the ancillary data; i.e., the data were typical of environmental results expected for these analytes. As usual, precision is better with samples where the concentration of the nutrients was relatively high and lower with samples that had lower concentrations of them.

Conclusions

The most important conclusion is that the holding time data are often dependent on the analyte concentrations. Exceptions included total nitrogen, total phosphorus, and ammonia data.

- The unfiltered and refrigerated samples analyzed for total nitrogen produced mean values less than ± 10% of the mean values of samples analyzed in < 48 hours with holding times up to and including 28 days.

- However, the total phosphorus and ammonia samples held longer than 48 hours produced mean values larger than ± 10% of the mean values of samples analyzed in < 48 hours. These analytes are therefore recommended to be analyzed in < 48 hours. The ammonia samples were preserved with both freezing and refrigeration and neither preservation technique helped to extend the holding time values using the methods in this study.

A second conclusion is that, with the exception of soluble reactive phosphate (SRP), the choice of freezing or refrigeration didn't significantly affect the results; i.e., the holding times with mean values within ± 10% of the mean values of samples analyzed in < 48 hours were about the same whether freezing or refrigeration was used in conjunction with the methods in this study.

- With the SRP samples where concentrations were ≥ the reporting level (RL) holding times of 7 days produced mean values within ± 10% of the mean values of samples analyzed in < 48 hours when freezing was employed for preservation. However, when similar samples were refrigerated then mean values that were ± 10% of the mean values of samples analyzed in < 48 hours only occurred with holding times up to 4 days.

Nitrite samples with concentrations about 5 X the RL or above produced mean values within ± 10% of the mean values of samples analyzed in < 48 hours for up to 28 days using either freezing or refrigeration. About the same results were obtained with nitrate samples (frozen or refrigerated) when the concentrations were around 2 X the RL or above.

Nitrate + nitrite samples (either frozen or refrigerated) analyzed within 7 days when the concentrations were ≥ the RL produced mean values within ± 10% of the mean values of samples analyzed in < 48 hours.

These conclusions are summarized in Table 1.1

Table 1.1 Holding Time Mean Values ± 10% of Mean Values for < 48 Hour Analyses

Nutrient Analyte	**Frozen / Refrigerated**	**Holding Time from Study**	**Requirement from Study**	**EPA Guidelines**
Total Nitrogen	Refrigerated	28 days	None	7 days
Total Phosphorus	Refrigerated	< 48 Hours	None	< 48 Hours
Nitrate + Nitrite	Either preservation	7 days	≥ RL	< 48 Hours
Nitrite	Either preservation	28 days	5 X RL	< 48 Hours
Nitrate	Either preservation	28 days	2 X RL	< 48 Hours
Ammonia	Either preservation	< 48 Hours	None	< 48 Hours
Soluble Reactive Phosphate	Frozen	7 days	≥ RL	< 48 Hours
Soluble Reactive Phosphate	Refrigerated	4 days	≥ RL	< 48 Hours

The implications of the results in Table 1.1 may be summarized as follows using the study methods:

- Total nitrogen unfiltered and refrigerated samples may be held for up to 28 days with low probability of any significant impact on the analytical values.

- Nitrate samples may be held for up to 28 days with low probability of any significant impact on the analytical values when they are field filtered and either frozen or refrigerated and when the anticipated analyte levels are ≥ 2 times the RL.

- Nitrite samples may be held for up to 28 days with low probability of any significant impact on the analytical values when they are field filtered and either frozen or refrigerated and when the anticipated analyte levels are ≥ 5 times the RL.

- Total nitrate + total nitrite samples may be held for up to 7 days with low probability of any significant impact on the analytical values when they are field filtered and either frozen or refrigerated and when the anticipated analyte levels are ≥ RL.

- Soluble reactive phosphate samples may be held for up to 7 days with low probability of any significant impact on the analytical values when they are field filtered and frozen and when the anticipated analyte levels are ≥ RL.

- Soluble reactive phosphate samples may be held for up to 4 days with low probability of any significant impact on the analytical values when they are field filtered and refrigerated and when the anticipated analyte levels are ≥ RL.

- Total phosphorus samples that are unfiltered and refrigerated should be analyzed in less than 48 hours.

- Ammonia samples that are field filtered and either frozen or refrigerated should be analyzed in less than 48 hours.

If different analytical methods or different preservation techniques are used for **total nitrogen** or **total phosphorus** or **orthophosphorus (SRP)** determinations then the above conclusions and implications for SWAMP probably will not apply or be accepted by U.S. EPA. However, the above conclusions and implications for SWAMP probably will apply and may be accepted by U.S. EPA for EPA Method 353.2 for **nitrate + nitrite** and for EPA Method 350.1 for **ammonia**.

Because of the many different results that are dependent on the various analytes, their concentrations, and the preservation technique used, an overall confidence level of the study design can not be calculated (i.e., data from many diverse variables can not be pooled and subjected to an overall study statistical analysis). However, it can be qualitatively stated that the study design was rigorous and that supporting statistical data for each "test" (as defined above) show good correlation and represent what would be expected from analyses that are produced from stable measurement systems in "statistical control." Statistical control is defined as the situation where all critical variables are controlled to the extent necessary and possible, resulting in stability of the process and reproducibility of the data within defined limits. [Taylor, Chapter 3, 1987]

2.0 Background Information

The goal of this study is to determine if any of the selected nutrients can be held longer than the accepted time of up to 48 hours with less than 10% variability in the data.

At each sampling site sufficient sample volume was collected to test freezing (with dry ice) and wet ice preservation at < 48 hour, 4 days, 7 days, and 28 days; seven replicates of each sample were analyzed. Method blanks were collected for filtered/unfiltered and frozen/wet ice preservation and were analyzed in triplicate at each time point. Every 20 samples (a batch) included a lab blank (DDI water), a LCS, and MS/MSD. Tahoe sites were spiked: 25 ug/L SRP, NO_3, NO_2, NH_4 (this will provide 50 ug/L NO_3+NO_2, and 75 ug/L TN).

Samples were taken from six sampling sites that represent three geographic areas in California.

- Two sites in the Central Coast (Franklin Creek and Orcutt Creek) – abbreviated as FC and OC, respectively.
- Two Tahoe sites (Upper Truckee River and West Fork Carson River) – abbreviated as UTR and WFCR, respectively.
- Two locations in the central valley (San Joaquin River at Vernalis and Sacramento River at Freeport) – abbreviated as SJR and SRF, respectively.

Analytical results from each of these sampling sites were summarized in separate Excel files by the analytical laboratory and the files were provided by SWAMP to Instant Reference Sources for further evaluation. As part of this evaluation, the confidence interval (CI) at the 95% confidence level was calculated from each of the means from seven replicate analyses. In addition, the relative standard deviation was calculated using the standard deviation associated with each mean value. These calculations were entered into each of the Excel files for all sample data (they appear in bold blue type to differentiate added calculations and data from existing calculations and data which appears in black type).

The most important data used to answer the question are the mean values for each of the samples. The mean values for each test (an analyte with its corresponding holding time) were compared with the mean value for the test conducted at a holding time of less than 48 hours as the reference point. The differences between mean values at holding times longer than 48 hours were expressed as percent change from the mean value of the corresponding test at less than 48 hours. These calculations are summarized in tables that are organized by test in Appendix A along with useful ancillary data that includes mean blank values, 95% confidence intervals, and the relative standard deviation.

As a visual aid the percent differences for each test were plotted together for all six sampling sites. These plots are provided in Section 3.0 to enhance the discussion and conclusions for each test.

3.0 Study Results and Discussion

The goal of this study is to determine if any of the selected nutrients can be held longer than the accepted time of up to 48 hours with less than 10% variability in the data. Freezing samples and refrigerating samples (4 ºC) were the two conditions under which holding times were examined.

Study results are organized by method since the objective of the study is to determine whether a method is able to produce data with less than 10% variability for holding times of 4, 7, and 28 days versus the currently accepted holding time of less than 48 hours.

Metadata reviewed included blank values (including the mean), matrix spikes (MS/MSD), and sample values (including the mean of 7 replicate values, standard deviation (δ or s), bias as percent recovery, relative standard deviation (RSD), and confidence intervals (CI) at the 95% confidence level).

- Standard deviation (in mg/L), confidence intervals (in mg/L), and relative standard deviation provide measurements of variance from random errors in the data sets.
- Matrix spikes provide measurements of bias (systematic high or low values) against known fortified sample values in the data sets and are useful for indicating errors caused by the sample matrix.

A suggestion included using a 60% confidence level instead of the typical 95% confidence level. A comparison of differences in confidence intervals obtained was tested using several representative values from the UTR sampling site with total nitrogen, total phosphorus, and reactive soluble phosphate data sets (see Table 3.1). The mg/L variance using 60% confidence levels was less than the variance using 95% confidence levels. But, increasing or decreasing the variance (as plus or minus mg/L values from the mean of a data set) does not significantly help to answer the question of whether the mean value from an analysis of samples held longer than 48 hours has more or less than a 10% difference from the 48 hour mean value. A general discussion of the relationship of numbers of samples analyzed, error (e.g., confidence intervals or tolerable error) and confidence levels (i.e., probability of inclusion of data in a data set within confidence intervals or tolerable errors) is provided with examples in Appendix B.

The 95% confidence intervals from the mean were calculated for all data. It is designated in the column labeled “95% CI” (in blue colored type) in each of the Excel spread sheets that are provided with this report. The 95% CI values were calculated using equation (1) from John K. Taylor’s book (Taylor, p. 27, 1987).

(1) $$\overline{X} \pm \frac{ts}{\sqrt{n}}$$

The 95% CI is one of the most common statistical calculations and it estimates, with a 95% probability, where the population mean lies with respect to a sample mean. The intervals calculated using equation 1 are expected to include the population mean 95% of the time. As the

equation shows, the confidence interval for the mean ($\bar{x}$) depends on the number of measurements (n), the standard deviation (s) and the level of confidence desired (e.g., 95%). The value for (t) in equation 1 depends on the level of confidence desired (found in statistical tables) and the number of degrees of freedom (v) associated with the estimation of the standard deviation. If the standard deviation is based on the set of measurements used to calculate the mean then v = n-1. For the data used in this study n = 7 replicate measurements and the square root of 7 is 2.645751. The value for t when 7 replicate samples are involved is 2.447 Equation 1 therefore becomes $\bar{x}$ = ± 2.224 (s)/2.645751 and this equation is applied to each data set using the standard deviation that was calculated with each corresponding mean.

The 60% CI values were estimated using the software program *DQO-PRO* (Keith, et al., 1996) and the equations in it are described in Appendix B. In these calculations the values for the standard deviation for each mean were entered with the desired confidence level of 60% and the process was iterated until the error associated with 7 samples was obtained.

