Analysis of Sampling Plan Options for Tank 16H from the Perspective of Statistical Uncertainty (U)

E.P. Shine

February 2013

Applied Computational Engineering and Statistics
Computational Sciences
Savannah River National Laboratory
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Executive Summary

Tank 16H is a Type II waste tank in the H-Tank Farm at the Savannah River Site (SRS) near Aiken, SC. Over the time of operation, Tank 16H had leaked material from the primary vessel to the annulus, so that both of these regions of the tank require estimates of analyte concentrations in the residual material. The primary tank vessel has had no material subpopulations identified, so a random sampling plan is an appropriate basis for selecting sample locations for either composite sampling or discrete sampling. The annulus has three identified subpopulations: the material inside the dehumidification duct, the material outside the duct in the Southern quadrant, and the material outside the duct in the Northern, Western, and Eastern quadrants. A stratified sampling plan is an appropriate method to select sample locations in the annulus.

Six sampling options have been outlined by Pavletich and Wiggins [2012] for evaluations to estimate mean analyte concentrations in the primary vessel and the annulus. The objective of this report is to rank these options based on the perspective of concentration uncertainty. To accomplish this, a model for analyte concentration in the residual material was developed to compute the variance of the mean of the measured concentrations, and then the model was used to compute an upper 95% confidence limit (UCL95) for the actual mean analyte concentration. The concentration model was based on a geostatistical concept called the semivariogram which describes the correlation between concentration measurements on pairs of samples as decreasing with increasing separation distance between the sample locations.

Despite the presence of cooling coils and the limited of number of access points, all sampling options were assumed to be feasible. A rank order (best to worst) of the sampling options from the perspective of statistical uncertainty follows.

- Option 1, Baseline Compositing, has been the general approach used to study analyte concentrations in the residual material in waste tanks. It has the lowest upper 95% confidence limit for the mean concentration (UCL95) of any of the options for the primary vessel and the annulus.
- Option 3, Reduced Baseline Compositing, has a higher UCL95 than the baseline case, but is a viable option since lowering the number of locations per composite sample to 4 does not have a substantial impact on the UCL95.
- Option 5, Composited Annulus and Discrete Primary, is the third most favorable plan from the perspective of statistical uncertainty. The annulus composite sampling plan is the same as Option 1, but the primary vessel is sampled and analyzed based on discrete locations. From an uncertainty perspective, the UCL95 for the actual mean analyte concentration in the primary vessel will be higher from a discrete plan than the baseline composite plan of Option 1. Discrete sampling is nearly the same as reducing the number of locations in composite sampling to one per sample. So Option 5 can be considered a limiting case for Option 3.

- Option 6, Discrete Annulus and Discrete Primary, is the next most viable option. The primary vessel's UCL95 and the annulus' UCL95 increase from the baseline plan. This plan is less

favorable from an uncertainty perspective than Option 5, because it switches from composite sampling to discrete sampling in the annulus which has not undergone the same mixing during cleaning as the primary vessel.

- Option 2, Combined Compositing, and Option 4, Composited and Discrete Analysis, are the least effective plans from an uncertainty perspective. Both of these options combine residual from the primary vessel and the annulus into each of the composite samples. This consolidation of material from two separate target regions creates a systematic error of unknown magnitude when the objective is to estimate the mean analyte concentrations in these two regions separately. There is potential to highly inflate the UCL95s, but the systematic effects are difficult to impossible to quantify. The addition of some analyses for key analytes in discrete samples in Option 4 provides only a marginal benefit over Option 2, and makes the statistical analysis of the results more complicated.

1. Introduction

Tank 16H is a Type II waste tank in the H-Tank Farm at the Savannah River Site (SRS) near Aiken, SC. This report develops a concentration variability model for Tank 16H in order to compare candidate sampling plans for assessing the concentrations of analytes in the residual material in the annulus and on the floor of the primary vessel. A concentration variability model is used to compare candidate sampling plans based on the expected upper 95% confidence limit (UCL95) for the mean. The result is expressed as a rank order of candidate sampling plans from lowest to highest expected UCL95, with the lowest being the most desirable from an uncertainty perspective.

Tank 16H is 27 feet in height and has a primary shell 85 feet in diameter surrounded by an annulus. The nominal capacity of the tank is 1,030,000 gallons. The tank was placed into service in 1959. The tank contains 44 cooling coils, 40 of which are vertical cooling coils and 4 of which run horizontally across the bottom of tank. Although these cooling coils and a limited number of accesses in the top of the tank may place limits on the candidate sampling plans, the uncertainty ranking was determined assuming that the candidate sampling plans as described in this report are feasible.

The residual material in the tank is located in two regions: approximately 300 gallons in then primary tank and 3,300 gallons in the tank annulus. A report by Pavletich and Wiggins [2012] estimates that Tank 16H has material in the annulus that can be partitioned into three subpopulations:

- Subpopulation 1 is approximately 1,200 gallons of residual material present in the dehumidification duct.
- Subpopulation 2 is approximately 800 gallons of residual material outside the duct in the Southern quadrant of the annulus.
- Subpopulation 3 is approximately 1,300 gallons of residual material outside the duct in the Northern, Eastern, and Western quadrants of the annulus.

Separate inventory inputs from the annulus and the primary vessel are needed for performance assessment modeling.

2. Candidate Sampling Plans

The report by Pavletich and Wiggins [2012] describes six candidate sampling plans to be ranked based on their ability to reduce uncertainty. The plans are summarized below and described in more detail in Table 1.

- Option 1, Baseline Compositing, is similar to compositing plans previously used to assess the analyte concentrations in residual material. It involves separate composite sampling plans for the primary vessel and the annulus.

- Option 2, Combined Compositing, uses a single compositing plan involving residuals from both the primary vessel and the annulus.

- Option 3, Reduced Baseline Compositing, is essentially the same as Option 1, but residual material from fewer sample locations is obtained for each composite sample.

- Option 4, Composited and Discrete Analysis, begins with the sampling plan in Option 2, but adds some discrete sample analyses for selected key analytes.

- Option 5, Composited Annulus and Discrete Primary, is the same as Option 1 in the annulus, but provides for 3 to 5 discrete samples in the primary vessel.

- Option 6, Discrete Annulus and Discrete Primary Sampling and Analysis, provides for separate discrete sampling g plans in the primary vessel and the annulus.

Table 1. Candidate Sampling Plans

Option	Description	Sampling Approach	General Impact On Uncertainty
1	*Baseline Compositing* 15 samples from annulus 15 samples from primary	15 primary tank samples collected for 3 composite samples. 15 annulus samples (inside and outside duct locations) collected for 3 composite samples. Three arrays of 5 sample locations per array would be used to build the composite samples. Treats primary and annulus as separate populations.	Since it follows Sampling and Analysis Program Plan (SAPP), Pavletich [2012a] and the Quality Assurance Program Plan (QAPP), Pavletich [2012b] impact on uncertainty would be low (i.e., generally the same as that for Tanks 5 and 6). Is applicable for three populations in annulus
2	*Combined Compositing* 15 samples total from primary and annulus	15 total samples collected from the primary and annulus (exact number from annulus and primary is to be determined, but assume 10 samples from annulus and 5 samples from the primary). Treats annulus and primary as one population (primary material is treated like a mound inside the tank). A total of 3 composite samples would be generated and analyzed. Does not meet the performance assessment (PA) need for separate annulus and primary	Since it follows SAPP and QAPP, impact on uncertainty would be low (i.e., generally the same as that for Tanks 5 and 6) but results would be biased high by virtue of using more material in the annulus for compositing. Annulus material might have higher concentrations of soluble constituents.
3	*Reduced Baseline Compositing* <15 samples in annulus <15 samples in primary	<15 samples (3 arrays of <5 samples per array) collected for 3 composite samples for tank primary <15 samples (3 arrays of <5 samples per array) collected for 3 composite samples for the annulus. Treats primary and annulus as separate populations. A total of 6 composite samples would be generated and analyzed. Meets PA need for separate annulus and primary inventory inputs for modeling.	Using fewer than 5 sample locations for each composite would increase Fundamental Sampling Error and uncertainty.

Table 1 (Continued). Candidate Sampling Plans

| Option	Description	Sampling Approach	General Impact On Uncertainty
4	*Composited and Discrete Analyses* 15 samples total from primary and annulus used for compositing. Some discrete samples analyzed for key radionuclides and chemicals.	Same as Option 2 with 15 total samples collected from primary and annulus (exact number from annulus and primary is to be determined, but assume 10 samples from annulus and 5 samples from the primary). Three composite samples created for analysis, but some discrete sample material analyzed for key radionuclides and chemicals and ratios established to estimate the residual tank inventories. Treats annulus and primary as one population (annulus material treated like a mound inside the tank) but some discrete samples (locations) would also be analyzed for selected key constituents. Would not meet the PA need for separate annulus and primary inventory inputs for modeling, so comparison of ratios from composite and discrete sample analyses might be used to determine the separate inventories.	This would have the highest uncertainty and the results and inventory probably would be highly biased toward the more soluble constituents in the annulus material.
5	Composited Annulus and Discrete Primary 15 samples in annulus 3 to 5 samples in primary	Collect 15 samples from annulus (3 arrays of 5 samples per array) for compositing (this would treat the material inside the duct as a mound in annulus.) Three composite samples would be analyzed. Collect discrete samples from primary. Assume a maximum of 5; most likely 3 to 4 discrete samples would be collected and analyzed, the actual number will depend on mapping. Meets the PA need for separate annulus and primary inventory inputs for modeling.	Expected lower level of primary tank inventory uncertainty, but higher uncertainty level in annulus. Impact unknown until analyses results received.

Table 1 (Continued). Candidate Sampling Plans

Option	Description	Sampling Approach	General Impact On Uncertainty
6	*Discrete Annulus and Discrete Primary Sampling and Analysis* ≥5 samples in annulus ±5 samples in primary	Collect discrete samples from annulus and primary. Assume at least 5 discrete samples would be collected in the annulus. Assume a maximum of 5; most likely 3 to 4 discrete samples would be collected and analyzed, the actual number will depend on mapping. Would meet the PA need for separate annulus and primary inventory inputs for modeling.	

3. Statistical Methods for Uncertainty Evaluation

Section 3 describes the common framework for comparing different sampling options based on a concentration variability model. A more detailed exposition can be found in Appendix A of this report. The objective is to develop a formula for the variance of the mean of concentration measurements of an analyte from tank residual material samples based on spatial and measurement variability. The variance of the mean of the analyte concentration measurements is used to determine a 95% upper confidence limit (UCL95) for the actual mean concentration in the targeted region of the vessel, whether that be only the primary vessel, only the annulus, or both the primary vessel and the annulus. This model does not include a systematic component of variability that arises when consolidating residual material from the primary vessel and the annulus to form composite samples (Option 2) when separate measurement results are needed for the primary vessel and the annulus.

The UCL95 is interpreted as an upper bound for the actual mean analyte concentration. Sampling plans with lower expected UCL95s are preferred from an uncertainty perspective. The uncertainty perspective is one of a number of attributes that must be evaluated in order to generate a sampling plan. Some other considerations outside the scope of this report include representativeness of the sampling scheme, engineering and feasibility considerations such as access to the residual material, and the economics of the plans.

Partitioning uncertainties by their source terms in the concentration variability model provides insight into how these components affect the variance of the mean of the concentration measurements and provides a basis for a spreadsheet tool to compare different sampling design configurations. The concentration variability model was developed from a geostatistical perspective as described by Journel and Huijbregts [1978]. The fundamental concept used to describe spatial variability in this report is the semivariogram shown in Figure 1. A semivariogram represents half of the variance of the difference between two measurements based on the distance between their sample locations.
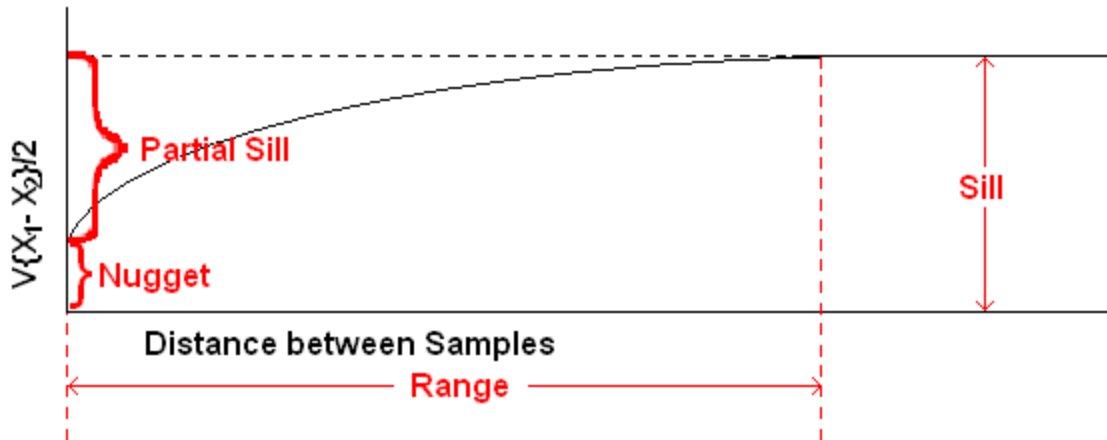
Figure 1. The Semivariogram

In Figure 1 it can be seen that the variance for the difference of two sample measurements increases with the distance between the samples. Eventually the variance of the difference between two sample measurements stops increasing after a separation distance called the range. The height (value of) the semivariogram for separation distances greater than the range is called the sill. The sill equals the variance of a measurement on a single sample. Measurements on samples separated by a distance greater than the range cannot be correlated. A key feature of the semivariogram is that as the distance between potential sample locations decreases to zero, the variance does not drop to zero. This non-zero semivariogram value, when two samples are essentially collocated, is called the nugget. The nugget arises from measurement error, sample preparation error, and a spatial discontinuity attributable to distinct (non-zero) differences from granule to granule of material. The measurement error is handled outside the variogram in this report, and the other factors that influence the semivariogram are considered nil. Therefore, the nugget will be set to zero in the semivariogram used in this report. The difference between the sill and the nugget is called the partial sill. The partial sill describes only the spatial component (less any particle to particle discontinuity) of the variance between measurements.

Two types of sampling plans are considered for selecting residual material sampling locations in the targeted areas of Tank 16H: random sampling and stratified random sampling. Random sampling is implemented by simply selecting all sample locations at random within the targeted region. When it is known that separate populations of residual material are present in the targeted region, then the populations are placed into separate nonoverlapping regions of the targeted area called strata. A basic stratified random sampling plan selects one location from each stratum for every composite sample. This concept can be extended by allowing for more than one location in some strata. More than one location in a stratum may be preferred when a stratum has more material than other strata, has more expected variability in an analyte concentration than in other strata, or may be cheaper to sample than other strata. Either random sampling or stratified random sampling can be used to select locations for

discrete or composite sampling plans. For simplicity, when composite sampling is considered, the variance formula was derived based on one location per composite sample per stratum.

Consider a composite sampling plan with m measurements on each of n composite samples based on k locations. The samples are obtained using a stratified random sampling plan. Appendix A provides an expression for the mean analyte concentration $\bar{M}_{n,k,m}^{strat}$ from a composite sampling plan based on stratified random sampling. It is

$$\bar{M}_{n,k,m}^{strat} = \frac{\sum_{j=1}^{n}\sum_{\ell=1}^{m} M_{j,\ell}}{mn} = \frac{\sum_{j=1}^{n}\sum_{\ell=1}^{m}\left[\left(\frac{\sum_{i=1}^{k} T_{j,i}}{k}\right)\left(1+\varepsilon_{j,\ell}\right)\right]}{mn}, \tag{1}$$

where $M_{j,\ell}$ is the ℓ-th measurement (ℓ = 1, 2, ..., m) on the j-th composite sample (j = 1, 2, ..., n). The actual mean analyte concentration in the entire targeted area of Tank 16H is T. The value of T is unknown, and the overall objective of the sampling plan is to obtain information from samples in order to estimate the value of T. The actual mean analyte concentration in the sample of residual material obtained from the i-th (stratum) location (i = 1, 2, ..., k) for composite sample j is $T_{j,i}$. Since the sample locations are selected according to a random scheme, the mean concentration value, $T_{j,i}$, for the sample from stratum i (i = 1, 2, ..., k) for composite sample j (j = 1, 2, ..., n) is a random variable. The sum $\sum_{i=1}^{k} T_{j,i}\Big/k$ is the true mean analyte concentration for the j-th composite sample (j = 1, 2, ..., n). This is a random variable because of the sample location selection process. The expected value is the mean result that would be obtained if a sampling plan could be executed a very large number of times. The expected value of $\sum_{i=1}^{k} T_{j,i}\Big/k$ is T. This means that each composite sample leads to an unbiased estimate of the actual analyte concentration in the targeted area. The (unknown) analytical and preparation error for measurement replicate ℓ (ℓ = 1, 2, ..., m) on composite sample j (j = 1, 2, ..., n) is $\varepsilon_{j,\ell}$. A relative semivariogram is used in the following expressions (and semivariogram terms for the partial sill, $PSill$, and the semivariogram values, γ, are tagged with the label "Rel" to indicate that they are parameters of a relative semivariogram), where the relative semivariogram equals the semivariogram divided by the square of the mean analyte concentration in the targeted region of the tank. For this stratified random sampling plan for composite sampling, the relative variance of the mean of the measurement results is as follows.

$$V_{Rel}\left\{\bar{M}_{n,k,m}^{strat}\right\} = \frac{\sigma_{meas}^{2}}{mn} + \left(PSill^{Rel} - \frac{n-1}{kn}\gamma_{within}^{Rel} - \frac{(k-1)}{k}\gamma_{among}^{Rel}\right) + \left(PSill^{Rel} - \frac{(k-1)}{k}\gamma_{among}^{Rel}\right)\frac{\sigma_{meas}^{2}}{mn} \tag{2}$$

where σ_{meas}^{2} is the relative measurement variance and $PSill^{Rel}$ is the relative partial sill (which is the relative spatial variance). The analyte concentrations from different sample locations in the targeted area of Tank 16H will be correlated if the sample locations are closer together than the range. The spatial correlation structure has been simplified for this analysis by considering separately any pair of

samples from locations that lie within the same stratum and any pair of samples from locations that lie in different strata. This natural partitioning comes about because the sample locations tend to be closer together when they are in the same stratum and further apart when they lie in different strata. Consequently, the analyte concentrations from pairs of samples obtained from locations within the same stratum tend to be more correlated than the analyte concentrations from pairs of samples from locations in different strata. The correlations for all pairs of samples that lie within the same stratum are averaged, and the correlations for all pairs of samples in different strata are averaged. The semivariogram (half the variance of the difference between two measurements) value γ_{within}^{Rel} is related to the mean correlation of pairs of measurements from sample locations in the same stratum, and γ_{among}^{Rel} is related to the mean correlation of pairs of measurements from sample locations in different strata. The relationship between the covariance (scaled correlation) between pairs of analyte concentration measurements and the semivariogram partial sill value is discussed in Appendix A Section A.1.

Assuming that the mean measured analyte concentrations for the individual composite samples are not significantly different from one another, the UCL95 is defined by the following expression,

$$UCL95 = \bar{M}_{n,k,m}^{strat}\left(1 + t\sqrt{V_{Rel}\left\{\bar{M}_{n,k,m}^{strat}\right\}}\right),$$

(3)

and the relative UCL95 is given by

$$UCL95_{Rel} = \frac{UCL95}{\bar{M}_{n,k,m}^{strat}} = 1 + t\sqrt{V_{Rel}\left\{\bar{M}_{n,k,m}^{strat}\right\}},$$

(4)

where t represents the 95-th percentile of a Student's t distribution with mn-1 degrees of freedom.

When the plan is discrete sampling with locations selected by random sampling, Formula (2) reduces to

$$V_{Rel}\left\{\bar{M}_{n,m}^{discrete}\right\} = \left(1 + PSill^{Rel}\right)\frac{\sigma_{meas}^2}{mn} + \left(PSill^{Rel} - \frac{n-1}{n}\gamma_{discrete}^{Rel}\right),$$

(5)

where $\bar{M}_{n,m}^{discrete}$ is the mean of the concentration measurements of the discrete samples with locations obtained by random sampling, and the relative semivariogram associated with the mean of the covariances of the concentrations between all pairs of discrete samples is $\gamma_{discrete}^{Rel}$. The UCL95 and the UCL95$_{Rel}$ are

$$UCL95 = \bar{M}_{n,m}^{discrete}\left(1 + t\sqrt{V_{Rel}\left\{\bar{M}_{n,m}^{discrete}\right\}}\right),$$

(6)

and the relative UCL95 is given by

$$UCL95_{Rel} = \frac{UCL95}{\bar{M}_{n,m}^{discrete}} = 1 + t\sqrt{V_{Rel}\left\{\bar{M}_{n,m}^{discrete}\right\}},$$

(7)

respectively, where t represents the 95-th percentile of a Student's t distribution with mn-1 degrees of freedom.

4. Evaluation of the Sampling Options

This section evaluates the sampling options based on the expected UCL95$_{Rel}$ for each plan. The variance of the mean of measurements for a composite sample plan based on stratified random sampling was given in Section 3. The statistical evaluation of the plan options will assume that the separation distances between pairs of samples from locations in different strata are effectively larger than the range. Therefore, the semivariogram, $\gamma_{among}^{Rel} = PSill^{Rel}$, which means that the concentrations for pairs of samples from locations in different strata are not correlated. The reduced formula for the relative variance of the mean of measurements on composite samples based on a stratified random sampling design is

$$V_{Rel}\left\{\overline{M}_{n,k,m}^{strat}\right\} = \frac{\sigma_{meas}^2}{mn} + \left(\frac{PSill^{Rel}}{k} - \frac{n-1}{kn}\gamma_{within}^{Rel}\right) + \left(\frac{PSill^{Rel}}{k}\right)\frac{\sigma_{meas}^2}{mn} \tag{8}$$

The sample uncertainty criteria in this report assume that the relative measurement standard deviation is 10% of the actual concentration. An examination of the relative measurement standard deviations from the Tank 5 concentration measurement results in Shine [2012], suggests the 10% is typical of the analytical results based on replicate runs. The relative spatial standard deviation of a single sample concentration is assumed to be 25% of the actual analyte concentration in the targeted region of the tank). Therefore, the relative partial sill is 0.0625, since it equals the relative spatial variance (square of the relative spatial standard deviation). The relative semivariogram value (half the variance difference in the analyte concentrations between pairs of samples from locations within the same stratum) is assumed to be 50% of the sill. These parameters appear to be better representations of the primary vessel than the annulus because the material in the primary vessel is assumed to be fairly homogeneous due to mixing whereas the material in the annulus did not undergo the type of mixing performed in the primary vessel. There is no prior history of executing a closure sampling plan for an annulus in another tank.

Table 2 is based on a composite sampling plan with the locations selected by stratified random sampling. All plans in Table 2 are based on 3 composite samples and 3 measurements per composite sample. The uncertainty results for Option 1, Baseline Compositing, are given in the top line (shaded in blue) of Table 2 with k = 5 locations per composite sample. Option 3, Reduced Baseline Compositing, is represented by the remaining lines in Table 2 in which only the number of locations per composite sample have been reduced. The relative standard deviation of the mean of the concentration measurements and the UCL95$_{Rel}$ are given in the two right columns of Table 2. The relative standard deviation is not seen to increase much dropping to 4 locations per composite sample. The relative standard deviation is expected to more than double if there were only one location per sample: this is the same as discrete sampling with 3 samples from locations selected by random sampling from the entire targeted region of the tank.

Table 2. UCL95 for the Mean Concentration Measurements from Composite Samples with Locations Selected by Stratified Random Sampling

n	k	m	σ^2_{meas}/mn	Term 2[♠]	Term 3[♠]	$V_{Rel}\{\bar{M}^{strat}_{n,k,m}\}$	$S_{Rel}\{\bar{M}^{strat}_{n,k,m}\}$	$UCL95_{Rel}$
3	5	3	0.001111	0.008333	0.000014	0.009458	9.73%	1.181
3	4	3	0.001111	0.010417	0.000017	0.011545	10.74%	1.200
3	3	3	0.001111	0.013889	0.000023	0.015023	12.26%	1.228
3	2	3	0.001111	0.020833	0.000035	0.021979	14.83%	1.276
3	1	3	0.001111	0.041667	0.000069	0.042847	20.70%	1.385

$$\text{♠}\ Term\ 2 = PSill^{Rel} - \frac{n-1}{kn}\gamma^{Rel}_{within} - \frac{(k-1)}{k}\gamma^{Rel}_{among}, \quad Term\ 3 = \left(PSill^{Rel} - \frac{(k-1)}{k}\gamma^{Rel}_{among}\right)\frac{\sigma^2_{meas}}{mn}, \text{ and}$$

$$UCL95_{Rel} = UCL95 \big/ \bar{M}^{strat}_{n,k,m}$$

Table 3 is similar in form to Table 2 but represents the results of a discrete sampling plan with the sample locations chosen by random sampling. Assuming the same semivariogram parameter values as in Table 2, the numbers of discrete samples in Table 3 were varied from 1 to 10, but the number of measurements per sample remained 3. Tables 2 and 3 have one case in common: 3 samples, 1 location per sample, and 3 measurements per sample. The common case is shaded gray in both tables. The relative standard deviations for the means of the concentration measurements are larger for the discrete sampling plans in Table 3 than the composite sampling plans in Table 2 (other than the one common case). A sensitivity analysis presented in Appendix B demonstrates that the relative standard deviations for the mean of the concentration measurements appear to increase proportionately with an increase in the relative spatial variance, the $PSill^{Rel}$, for all of the composite sampling plans evaluated in Table 2 and all of the discrete sampling plans evaluated in Table 3. So the relative ordering of the sampling plans based on the relative standard deviation of the mean of the concentration measurements is not sensitive to increases in the relative spatial variance, $PSill^{Rel}$.

The discrete sampling plans considered in Table 3 have larger $UCL95_{Rel}$s than the composite sampling plan in Option 1. The sensitivity study in Appendix B, shows similar results when the relative spatial standard deviation, $\sqrt{PSill_{Rel}}$[1], increases from 25% to 50%.

The relative standard deviation of the mean of the concentration measurements and the $UCL95_{Rel}$ both assume that there will be no statistically significant sample-to-sample variance when the results are analyzed. The $UCL95_{Rel}$s display significantly greater differences among the discrete sampling plans in Table 3 than among the composite sampling plans in Table 2. The reason for this is that the $UCL95_{Rel}$ in Table 2 is based on an unchanging Student's t value since every plan had precisely 3 measurements on 3 composite samples, whereas the Student's t values in the calculations of the $UCL95_{Rel}$s in Table 3 reflect considerably different numbers of measurements for each case beginning with 30 measurements in the top line and decreasing to just 3 measurements on a single sample in the last line. Note that any sampling plan based on analyses of a single sample, whether it is a composite sample or a discrete sample, results in a set of measurements, that when analyzed, understates the true uncertainty because the spatial variance component has not been captured in the data.

Table 3. UCL95 for the Mean Concentration Measurements from Discrete Samples with Locations Selected by Random Sampling

n	k	m	σ^2_{meas}/mn	Term 2♠	Term 3♠	$V_{Rel}\{\bar{M}^{discrete}_{n,m}\}$	$S_{Rel}\{\bar{M}^{discrete}_{n,m}\}$	$UCL95_{Rel}$
10	1	3	0.000333	0.034375	0.000021	0.034729	18.64%	1.317
9	1	3	0.000370	0.034722	0.000023	0.035116	18.74%	1.320
8	1	3	0.000417	0.035156	0.000026	0.035599	18.87%	1.323
7	1	3	0.000476	0.035714	0.000030	0.036220	19.03%	1.328
6	1	3	0.000556	0.036458	0.000035	0.037049	19.25%	1.335
5	1	3	0.000667	0.037500	0.000042	0.038208	19.55%	1.344
4	1	3	0.000833	0.039063	0.000052	0.039948	19.99%	1.359
3	1	3	0.001111	0.041667	0.000069	0.042847	20.70%	1.385
2	1	3	0.001667	0.046875	0.000104	0.048646	22.06%	1.444
1	1	3	0.003333	0.062500	0.000208	0.066042	25.70%	1.750

$$\spadesuit \, Term\,2 = PSill^{Rel} - \frac{n-1}{n}\gamma^{Rel}_{within}, \, Term\,3 = PSill^{Rel}\frac{\sigma^2_{meas}}{mn}, \text{ and } UCL95_{Rel} = UCL95/\bar{M}^{discrete}_{n,m}$$

Now the sampling options can be considered. For Option 1, Baseline Compositing Plan, the relative standard deviation of the mean of the concentration measurements, $S_{Rel}\{\bar{M}_{n,k,m}\}$, is 9.73%. The UCL95 is 1.18 times the actual analyte concentration in the targeted region of the tank.