Table 3.1 Example Confidence Intervals at 95 x and 60% Confidence Levels

Analyte	Holding Time	Mean * mg/L	CI at 60% CL in mg/L	CI at 95% CL in mg/L	Difference in CI from 60 to 95% CL
Total N	< 48 Hours	0.163	± 0.005	± 0.013	0.008 mg/L (5% of mean)
Total N	4 Days	0.151	± 0.003	± 0.007	0.004 mg/L (3% of mean)
Total N	7 Days	0.178	± 0.008	± 0.021	0.013 mg/L (7% of mean)
Total P	< 48 Hours	0.036	± 0.006	± 0.016	0.010 mg/L (28% of mean)
Total P	4 Days	0.040	± 0.002	± 0.005	0.003 mg/L (8% of mean)
Total P	7 Days	0.045	± 0.003	± 0.008	0.005 mg/L (11% of mean)
SRP Frozen	< 48 Hours	0.033	± 0.003	± 0.009	0.006 mg/mL (27% of mean)
SRP Frozen	4 Days	0.035	± 0.002	± 0.004	0.002 mg/mL (6% of mean)
SRP Frozen	7 Days	0.036	± 0.002	± 0.004	0.002 mg/mL (6% of mean)

References

Keith, L. H., et. al., *DQO-PRO*, 1996, American Chemical Society Division of Environmental Chemistry, EnvirofACS Online, www.envirofacs.org.

Taylor, J. K., Quality Assurance of Chemical Measurements, Lewis Publishers, 1987.

3.1 Total Nitrogen

The total nitrogen samples were unfiltered and refrigerated for storage. The Method Detection Limit (MDL) for total nitrogen analysis is 0.010 mg/L and the Reporting Limit (RL) is 0.050 mg/L. Detailed comparisons of metadata from all six sample sites are provided in Tables A 1.1 to A.1.6 in Appendix A.

In general, the metadata in Tables A 3.1 to A 3.6 and the plots in Figure 3.1 show that holding times for samples that are unfiltered may be stored refrigerated for up to 28 days with the exception of two data points (circled in Figure 3.1). These include a 25% change after 28 days for the UTR samples and a -11% change after 4 days for the WFCR samples.

Two factors contributed to the high percentage change with the UTR samples: a high bias of 116% recovery and a high RSD of 24%. The SD of this data set was ± 0.049 mg/L from the average of 0.204 mg/L. It may thus be considered an outlier from the other data as shown in Figure 3.1.

The WFCR data set shows no unusual blank values or bias from percent recovery and the apparent systematic decrease in difference from the < 48 hour reference data set is not able to be explained from the data at hand. However, the fact that the differences become less with time, rather than the usual opposite trend, diminishes the importance of the 4 day data set values when considering the influence of holding time with total nitrogen sample measurements.

Conclusion: unfiltered and refrigerated samples for total nitrogen analysis were held for up to 28 days with no significant impact on the analytical values obtained from the measurement process used in this evaluation.

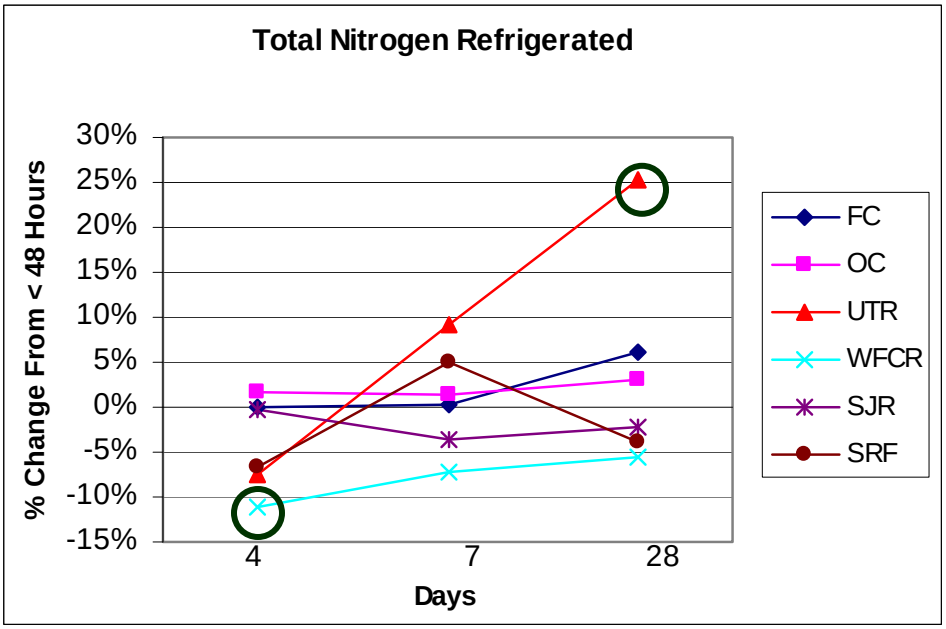

Figure 3.1 – Plots of % Change Relative to < 48 Hour Sample Values for Total Nitrogen

3.2 Total Phosphorus

The total phosphorus samples were unfiltered and refrigerated for storage. The MDL for total phosphorus analysis is 0.005 mg/L and the RL is 0.050 mg/L. Detailed comparisons of metadata from all six sample sites are provided in Tables A 2.1 to A.2.6 in Appendix A.

In general, the metadata in Tables A 2.1 to A 2.6 and the plots in Figure 3.2 show that the holding times for total phosphorus samples may not be held past the < 48 hour referenced holding time.

Figure 3.2 shows widely varying trends, from consistently high percent changes (e.g., UTR samples) to acceptable to high (e.g., WFCR samples), to unacceptable low to acceptable (e.g., OC samples) to acceptable changes (i.e., less than 10% with FC samples).

Tables A 2.1 to A 2.6 also reflect this same variability in the data. Furthermore, there is no obvious source of the variability; i.e., there are no unusually high blank values, no widely fluctuating percent recovery, etc. The variability is high – for example, RSDs range from 4% to 48% and the majority of them are higher than 10%.

Conclusion: unfiltered and refrigerated samples for total phosphorus analysis may be held for no longer than the referenced procedure of < 48 hours. Holding total phosphorus samples for longer times poses a significant risk of obtaining unreliable data.

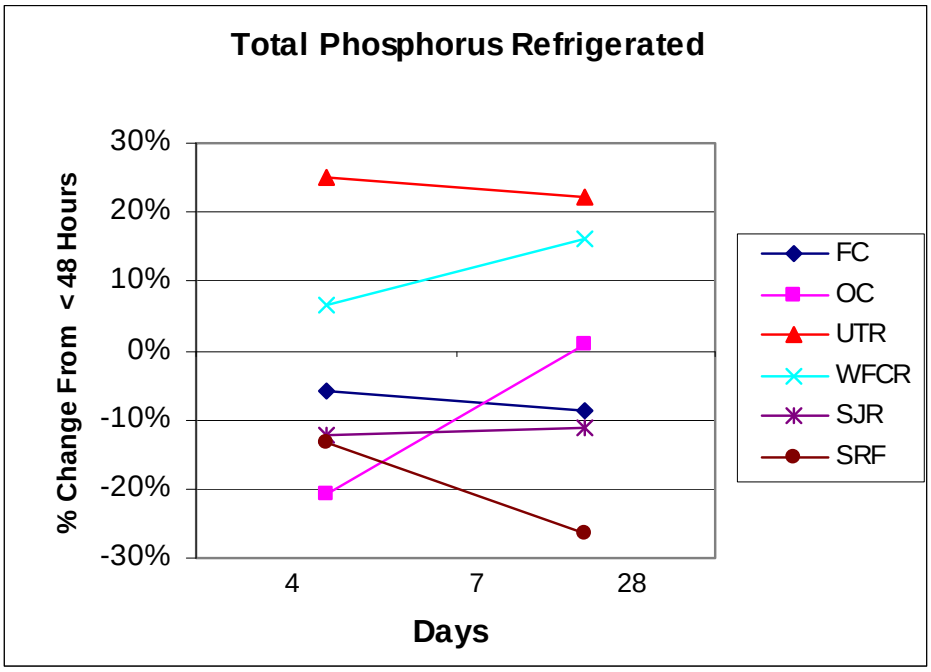

Figure 3.2 – Plots of % Change Relative to < 48 Hour Sample Values for Total Phosphorus

3.3 Nitrate + Nitrite – Field Filtered and Frozen

The nitrate + nitrite samples were field filtered and frozen for storage. The MDL for nitrate + nitrite analysis is 0.010 mg/L and the RL is 0.050 mg/L. Detailed comparisons of metadata from all six sample sites are provided in Tables A 3.1 to A.3.6 in Appendix A.

In general, the metadata in Tables A 3.1 to A 3.6 and the plots in Figure 3.3 show that the changes in data values for holding times for nitrate + nitrite samples were within ± 10% for up to 28 days with the exception of the samples from Sacramento River at Freeport site (SRF).

Figure 3.3 shows that samples from the other five sites are all within ± 10% of the samples held < 48 hours. However, the values from 28 days holding time are clearly more variable for half of the sites than those held from 4 to 7 days.

An examination of the metadata in Table A 3.6 for the SRF site shows that the mean concentration values for nitrate + nitrite are the lowest of all the sampling sites studied. In fact, the difference between the 28 day holding time average (0.024 mg/L) and the < 48 hour holding time (0.19 mg/L) is only 5 mg/L. The mean values for the other sites are larger and range from 0.042 mg/L to 35.5 mg/L. In addition, the mean value for the blank for the < 48 hour sample was -11 mg/L and the mean value of those replicate analyses was 19 mg/L.

Conclusion: field filtered and frozen nitrate + nitrite samples with concentrations at the reporting level (RL) or above were held for up to 7 days with low probability of any significant impact on the analytical values obtained from the measurement process used in this evaluation. Samples with nitrate + nitrite concentrations less than the RL are not recommended to be held past 48 hours.

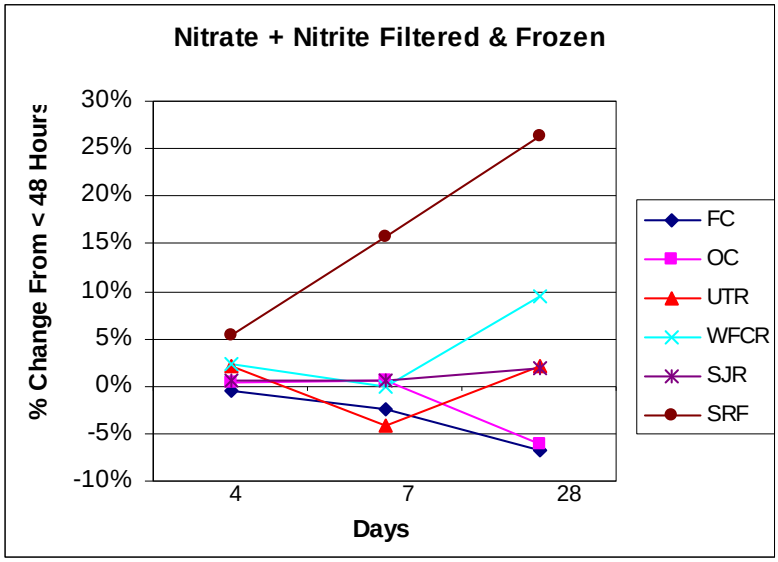

Figure 3.3 – Plots of % Change Relative to < 48 Hour Sample Values for Nitrate + Nitrite Filtered and Frozen

3.4 Nitrate + Nitrite – Field Filtered and Refrigerated

The nitrate + nitrite samples were field filtered and refrigerated for storage. The MDL for nitrate + nitrite analysis is 0.010 mg/L and the RL is 0.050 mg/L. Detailed comparisons of metadata from all six sample sites are provided in Tables A 4.1 to A.4.6 in Appendix A.

In general, the metadata in Tables A 4.1 to A 4.6 and the plots in Figure 3.4 show similar trends to those obtained from samples that were field filtered and frozen. Again, the Sacramento River at Freeport (SRF) sample showed much larger variations compared to the < 48 hour samples than samples from the other five sites. And, again the mean concentration of the < 48 hour sample was the lowest (0.017 mg/L) and had a corresponding mean concentration of the blanks of -0.010 mg/L.