Option 3 is the same sampling plan as Option 1 but with fewer locations per composite sample. For 4 locations per composite sample, the relative standard deviation of the mean of the analyte concentration measurements is 10.74%, and the UCL95 is 1.20 times the actual analyte concentration in the targeted region of the tank. For 3 locations per composite sample, the relative standard deviation of the mean of the analyte concentration measurements is 12.26%, and the UCL95 is 1.23 times the actual analyte concentration in the targeted region of the tank. Fewer than 3 locations per composite sample were not considered. Option 3 with 4 or 3 locations does not appear to drive the UCL95 substantially higher than observed in Option 1, Baseline Compositing, based on the assumed measurement and spatial uncertainties. This evaluation does not consider the representativeness of the sampling plan.

Option 2, Combined Compositing, is basically the same sampling plan as Option 1, Baseline Compositing, except the sampled region of the tank in Option 2 is both the primary vessel and the annulus. The random uncertainty evaluation is the same as Option 1, but Option 2 also brings in a systematic error component, since Option 2 estimates a volumetrically weighted mean of the entire Tank 16H (primary vessel and annulus together). When this estimate is applied to just the primary vessel or just the annulus, there is a systematic difference not considered in Formula (8). This systematic difference will vary by analyte. If the analyte concentration is roughly the same in the primary vessel and the annulus, this systematic error component will be relatively low. However, when key analyte concentrations differ between the primary vessel and the annulus, one of the estimates will be overestimated and the other will be underestimated. This systematic error is not quantified in this report, but the potential for large

systematic differences between the primary vessel and the annulus relegates Options 2 and 4 to be the least desirable sampling plans based on expected uncertainty.

Sampling Options 5 and 6 involve a discrete sampling plan. The variance of the mean of concentration measurements for discrete sampling, where the locations were selected by random sampling from the targeted region of the tank is given by Appendix A Formula (A16). This also corresponds to $k = 1$ (one location per sample) from the limiting case of composite sampling with one stratum when the locations were selected by stratified sampling. It is assumed that the discrete samples will be separated by a distance greater than the range, making $\gamma_{discrete}^{Rel}$ equal to the PSill^{Rel}.

$$V_{Rel}\left\{\overline{M}_{n,k,m}^{strat}\right\} = \left(1 + PSill^{Rel}\right)\left(1 + \frac{\sigma_{meas}^2}{mn}\right) - 1 \tag{9}$$

All of the UCL95s computed for discrete sampling appear to be larger than those for composite sampling (except for the common case). The assumption that discrete samples could be located sufficiently far apart for their analyte concentrations to be uncorrelated lowers their relative standard deviations and relative UCL95s. Correlated concentrations from samples from pairs of locations closer than the range will produce higher values for the relative standard deviations and the relative UCL95s, making the composite sampling plans even more favorable than the discrete plans from the perspective of uncertainty.

5. Summary and Conclusions

The sampling options have been compared on the basis of their uncertainties. The uncertainty perspective is one of a number of attributes that must be evaluated in order to generate a sampling plan. Some other considerations outside the scope of this report include representativeness of the sampling scheme, engineering and feasibility considerations such as access to the residual material, and the economics of the plans.

The following sampling options are ranked best to worst based on their capability of producing low expected UCL95s for mean analyte concentrations.

1. Sampling Option 1, Baseline Compositing, provides the lowest UCL95.
2. Sampling Option 3, Reduced Compositing, raises the UCL95s from the Baseline Composing Case. However, the increase in the UCL95 for 4 locations per composite sample does not substantially raise the UCL95 based on the assumptions given in Section 4 of this report.
3. Sampling Option 5, Composited Annulus and Discrete Primary, has an identical sampling plan for the annulus to Option 1, but uses discrete sampling in the primary vessel. Therefore, the UCL95 for the annulus is the same as Option 1, but the UCL95 for the primary vessel is the same as Option 6, Discrete Annulus and Discrete Primary Sampling and Analysis, which has a higher UCL95 than sampling Option 1.
4. Sampling Option 6, Discrete Annulus and Discrete Primary Sampling and Analysis, has higher UCL95s in the annulus and the primary vessel than Options 1 and 3. Sampling Option 6 has the same UCL95 as sampling Option 5 in the primary vessel, but a higher UCL95 than for the annulus.
5. Sampling Option 4, Composited and Discrete Analysis, consolidates material from the primary vessel and the annulus in every sample. The potential systematic error when considering this bound for the mean of only the annulus material or for the mean of only the primary vessel material makes this option undesirable from an uncertainty perspective. The addition of analyses of discrete samples for key constituents layers a discrete plan for a partial set of analytes on top of the composite plan. Since this plan has about the same number of samples as Sampling Option 5, it is less desirable from an uncertainty perspective for those constituents only analyzed on the composite samples.
6. Sampling Option 2, Combined Compositing, leads to systematic errors in using the results to represent only the primary vessel or only the annulus. It is the least favorable sampling plan from an uncertainty perspective.

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Appendix A: Tank Sampling Framework

This appendix develops a common framework for comparing different sampling options. The objective is to develop a general formula for the variance of the mean of concentration measurements of an analyte based on components of spatial and measurement variability. Partitioning uncertainties by their source terms provides insight into how these components affect the variance of the mean of the concentration measurements and provides a basis for a spreadsheet tool to compare different sampling design configurations.

Section A.1 describes the concept of intrinsic stationarity and introduces the semivariogram, a concept arising from geology and mining applications that is useful in describing variability between samples based on the distance between their locations. Section A.2 describes the concept of a proportional effect and introduces the relative semivariogram. Section A.3 describes an analysis of variance (ANOVA) procedure to compute a variance of a possibly nonlinear function involving correlated variables and then describes a special case for the variance of a product of two independent variables. Section A.4 applies the variance calculation procedures in Section A. to determine the variance of the mean of sample measurements when the sampling plan involves (1) discrete samples with locations selected by random sampling, (2) composite samples with locations selected by random sampling, and (3) composite samples with locations selected by stratified random sampling.

A general discussion of semivariograms, relative semivariograms, and the proportional effect can be found in references by Journel and Huijbregts [1978], Deutsch and Journel {1992], and Cressie [1993].

A.1.   Intrinsic Stationarity and the Semivariogram

Consider the concentration of an analyte in the residual material on the floor of a tank once the process of cleaning and removing of material from the tank floor is complete. Initially assume that there are no distinct material populations within the tank. The analyte concentrations Z in the residual material typically exhibit some spatial variability across the expanse of the tank floor. The concentration at a particular location identified by the vector coordinates s is denoted as $Z(s)$, and the concentration at a location h (direction and distance) units away from s is denoted by $Z(s+h)$. To describe this spatial variability, a model called intrinsic stationarity is employed. Assuming isotropic conditions, intrinsic stationarity is defined by the following two relations:

$$E\{Z(s+h)-Z(s)\}=0$$
$$V\{Z(s+h)-Z(s)\}=2\gamma(\|h\|)$$

(A1)

where E and V denote mathematical expectation and variance, respectively, and $\|h\|$ is the Euclidean distance norm. Isotropy implies that only the separation distance not the direction defines the nature of the expected difference between the measurements at two locations. Formula (A1) describes the spatial distribution of the actual concentration of an analyte in the residual material as having a constant mean concentration and having the variance of the difference between actual concentrations at pairs of

locations as depending on the distance between two locations regardless of direction. The function $\gamma(\boldsymbol{h})$ is called the semivariogram and, in general, may depend on the direction as well as distance between pairs of sample locations, and the function $\gamma(\|\boldsymbol{h}\|)$ is called an isotropic semivariogram because the latter depends only on the distance between samples, not the direction of the difference between locations. The covariance among measurements on two samples within the tank can be characterized by plotting them as a function of distance between their measurement locations. It is expected that the covariance between pairs of measurements decreases as a function of increasing separation distance. Alternatively a semivariogram can be used in place of the covariance function.

The semivariogram in Figure A.1 (repeated from Figure 1 in Section 3) portrays half of the variance of the difference between concentration measurements on two samples as a function of their sample separation distance. In Figure A.1 the expected difference between two measurements is a nondecreasing function of the separation distance. Once two measurements are separated by at least a distance referred to as the range, they are considered uncorrelated[1]. The height of the semivariogram at distances greater than the range is called the sill. The sill is also equal to the variance of a single measurement:

$$Sill = \frac{V\left\{X_1 - X_2 \mid d_{X_1,X_2} \geq Range\right\}}{2} = \frac{V\left\{X_1\right\} + V\left\{X_2\right\}}{2} = \frac{\sigma_X^2 + \sigma_X^2}{2} = \sigma_X^2 \tag{A2}$$

where X_1 and X_2 are two measurements on samples from locations separated by distance d_{X_1,X_2}. The notation V denotes the variance operation, and the fence "|" indicates the variance is conditional on the expression to the right of "|" in Formula (A2).
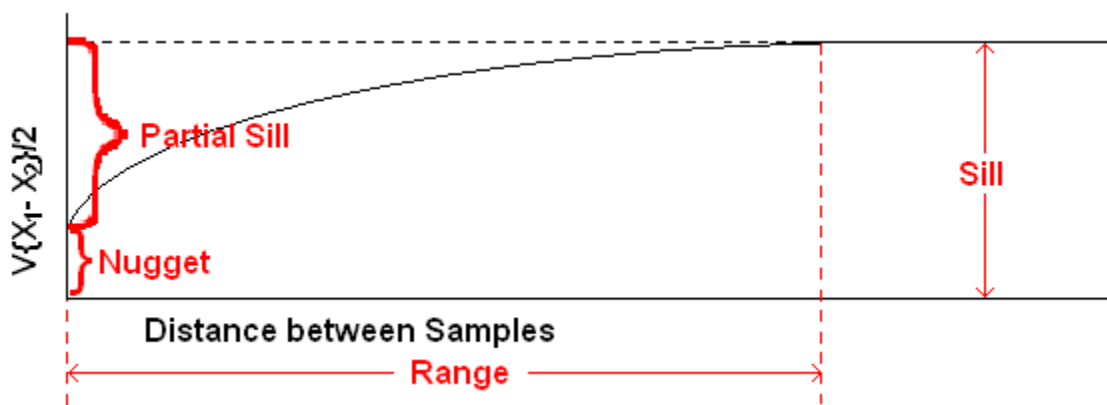
Figure A.1 The Semivariogram

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[1] In this report, the semivariogram model assumes that the maximum value of the semivariogram is attained when two sample locations are separated by a distance at least as large as the range, as opposed to semivariogram models that asymptote to the largest semivariogram value. For those latter models, the range is defined as the sample separation distance when the variogram is practically close to the sill value.

As the distance between two potential sample locations shrinks toward zero, the semivariogram can intercept the y-axis at a value greater than zero: this is called the nugget effect that can arise from measurement error, material preparation error, or a spatial discontinuity attributable to distinct non-zero differences from granule to granule of material. The partial sill (*PSill*) equals the sill minus the nugget effect, and is the difference between the sill and the limit point of the semivariogram when the separation distance shrinks to zero. The semivariogram has units of measure equal to the concentration units squared. The relationship between the covariance function and the semivariogram is as follows.

$$Cov\{Z(\boldsymbol{s}+\boldsymbol{h}),Z(\boldsymbol{s})\}=Sill-\gamma(\|\boldsymbol{h}\|)=PSill+Nugget-\gamma(\|\boldsymbol{h}\|).$$ (A3)

A.2. The Proportional Effect and the Relative Semivariogram

A common situation occurs when the targeted region of a tank such as the primary vessel or the annulus can be partitioned into nonoverlapping regions defining distinct populations of residual material based on earlier sampling and tank history. The partitioned areas are called strata. Generally, samples of residual material within the same stratum are assumed to be obtained from locations that are considerably closer together than samples located in different strata. Consequently, actual analyte concentrations in pairs of samples from the same stratum are considered to be at least as correlated as those pairs of actual analyte concentrations in pairs of samples located in different strata. Although the concentration of an analyte in the residual material within each stratum in the tank may exhibit intrinsic stationarity, the concentration of the residual material will not generally exhibit intrinsic stationarity across strata. However, if one assumes that a proportional effect[2] exists between the stratum semivariograms and their means, then a relative semivariogram can be used to model the residual material across the entire tank floor. Thus, the relative semivariogram is

$$\gamma(\|\boldsymbol{h}\|)^{Rel}=\gamma(\|\boldsymbol{h}\|)\Big/E^2\{Z(\|\boldsymbol{h}\|)\},$$ (A4)

and it is not limited to any particular stratum. The shape of the relative semivariogram is the same as the semivariogram in Figure A.1, since they differ by only the scale factor in the denominator of Formula (A4).

A.3. Formulas for the Variance

Two variance formulas will be used in the next section to express the variance of a mean of composite sample results as a function of spatial variability of the residual material on the tank floor and the measurement variability.

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[2] A proportional effect arises when semivariograms in different neighborhoods can be made to coincide by dividing them by a function of their means.

The following expression for the expectation of a function B of two random variables X and Y will be used to determine the expressions for the variance.

$$E\{B\}=\sum_x\sum_y p_{(x,y)}b_{(x,y)}=\sum_x p_x\sum_y p_{y|x}b_{(x,y)}=\sum_x p_x E_Y\left\{b_{(x,y)}\,|\,X=x\right\}=E_X\left\{E_Y\{B|X=x\}\right\},\qquad\text{(A5)}$$

where $p_{(x,y)}, p_x,$ and $p_{y|x}$ are the joint probability of random variables X and Y, the marginal probability of X, and the conditional probability of Y given $X = x$, respectively, and the set of all possible values for B is the set $\left\{b_{(x,y)}, \text{for all possible values of } x \text{ and } y\right\}$.

Two variance formulas will be used in the next section. Let E be the expectation operator and V be the variance operator. The expression $Q\{B|\underline{X}=\underline{x}\}$ refers to applying some operation Q (such as the expectation or variance operation) on a function B while holding the variable X equal to a constant value x.

Since the variance is defined as $V\{B\}=E\{B^2\}-\left(E\{B\}\right)^2$, in terms of the expectation operation the variance of a function B of variables X and Y can be computed using the analysis of variance (ANOVA) formula,

$$V\{B\}=E\{B^2\}-\left(E\{B\}\right)^2=E_X\left\{E_Y\{B^2|\underline{X}=\underline{x}\}\right\}-\left(E_X\{E_Y\{B|\underline{X}=\underline{x}\}\}\right)^2$$

$$=E_X\left\{E_Y\{B^2|\underline{X}=\underline{x}\}\right\}+\left[-E_X\left\{\left(E_Y\{B|\underline{X}=\underline{x}\}\right)^2\right\}+E_X\left\{\left(E_Y\{B|\underline{X}=\underline{x}\}\right)^2\right\}\right]-\left(E_X\{E_Y\{B|\underline{X}=\underline{x}\}\}\right)^2$$

$$=\left[E_X\left\{E_Y\{B^2|\underline{X}=\underline{x}\}\right\}-E_X\left\{\left(E_Y\{B|\underline{X}=\underline{x}\}\right)^2\right\}\right]+\left[E_X\left\{\left(E_Y\{B|\underline{X}=\underline{x}\}\right)^2\right\}-\left(E_X\{E_Y\{B|\underline{X}=\underline{x}\}\}\right)^2\right]$$

$$=E_X\left\{V_Y\{B|\underline{X}=\underline{x}\}\right\}+V_X\left\{E_Y\{B|\underline{X}=\underline{x}\}\right\}\qquad\text{(A6)}$$

The first term on the right side of Formula (A6) is the "within" portion of the variability, and the second term on the right side of Formula (A6) is the "between" term of the variability. Formulas (A5) and (A6) hold even if the variables X and Y are dependent and B is a nonlinear function of X and Y.

In the special case where A is the product of two independent variables X and Y, the variance of $A = XY$ is

$$V\{A\}=E_X\left\{V_Y\{XY|\underline{X}=\underline{x}\}\right\}+V_X\left\{E_Y\{XY|\underline{X}=\underline{x}\}\right\}=E_X\left\{X^2V_Y\{Y|\underline{X}=\underline{x}\}\right\}+V_X\left\{XE_Y\{Y|\underline{X}=\underline{x}\}\right\}$$

$$=E_X\left\{X^2V_Y\{Y\}\right\}+V_X\left\{XE_Y\{Y\}\right\}=E_X\{X^2\}V_Y\{Y\}+V_X\{X\}\left(E_Y\{Y\}\right)^2$$

$$=\left[V_X\{X\}+\left(E_X\{X\}\right)^2\right]V_Y\{Y\}+V_X\{X\}\left(E_Y\{Y\}\right)^2$$

$$=V_X\{X\}V_Y\{Y\}+\left(E_X\{X\}\right)^2V_Y\{Y\}+V_X\{X\}\left(E_Y\{Y\}\right)^2.\qquad\text{(A7)}$$

The exact formula for the variance of $A = XY$ can be approximated by variance (error) propagation of the first order Taylor series expansion for A,

$$V\{A\} \approx \left(E_X\{X\}\right)^2 V_Y\{Y\} + V_X\{X\}\left(E_Y\{Y\}\right)^2 , \tag{A8}$$

as described by Coleman and Steele [2009]. The result is in good agreement with the exact variance in Formula (A7) when X and Y are independent and both of the variances of X and Y are moderately small.

A.4. Models for Concentration Variability

Generally the target region of interest is the primary vessel or the annulus of a tank. The objective is to obtain representative samples of residual material from the target region, measure the samples for analyte concentration, then estimate the mean concentration and provide a *UCL95* for the mean concentration of the residual material in the target region of the tank.

Discrete sampling and composite sampling plans are common approaches to sample design. In discrete sampling each sample is separately measured at least once and, in this report, the samples are obtained using simple random sampling over the target region of the tank. In composite sampling, the material is volumetrically combined from different sample locations within the target region of the tank in a manner such that the analyte concentration in each composite sample is an unbiased estimate of the mean concentration over the target region of the tank. There are several methods in common use for selecting sample locations for composite samples. The two considered in the report are random sampling and stratified random sampling.

In random sampling, the sample locations to obtain residual material for each composite sample are chosen randomly from the target region of the tank. Alternatively, separate populations of residual material may be identified within the target region. The populations are identified by having distinct characteristics, usually based on prior sampling, tank history, material coloration, and the configuration of the residual material such as the existence of mounds of material. The populations of residual material are partitioned into nonoverlapping sections of the target region called strata. In the simplest implementation of stratified random sampling, each composite sample is composed of the material randomly assigned from one location in each stratum.

In a slightly more general form, composite samples could be constructed from one or more random locations within each stratum. This latter form permits more than one location to be sampled from strata with relatively large volumes of residual material, regions where the concentration of residual material may be expected to have high variability, or where sampling costs are lower than other strata. As an example, the residual material in the target region may have been stratified into two populations: the first population twice as large in volume as the second population. Therefore, each composite sample could be made by combining material from two locations in population 1 and from one location in population 2.

A.4.1   The Variance of the Mean of Measurements in Discrete Sampling

Consider a random sampling plan that supports discrete samples, that is, residual material in samples from individual locations are not consolidated with residual material from other samples prior to measurement. The measurement model for the mean of the concentration measurements $\bar{M}_{n,m}^{discrete}$ using discrete sampling is

$$\bar{M}_{n,m}^{discrete} = \frac{\sum_{j=1}^{n}\sum_{\ell=1}^{m} M_{j,\ell}}{mn} = \frac{\sum_{j=1}^{n}\sum_{\ell=1}^{m}\left[T_j\left(1+\varepsilon_{j,\ell}\right)\right]}{mn} = \frac{\sum_{j=1}^{n} T_j \sum_{\ell=1}^{m}\left[\left(1+\varepsilon_{j,\ell}\right)\right]}{mn},$$
(A9)

where the n random samples have actual mean concentrations $T_j, j=1,2,\ldots,n$, and, due to random selection, the mean concentration of each sample is an unbiased estimator of the actual concentration T in the targeted region of the tank: the expected value of the concentration in the j-th random sample is $E\{T_j\}=T, j=1,2,\cdot\cdot,\ldots n$. The vector of concentration variables is $\underline{T}=(T_1,T_2,\ldots,T_n)'$, and the vector of measurement error variables is $\underline{\varepsilon}=(\varepsilon_{1,1},\varepsilon_{1,2},\ldots,\varepsilon_{1,m},\varepsilon_{2,1},\varepsilon_{2,2},\ldots,\varepsilon_{2,m},\ldots,\varepsilon_{n,1},\varepsilon_{n,2},\ldots,\varepsilon_{n,m})'$, where the subscripts on each element $\varepsilon_{j,\ell}$ of the vector denote the sample (j = 1, 2, ..., n) and the replicate measurement (ℓ = 1, 2, ..., m).

The variance of the mean of the measurements is derived using Formula (A6). The conditional expectation of $\bar{M}_{n,m}^{discrete}$ is

$$E_{\underline{T}}\left\{\bar{M}_{n,m}^{discrete}\,\middle|\,\underline{\varepsilon}\right\}=E_{\underline{T}}\left\{\frac{\sum_{j=1}^{n}T_j\sum_{\ell=1}^{m}\left[\left(1+\varepsilon_{j,\ell}\right)\right]}{mn}\,\middle|\,\underline{\varepsilon}=\underline{e}\right\}=\frac{\sum_{j=1}^{n}E_{\underline{T}}\left\{T_j\,\middle|\,\underline{\varepsilon}=\underline{e}\right\}\sum_{\ell=1}^{m}\left[\left(1+e_{j,\ell}\right)\right]}{mn}=\frac{\sum_{j=1}^{n}E_{\underline{T}}\left\{T_j\right\}\sum_{\ell=1}^{m}\left[\left(1+e_{j,\ell}\right)\right]}{mn}$$

$$=\frac{T\sum_{j=1}^{n}\sum_{\ell=1}^{m}\left[\left(1+e_{j,\ell}\right)\right]}{mn},$$
(A10)

and the unconditional variance of the conditional expectation is

$$V_{\underline{\varepsilon}}\left\{E_{\underline{T}}\left\{\bar{M}_{n,m}^{discrete}\,\middle|\,\underline{\varepsilon}=\underline{e}\right\}\right\}=V_{\underline{\varepsilon}}\left\{\frac{T\sum_{j=1}^{n}\sum_{\ell=1}^{m}\left[\left(1+\varepsilon_{j,\ell}\right)\right]}{mn}\right\}=\left\{\frac{T^2\sum_{j=1}^{n}\sum_{\ell=1}^{m}V_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\right\}}{m^2n^2}\right\}=\frac{T^2\sigma_{meas}^2}{mn}.$$
(A11)

The conditional variance of $\bar{M}_{n,m}^{discrete}$ is

$$V_{\underline{T}}\left\{\bar{M}_{n,m}^{discrete}\,\middle|\,\underline{\varepsilon}=\underline{e}\right\}=V_{\underline{T}_d}\left\{\frac{\sum_{j=1}^{n}T_j\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)}{mn}\,\middle|\,\underline{\varepsilon}=\underline{e}\right\}$$

$$=\frac{1}{m^2n^2}V_{\underline{T}}\left\{T_1\right\}\sum_{j=1}^{n}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)^2+\frac{1}{m^2n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T},\underline{T}}\left\{T_j,T_{j'}\right\}\sum_{\ell=1}^{m}\sum_{\ell'=1}^{m}\left(1+e_{j,\ell}\right)\left(1+e_{j',\ell'}\right)$$
(A12)

$$E_{\underline{\varepsilon}}\left\{V_T\left\{\bar{M}_{n,m}^{discrete}\mid\underline{\varepsilon}=\underline{e}\right\}\right\}=\frac{1}{m^2n^2}V_T\{T_1\}\sum_{j=1}^{n}E_{\underline{\varepsilon}}\left[\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)^2\right]+\frac{1}{m^2n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T},\underline{T}}\{T_j,T_{j'}\}E_{\underline{\varepsilon}}\left\{\sum_{\ell=1}^{m}\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\left(1+\varepsilon_{j',\ell'}\right)\right\}$$

$$=\frac{1}{m^2n^2}V_{\underline{T}}\{T_1\}\sum_{j=1}^{n}\left[\left(\sum_{\ell=1}^{m}\left(1+E_{\underline{\varepsilon}}\{\varepsilon_{j,\ell}\}\right)\right)^2+\sum_{\ell=1}^{m}V_{\underline{\varepsilon}}\{\varepsilon_{j,\ell}\}\right]$$

$$+\frac{1}{m^2n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T},\underline{T}}\{T_j,T_{j'}\}\sum_{\ell=1}^{m}\left(1+E_{\underline{\varepsilon}}\{\varepsilon_{j,\ell}\}\right)\sum_{\ell'=1}^{m}\left(1+E_{\underline{\varepsilon}}\{\varepsilon_{j,\ell'}\}\right)$$

$$=\frac{1}{m^2n^2}V_{\underline{T}}\{T_1\}\sum_{j=1}^{n}\left[\left(\sum_{\ell=1}^{m}(1+0)\right)^2+\sum_{\ell=1}^{m}\sigma_{meas}^2\right]+\frac{1}{m^2n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T},\underline{T}}\{T_j,T_{j'}\}\sum_{\ell=1}^{m}(1+0)\sum_{\ell'=1}^{m}(1+0)$$

$$=\frac{1}{m^2n^2}V_{\underline{T}}\{T_1\}\sum_{j=1}^{n}\left(m^2+m\sigma_{meas}^2\right)+\frac{1}{m^2n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T},\underline{T}}\{T_j,T_{j'}\}m^2$$

$$=\frac{1}{n}V_{\underline{T}}\{T_1\}\left(1+\frac{\sigma_{meas}^2}{m}\right)+\frac{n-1}{n}\overline{Cov_{\underline{T},\underline{T}}\{T_j,T_{j'}\}}=\frac{1}{n}PSill\left(1+\frac{\sigma_{meas}^2}{m}\right)+\frac{n-1}{n}\left(PSill-\gamma_{discrete}\right)$$

$$=PSill\left(1+\frac{\sigma_{meas}^2}{mn}\right)-\frac{n-1}{n}\gamma_{discrete}, \tag{A13}$$

where the mean of the covariances of the concentrations for pairs of the samples is

$$\overline{Cov_{\underline{T},\underline{T}}\{T_j,T_{j'}\}}=\frac{\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T},\underline{T}}\{T_j,T_{j'}\}}{n^2-n}=\frac{\sum_{j=1}^{n}\sum_{j'>j}^{n}Cov_{\underline{T},\underline{T}}\{T_j,T_{j'}\}}{\left(n^2-n\right)/2}, \tag{A14}$$

where the relative measurement error variance is σ_{meas}^2, and the semivariogram value $\gamma_{discrete}$ is the mean of the semivariogram values of the individual pairs of concentration measurements. The spatial variances of all of the concentrations for the samples are equal, that is, $V_{\underline{T}_d}\{T_1\}=V_{\underline{T}_d}\{T_2\}=\ldots=V_{\underline{T}_d}\{T_n\}=PSill$.