Figure 3.4 shows that half of the values from the 28 day samples had differences from the < 48 hour samples by more than 10%. In addition to the SRF samples, those from Upper Truckee River (UTR) and West Fork Carson River (WFCR) also had differences from the < 48 hour samples by more than 10%. All three of these sampling sites had mean sample concentrations that were below the reporting level and the SRF samples had the lowest concentrations of the three.

Conclusion: field filtered and refrigerated nitrate + nitrite samples with concentrations at the reporting level (RL) or above were held for up to 7 days with low probability of any significant impact on the analytical values obtained from the measurement process used in this evaluation. Samples with nitrate + nitrite concentrations less than the RL are not recommended to be held past 48 hours.

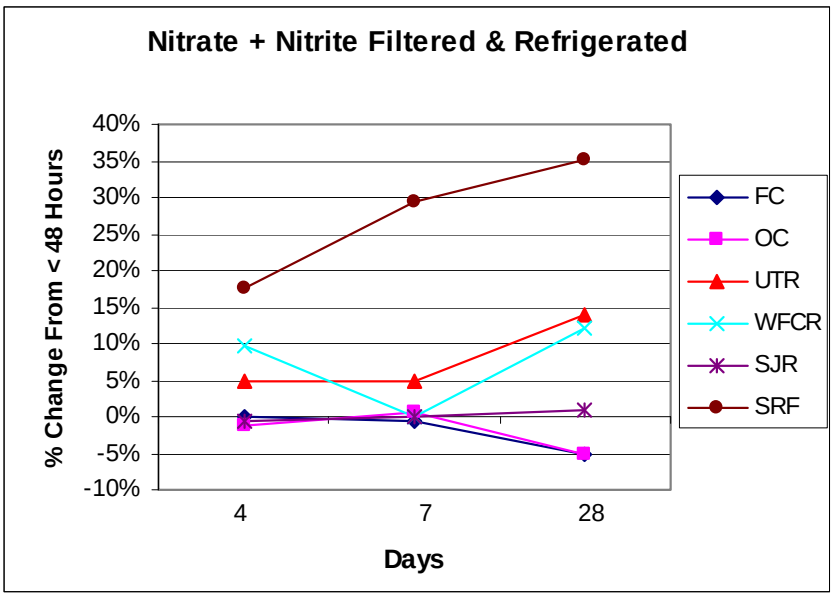

Figure 3.4 – Plots of % Change Relative to < 48 Hour Sample Values for Nitrate + Nitrite Filtered and Refrigerated

3.5 Nitrite – Field Filtered and Frozen

The nitrite samples were field filtered and frozen for storage. The MDL for nitrite analysis is 0.010 mg/L and the RL is 0.020 mg/L. Detailed comparisons of metadata from all six sample sites are provided in Tables A 5.1 to A.5.6 in Appendix A.

In general, the metadata in Tables A 5.1 to A 5.6 and the plots in Figure 3.5 show that four of the six sampling sites where samples were held for four days have mean concentrations of nitrite that vary less than 10% from corresponding samples held for < 48 hours. Variability increases when samples are held past four days except for data sets from the FC and OC sites.

Figure 3.5 shows that the change in concentration of nitrite values compared to those from samples held < 48 hours is much less than 10% for the FC and OC sites even up to 28 days holding time. An examination of the data to explain these large differences reveals that the concentration of nitrite in the FC and OC data sets is much higher than in the samples from the other four sites. The average nitrite concentrations in the FC and OC sites are about 0.140 mg/L and 0.245 mg/L respectively whereas they range from less than 10 mg/L to about 30 mg/L in the other four sites.

Conclusion: field filtered and frozen nitrite samples with concentrations at 5X the reporting level (RL) or above were held for up to 28 days with low probability of any significant impact on the analytical values obtained from the measurement process used in this evaluation. Samples with nitrite concentrations less than the 5X RL are not recommended to be held past 48 hours.

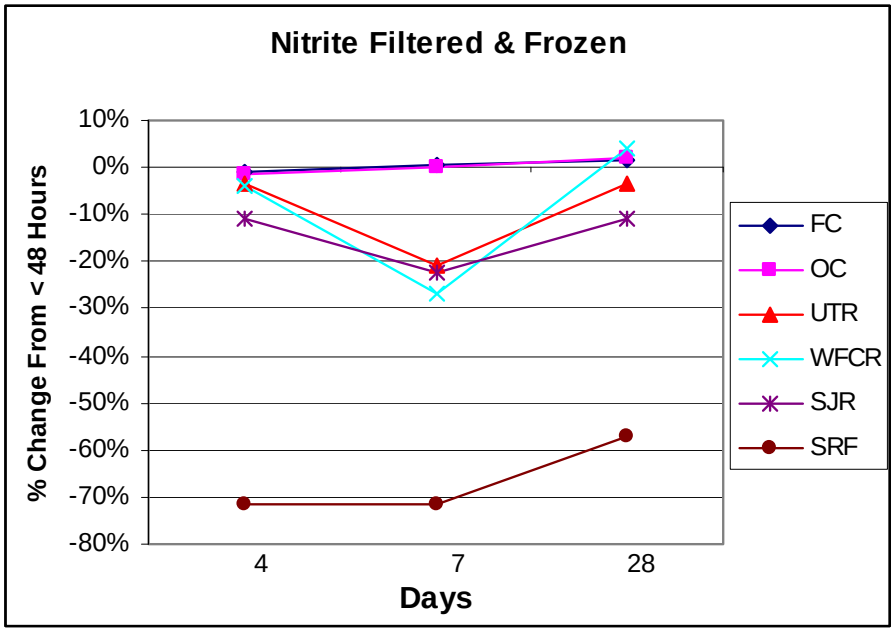

Figure 3.5 – Plots of % Change Relative to < 48 Hour Sample Values for Nitrite Filtered and Frozen

3.6 Nitrite – Field Filtered and Refrigerated

The nitrite samples were field filtered and refrigerated for storage. The MDL for nitrite analysis is 0.010 mg/L and the RL is 0.020 mg/L. Detailed comparisons of metadata from all six sample sites are provided in Tables A 6.1 to A.6.6 in Appendix A.

In general, the metadata in Tables A 6.1 to A 6.6 and the plots in Figure 3.6 show similar trends to those obtained from samples that were field filtered and frozen. Again, the concentrations of nitrite in these samples were similar to those found in the samples that were stored frozen.

Figure 3.6 shows that the change in concentration of nitrite values compared to those from samples held < 48 hours is much less than 10% for the FC and OC sites even up to 28 days holding time. The concentration of nitrite in the FC and OC data sets is much higher than in the samples from the other four sites. The average nitrite concentrations in the FC and OC sites are about 0.140 mg/L and 0.240 mg/L respectively whereas they range from less than 0.010 mg/L to about 0.030 mg/L in the other four sites.

Conclusion: field filtered and refrigerated nitrite samples with concentrations at 5X the reporting limit (RL) or above were held for up to 28 days with low probability of any significant impact on the analytical values obtained from the measurement process used in this evaluation. Samples with nitrite concentrations less than the 5X RL are not recommended to be held past 48 hours.

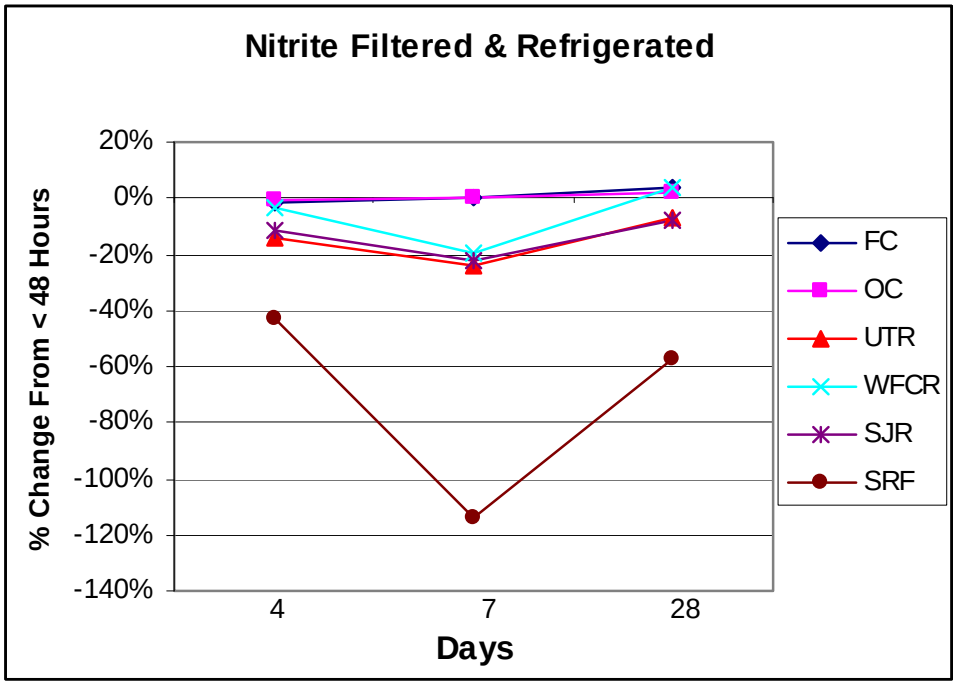

Figure 3.6 – Plots of % Change Relative to < 48 Hour Sample Values for Nitrite Filtered and Refrigerated

3.7 Nitrate – Field Filtered and Frozen

This data was obtained from calculations using the nitrate + nitrite samples and subtracting the nitrate values from them. These samples were field filtered and frozen for storage. The MDL for nitrate analysis is assumed to be the same as for nitrite which is 0.010 mg/L and the RL is likewise assumed to be 0.020 mg/L. Detailed comparisons of metadata from all six sample sites are provided in Tables A 7.1 to A.7.6 in Appendix A.

In general, the metadata in Tables A 7.1 to A 7.6 and the plots in Figure 3.7 show that some of the samples have less than 10% difference from the corresponding samples held less than 48 hours even up to 28 days holding time while others exhibit widely varying percentage changes.

Figure 3.7 shows that the change in concentration of nitrate values compared to those from samples held < 48 hours is much less than 10% for the FC, OC, and SJR sites even up to 28 days holding time. An examination of the data to explain these large differences reveals that the concentration of nitrate in these three data sets is higher than in the samples from the other data sets. The average nitrate concentrations in the FC and OC sites are about 0.025 mg/L and 0.030 mg/L respectively and about 0.015 mg/L for the SJR site whereas they range from 0.012 mg/L to 0.024 mg/L in the other three sites.

Conclusion: field filtered and frozen nitrate samples with concentrations of 2X the reporting limit (RL) or above were held for up to 28 days with low probability of any significant impact on the analytical values obtained from the measurement process used in this evaluation. Samples with nitrate concentrations less than 2X the RL are not recommended to be held past 2 days.

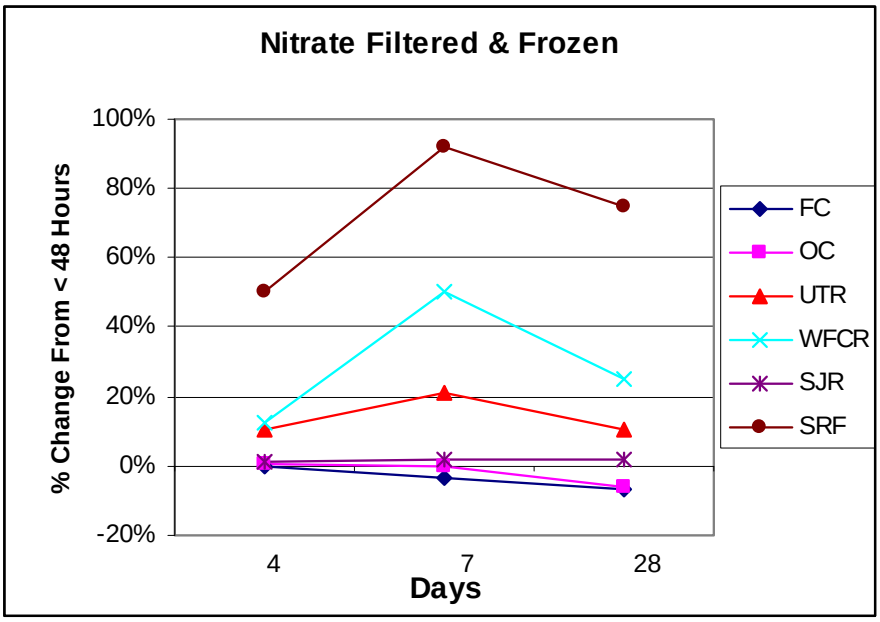

Figure 3.7 – Plots of % Change Relative to < 48 Hour Sample Values for Nitrate Filtered and Frozen

3.8 Nitrate – Field Filtered and Refrigerated

This data was obtained from calculations using the nitrate + nitrite samples and subtracting the nitrate values from them. These samples were field filtered and refrigerated for storage. The MDL for nitrate analysis is assumed to be the same as for nitrite which is 0.010 mg/L and the RL is likewise assumed to be 0.020 mg/L. Detailed comparisons of metadata from all six sample sites are provided in Tables A 8.1 to A.8.6 in Appendix A.

In general, the metadata in Tables A 8.1 to A 8.6 and the plots in Figure 3.8 show that some of the samples have less than 10% difference from the corresponding samples held less than 48 hours even up to 28 days holding time while others exhibit widely varying percentage changes.

Figure 3.8 shows that the change in concentration of nitrate values compared to those from samples held < 48 hours is much less than 10% for the FC, OC, and SJR sites even up to 28 days holding time. An examination of the data to explain these large differences reveals that the concentration of nitrate in these three data sets is much higher than in the samples from the other data sets. The average nitrate concentrations in the FC and OC sites are about 0.025 mg/L and 0.030 mg/L respectively and about 0.015 mg/L for the SJR site whereas they range from 0.010 mg/L to 0.023 mg/L in the other three sites.

Conclusion: field filtered and refrigerated nitrate samples with concentrations of 2X the reporting limit (RL) or above were held for up to 28 days with low probability of any significant impact on the analytical values obtained from the measurement process used in this evaluation. Samples with nitrate concentrations less than 2X the RL are not recommended to be held past 2 days.

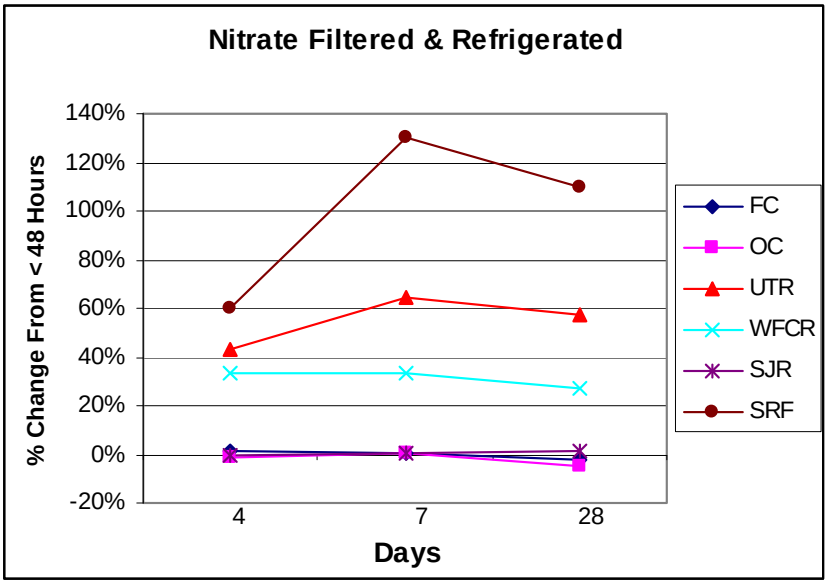

Figure 3.8 – Plots of % Change Relative to < 48 Hour Sample Values for Nitrate Filtered and Refrigerated

3.9 Ammonia – Field Filtered and Frozen

The ammonia samples were field filtered and frozen for storage. The MDL for ammonia analysis is 0.010 mg/L and the RL is 0.020 mg/L. Detailed comparisons of metadata from all six sample sites are provided in Tables A 9.1 to A.9.6 in Appendix A.

In general, the metadata in Tables A 9.1 to A 9.6 and the plots in Figure 3.9 show that the data sets are widely variable with respect to comparisons made with respective samples held for < 48 hours before analysis. Unlike other analyses where similar trends were observed, the concentrations of ammonia were not greatly different from one another and ranged from a little less than 0.02 mg/L to a little more than 0.1 mg/L.

None of the blanks were excessively high and ranged from -0.002 mg/L to 0.010 mg/L. Likewise, the precision within each of the data sets remained tight. For example, the Confidence Intervals at a 95% Confidence Level ranged from 0 to 0.002 mg/L. However, changes in concentrations from the referenced ammonia concentrations in samples held < 48 hours ranged from -0.009 mg/L to 0.006 mg/mL and, further, the values at the two ends of this range corresponded to the samples with lower concentrations. For example, a change of only 0.002 mg/L from the < 48 hour result of 0.021 mg/L represents about a 10% difference.

Conclusion: field filtered and frozen samples for ammonia analysis should be analyzed within 48 hours of collection.

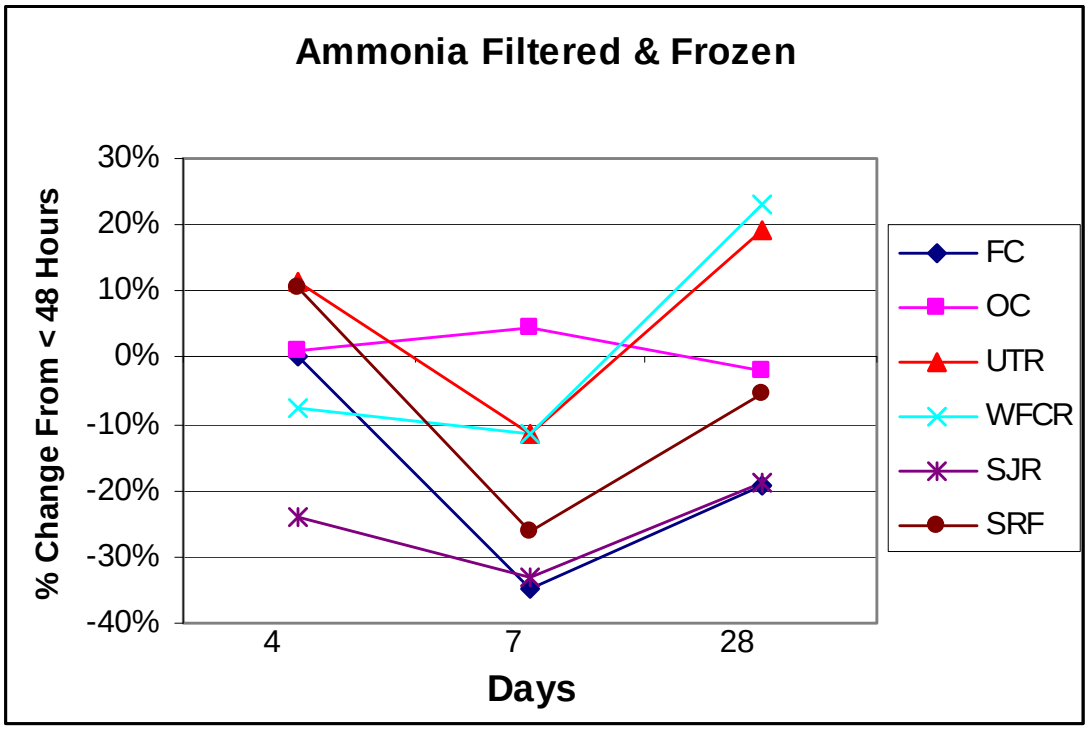

Figure 3.9 – Plots of % Change Relative to < 48 Hour Sample Values for Ammonia Filtered and Frozen

3.10 Ammonia – Field Filtered and Refrigerated

The ammonia samples were field filtered and refrigerated for storage. The MDL for ammonia analysis is 0.010 mg/L and the RL is 0.020 mg/L. Detailed comparisons of metadata from all six sample sites are provided in Tables A 10.1 to A.10.6 in Appendix A.

In general, the metadata in Tables A 10.1 to A 10.6 and the plots in Figure 3.10 show that the data sets are widely variable with respect to comparisons made with respective samples held for < 48 hours before analysis. Unlike other analyses where similar trends were observed, the concentrations of ammonia were not greatly different from one another and ranged from 0.006 mg/L to a little more than 0.1 mg/L.

One of the blanks (from UTR) was high (0.027 mg/L) but the others were in a typical range from -0.001 mg/L to 0.007 mg/L. Likewise, the precision within each of the data sets remained reasonable. For example, the Confidence Intervals at a 95% Confidence Level ranged from 0 to 0.006 mg/L. However, changes in concentrations from the referenced ammonia concentrations in samples held < 48 hours ranged from -0.015 mg/L to 0.006 mg/mL.

Conclusion: field filtered and refrigerated samples for ammonia analysis should be analyzed within 48 hours of collection.