Combining the within and between components in Formulas (A11) and (A13), the variance of the mean of the discrete sample measurements in the units of the concentration measurement squared is

$$V\left\{\bar{M}_{n,m}^{discrete}\right\}=\frac{T^2\sigma_{meas}^2}{mn}+PSill\left(1+\frac{\sigma_{meas}^2}{mn}\right)-\frac{n-1}{n}\gamma_{discrete}. \tag{A15}$$

Dividing Formula (A15) by T^2, the relative variance of $\bar{M}_{n,m}^{discrete}$ is

$$V_{Rel}\left\{\bar{M}_{n,m}^{discrete}\right\}=\frac{V\left\{\bar{M}_{n,m}^{discrete}\right\}}{T^2}=\frac{\dfrac{T^2\sigma_{meas}^2}{mn}+PSill\left(1+\dfrac{\sigma_{meas}^2}{mn}\right)-\dfrac{n-1}{n}\gamma_{discrete}}{T^2}$$

$$=\left(1+PSill^{Rel}\right)\left(1+\frac{\sigma_{meas}^2}{mn}\right)-\frac{n-1}{n}\gamma_{discrete}^{Rel}-1 \tag{A16}$$

$$=\left(1+PSill^{Rel}\right)\frac{\sigma_{meas}^2}{mn}+\left(PSill^{Rel}-\frac{n-1}{n}\gamma_{discrete}^{Rel}\right)$$

Assuming that the mean of the analyte concentrations from replicate measurements of the discrete samples are not significantly different from one another, the 95% upper confidence bound (*UCL95*) for

the actual mean analyte concentration in the targeted region of the tank is defined by the following expression,

$$UCL95 = \bar{M}_{n,m}^{discrete}\left(1 + t\sqrt{V_{Rel}\left\{\bar{M}_{n,m}^{discrete}\right\}}\right),$$

(A17)

where t represents the 95 percentile of a Student's t distribution with $mn-1$ degrees of freedom.

A.4.2   The Variance of the Mean of Measurements in Composite Sampling based on Random Sampling of Locations

The variance of the mean of composite samples can be obtained when the underlying sampling plan to select sample locations is based on simple random sampling. This is a typical approach when no subpopulations of material have been identified a'priori to sampling.

The basic model for the mean of the measurements $\bar{M}_{n,k,m}^{ran}$ is given by Formula (A18):

$$\bar{M}_{n,k,m}^{ran} = \frac{\sum_{j=1}^{n}\sum_{\ell=1}^{m}M_{j,\ell}}{mn} = \frac{\sum_{j=1}^{n}\sum_{\ell=1}^{m}\left[\left(\frac{\sum_{i=1}^{k}T_{j,i}}{k}\right)(1+\varepsilon_{j,\ell})\right]}{mn} = \sum_{j=1}^{n}\sum_{i=1}^{k}\left[\frac{T_{j,i}}{kn}\sum_{\ell=1}^{m}\frac{(1+\varepsilon_{j,\ell})}{m}\right].$$

(A18)

where the vector of concentration variables is $\underline{T} = \left(T_{1,1}, T_{1,2}, \ldots, T_{1k}, T_{2,1}, T_{2,2}, \ldots, T_{2k}, \ldots, T_{n,1}, T_{n,2}, \ldots, T_{nk},\right)'$ and

the vector of measurement error variables is $\underline{\varepsilon} = \left(\varepsilon_{1,1}, \varepsilon_{1,2}, \ldots, \varepsilon_{1,m}, \varepsilon_{2,1}, \varepsilon_{2,2}, \ldots, \varepsilon_{2,m}, \ldots, \varepsilon_{n,1}, \varepsilon_{n,2}, \ldots, \varepsilon_{n,m}\right)'$,
and there are n composite samples (j = 1, 2, ..., n), m replicate measurement (ℓ = 1, 2, ..., m), and k locations per composite sample (i = 1, 2, ..., k).

The total number of sample locations in the tank is kn, and the sample locations are randomly selected in the targeted region of the tank, and the kn selected samples are randomly divided into n sets of k samples where each set of k samples is combined to form each of the n composite samples. The mean concentration in each composite sample j is an unbiased estimator for the actual concentration in the targeted area of the tank: the expected value of the mean concentration of the j-th composite sample is

$$E_{\underline{T}}\left\{\sum_{i=1}^{k}T_{ji}\Big/k\right\} = T, j = 1, 2, \ldots, n.$$

The conditional expectation of $\bar{M}_{n,k,m}^{ran}$ is

$$E_{\underline{T}}\left\{\bar{M}_{n,k,m}^{ran}\Big|\underline{\varepsilon}\right\} = E_{\underline{T}}\left\{\sum_{j=1}^{n}\sum_{i=1}^{k}\left[\frac{T_{j,i}}{kn}\sum_{\ell=1}^{m}\frac{(1+\varepsilon_{j,\ell})}{m}\right]\Big|\underline{\varepsilon}=\underline{e}\right\} = \sum_{j=1}^{n}\left[\frac{\sum_{i=1}^{k}E_{\underline{T}}\left\{T_{j,i}\Big|\underline{\varepsilon}=\underline{e}\right\}}{kn}\sum_{\ell=1}^{m}\frac{(1+e_{j,\ell})}{m}\right]$$

$$= \sum_{j=1}^{n}\left[\frac{\sum_{i=1}^{k}E_{\underline{T}}\left\{T_{j,i}\right\}}{kn}\sum_{\ell=1}^{m}\frac{(1+e_{j,\ell})}{m}\right] = \frac{T}{n}\sum_{j=1}^{n}\left[\sum_{\ell=1}^{m}\frac{(1+e_{j,\ell})}{m}\right],$$

(A19)

and the unconditional variance of the conditional expectation in the units of measure squared is

$$V_{\underline{\varepsilon}}\left\{E_{\underline{T}}\left\{\bar{M}_{n,k,m}^{ran}\big|\underline{\varepsilon}=\underline{e}\right\}\right\}=V_{\underline{\varepsilon}}\left\{\frac{T}{n}\sum_{j=1}^{n}\left[\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\right]\right\}=\frac{T^2\displaystyle\sum_{j=1}^{n}\sum_{\ell=1}^{m}V_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\right\}}{n^2}=\frac{T^2\sigma_{meas}^2}{mn}\ .\tag{A20}$$

The components of the variance of the mean of the concentration measurements are partitioned into three classes: (1) the set of spatial variances, (2) the set of covariances associated with pairs of concentrations arising from samples that were combined in the same composite sample, and (3) the set of covariances associated with pairs of concentrations arising from samples that were assigned to different composite samples.

The conditional variance of $\bar{M}_{n,k,m}^{ran}$ is

$$\begin{aligned}
V_{\underline{T}}\left\{\bar{M}_{n,k,m}^{ran}\big|\underline{\varepsilon}=\underline{e}\right\}&=V_{\underline{T}}\left\{\sum_{j=1}^{n}\sum_{i=1}^{k}\left[\frac{T_{j,i}}{kn}\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\right]\Big|\underline{\varepsilon}=\underline{e}\right\}\\
&=\frac{1}{k^2m^2n^2}\sum_{j=1}^{n}\sum_{i=1}^{k}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)^2 V_{\underline{T}}\left\{T_{j,i}\big|\underline{\varepsilon}=\underline{e}\right\}\\
&\quad+\frac{1}{k^2m^2n^2}\sum_{j=1}^{n}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+e_{j,\ell'}\right)\right)Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\big|\underline{\varepsilon}=\underline{e}\right\}\\
&\quad+\frac{1}{k^2m^2n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}\sum_{i=1}^{k}\sum_{i'=1}^{k}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+e_{j',\ell'}\right)\right)Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\big|\underline{\varepsilon}=\underline{e}\right\}\\
&=\frac{1}{k^2m^2n^2}\sum_{j=1}^{n}\sum_{i=1}^{k}V_{\underline{T}}\left\{T_{j,i}\right\}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)^2\\
&\quad+\frac{1}{k^2m^2n^2}\sum_{j=1}^{n}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+e_{j,\ell'}\right)\right)\\
&\quad+\frac{1}{k^2m^2n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}\sum_{i=1}^{k}\sum_{i'=1}^{k}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+e_{j',\ell'}\right)\right),
\end{aligned}\tag{A21}$$

and the unconditional expectation of the conditional variance in the units of the concentration measurement squared is

$$E_{\underline{\varepsilon}}\left\{V_T\left\{\overline{M}_{n,k,m}^{ran}\,\big|\,\underline{\varepsilon}=\underline{e}\right\}\right\}=E_{\underline{\varepsilon}}\left\{\frac{1}{k^2 m^2 n^2}\sum_{j=1}^{n}\sum_{i=1}^{k}V_{\underline{T}}\left\{T_{j,i}\right\}\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)^2\right\}$$

$$+E_{\underline{\varepsilon}}\left\{\frac{1}{k^2 m^2 n^2}\sum_{j=1}^{n}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j,\ell'}\right)\right)\right\}$$

$$+E_{\underline{\varepsilon}}\left\{\frac{1}{k^2 m^2 n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}\sum_{i=1}^{k}\sum_{i'=1}^{k}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j',\ell'}\right)\right)\right\}$$

$$=\frac{1}{k^2 m^2 n^2}\sum_{j=1}^{n}\sum_{i=1}^{k}V_{\underline{T}}\left\{T_{j,i}\right\}E_{\underline{\varepsilon}}\left\{\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)^2\right\}$$

$$+\frac{1}{k^2 m^2 n^2}\sum_{j=1}^{n}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}E_{\underline{\varepsilon}}\left\{\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j,\ell'}\right)\right)\right\}$$

$$+\frac{1}{k^2 m^2 n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}\sum_{i=1}^{k}\sum_{i'=1}^{k}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}E_{\underline{\varepsilon}}\left\{\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j',\ell'}\right)\right)\right\}$$

$$=\frac{1}{k^2 m^2 n^2}\sum_{j=1}^{n}\sum_{i=1}^{k}V_{\underline{T}}\left\{T_{j,i}\right\}\left[\left(\sum_{\ell=1}^{m}\left(1+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\right\}\right)\right)^2+\left\{\sum_{\ell=1}^{m}V_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\right\}\right\}\right]$$

$$+\frac{1}{k^2 m^2 n^2}\sum_{j=1}^{n}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}\left(\sum_{\ell=1}^{m}\sum_{\ell'=1}^{m}\left(1+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\right\}+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell'}\right\}+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\varepsilon_{j,\ell'}\right\}\right)\right)$$

$$+\frac{1}{k^2 m^2 n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}\sum_{i=1}^{k}\sum_{i'=1}^{k}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}\left(\sum_{\ell=1}^{m}\left(1+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\right\}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+E_{\underline{\varepsilon}}\left\{\varepsilon_{j',\ell'}\right\}\right)\right)$$

$$=\frac{1}{k^2 m^2 n^2}\sum_{j=1}^{n}\sum_{i=1}^{k}V_{\underline{T}}\left\{T_{j,i}\right\}\left[\left(\sum_{\ell=1}^{m}\left(1+0\right)\right)^2+m\sigma_{meas}^2\right]$$

$$+\frac{1}{k^2 m^2 n^2}\sum_{j=1}^{n}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}\left(\sum_{\ell=1}^{m}\sum_{\ell'=1}^{m}\left(1+0+0+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\varepsilon_{j,\ell'}\right\}\right)\right)$$

$$+\frac{1}{k^2 m^2 n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}\sum_{i=1}^{k}\sum_{i'=1}^{k}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}\left(\sum_{\ell=1}^{m}\left(1+0\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+0\right)\right)$$

$$=\frac{1}{k^2 n^2}\left(1+\frac{\sigma_{meas}^2}{m}\right)\sum_{j=1}^{n}\sum_{i=1}^{k}V_{\underline{T}}\left\{T_{j,i}\right\}+\frac{1}{k^2 n^2}\left(1+\frac{\sigma_{meas}^2}{m}\right)\sum_{j=1}^{n}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}$$

$$+\frac{1}{k^2 n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}\sum_{i=1}^{k}\sum_{i'=1}^{k}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}$$

$$=\frac{1}{kn}V_{\underline{T}}\left\{T_{1,1}\right\}\left(1+\frac{\sigma_{meas}^2}{m}\right)+\frac{(k-1)}{kn}\overline{Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}}\left(1+\frac{\sigma_{meas}^2}{m}\right)+\frac{(n-1)}{n}\overline{Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}}$$

$$=\frac{1}{kn}PSill\left(1+\frac{\sigma_{meas}^2}{m}\right)+\frac{(k-1)}{kn}\left(PSill-\gamma_{ran}\right)\left(1+\frac{\sigma_{meas}^2}{m}\right)+\frac{(n-1)}{n}\left(PSill-\gamma_{ran}\right)$$

$$=\left(\frac{1}{kn}+\frac{(k-1)}{kn}+\frac{(n-1)}{n}\right)PSill+\left(\frac{1}{kn}+\frac{(k-1)}{kn}\right)PSill\frac{\sigma_{meas}^2}{m}-\left(\frac{(k-1)}{kn}+\frac{(kn-k)}{kn}+\frac{(k-1)}{kn}\frac{\sigma_{meas}^2}{m}\right)\gamma_{ran}$$

$$=PSill\left(1+\frac{\sigma_{meas}^2}{mn}\right)-\left(\frac{(kn-1)}{kn}+\frac{(k-1)}{k}\frac{\sigma_{meas}^2}{mn}\right)\gamma_{ran}, \tag{A22}$$

where γ_{ran} is the mean semivariogram value associated the actual concentrations in samples from all pairs of locations in units of the concentration measurement squared.

Combining the within and between components in Formulas (A20) and (A22), the variance of the mean of the composite sample measurements is

$$V\left\{\bar{M}_{n,k,m}^{ran}\right\} = \frac{T^2\sigma_{meas}^2}{mn} + PSill\left(1+\frac{\sigma_{meas}^2}{mn}\right) - \left(\frac{(kn-1)}{kn}+\frac{(k-1)}{k}\frac{\sigma_{meas}^2}{mn}\right)\gamma_{ran} \tag{A23}$$

Dividing Formula (23) by T^2, the relative variance of $\bar{M}_{n,k,m}$ is

$$V_{Rel}\left\{\bar{M}_{n,k,m}^{ran}\right\} = \frac{V\left\{\bar{M}_{n,k,m}^{ran}\right\}}{T^2} = \frac{\dfrac{T^2\sigma_{meas}^2}{mn} + PSill\left(1+\dfrac{\sigma_{meas}^2}{mn}\right) - \left(\dfrac{(kn-1)}{kn}+\dfrac{(k-1)}{k}\dfrac{\sigma_{meas}^2}{mn}\right)\gamma_{ran}}{T^2}$$
$$= \frac{\sigma_{meas}^2}{mn} + PSill^{Rel}\left(1+\frac{\sigma_{meas}^2}{mn}\right) - \left(\frac{(kn-1)}{kn}+\frac{(k-1)}{k}\frac{\sigma_{meas}^2}{mn}\right)\gamma_{ran}^{Rel} \tag{A24}$$

Assuming that the mean of the analyte concentrations from replicate measurements of the composite samples are not significantly different from one another, the *UCL95* is defined by the following expression,

$$UCL95 = \bar{M}_{n,k,m}^{ran}\left(1+t\sqrt{V_{Rel}\left\{\bar{M}_{n,k,m}^{ran}\right\}}\right), \tag{A25}$$

where *t* represents the 95 percentile of a Student's t distribution with *mn*-1 degrees of freedom.