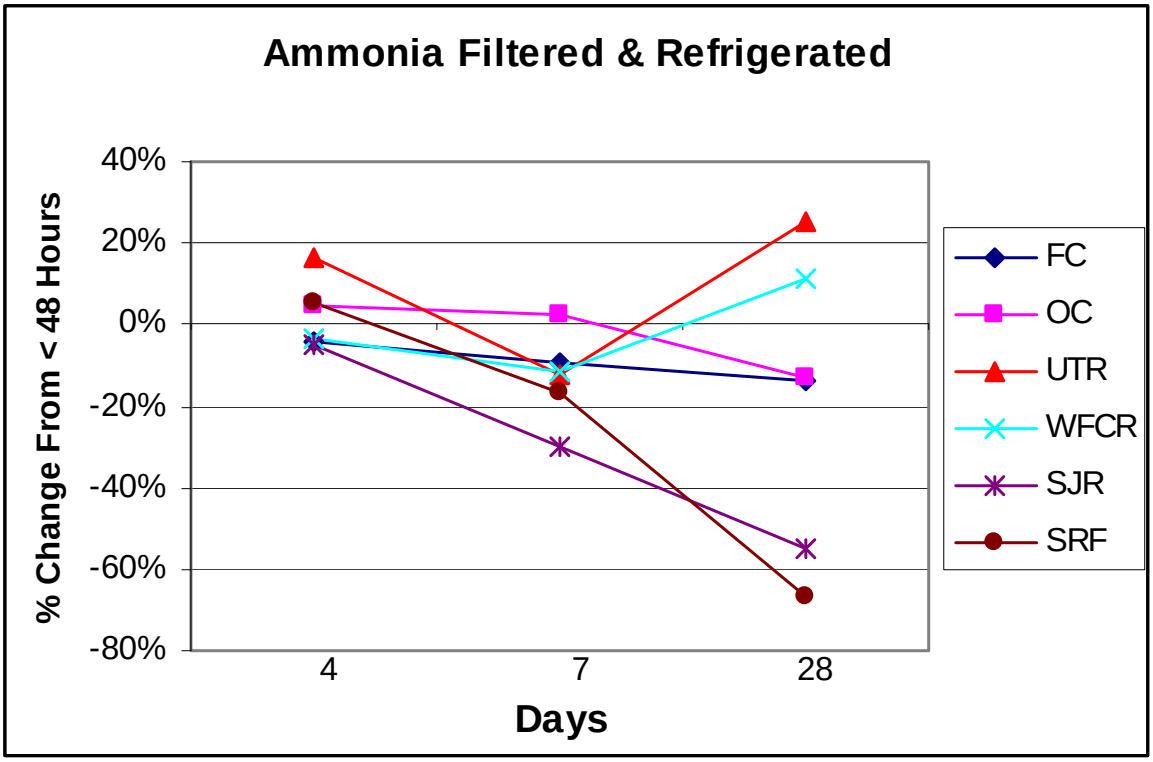

Figure 3.10 – Plots of % Change Relative to < 48 Hour Sample Values for Ammonia Filtered and Refrigerated

3.11 Soluble Reactive Phosphate (SRP) – Field Filtered and Frozen

The SRP samples were field filtered and frozen for storage. The MDL for SRP analysis is 0.005 mg/L and the RL is 0.050 mg/L. Detailed comparisons of metadata from all six sample sites are provided in Tables A 11.1 to A.11.6 in Appendix A.

In general, the metadata in Tables A 11.1 to A 11.6 and the plots in Figure 3.11 show that samples may be held frozen for up to 4 days with less than 10% difference from samples analyzed in < 48 hours. Most of the data for samples held up to 7 days also meets the < 10% difference objective; the Franklin Creek (FC) data was the single exception with a difference in mean concentration of 11.8%. It should be noted that the FC concentration data ranged from 0.017 – 0.019 mg/L whereas concentrations of SRP in the other five sites ranged from 0.024 to 0.073 mg/L so that a small change of 0.002 mg/L results in a relatively high percentage change.

Conclusion: field filtered and frozen soluble reactive phosphorus (SRP) samples with concentrations at the reporting level (RL) or above were held for up to 7 days with low probability of any significant impact on the analytical values obtained from the measurement process used in this evaluation. Samples with SRP concentrations less than the RL are not recommended to be held past 48 hours.

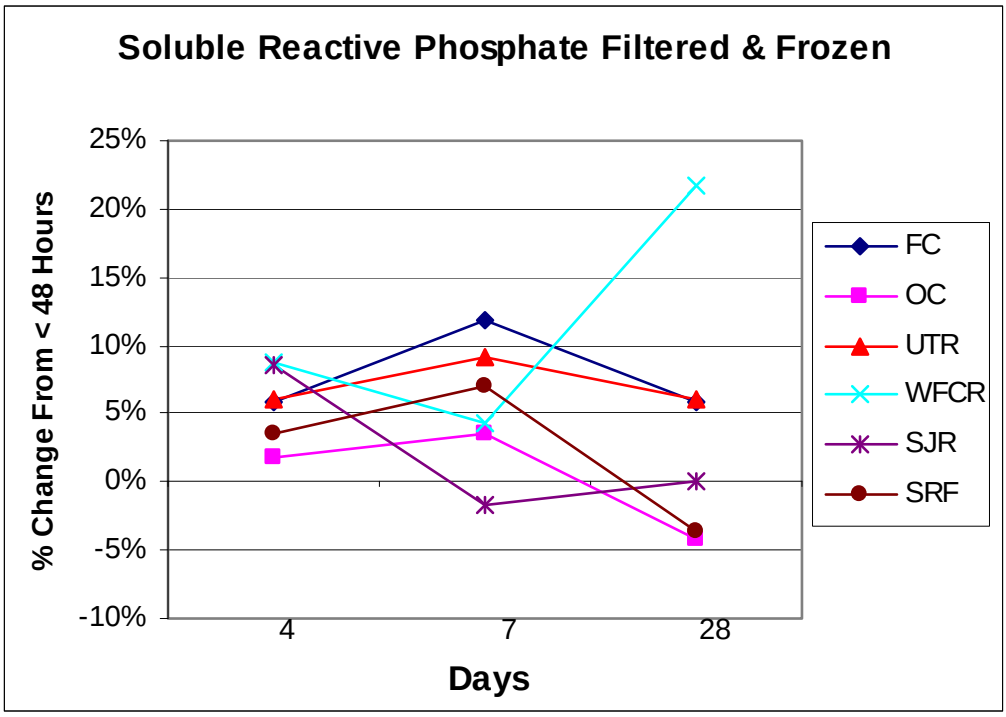

Figure 3.11 – Plots of % Change Relative to < 48 Hour Sample Values for Soluble Reactive Phosphate Filtered and Frozen

3.12 Soluble Reactive Phosphate (SRP) – Field Filtered and Refrigerated

The SRP samples were field filtered and refrigerated for storage. The MDL for SRP analysis is 0.005 mg/L and the RL is 0.050 mg/L. Detailed comparisons of metadata from all six sample sites are provided in Tables A 12.1 to A.12.6 in Appendix A.

In general, the metadata in Tables A 12.1 to A 12.6 and the plots in Figure 3.12 show that samples may be held refrigerated for up to 4 days with less than 10% difference from samples analyzed in < 48 hours. Samples for soluble reactive phosphate that are held longer than 4 days begin to exhibit more widely variable data.

Conclusion: field filtered and refrigerated soluble reactive phosphorus samples with concentrations at the reporting level (RL) or above were held for up to 4 days with low probability of any significant impact on the analytical values obtained from the measurement process used in this evaluation. Samples with SRP concentrations less than the RL are not recommended to be held past 48 hours.

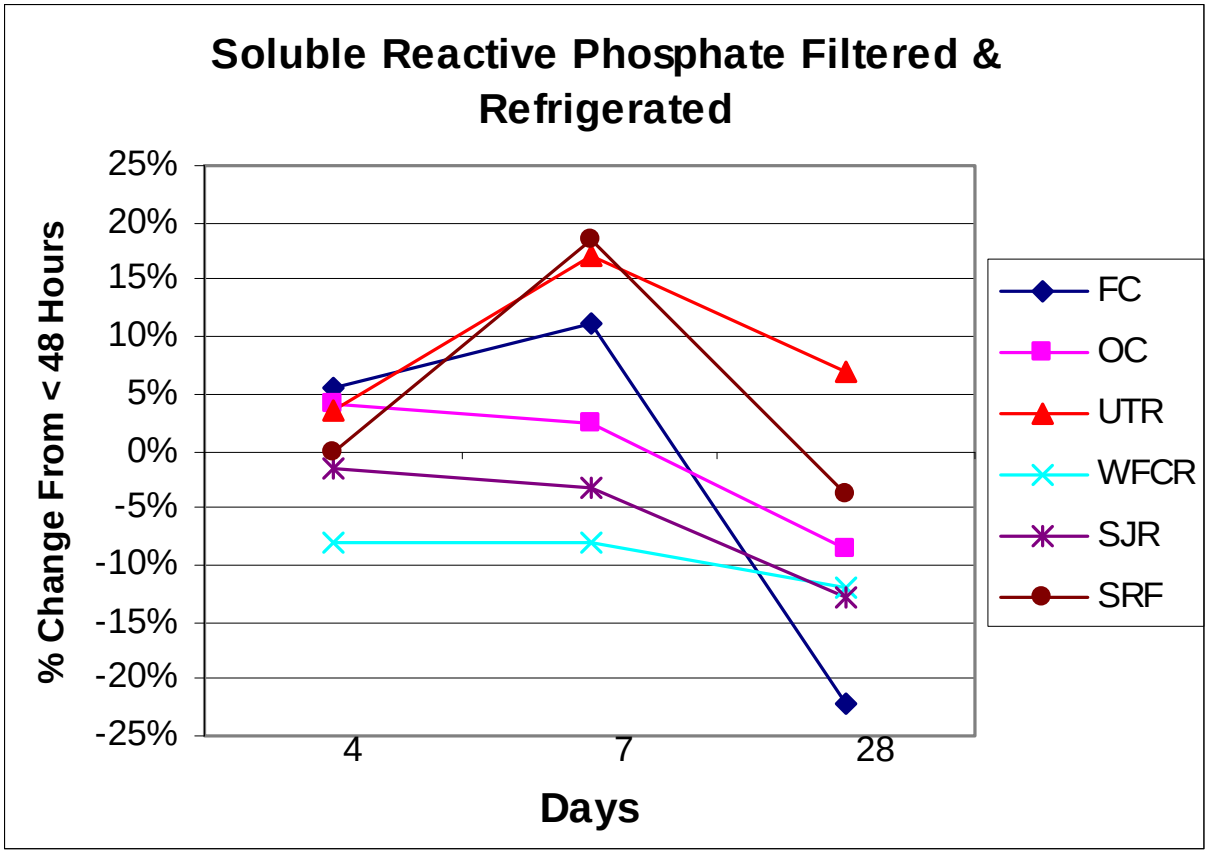

Figure 3.12 – Plots of % Change Relative to < 48 Hour Sample Values for Soluble Reactive Phosphate Filtered and Refrigerated

Appendix A – Data Trends By Sampling Site

1 - Total Nitrogen Data Trends By Sampling Site - Refrigerated

All Samples are Unfiltered and Refrigerated

Table A 1.1 - FC (Franklin Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days *	25.286	0.000	0.800	3.4%	-	-
4 Days **	25.314	-0.215	0.415	1.8%	0.028	0.1%
7 Days **	25.357	-0.133	0.667	2.8%	0.071	0.3%
28 Days **	26.857	-0.202	1.048	4.2%	1.571	6.2%

* Analyzed at 10 X
** Diluted 10 X before digestion

Table A 1.2 - OC (Orcutt Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	32.8	0.448	0.618	2.0%	-	-
4 Days	34.414	0.334	0.715	2.2%	0.614	1.8%
7 Days	34.286	0.413	1.920	6.1%	0.486	1.4%
28 Days	34.843	0.454	0.757	2.3%	1.043	3.1%

Table A 1.3 - UTR (Upper Truckee River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.163	0.005	0.013	8.5%	-	-
4 Days	0.151	-0.012	0.007	5.0%	-0.012	-7.4%
7 Days	0.178	-0.004	0.021	12.7%	0.015	9.2%
28 Days	0.204	0.002	0.046	24.2%	0.041	25.2%

Table A 1.4 - WFCR (West Fork Carson River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.164	-0.010	0.008	5.6%	-	-
4 Days	0.146	-0.013	0.004	2.9%	-0.018	-11.0%
7 Days	0.152	-0.012	0.009	6.6%	-0.012	-7.3%
28 Days	0.155	0.001	0.016	11.5%	-0.009	-5.5%