A.4.3   The Variance of the Mean of Measurements in Composite Sampling based on Stratified Random Sampling of Locations

Consider a single composite sample that was formed from the material from *k* locations in the tank. The k locations can be specified by random sampling over the entire tank floor or random sampling one location from each of *k* strata. The measurement model for the mean of *m* concentration measurements on one composite sample composed of *k* locations is

$$\bar{M}_{1,k,m}^{strat} = \frac{\sum_{\ell=1}^{m}\left(\dfrac{\sum_{i=1}^{k}T_i}{k}\right)(1+\varepsilon_\ell)}{m} = \left(\frac{\sum_{i=1}^{k}T_i}{k}\right)\left(\frac{\sum_{\ell=1}^{m}(1+\varepsilon_\ell)}{m}\right) \tag{A26}$$

where the mean of the measurements is denoted by $\bar{M}_{1,k,m}$, and the subscript $(1,k,m)$ denotes that the mean of the measurements is obtained from 1 composite sample formed from *k* locations, and then measured once on each of *m* aliquots of material from the sample. The true analyte concentration for

the composite sample formed from volumetrically equal parts[3] of material from the k locations is $\sum_{i=1}^{k} T_i \Big/ k$. Since each location was randomly chosen, $\sum_{i=1}^{k} T_i \Big/ k$ is an unbiased estimator of T, the actual concentration of all of the residual material on the tank floor.

Formula (A26) fits the model of a product of two independent variables: analyte concentrations at random locations and measurement errors. Therefore, Formula (A7) can be used to derive the variance of the mean of concentration measurements defined by Formula (A26).

The variance of the mean of m concentration measurements on one composite sample is

$$
\begin{aligned}
V\{\overline{M}_{1,k,m}^{strat}\} &= V\left\{ \frac{\sum_{\ell=1}^{m} M_\ell}{m} \right\} = \left[E\left\{ \frac{\sum_{i=1}^{k} T_i}{k} \right\} \right]^2 \left[\frac{\sum_{\ell=1}^{m} V\{\varepsilon_\ell\}}{m^2} \right] + \left[\frac{V\left\{\sum_{i=1}^{k} T_i\right\}}{k^2} \right]\left[E\left\{ \frac{\sum_{\ell=1}^{m}(1+\varepsilon_\ell)}{m} \right\} \right]^2 + \left[\frac{V\left\{\sum_{i=1}^{k} T_i\right\}}{k^2} \right]\left[\frac{\sum_{\ell=1}^{m} V\{\varepsilon_\ell\}}{m^2} \right] \\
&= T^2 \frac{\sigma_{meas}^2}{m} + \left(\frac{V\{T_1\}}{k} + \frac{(k-1)\overline{Cov\{T_i,T_{i'}\}}}{k} \right) + \left(\frac{V\{T_1\}}{k} + \frac{(k-1)\overline{Cov\{T_i,T_{i'}\}}}{k} \right) \frac{\sigma_{meas}^2}{m} \\
&= T^2 \frac{\sigma_{meas}^2}{m} + \left(PSill - \frac{(k-1)\gamma_{among}}{k} \right) + \left(PSill - \frac{(k-1)\gamma_{among}}{k} \right) \frac{\sigma_{meas}^2}{m} \quad , \\
&= T^2 \left[\frac{\sigma_{meas}^2}{m} + \left(PSill^{Rel} - \frac{(k-1)\gamma_{among}^{Rel}}{k} \right)\left(1 + \frac{\sigma_{meas}^2}{m} \right) \right] \\
&= T^2 \left[\left(1 + PSill^{Rel} - \frac{(k-1)\gamma_{among}^{Rel}}{k} \right)\left(1 + \frac{\sigma_{meas}^2}{m} \right) - 1 \right] \qquad\qquad\qquad (A27)
\end{aligned}
$$

where γ_{among} is the mean semivariogram value associated the actual concentrations in samples from pairs of locations associated with a single composite sample in units of the concentration measurement squared. The term

$$
\overline{Cov\{T_i,T_{i'}\}} = \sum_{i=1}^{k}\sum_{i'\neq i}^{k} Cov\{T_i,T_{i'}\} \Big/ \left(k^2-k\right) = \sum_{i=1}^{k}\sum_{i'>i}^{k} Cov\{T_i,T_{i'}\} \Big/ \left(\left(k^2-k\right)/2\right), \qquad (A28)
$$

is the mean covariance of the actual concentrations of residual material from pairs of samples obtained from different spatial locations associated with the same composite sample (that means the locations are in separate strata).

---

[3] Assuming that each composite sample is comprised of equal volumetric parts of material from each location simplifies the presentation of these statistical results. More commonly, composite samples are formed from material from sampled locations where the volumetric proportion of material from a particular location equals the relative volume of the stratum from which the sample was obtained.

The relative variance of $\bar{M}_{1,k,m}^{strat}$ is

$$V_{Rel}\left\{\bar{M}_{1,k,m}^{strat}\right\}=\frac{V\left\{\bar{M}_{1,k,m}^{strat}\right\}}{T^2}=\frac{T^2\left[\left(1+PSill^{Rel}-\frac{(k-1)\gamma_{among}^{Rel}}{k}\right)\left(1+\frac{\sigma_{meas}^2}{m}\right)-1\right]}{T^2}$$

$$=\left(1+PSill^{Rel}-\frac{(k-1)}{k}\gamma_{among}^{Rel}\right)\left(1+\frac{\sigma_{meas}^2}{m}\right)-1. \tag{A29}$$

In the limiting case of $k = 1$ location and $m = 1$ measurement on the sample from that location, Formula (A29) reduces to

$$V_{Rel}\left\{\bar{M}_{1,1,1}^{strat}\right\}=\left(1+PSill^{Rel}\right)\left(1+\sigma_{meas}^2\right)-1. \tag{A30}$$

Formula (A30) can be used to compare sample plans based on prior estimates of the $PSill^{Rel}$ and σ_{meas}^2. However, by itself, one measurement result does not provide even minimal information to calculate the values $PSill^{Rel}$ and σ_{meas}^2 based on sample results.

Now consider the mean of m measured concentrations on each of n composite samples that were each constructed from residual material from one random location. The mean of the measurements is

$$\bar{M}_{n,1,m}^{strat}=\frac{\sum_{j=1}^{n}\left(\frac{\sum_{\ell=1}^{m}M_{j,\ell}}{m}\right)}{n}=\frac{\sum_{j=1}^{n}\sum_{\ell=1}^{m}\left[T_j\left(1+\varepsilon_{j,\ell}\right)\right]}{mn}=\sum_{j=1}^{n}\left[\frac{T_j}{n}\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\right] \tag{A31}$$

The mean in Formula (A31) is not in the form of a product of two independent random variables, so the variance is obtained from Formula (A6).

$$V\left\{\overline{M}_{n,1,m}^{strat}\right\}=E_{\varepsilon}\left\{V_{T_0}\left\{\sum_{j=1}^{n}\left[\frac{T_j}{n}\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\Big|\underline{\varepsilon}=\underline{e}\right]\right\}\right\}+V_{\varepsilon}\left\{E_{T_0}\left\{\sum_{j=1}^{n}\left[\frac{T_j}{n}\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\Big|\underline{\varepsilon}=\underline{e}\right]\right\}\right\}$$

$$=\sum_{j=1}^{n}\frac{V\{T_j\}}{n^2}E_{\varepsilon}\left\{\left(\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\right)^2\right\}$$

$$+\frac{1}{m^2 n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov\{T_j,T_{j'}\}E_{\varepsilon}\left\{\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j',\ell'}\right)\right\}+V_{\varepsilon}\sum_{j=1}^{n}\left[\frac{T}{n}\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\right]$$

$$=\sum_{j=1}^{n}\frac{V\{T_j\}}{n^2}\left[\left(\sum_{\ell=1}^{m}\frac{\left(1+E_{\varepsilon}\left\{\varepsilon_{j,\ell}\right\}\right)}{m}\right)^2+V_{\varepsilon}\left\{\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\right\}\right]\qquad(A32)$$

$$+\frac{1}{m^2 n^2}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov\{T_j,T_{j'}\}E_{\varepsilon}\left\{\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j',\ell'}\right)\right\}+V_{\varepsilon}\sum_{j=1}^{n}\left[\frac{T}{n}\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\right]$$

$$=\frac{V\{T_1\}}{n}\left(1+\frac{\sigma_{meas}^2}{m}\right)+\frac{(n-1)}{n}\overline{Cov\{T_j,T_{j'}\}}+\frac{T^2\sigma_{meas}^2}{mn}$$

$$=\left(T^2+PSill\right)\left(1+\frac{\sigma_{meas}^2}{mn}\right)-\frac{(n-1)}{n}\gamma_{within}-T^2$$

The relative variance is

$$V^{Rel}\left\{\overline{M}_{n,1,m}^{strat}\right\}=\frac{V\left\{\overline{M}_{n,1,m}^{strat}\right\}}{T^2}=\frac{\left(T^2+PSill\right)\left(1+\frac{\sigma_{meas}^2}{mn}\right)-\frac{(n-1)}{n}\gamma_{within}-T^2}{T^2}\,.\qquad(A33)$$

$$=\left(1+PSill^{Rel}\right)\left(1+\frac{\sigma_{meas}^2}{mn}\right)-\frac{(n-1)}{n}\gamma_{within}^{Rel}-1$$

More generally, suppose that each of n ($j = 1, 2, ..., n$) composite samples is measured m ($\ell = 1, 2, ..., m$) times. We are concerned with the mean of the mn analytical results, where each composite sample is composed of material from k ($i = 1, 2, ..., k$) distinct locations (one from each of the k strata). Denoting the ℓ-th measurement on the j-th composite sample as $M_{j,\ell}$, the measurement model is

$$\overline{M}_{n,k,m}^{strat}=\frac{\sum_{j=1}^{n}\sum_{\ell=1}^{m}M_{j,\ell}}{mn}=\frac{\sum_{j=1}^{n}\sum_{\ell=1}^{m}\left[\left(\frac{\sum_{i=1}^{k}T_{j,i}}{k}\right)\left(1+\varepsilon_{j,\ell}\right)\right]}{mn}=\sum_{j=1}^{n}\sum_{i=1}^{k}\left[\frac{T_{j,i}}{kn}\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\right]\qquad(A34)$$

The mean $\overline{M}_{n,k,m}^{strat}$ depends on the vector of actual concentrations at the randomly sampled locations $\underline{T_0}=\left(T_{1,1},T_{1,2},...,T_{1,n},T_{2,1},T_{2,2},...,T_{2,n},...,T_{k,1},T_{k,2},...,T_{k,n}\right)'$ and the vector of measurement errors $\underline{\varepsilon}=\left(\varepsilon_{1,1},\varepsilon_{1,2},...,\varepsilon_{1,m},\varepsilon_{2,1},\varepsilon_{2,2},...,\varepsilon_{2,m},...,\varepsilon_{n,1},\varepsilon_{n,2},...,\varepsilon_{n,m}\right)'$. The variance of the mean of measured concentrations can be determined via the ANOVA Formula (A6). The notation $\big|\underline{\varepsilon}=\underline{e}$ indicates that the

intended operation is performed holding the vector of measurement errors $\underline{\varepsilon}$ constant to some vector of values $\underline{e}$.

The conditional expectation of $\bar{M}_{n,k,m}^{strat}$ is

$$E_{\underline{T}}\left\{\bar{M}_{n,k,m}^{strat}\,\middle|\,\underline{\varepsilon}\right\}=E_{\underline{T}}\left\{\sum_{j=1}^{n}\sum_{i=1}^{k}\left[\frac{T_{j,i}}{kn}\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\right]\middle|\underline{\varepsilon}=\underline{e}\right\}=\sum_{j=1}^{n}\left[\frac{E_{\underline{T}}\left\{\dfrac{\sum_{i=1}^{k}T_{j,i}}{k}\middle|\underline{\varepsilon}=\underline{e}\right\}}{n}\sum_{\ell=1}^{m}\frac{\left(1+e_{j,\ell}\right)}{m}\right]$$

$$=\sum_{j=1}^{n}\left[\frac{E_{\underline{T}}\left\{\dfrac{\sum_{i=1}^{k}T_{j,i}}{k}\right\}}{n}\sum_{\ell=1}^{m}\frac{\left(1+e_{j,\ell}\right)}{m}\right]=\frac{T}{n}\sum_{j=1}^{n}\left[\sum_{\ell=1}^{m}\frac{\left(1+e_{j,\ell}\right)}{m}\right],\tag{A35}$$

where the expected concentration for composite sample j (j = 1, 2, ..., n) is $E_{\underline{T}}\left\{\sum_{i=1}^{k}T_{j,i}\middle/k\right\}=T$, the actual

concentration of the analyte in the residual material over the entire tank floor, and the unconditional variance of the conditional expectation is

$$V_{\underline{\varepsilon}}\left\{E_{\underline{T}}\left\{\bar{M}_{n,k,m}^{strat}\,\middle|\,\underline{\varepsilon}=\underline{e}\right\}\right\}=V_{\underline{\varepsilon}}\left\{\frac{T}{n}\sum_{j=1}^{n}\left[\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\right]\right\}=\frac{T^{2}\sum_{j=1}^{n}\sum_{\ell=1}^{m}V_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\right\}}{n^{2}\,m^{2}}=\frac{T^{2}\sigma_{meas}^{2}}{mn}\tag{A36}$$

In the derivation of the conditional variance of $\bar{M}_{n,k,m}^{strat}$, the components of variances and covariance are partitioned into three sets of sums: (1) the variances involving the individual elements of the vector $\underline{T}_{0}$, (2) the covariances of pairs of elements of the vector $\underline{T}_{0}$ that are both in the same stratum (same stratum i but different composite samples j and j'), (3) and the covariances of pairs of elements of the vector $\underline{T}_{0}$ that are in different strata (different i and i' and no restriction on j).

The number of variances and covariances in these classes will need to be computed, and Figure 2 is provided to organize the variances and covariances to make the computations easier. Figure 2 depicts a large square that represents all of the spatial variances of the concentrations for the samples once along the blue diagonal and all of the spatial covariances of the concentrations for the samples twice (once in the off-diagonal area above the blue diagonal and once in the off-diagonal area below the blue diagonal). The arrangement of the variances and covariances is symmetrical about the blue diagonal. Figure 2 can be used to compute the number of spatial variances and the number of spatial covariances of different kinds. The total number of sample locations is kn, and it equals the length of vector $\underline{T}_{0}$.
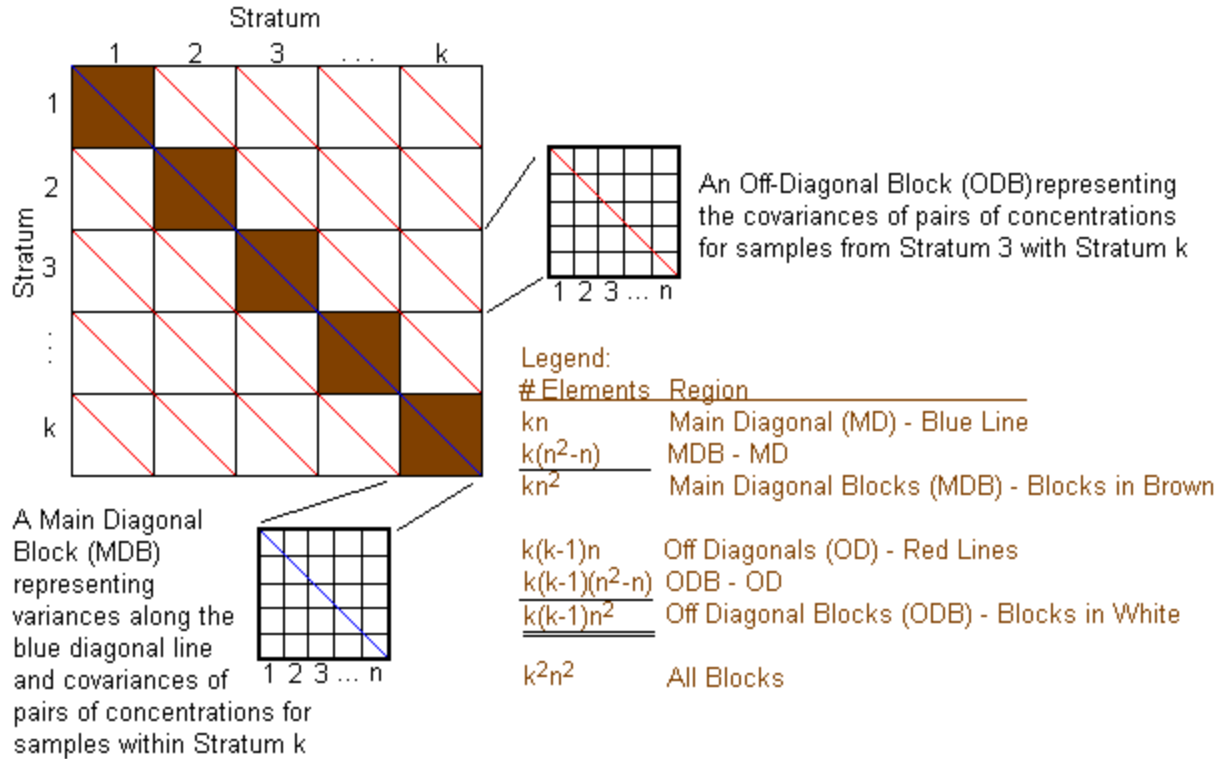
Figure A.2. Diagram to Compute the Number of Variances and Covariances

The main diagonal blocks (MDB) that lie along the blue main diagonal (MD) line are shaded brown. The top left MDB represents the variances and covariances of concentrations in samples from locations only within Stratum 1, the second MDB from only within Stratum 2, and the bottom right MDB from only within the Stratum k. The n variances along the blue main diagonal line in one MDB are associated with composite samples 1, 2, ..., n (from left to right in numerical order) from samples obtained from locations within a single stratum. Similarly, the $(n^2-n)/2$ covariances, represented by the $(n^2-n)/2$ elements above the MD and repeated on the $(n^2-n)/2$ elements below the MD in each MDB, are associated with the sample concentrations for samples from pairs of locations within a single stratum. Since there are k strata (brown blocks), the total number of variances is kn and the total number of covariances for pairs of concentrations for samples from locations within the same stratum is $k(n^2-n)/2$. Since there are k diagonal blocks (strata), there are a grand total of kn variances arising from the kn sample locations and $k(n^2-n)/2$ covariances of samples from the same stratum are each placed on two of the off-diagonal elements, one above and one below the MD. Adding the number of MD elements to the number of off-diagonal elements (the number of variances plus twice the number of covariances) in the brown blocks totals kn^2.

The white blocks represent the covariances of concentrations arising from different strata. The red diagonal lines above the blue main diagonal line represent the $(k^2-k)n/2$ covariances of concentrations for pairs of samples from locations within different strata that associated with the same composite sample: the remaining portions of the white blocks (off the red line) represent the covariances for concentrations for samples from locations within different strata that are associated with different

composite samples. There are $(k^2-k)(n^2-n)/2$ such covariances. Adding the number of elements on the red lines to the number of off-diagonal elements (the number of variances plus twice the number of covariances) in the white blocks totals $(k^2-k)n^2$. The total number of variances and (twice the) covariances in the large square is k^2n^2.

Using the fact that the variances and covariances of the elements in the vector $\underline{T}_0$ are not dependent on the elements in the vector $\underline{\varepsilon}$, the conditional variance of $\bar{M}_{n,k,m}$ in the concentration units of measure (squared) is

$$
\begin{aligned}
V_{\underline{T}}\left\{\bar{M}_{n,k,m}^{strat}\,\middle|\,\underline{\varepsilon}=\underline{e}\right\} &= V_{\underline{T}}\left\{\sum_{i=1}^{k}\sum_{j=1}^{n}\left[\frac{T_{j,i}}{kn}\sum_{\ell=1}^{m}\frac{\left(1+\varepsilon_{j,\ell}\right)}{m}\right]\middle|\underline{\varepsilon}=\underline{e}\right\} \\
&= \frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)^2 V_{\underline{T}}\left\{T_{j,i}\,\middle|\,\underline{\varepsilon}=\underline{e}\right\} \\
&\quad+\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+e_{j',\ell'}\right)\right)Cov_{\underline{T}}\left\{T_{j,i},T_{j',i}\,\middle|\,\underline{\varepsilon}=\underline{e}\right\} \\
&\quad+\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}\sum_{j'=1}^{n}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+e_{j',\ell'}\right)\right)Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\,\middle|\,\underline{\varepsilon}=\underline{e}\right\} \\
&= \frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)^2 V_{\underline{T}}\left\{T_{j,i}\right\} \\
&\quad+\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+e_{j',\ell'}\right)\right)Cov_{\underline{T}}\left\{T_{j,i},T_{j',i}\right\} \\
&\quad+\left(\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+e_{j,\ell'}\right)\right)Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}\right. \\
&\quad\left.+\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}\left(\sum_{\ell=1}^{m}\left(1+e_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+e_{j',\ell'}\right)\right)Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}\right)
\end{aligned}
\tag{A37}
$$

The variance of $\bar{M}_{n,k,m}^{strat}$ was partitioned into three sums containing spatial variances, spatial covariances within the same strata, and spatial covariances in different strata. The rational for this is that the mean of the spatial covariances associated with pairs of sample locations in different strata should be no more, and usually less, than the mean of the covariances associated with pairs of sample locations within the same strata because the mean distance between pairs of locations is generally less within strata than between strata. The third sum containing spatial covariances for locations in different strata was further partitioned in the last line of Formula (A37) into a sum over terms associated with the same composite sample and a sum of terms associated with different composite samples.

The unconditional expectation of the conditional variance in the units of measure (squared) is

$$E_{\underline{\varepsilon}}\left\{V_T\left\{\overline{M}_{n,k,m}^{strat}\big|\underline{\varepsilon}=\underline{e}\right\}\right\}=E_{\underline{\varepsilon}}\left\{\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}V_{\underline{T}}\left\{T_{j,i}\right\}\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)^2\right\}$$

$$+E_{\underline{\varepsilon}}\left\{\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i}\right\}\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j',\ell'}\right)\right)\right\}$$

$$+\left(E_{\underline{\varepsilon}}\left\{\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j,\ell'}\right)\right)\right\}\right.$$

$$\left.+E_{\underline{\varepsilon}}\left\{\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j',\ell'}\right)\right)\right\}\right)$$

$$=\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}V_{\underline{T}}\left\{T_{j,i}\right\}E_{\underline{\varepsilon}}\left\{\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)^2\right\}$$

$$+\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i}\right\}E_{\underline{\varepsilon}}\left\{\sum_{\ell=1}^{m}\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\left(1+\varepsilon_{j',\ell'}\right)\right\}$$

$$+\left(\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}E_{\underline{\varepsilon}}\left\{\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j,\ell'}\right)\right)\right\}\right.$$

$$\left.+\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}E_{\underline{\varepsilon}}\left\{\left(\sum_{\ell=1}^{m}\left(1+\varepsilon_{j,\ell}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+\varepsilon_{j',\ell'}\right)\right)\right\}\right)$$

$$=\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}V_{\underline{T}}\left\{T_{j,i}\right\}\left[\left(\sum_{\ell=1}^{m}\left(1+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\right\}\right)\right)^2+\left\{\sum_{\ell=1}^{m}V_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\right\}\right\}\right]$$

$$+\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i}\right\}\sum_{\ell=1}^{m}\sum_{\ell'=1}^{m}\left(1+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\right\}+E_{\underline{\varepsilon}}\left\{\varepsilon_{j',\ell'}\right\}+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\varepsilon_{j',\ell'}\right\}\right)$$

$$+\left(\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}\sum_{\ell=1}^{m}\sum_{\ell'=1}^{m}\left(1+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\right\}+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell'}\right\}+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\varepsilon_{j,\ell'}\right\}\right)\right.$$

$$\left.+\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}\left(\sum_{\ell=1}^{m}\left(1+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\right\}\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+E_{\underline{\varepsilon}}\left\{\varepsilon_{j',\ell'}\right\}\right)\right)\right)$$

$$=\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}\left[\left(\sum_{\ell=1}^{m}\left(1+0\right)\right)^2+m\sigma_{meas}^2\right]V_{\underline{T}}\left\{T_{j,i}\right\}$$

$$+\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i}\right\}\sum_{\ell=1}^{m}\sum_{\ell'=1}^{m}\left(1+0+0+0\right)$$

$$+\left(\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}\sum_{\ell=1}^{m}\sum_{\ell'=1}^{m}\left(1+0+0+E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}\varepsilon_{j,\ell'}\right\}\right)\right.$$

$$\left.+\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}\left(\sum_{\ell=1}^{m}\left(1+0\right)\right)\left(\sum_{\ell'=1}^{m}\left(1+0\right)\right)\right)$$

$$=\frac{m^2+m\sigma_{meas}^2}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}V_{\underline{T}}\left\{T_{j,i}\right\}+\frac{m^2}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i}\right\}$$

$$+\left(\frac{1}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}\left(m^2+\sum_{\ell=1}^{m}E_{\underline{\varepsilon}}\left\{\varepsilon_{j,\ell}^2\right\}\right)Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}+\frac{m^2}{k^2m^2n^2}\sum_{i=1}^{k}\sum_{i'\neq i}^{k}\sum_{j=1}^{n}\sum_{j'\neq j}^{n}Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}\right)$$

$$=\left(\frac{1}{kn}+\frac{\sigma_{meas}^2}{kmn}\right)V_{\underline{T}}\left\{T_{1,1}\right\}+\frac{k\left(n^2-n\right)}{k^2n^2}\overline{Cov_{\underline{T}}\left\{T_{j,i},T_{j',i}\right\}}$$

$$+\frac{\left(k^2-k\right)n}{k^2n^2}\left(1+\frac{\sigma_{meas}^2}{m}\right)\overline{Cov_{\underline{T}}\left\{T_{j,i},T_{j,i'}\right\}}+\frac{\left(k^2-k\right)\left(n^2-n\right)}{k^2n^2}\overline{Cov_{\underline{T}}\left\{T_{j,i},T_{j',i'}\right\}}$$

$$= \left(\frac{1}{kn} + \frac{\sigma_{meas}^2}{kmn} \right) V_{\underline{T}}\{T_{1,1}\} + \frac{n-1}{kn}\overline{Cov_{\underline{T}}\{T_{j,i}, T_{j',i}\}} + \frac{k-1}{kn}\left(1 + \frac{\sigma_{meas}^2}{m} \right)\overline{Cov_{\underline{T}}\{T_{j,i}, T_{j,i'}\}}$$
$$+ \frac{(k-1)(n-1)}{kn}\overline{Cov_{\underline{T}}\{T_{j,i}, T_{j',i'}\}} \tag{A38}$$

$$E_{\underline{\varepsilon}}\{V_T\{\overline{M}_{n,k,m}^{strat}|\underline{\varepsilon}=\underline{e}\}\} = \left(\frac{1}{kn} + \frac{\sigma_{meas}^2}{kmn} \right) V_{\underline{T}}\{T_{1,1}\} + \frac{n-1}{kn}\overline{Cov_{\underline{T}}\{T_{j,i}, T_{j',i}\}} + \frac{k-1}{kn}\left(1 + \frac{\sigma_{meas}^2}{m} \right)\overline{Cov_{\underline{T}}\{T_{j,i}, T_{j,i'}\}}$$
$$+ \frac{(k-1)(n-1)}{kn}Cov_{\underline{T}}\{T_{j,i}, T_{j',i'}\}$$

$$= \left(\frac{1}{kn} + \frac{\sigma_{meas}^2}{kmn} \right) PSill + \frac{n-1}{kn}\left(PSill - \gamma_{within} \right) + \frac{k-1}{kn}\left(1 + \frac{\sigma_{meas}^2}{m} \right)\left(PSill - \gamma_{among} \right)$$
$$+ \frac{(k-1)(n-1)}{kn}\left(PSill - \gamma_{among} \right)$$

$$= \left(\frac{1}{kn} + \frac{n-1}{kn} + \frac{k-1}{kn} + \frac{(k-1)(n-1)}{kn} \right) PSill + (1+k-1)\frac{\sigma_{meas}^2}{kmn} PSill$$
$$- \frac{n-1}{kn}\gamma_{within} - \left(\frac{(k-1)(n-1)}{kn} + \frac{k-1}{kn} + \frac{(k-1)}{k}\frac{\sigma_{meas}^2}{mn} \right)\gamma_{among}$$

$$= -\frac{n-1}{kn}\gamma_{within} + \left(PSill - \frac{(k-1)}{k}\gamma_{among} \right)\left(1 + \frac{\sigma_{meas}^2}{mn} \right) \tag{A39}$$

where $\overline{Cov_{\underline{T}}\{T_{j,i}, T_{j',i}\}}$ is the mean of the covariances between pairs of measurements on samples from the same stratum, and $\overline{Cov_{\underline{T}}\{T_{j,i}, T_{j',i'}\}}$ is the mean of the covariances between pairs of measurements on samples from different strata. The variance is the same for any random location, so $V_{\underline{T}}\{T_{j,i}\} = V_{\underline{T}}\{T_{1,1}\}$, $j = 1, 2, ..., n, i = 1, 2, ..., k$.