Table A 1.5 - SJR (San Joaquin River at Vernalis) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	2.154	-0.124	0.053	2.7%	-	-
4 Days	2.146	-0.194	0.044	2.2%	-0.008	-0.4%
7 Days	2.079	-0.064	0.047	2.4%	-0.075	-3.5%
28 Days	2.107	-0.082	0.044	2.3%	-0.047	-2.2%

Table A 1.6 - SRF (Sacramento River at Freeport) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.176	-0.007	0.028	17.2%	-	-
4 Days	0.164	-0.003	0.008	5.0%	-0.012	-6.8%
7 Days	0.185	0.032	0.017	9.8%	0.009	5.1%
28 Days	0.169	-0.007	0.012	7.5%	-0.007	-4.0%

2 - Total Phosphorus Data Trends By Sampling Site - Refrigerated

All Samples are Unfiltered and Refrigerated

Table A 2.1 - FC (Franklin Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.035	0.001	0.005	16.9%	-	-
4 Days	0.012	-0.009	0.002	18.6%	-0.023	-65.7%
7 Days	0.033	-0.002	0.007	23.3%	-0.002	-5.7%
28 Days	0.032	-0.007	0.004	13.0%	-0.003	-8.6%

Table A 2.2 - OC (Orcutt Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days *	2.540	0.003	0.115	4.9%	-	-
4 Days **	1.668	-0.011	0.085	5.5%	-0.872	-34.3%
7 Days *	2.013	-0.001	0.092	5.0%	-0.527	-20.7%
28 Days *	2.561	-0.006	0.161	6.8%	0.021	0.8%

* Diluted 10 X before digestion
** Diluted 5 X before digestion

Table A 2.3 - UTR (Upper Truckee River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.036	0.002	0.016	48.5%	-	-
4 Days	0.040	0.003	0.005	14.5%	0.004	11.1%
7 Days	0.045	0.001	0.008	20.3%	0.009	25.0%
28 Days	0.044	0.005	0.004	10.6%	0.008	22.2%

Table A 2.4 - WFCR (West Fork Carson River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.031	-0.009	0.004	13.6%	-	-
4 Days	0.031	0.003	0.005	16.4%	0	0.0%
7 Days	0.033	-0.003	0.004	11.8%	0.178	6.5%
28 Days	0.036	0.001	0.001	3.0%	0.005	16.1%

Table A 2.5 - SJR (San Joaquin River at Vernalis) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.178	No Value	0.012	7.4%	-	-
4 Days	0.182	-0.009	0.007	4.0%	0.004	2.2%
7 Days	0.156	0.002	0.011	7.3%	-0.022	-12.4%
28 Days	0.158	0.002	0.015	10.2%	-0.020	-11.2%

Table A 2.6 - SRF (Sacramento River at Freeport) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.053	No Value	0.005	11.1%	-	-
4 Days	0.048	0.001	0.002	4.2%	-0.005	-9.4%
7 Days	0.046	0.00	0.010	23.7%	-0.007	-13.2%
28 Days	0.039	0.003	0.011	29.3%	-0.014	-26.4%

3 - Nitrate + Nitrite Data Trends By Sampling Site - Frozen

All Samples are Field Filtered and Frozen

Table A 3.1 -FC (Franklin Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days *	25.786	0	0.135	0.6%	-	-
4 Days **	25.686	-0.023	0.112	0.5%	-0.1	-0.4%
7 Days **	25.157	-.215	0.315	1.4%	-0.629	-2.4%
28 Days **	24.029	-0.097	0.045	0.2%	-1.757	-6.8%

* Analyzed at 5 X dilution
** Analyzed at 10 X dilution

Table A 3.2 -OC (Orcutt Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days *	32.471	0.406	0.148	0.5%	-	-
4 Days **	32.571	0.352	0.158	0.5%	0.1	0.3%
7 Days **	32.314	0.406	0.099	0.3%	-0.157	-0.5%
28 Days **	30.486	0.492	0.083	0.3%	-1.985	-6.1%

* Analyzed at 5 X dilution
** Analyzed at 10 X dilution

Table A 3.3 -UTR (Upper Truckee River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.048	-0.007	0.002	4.9%	-	-
4 Days	0.049	-0.002	0.003	5.9%	0.001	2.1%
7 Days	0.046	-0.007	0.001	3.0%	-0.002	-4.2%
28 Days	0.049	-0.002	0.001	2.0%	0.001	2.1%

Table A 3.4 -WFCR (West Fork Carson River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.042	-010	0.001	2.3%	-	-
4 Days	0.043	-0.005	0.002	4.6%	0.001	2.4%
7 Days	0.042	-0.007	0.001	2.5%	0	0.0%
28 Days	0.046	-0.001	0	1.2%	0.004	9.5%

Table A 3.5 -SJR (San Joaquin River at Vernalis) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	1.474	-0.162	0.019	1.4%	-	-
4 Days	1.484	-0.092	0.010	0.8%	0.010	0.7%
7 Days	1.483	-0.082	0.007	0.5%	0.009	0.6%
28 Days	1.500	-0.105	0	0	0.026	1.8%

Table A 3.6 -SRF (Sacramento River at Freeport) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.019	-0.011	0.002	12.6%	-	-
4 Days	0.020	-0.007	0.003	17.5%	0.001	5.3%
7 Days	0.022	-0.004	0.001	4.5%	0.003	15.8%
28 Days	0.024	-0.003	0.001	4.8%	0.005	26.3%

4 - Nitrate + Nitrite Data Trends By Sampling Site - Refrigerated

All Samples are Field Filtered and Refrigerated

Table A 4.1 - FC (Franklin Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	25.400	0	0.456	1.9%	-	-
4 Days	25.429	-0.239	0.116	0.5%	0.029	0.1%
7 Days	25.271	-0.209	0.166	0.7%	-0.129	-0.5%
28 Days	24.471	-0.095	0.070	0.3%	-0.929	-3.7%

Table A 4.2 - OC (Orcutt Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	32.400	0.408	0.160	0.5%	-	-
4 Days	32.000	0.495	0.107	0.4%	-0.4	-1.2%
7 Days	32.557	0.389	0.159	0.5%	0.157	0.5%
28 Days	30.771	0.624	0.158	0.6%	-1.629	-5.0%

Table A 4.3 - UTR (Upper Truckee River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.043	-0.010	0.001	2.5%	-	-
4 Days	0.045	-0.006	0.001	2.8%	0.002	4.7%
7 Days	0.045	-0.007	0.001	2.1%	0.002	4.7%
28 Days	0.049	-0.001	0.001	2.0%	0.006	14.0%

Table A 4.4 - WFCR (West Fork Carson River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.041	-0.010	0.002	4.0%	-	-
4 Days	0.045	-0.003	0.001	3.6%	0.004	9.8%
7 Days	0.041	-0.007	0.001	1.8%	0	0.0%
28 Days	0.046	-0.001	0	1.2%	0.005	12.2%

Table A 4.5 - SJR (San Joaquin River at Vernalis) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	1.494	-0.208	0.014	1.0%	-	-
4 Days	1.484	-0.092	0.005	0.4%	-0.010	-0.7%
7 Days	1.496	-0.-79	0.005	0.4%	0.002	0.1%
28 Days	1.506	-0.105	0.007	0.5%	0.012	0.8%

Table A 4.6 - SRF (Sacramento River at Freeport) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.017	-0.010	0.001	9.1%	-	-
4 Days	0.020	-0.007	0.05	26%	0.003	17.6%
7 Days	0.022	-0.001	-.001	5.0%	0.005	29.4%
28 Days	0.023	-0.003	0.001	4.8%	0.006	35.3%

5 -Nitrite Data Trends By Sampling Site - Frozen

All Samples are Field Filtered and Frozen

Table A 5.1 - FC (Franklin Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.140	0.002	0.002	1.5%	-	-
4 Days	0.139	0.001	0.003	2.0%	-0.001	-0.7%
7 Days	0.141	0.002	0.001	0.7%	0.001	0.7%
28 Days	0.142	0.004	0.002	1.7%	0.002	1.4%

Table A 5.2 - OC (Orcutt Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.243	0.002	0.001	0.4%	-	-
4 Days	0.240	0.001	0.004	1.7%	-0.003	-1.2%
7 Days	0.243	0.002	0	0.2%	0	0.0%
28 Days	0.248	0.005	0.001	0.6%	0.005	2.1%

Table A 5.3 - UTR (Upper Truckee River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.029	0.005	0.001	3.7%	-	-
4 Days	0.028	0.005	0.001	3.8%	-0.001	-3.4%
7 Days	0.023	0	0.001	4.3%	-0.006	-20.7%
28 Days	0.028	0.006	0	1.9%	-0.001	-3.4%

Table A 5.4 - WFCR (West Fork Carson River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.026	0.005	0.001	2.2%	-	-
4 Days	0.025	0.004	0	0%	-0.001	-3.8%
7 Days	0.019	-0.002	0.004	21.1%	-0.007	-26.9%
28 Days	0.027	0.002	0.001	2.8%	0.001	3.8%

Table A 5.5 - SJR (San Joaquin River at Vernalis) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.036	0.005	0	1.1%	-	-
4 Days	0.032	0.001	0	0	-0.004	-11.1%
7 Days	0.028	-0.002	0	1.4%	-0.008	-22.2%
28 Days	0.032	0.002	0.001	3.3%	-0.004	-11.1%

Table A 5.6 - SRF (Sacramento River at Freeport) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.007	0.005	0	5.3%	-	-
4 Days	0.002	0.002	0.001	33.1%	-0.005	-71.4%
7 Days	-0.002	-0.002	0.001	-44.1%	-0.005	-71.4%
28 Days	0.003	0.002	0	0%	-0.004	-57.1%

6 - Nitrite Data Trends By Sampling Site - Refrigerated

All Samples are Field Filtered and Refrigerated

Table A 6.1 - FC (Franklin Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.140	0.002	0.001	0.6%	-	-
4 Days	0.138	-0.001	0.001	1.2%	-0.002	-1.4%
7 Days	0.140	0.003	0.001	0.9%	0	0.0%
28 Days	0.145	0.004	0.002	1.6%	0.005	3.6%

Table A 6.2 - OC (Orcutt Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.241	0.002	0.001	0.6%	-	-
4 Days	0.239	0.001	0.004	2.0%	-0.002	-0.8%
7 Days	0.241	0.001	0.002	0.8%	0	0.0%
28 Days	0.246	0.004	0.002	1.0%	0.005	2.1%

Table A 6.3 - UTR (Upper Truckee River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.029	0.005	0.002	6.3%	-	-
4 Days	0.025	0.004	0.001	3.0%	-0.004	-13.8%
7 Days	0.022	0	0.001	3.4%	-0.007	-24.1%
28 Days	0.027	0.005	0	1.8%	-0.002	-6.9%

Table A 6.4 - WFCR (West Fork Carson River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.026	0.005	0	2.0%	-	-
4 Days	0.025	0.004	0	1.5%	-0.001	-3.8%
7 Days	0.021	0	0	0%	-0.005	-19.2%
28 Days	0.027	0.006	0	0%	0.001	3.8%

Table A 6.5 - SJR (San Joaquin River at Vernalis) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.036	0.005	0	1.5%	-	-
4 Days	0.032	0.002	0	1.2%	-0.004	-11.1%
7 Days	0.028	-0.002	0	0%	-0.008	-22.2%
28 Days	0.033	0.002	0	0%	-0.003	-8.3%

Table A 6.6 - SRF (Sacramento River at Freeport) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.007	0.005	0	0%	-	-
4 Days	0.004	0.002	0	0%	-0.003	-42.9%
7 Days	-0.001	-0.002	0.001	-124%	-0.008	-114.3%
28 Days	0.003	0.002	0	13.2%	-0.004	-57.1%

7 -Nitrate Data Trends By Sampling Site - Frozen

All Samples are Field Filtered and Frozen

Table A 7.1 - FC (Franklin Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	25.639	No Value	0.132	0.6%	-	-
4 Days	25.564	No Value	0.131	0.6%	-0.075	-0.3%
7 Days	24.816	No Value	0.131	0.6%	-0.823	-3.2%
28 Days	23.980	No Value	0.134	0.6%	-1.659	-6.5%

Table A 7.2 - OC (Orcutt Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	32.311	No Value	0.226	0.8%	-	-
4 Days	32.401	No Value	0.225	0.8%	0.09	0.3%
7 Days	32.207	No Value	0.226	0.8%	-0.104	-0.3%
28 Days	30.396	No Value	0.230	0.8%	-1.915	-5.9%

Table A 7.3 - UTR (Upper Truckee River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.019	No Value	0.002	12.9%	-	-
4 Days	0.021	No Value	0.003	15.9%	0.002	10.5%
7 Days	0.023	No Value	0.002	8.4%	0.004	21.1%
28 Days	0.021	No Value	0.001	5.1%	0.002	10.5%

Table A 7.4 - WFCR (West Fork Carson River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.016	No Value	0.001	4.8%	-	-
4 Days	0.018	No Value	0.002	10.9%	0.002	12.5%
7 Days	0.024	No Value	0.004	19.0%	0.008	50.0%
28 Days	0.020	No Value	0.001	5.6%	0.004	25.0%

Table A 7.5 - SJR (San Joaquin River at Vernalis) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	1.438	No Value	0.019	1.5%	-	-
4 Days	1.452	No Value	0.010	0.8%	0.014	1.0%
7 Days	1.465	No Value	0.007	0.5%	0.027	1.9%
28 Days	1.468	No Value	0.001	0.1%	0.030	2.1%

Table A 7.6 - SRF (Sacramento River at Freeport) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.012	No Value	0.003	23.1%	-	-
4 Days	0.018	No Value	0.001	6.4%	0.006	50%
7 Days	0.023	No Value	0.002	7.4%	0.011	92%
28 Days	0.021	No Value	0.001	5.5%	0.009	75%

8- Nitrate Data Trends By Sampling Site - Refrigerated

All Samples are Field Filtered and Refrigerated

Table A 8.1 - FC (Franklin Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	24.907	0.001	0.130	0.6%	-	-
4 Days	25.303	-0.001	0.129	0.6%	0.396	1.6%
7 Days	25.091	0.003	0.131	0.6%	0.184	0.7%
28 Days	24.396	0.004	0.136	0.6%	-0.511	-2.1%

Table A 8.2 - OC (Orcutt Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	32.227	0.002	0.224	0.8%	-	-
4 Days	31.885	0.001	0.226	0.8%	-0.342	-1.1%
7 Days	32.385	0.001	0.225	0.8%	0.158	0.5%
28 Days	30.601	0.004	0.230	0.8%	-1.626	-5.0%

Table A 8.3 - UTR (Upper Truckee River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.014	0.005	0.001	8.8%	-	-
4 Days	0.020	0.004	0.002	8.7%	0.006	42.9%
7 Days	0.023	0	9.001	6.8%	0.009	64.3%
28 Days	0.022	0.005	0.001	5.1%	0.008	57.1%

Table A 8.4 - WFCR (West Fork Carson River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.015	0.005	0.002	11.8%	-	-
4 Days	0.020	0.004	0.002	8.9%	0.005	33.3%
7 Days	0.020	0	0.001	3.7%	0.005	33.3%
28 Days	0.019	0.006	0	2.8%	0.004	26.7%

Table A 8.5 - SJR (San Joaquin River at Vernalis) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	1.459	0.005	0.014	1.1%	-	-
4 Days	1.452	0.001	0.005	0.4%	-0.007	-0.5%
7 Days	1.468	-0.002	0.005	0.4%	0.009	0.6%
28 Days	1.473	0.002	0.007	0.5%	0.014	1.0%

Table A 8.6 - SRF (Sacramento River at Freeport) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.010	0.005	0.001	15.8%	-	-
4 Days	0.016	0.002	0.001	5.7%	0.006	60%
7 Days	0.023	-0.002	0.002	10.3%	0.013	130%
28 Days	0.021	0.002	0.001	7.3%	0.011	110%

9- Ammonia Data Trends By Sampling Site - Frozen

All Samples are Field Filtered and Frozen

Table A 9.1 - FC (Franklin Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.026	0.002	0.005	19.0%	-	-
4 Days	0.026	0.003	0.003	13.1%	0	0
7 Days	0.017	0.001	0.001	4.4%	-0.009	-34.6%
28 Days	0.021	0	0.003	15.5%	-0.005	-19.2%

Table A 9.2 - OC (Orcutt Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.114	0.001	0.001	0.9%	-	-
4 Days	0.115	0.003	0.002	1.8%	0.001	0.9%
7 Days	0.119	0.002	0.001	0.8%	0.005	4.4%
28 Days	0.112	0.002	0.002	1.7%	-0.002	-1.8%

Table A 9.3 - UTR (Upper Truckee River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.026	0.002	0.001	2.9%	-	-
4 Days	0.029	0	0.002	6.8%	0.003	11.5%
7 Days	0.023	-0.002	0.002	9.8%	-0.003	-11.5%
28 Days	0.031	0.006	0.001	3.2%	0.005	19.2%

Table A 9.4 - WFCR (West Fork Carson River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.026	0.010	0.001	2.9%	-	-
4 Days	0.024	0.003	0.002	11.0%	-0.002	-7.7%
7 Days	0.023	0	0.001	6.9%	-0.003	-11.5%
28 Days	0.032	0.006	0.001	2.3%	0.006	23.1%

Table A 9.5 - SJR (San Joaquin River at Vernalis) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.021	0.003	0.001	6.5%	-	-
4 Days	0.016	-0.001	0.001	4.6%	-0.005	-23.8%
7 Days	0.014	-0.001	0	0%	-0.007	-33.3%
28 Days	0.017	0.002	0.001	9.2%	-0.004	-19.0%

Table A 9.6 - SRF (Sacramento River at Freeport) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.019	0.004	0.002	8.8%	-	-
4 Days	0.021	0	0.002	9.9%	0.002	10.5%
7 Days	0.014	-0.002	0	0%	-0.005	-26.3%
28 Days	0.018	0.001	0.002	13.7%	-0.001	-5.3%

10- Ammonia Data Trends By Sampling Site - Refrigerated

All Samples are Field Filtered and Refrigerated

Table A 10.1 - FC (Franklin Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.022	0.002	0.002	7.6%	-	-
4 Days	0.021	0.001	0.001	5.3%	-0.001	-4.5%
7 Days	0.020	0.001	0.001	5.4%	-0.002	-9.1%
28 Days	0.019	0	0.001	5.7%	-0.003	-13.6%

Table A 10.2 - OC (Orcutt Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.114	0.002	0.002	1.7%	-	-
4 Days	0.119	0.002	0.006	5.1%	0.005	4.4%
7 Days	0.117	0.002	0.002	1.7%	0.003	2.6%
28 Days	0.099	-0.001	0.002	1.7%	-0.015	-13.2%

Table A 10.3 - UTR (Upper Truckee River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.024	0.027	0.001	5/7%	-	-
4 Days	0.028	0.005	0.003	10.9%	0.004	16.7%
7 Days	0.021	0.006	0.001	2.5%	-0.003	-12.5%
28 Days	0.030	0.006	0.001	2.5%	0.006	25.0%

Table A 10.4 - WFCR (West Fork Carson River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.026	0.001	0.001	2.9%	-	-
4 Days	0.025	0.006	0.001	4.3%	-0.001	-3.8%
7 Days	0.023	-0.001	0.001	6.7%	-0.003	-11.5%
28 Days	0.029	0.007	0.001	3.7%	0.003	11.5%

Table A 10.5 - SJR (San Joaquin River at Vernalis) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.020	0.005	0.001	5.0%	-	-
4 Days	0.019	-0.001	0.003	16.9%	-0.001	-5.0%
7 Days	0.014	-0.001	0	0%	-0.006	-30%
28 Days	0.009	0.002	0.001	17.6%	-0.011	-55%

Table A 10.6 - SRF (Sacramento River at Freeport) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.018	0.003	0.001	9.1%	-	-
4 Days	0.019	0	0.001	7.8%	0.001	5.6%
7 Days	0.015	-0.001	0.001	6.7%	-0.003	-16.7%
28 Days	0.006	0.003	0.006	111.5%	-0.012	-66.7%

11 - SRP Data Trends By Sampling Site - Frozen

All Samples are Field Filtered and Frozen

Table A 11.1 - FC (Franklin Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.017	-0.004	0.001	8.7%	-	-
4 Days	0.018	-0.003	0.002	13.2%	0.001	5.9%
7 Days	0.019	-0.002	0.003	16.2%	0.002	11.8%
28 Days	0.018	-0.001	0.002	11.7%	0.001	5.9%

Table A 11.2 - OC (Orcutt Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days *	0.457	-0.003	0.008	1.9%	-	-
4 Days *	0.465	-0.003	0.009	2.1%	0.008	1.8%
7 Days *	0.473	0	0.008	1.9%	0.016	3.5%
28 Days *	0.438	-0.001	0.005	1.3%	-0.019	-4.2%

* Analyzed at 3 X dilution

Table A 11.3 - UTR (Upper Truckee River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.033	-0.006	0.009	28.3%	-	-
4 Days	0.035	-0.001	0.004	12.2%	0.002	6.1%
7 Days	0.036	-0.001	0.004	13.2%	0.003	9.1%
28 Days	0.035	-0.001	0.001	3.2%	0.002	6.1%

Table A 11.4 - WFCR (West Fork Carson River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.023	-0.007	0.003	14.4%	-	-
4 Days	0.025	0	0.002	10.0%	0.002	8.7%
7 Days	0.024	-0.001	0.001	5.7%	0.001	4.3%
28 Days	0.028	0	0.003	13.0%	0.005	21.7%

Table A 11.5 - SJR (San Joaquin River at Vernalis) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.059	-0.005	0.001	2.5%	-	-
4 Days	0.064	0	0.001	2.5%	0.005	8.5%
7 Days	0.058	0.001	0.003	6.3%	-0.001	-1.7%
28 Days	0.059	-0.001	0.002	3.6%	0.0	0%

Table A 11.6 - SRF (Sacramento River at Freeport) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.028	-0.005	0.001	4.6%	-	-
4 Days	0.029	0	0.002	7.2%	0.001	3.6%
7 Days	0.030	0.001	0.001	5.9%	0.002	7.1%
28 Days	0.027	-0.001	0.001	4.7%	-0.001	-3.6%

12 - SRP Data Trends By Sampling Site - Refrigerated

All Samples are Field Filtered and Refrigerated

Table A 12.1 - FC (Franklin Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.018	-0.004	0.001	6.5%	-	-
4 Days	0.019	-0.004	0.001	6.5%	0.001	5.6%
7 Days	0.020	-0.001	0.002	11.6%	0.002	11.1%
28 Days	0.014	-0.001	0.002	15.8%	-0.004	-22.2%