Combining the within and between components in Formulas (A36) and (A39), the variance of the mean of the composite sample measurements is

$$V\{\overline{M}_{n,k,m}^{strat}\} = \frac{T^2\sigma_{meas}^2}{mn} - \frac{n-1}{kn}\gamma_{within} + \left(PSill - \frac{(k-1)}{k}\gamma_{among} \right)\left(1 + \frac{\sigma_{meas}^2}{mn} \right) \tag{A40}$$

Dividing Formula (A40) by T^2, the relative variance of $\overline{M}_{n,k,m}$ is

$$V_{Rel}\{\overline{M}_{n,k,m}^{strat}\} = \frac{V\{\overline{M}_{n,k,m}^{strat}\}}{T^2} = \frac{\frac{T^2\sigma_{meas}^2}{mn} - \frac{n-1}{kn}\gamma_{within} + \left(PSill - \frac{(k-1)}{k}\gamma_{among} \right)\left(1 + \frac{\sigma_{meas}^2}{mn} \right)}{T^2}$$

$$= \frac{\sigma_{meas}^2}{mn} - \frac{n-1}{kn}\gamma_{within}^{Rel} + \left(PSill^{Rel} - \frac{(k-1)}{k}\gamma_{among}^{Rel} \right)\left(1 + \frac{\sigma_{meas}^2}{mn} \right)$$

$$= \frac{\sigma_{meas}^2}{mn} + \left(PSill^{Rel} - \frac{n-1}{kn}\gamma_{within}^{Rel} - \frac{(k-1)}{k}\gamma_{among}^{Rel} \right) + \left(PSill^{Rel} - \frac{(k-1)}{k}\gamma_{among}^{Rel} \right)\frac{\sigma_{meas}^2}{mn} \tag{A41}$$

The permissible range for both of the relative semivariogram values, γ_{within}^{Rel} and γ_{among}^{Rel}, is 0 to $PSill^{Rel}$, and a rational ordering of values would be $0 \leq \gamma_{within}^{Rel} \leq \gamma_{among}^{Rel} \leq PSill$, since the expected absolute

difference between two measurements would generally be expected to be smaller within a stratum than between strata. For $\gamma_{within}^{Rel}=0$, the actual concentration would be constant within strata (but could vary from stratum to stratum), and, for $\gamma_{within}^{Rel}=\gamma_{among}^{Rel}=PSill^{Rel}=0$, the actual concentration would be constant over the entire targeted area of the tank. For $\gamma_{among}^{Rel}=PSill^{Rel}>0$, the concentrations would be uncorrelated for pairs of samples from locations in different strata, and, for $\gamma_{within}^{Rel}=\gamma_{among}^{Rel}=PSill^{Rel}>0$, the concentrations would be uncorrelated for pairs of samples from locations throughout the targeted region of the tank. Substituting $\gamma_{within}^{Rel}=\gamma_{among}^{Rel}=PSill^{Rel}=0$, into Formula (A41) produces a variance for the concentration measurements that depends solely on the measurement uncertainty: $V_{Rel}\left\{\overline{M}_{n,k,m}^{strat}\right\}=\dfrac{\sigma_{meas}^2}{mn}$.

Substituting $\gamma_{within}^{Rel}=\gamma_{among}^{Rel}=PSill^{Rel}>0$, into Formula (A41) yields $V_{Rel}\left\{\overline{M}_{n,k,m}^{strat}\right\}=\left(1+\dfrac{PSill^{Rel}}{kn}\right)\left(1+\dfrac{\sigma_{meas}^2}{m}\right)-1$.

Assuming that the mean of the analyte concentrations from replicate measurements of the composite samples are not significantly different from one another, the *UCL95* is defined by the following expression,

$$UCL95=\overline{M}_{n,k,m}^{strat}\left(1+t\sqrt{V_{Rel}\left\{\overline{M}_{n,k,m}^{strat}\right\}}\right),\tag{A42}$$

where *t* represents the 95 percentile of a Student's t distribution with *mn*-1 degrees of freedom.

A.5 Special Cases.

Substituting *n* = 1 composite sample in Formula (A41) where there are *k* locations and *m* measured times, the variance of the mean of the concentration measurements is

$$\begin{aligned}V_{Rel}\left\{\overline{M}_{1,k,m}^{strat}\right\}&=\frac{\sigma_{meas}^2}{m}+\left(PSill^{Rel}-\frac{(k-1)}{k}\gamma_{among}^{Rel}\right)\left(1+\frac{\sigma_{meas}^2}{m}\right)\\[2mm]&\quad\left(1+\frac{\sigma_{meas}^2}{m}\right)+\left(PSill^{Rel}-\frac{(k-1)}{k}\gamma_{among}^{Rel}\right)\left(1+\frac{\sigma_{meas}^2}{m}\right)-1\\[2mm]&=\left(1+PSill^{Rel}-\frac{(k-1)}{k}\gamma_{among}^{Rel}\right)\left(1+\frac{\sigma_{meas}^2}{m}\right)-1\end{aligned}\tag{A43}$$

This special case of the variance of $\overline{M}_{n,k,m}^{strat}$ for *n* = 1 composite sample using the variance computational method in Formula (A6) agrees with the relative variance of $\overline{M}_{1,k,m}^{strat}$ in Formula (A29) which is a direct derivation of the variance of $\overline{M}_{1,k,m}^{strat}$ using the variance computational method of Formula (A7).

Substituting *k* = 1 location per composite sample[4] in Formula (A41), where there are *n* composite samples and *m* measured times, the variance of the mean of the concentration measurements is

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[4] With one location per sample, we can drop the descriptor "composite" from composite sample: this is a discrete sample, and the sampled locations are obtained randomly from the entire tank floor.

$$V_{Rel}\left\{\overline{M}_{n,1,m}^{strat}\right\} = \frac{\sigma_{meas}^2}{mn} - \frac{n-1}{n}\gamma_{within}^{Rel} + PSill^{Rel}\left(1+\frac{\sigma_{meas}^2}{mn}\right)$$

$$= \left(1+\frac{\sigma_{meas}^2}{mn}\right) - \frac{n-1}{n}\gamma_{within}^{Rel} + PSill^{Rel}\left(1+\frac{\sigma_{meas}^2}{mn}\right) - 1$$

$$= \left(1+PSill^{Rel}\right)\left(1+\frac{\sigma_{meas}^2}{mn}\right) - \frac{n-1}{n}\gamma_{within}^{Rel} - 1 \qquad (A44)$$

This special case of the variance of $\overline{M}_{n,k,m}^{strat}$ for $k = 1$ stratum agrees with the relative variance of $\overline{M}_{n,1,m}^{strat}$ in Formula (A33). Both results were based on the variance computational method of Formula (A6), but Formula (A29) starts with a simplified model for the mean of measurements in Formula (A31), while Formula (A44) begins with a general model for the mean of measurements in Formula (A34).

Formula (A44) also is the same as Formula (A16), the variance of the mean of concentration measurements under random sampling.

Appendix B: Sensitivity Analyses for the Uncertainty Results.

This appendix presents a sensitivity analysis of the results discussed in Section 4.

Consider the composite sampling plans with locations selected based on stratified random sampling. Table B.1 summarizes the impact on the relative standard deviation of the mean of the concentration measurements, $S_{Rel}\left\{\bar{M}_{n,k,m}^{strat}\right\}$, and on the UCL95$_{Rel}$ from increasing the relative spatial standard deviation, $S_{Rel}\left\{\bar{M}_{n,m}^{discrete}\right\}$ from the baseline case of 25% of the true concentration to 50% and 100% of the true concentration. Since the relative measurement error standard deviation has not been changed from 10% of the true concentration, this also amounts to increasing the ratio of the relative spatial standard deviation to the relative measurement error standard deviation from 2.5 to 5.0 and 10.0, respectively. The correlation patterns remain unchanged.

The results from Section 4 Table 2 are shaded in gray in Table B.1 below. Moving from left to right in Table B.1, the relative standard deviation of the mean of the concentration measurements, $S_{Rel}\left\{\bar{M}_{n,k,m}^{strat}\right\}$ follows a simple pattern increasing in proportion to the inflation in the relative spatial standard deviation, $\sqrt{PSill^{Rel}}$: if the relative spatial standard deviation doubles so does the relative standard deviation of $\bar{M}_{n,k,m}^{strat}$.

Table B.1. Sensitivity Results for the UCL95 for the Mean Concentration Measurements from Composite Samples with Locations Selected by Stratified Random Sampling by Varying the PSill

PSill^{Rel}			25%		50%		100%	
PSill^{Rel}/ σ_{meas}^2			2.5		5.0		10.0	
n	k	m	$S_{Rel}\left\{\bar{M}_{n,k,m}^{strat}\right\}$	UCL95$_{Rel}$	$S_{Rel}\left\{\bar{M}_{n,k,m}^{strat}\right\}$	UCL95$_{Rel}$	$S_{Rel}\left\{\bar{M}_{n,k,m}^{strat}\right\}$	UCL95$_{Rel}$
3	5	3	9.73%	1.181	18.57%	1.345	36.70%	1.682
3	4	3	10.74%	1.200	20.70%	1.385	40.99%	1.762
3	3	3	12.26%	1.228	23.82%	1.443	47.30%	1.880
3	2	3	14.83%	1.276	29.08%	1.541	57.88%	2.076
3	1	3	20.70%	1.385	40.99%	1.762	81.79%	2.521

Table B.2 summarizes the results of increasing the relative spatial standard deviation, $\sqrt{PSill^{Rel}}$, from the baseline case of 25% of the true concentration value to 50% and 100% of the true value for the discrete sampling plans. The correlation patterns remain unchanged. The results from Section 4 Table 3 are shaded in gray in Table B.2. Similar to the composite sample sensitivity results, the relative standard deviation of the mean of the concentration measurements, $S_{Rel}\left\{\bar{M}_{n,m}^{discrete}\right\}$, follows a simple pattern it increasing in proportion to the inflation in the $\sqrt{PSill^{Rel}}$: if the relative spatial standard deviation doubles so does the relative standard deviation of $\bar{M}_{n,m}^{discrete}$.

Table B.2. Sensitivity Results for the UCL95 for the Mean Concentration Measurements from Discrete Samples with Locations Selected by Random Sampling by Varying the PSill

PSill^{Rel}			25%		50%		100%	
PSill^{Rel}/σ^2_{meas}			2.5		5.0		10.0	
n	k	m	$S_{Rel}\left\{\overline{M}^{discrete}_{n,m}\right\}$	$UCL95_{Rel}$	$S_{Rel}\left\{\overline{M}^{discrete}_{n,m}\right\}$	$UCL95_{Rel}$	$S_{Rel}\left\{\overline{M}^{discrete}_{n,m}\right\}$	$UCL95_{Rel}$
10	1	3	18.64%	1.317	37.14%	1.631	74.21%	2.261
9	1	3	18.74%	1.320	37.33%	1.637	74.59%	2.272
8	1	3	18.87%	1.323	37.57%	1.644	75.06%	2.286
7	1	3	19.03%	1.328	37.88%	1.653	75.66%	2.305
6	1	3	19.25%	1.335	38.28%	1.666	76.45%	2.330
5	1	3	19.55%	1.344	38.84%	1.684	77.55%	2.366
4	1	3	19.99%	1.359	39.66%	1.712	79.16%	2.422
3	1	3	20.70%	1.385	40.99%	1.762	81.79%	2.521
2	1	3	22.06%	1.444	43.54%	1.877	86.79%	2.749
1	1	3	25.70%	1.750	50.41%	2.472	100.33%	3.930

Comparison of composite and discrete sampling plans based on the relative standard deviation of the mean of the concentration measurements follows a consistent pattern regardless of the value of the relative spatial standard deviation, $\sqrt{PSill^{Rel}}$, and in the range where the ratio of the relative spatial standard deviation to the relative measurement error standard deviation changes from a ratio of 2.5:1 to 10:1.

The changes in the UCL95^{Rel} when the PSill^{Rel} is varied are consistent with the previous results in Section 4 where all of the discrete sampling plans had larger UCL95^{Rel}s than all of the composite sampling plans (except for the common case). When the relative spatial standard deviation, $\sqrt{PSill^{Rel}}$, was doubled to 50% of the true concentration value, the UCL95^{Rel} for the sampling plans followed the same ordering. Unlike the primary vessel with well-mixed material, the annulus may be expected to display a higher spatial variability (there is no previous tank data set with annulus samples to predict how large this could be), because the material did not undergo the same mixing process as the material in the primary vessel. The compositing plans may offer greater benefits in term of lower UCL95^{Rel}s than the discrete plans, and the results do not seem to be sensitive to the relative spatial standard deviation.

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