Table A 12.2 - OC (Orcutt Creek) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days *	0.454	-0.003	0.008	2.0%	-	-
4 Days *	0.473	-0.001	0.006	1.4%	0.019	4.2%
7 Days *	0.465	0	0.003	0.7%	0.011	2.4%
28 Days *	0.415	-0.001	0.016	4.1%	-0.039	-8.6%

* Analyzed at 3 X dilution

Table A 12.3 - UTR (Upper Truckee River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.029	-0.005	0.003	10.7%	-	-
4 Days	0.030	0	0.004	13.6%	0.001	3.4%
7 Days	0.034	0.001	0	1.6%	0.005	17.2%
28 Days	0.031	-0.001	0.001	5.1%	0.002	6.9%

Table A 12.4 - WFCR (West Fork Carson River) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.025	-0.002	0.007	32.0%	-	-
4 Days	0.023	-0.001	0.003	13.5%	-0.002	-8.0%
7 Days	0.023	-0.004	0.002	11.3%	-0.002	-8.0%
28 Days	0.022	-0.001	0.001	5.8%	-0.003	-12.0%

Table A 12.5 - SJR (San Joaquin River at Vernalis) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.062	-0.005	0.003	4.8%	-	-
4 Days	0.061	0	0.001	2.4%	-0.001	-1.6%
7 Days	0.060	0.002	0.001	2.4%	-0.002	-3.2%
28 Days	0.054	-0.002	0.008	15.9%	-0.008	-12.9%

Table A 12.6 - SRF (Sacramento River at Freeport) Sampling Site

	Mean Conc. (mg/L)	Mean Blank (mg/L)	95% Conf. Interval (mg/L)	RSD	Change in mg/L	%Change from <2 Days
< 2 Days	0.027	-0.005	0.001	4.6%	-	-
4 Days	0.027	-0.001	0.001	4.6%	0.000	0%
7 Days	0.032	0.002	0.004	13.9%	0.005	18.5%
28 Days	0.026	-0.002	0.001	4.8%	-0.001	-3.7%

Appendix B – Confidence Intervals and Confidence Levels

When using environmental analytical data to form conclusions or to make decisions, confidence levels and the amount of variance in data sets are important values when assessing the data quality of analytical data generated in a project.

- For example, consider a data set where the average concentration of an analyte is 50 ug/L and decisions will be made based on whether a ± 10% change over time (i.e., ± 5 ug/L) occurred. If the average variance in the data is ± 2 ug/L then a 10% change in the average concentration of the analyte can be determined. But, if the average variance in the data is more than ± 5 ug/L then the variance is as large as the decision criterion (± 10%) making it unlikely that a ± 10% change in average concentration of the analyte can be determined.

All environmental analytical data contain variance (often called "error"). The operation of a measurement process does not produce one number but, rather, a variety of numbers. Each time a measurement process is used it can be expected to produce a slightly different number or set of numbers. This means that sets of numbers will differ among themselves, but to a lesser degree than the individual values. The difference among numbers or sets of numbers may be described as "variance" which is defined as the value approached by the average of a sum of the squares of deviations of individual measurements from the mean. [Taylor, Chapter 4, 1987]

Variance is calculated using standard deviation (δ) values. The standard deviation is the positive square root of variance and variance (sometimes designated with a "V") is thus $(\delta)^2$. Sources of variance may be broadly classified as errors from measurement sources of variance and errors from sample population sources of variance. Errors are usually expressed in terms of standard deviation (δ) [Taylor, Chapter 4, 1987]. An overall (or total) error may then be expressed by equation (1) where "error" is defined as "the difference between a measured value and the true value of the parameter measured." In equation (1) δ_o is an overall standard deviation, δ_m is the standard deviation of the measurement technique, and δ_p is the standard deviation of the sample population [Keith, et. al., 1983].

$$(1) \qquad (\delta_o)^2 = (\delta_m)^2 + (\delta_p)^2$$

The confidence interval is defined as the range of values within which some parameters may be expected to lie with a stated confidence. The confidence level is a percentage which is related to the probability of inclusion of the parameter of interest [Taylor, Chapter 4, 1987]. Using the previous example, there is a 95% probability (confidence level) that the variance will be ± 2 ug/L (error or confidence interval) of the average sample concentration of 50 ug/L of the target analyte.

Confidence level and variance are integrally related to each other and to a third parameter of a data set – the number of samples (or population) in it. In fact, one of the most frequently asked questions is how many samples should be analyzed in order to meet the data quality objectives of a project. The answer to that question was described in the relationship shown in equation (2) where N_s is the number of samples, *z* is the value of the standard normal variate based on the

level of confidence desired, δ_p is the standard deviation of the sample population, and *e* is the tolerable error in the estimate of the mean for the characteristic of interest [Keith, et. al., 1983].

$$N_s = \left(\frac{z\,\delta_p}{e} \right)^2 \qquad (2)$$

Using equation (2) if the sample population is expected to have a mean concentration of 0.1 mg/L with a standard deviation of 0.05 mg/L and the tolerable error (i.e., a desired error limit) in the mean at a 95% confidence level (where z = 1.96) is not to exceed 0.02 mg/L, then the estimated number of samples needed would be calculated in equation (3).

$$(3) \quad N_s = (1.96 \times 0.05 / 0.02)^2 = (0.098/0.02)^2 = (4.9)^2 = 24$$

It is important to know that each of these parameters affects the others by relatively different degrees (i.e., they do not exert equivalent changes to each other). This is shown graphically by Figures B1 – B3.

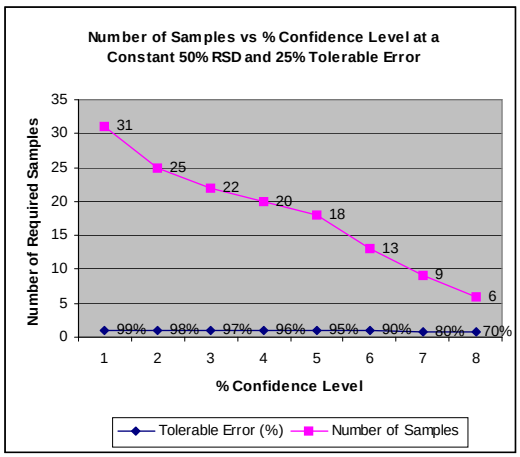

Figure B1 – Decreasing Confidence Levels

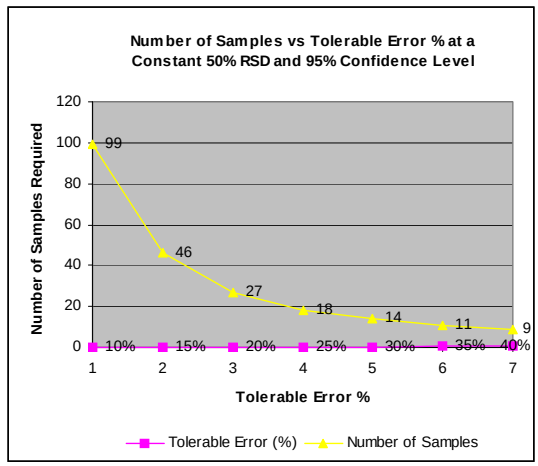

Figure B2 – Increasing Tolerable Error

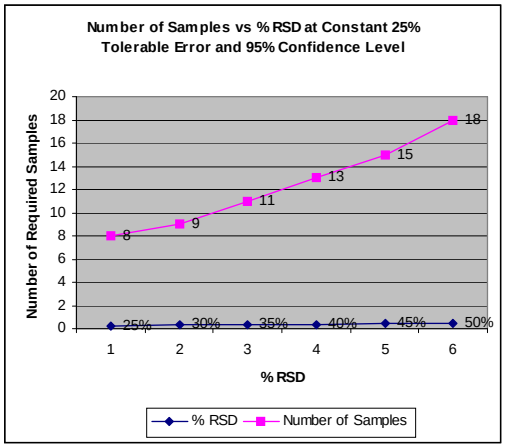

Figure B3 – Increasing Relative Standard Deviation

The three figures show that

- As the confidence level decreases from 99% to 70%, the number of samples required decreases from 31 to 6 (a five-fold decrease) with constant 50% RSD and 25% tolerable error.

- As the tolerable error increases from 10% to 40% the number of samples required decreases from 99 to 9 (an eleven fold decrease) with constant 50% tolerable error and 95% confidence level

- As the precision worsens (measured by doubling the RSD from 25% to 50%) the number of samples required increases from 8 to 18 (also roughly doubling) with a constant 25% tolerable error and 95% confidence level.

In general, the amount of error in a data set has the largest effect while the precision of the measurement operation has the least effect as demonstrated by the number of samples required.

Statistical Calculations

Equation (2) is one way of performing statistical calculations on data sets. While preparing a study design the number of samples required for a desired confidence level and tolerable error can be calculated as shown in the equation (3) example [Keith, et. al, 1983].

However, a more accurate set of equations which perform iterative determinations may also be used to meet the objectives for tolerable error and the confidence in estimating a mean concentration. Iterations are more accurate because the "t" distribution is the most appropriate for determining the number of samples when variability is estimated from sampling data. However, since one rarely has historical data to estimate the variability in a process or at an investigative site (the coefficient of variation (CV) or standard deviation are used to estimate variability) the "Z" distribution must be used to initially determine a number of samples. The number of samples calculated via the Z distribution is then fed into the equation using "t" (retaining all other parameters as specified for the Z) and the required "n" calculated again. This should be iterated until the "n" stabilizes. These equations have been incorporated into a software program that uses 3 iterations. The software program is named “Enviro-Calc” and it is one of three programs incorporated into a master utility named “DQO-PRO” [Keith et al., 1996]. These software programs were produced for a classified U.S. intelligence agency and are widely distributed and currently used by thousands of scientists from downloads through the American Chemical Society’s Division of Environmental Chemistry web site at www.EnvirofACS.org.

Two sets of equations implemented in the software program are presented below [Gilbert, 1987]. The first set will be used when the variability estimate is presented in absolute terms using the standard deviation. The second set of equations can be used when the variability is presented in relative terms using the coefficient of variation (i.e., % Relative Standard Deviation).

The equations for determining the number of samples needed to estimate a mean concentration when variability is estimated in absolute terms using the standard deviation are:

(4.A). First Pass Equation: $n = [Z(1\text{-alpha}/2)*s.d./d]^2$
(4.B). Second Pass Equation: $n = [t(1\text{-alpha}/2)*s.d./d]^2$

The equations for determining the number of samples to estimate a mean concentration when variability is estimated in relative terms using the coefficient of variation (relative standard deviation) are:

(5.A) First Pass Equation: $n = [Z(1\text{-alpha}/2)*CV/d(r)]^2$
(5.B) Second Pass Equation: $n = [t(1\text{-alpha}/2)*CV/d(r)]^2$

In these equations:

- Absolute (4 A and 4 B) - the standard deviation will be used and the allowable error also will be stated in absolute terms (the standard deviation and the allowable error must be in the same terms).
- Relative (5 A and 5 B) - the coefficient of variation will be used and the allowable error will be stated in relative terms.
- Z = the standard normal deviate from the Z distribution using alpha for a two-tailed distribution;
- s.d. = the standard deviation for a sample set;
- d = the amount of error tolerable in the estimate of the average in absolute terms (e.g., 4 mg/L);
- d(r) = the amount of error tolerable in the estimate of the average in relative terms (e.g., 5%); and,
- ^{2} = square the previous product.

We used these more accurate iterative equations to estimate confidence intervals with a 60% confidence level and seven samples.

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