

Extensions to the Theory of Sampling 2. The Sampling Uncertainty (SU), and SU as alternative to variographic analysis

Bo Svensmark

Department of Plant and Environmental Sciences, University of Copenhagen, Faculty of Science, Thorvaldsensvej 40, DK-1871, Frederiksberg C, Denmark, E-mail: svensmark@plen.ku.dk

DOI: [to be added by publishers]

Abstract: In the Theory of Sampling the Grouping and Segregation Error (GSE) is expressed relative to the Fundamental Sampling Error (FSE) by $GSE = Y \cdot Z \cdot FSE$. Unfortunately, estimation of Z seems difficult or impossible. The problem seems to be the attempt to link GSE to FSE. However, the sampling uncertainty due to $FSE + GSE$ can be estimated from the distributional heterogeneity, with a small modification, by a new function, the Sampling Uncertainty (SU) proposed here. SU is calculated from the spatial distribution of the analyte in a manner similar to cyclic convolution. The new method was validated by a riffle splitter mass reduction experiment and by variographic analysis of theoretical data. For 1-dimensional sampling SU is shown to be better than variogram integration in case of cyclic or non-stationary variations and by being independent of the nugget effect when the nugget effect is close to zero. Thus, the extensions allow accurate predictions of the correct sampling uncertainty for 1-dimensional sampling and are proposed as a supplement to variographic analysis. The rationale for using SU is to be able to set up plausible theoretical scenarios for a sampling problem, and to predict the effect of variations in sample size, increment number, increment orientation and sampling method (random systematic, stratified random, random or single increment sampling). SU can also give numeric results for 2-dimensional sampling. The use of SU will mainly be for teaching and for a quantitative understanding of Theory of Sampling and of the benefits of compositional sampling.

Introduction

According to Theory of Sampling (TOS) as developed by Pierre Gy, a representative sample has an acceptable (for the intended use) bias and precision, and bias can be minimized by taking the sample correctly according to the Fundamental Sampling Principle [1-3]. When that is the case, sampling precision is given by FSE and GSE alone, where the latter is often much higher than the former and in practice is responsible for most of the sampling variance. Minkinen [4] has estimated the effects of GSE on simulated lots and Minkinen and Esbensen [5] have made important work with a modification of the factors used for GSE. Unfortunately it is difficult to use the present theory to predict the sampling variance due to GSE, as shown by Geelhoed [6], see Supplementary materials S1 in [14]. A theoretical solution to this is proposed here.

The Sampling Uncertainty (SU) proposed here is a method for estimation of the relative standard deviation for a specific sampling protocol, where a sampling protocol includes sampling method (single increment, random systematic, stratified random or random sampling), number of increments, sampling ratio (mass of the sample divided by mass of the lot), and the specific orientation of the increments relative to the segregation in the lot. Thus SU depends on the combined properties of the lot and of the sampling process. For the lot, input data are spatial distributions of fragments or analytes, which in most cases are not known beforehand, but it is often possible to set up realistic scenarios with reasonable distributions based on prior knowledge or in parallel to similar cases.

So what can it be used for? SU is very well suited for pedagogical purposes, because all aspects of grouping and segregation and distributional heterogeneity can be simulated with greater accuracy, e.g. to show the benefits of composite sampling by real numbers. In a teaching environment it is also possible to make practical experiments with lots which have been prepared with well known properties [7]. But SU can also estimate sampling errors for 1-dimensional (and higher dimensional) cases in the same way as variographic analysis, i.e. the results are estimated based on a series of real samples, and in such cases concentrations are known as function of position. In other cases, e.g. for preparing a series of secondary samplings, it is also possible to make a first sampling round to estimate the distribution of analytes and/or fragments, and then to use SU to make the best protocol for the following many samples. So for many practical cases SU allows a quantitative comparison of different sampling schemes and a better-informed selection of the best compromise between precision and 'cost'.

In most cases SU will be a prediction of the Grouping and Segregation Error (GSE) because the input for the calculations does only contain average concentrations. In other cases, when the input are data from real samples like samples for variographic analysis, the data are affected by the Fundamental Sampling Error (FSE) and long range errors in addition to GSE, so the result from SU will be estimates of the Correct Sampling Error. This double meaning is the main reason for choosing a separate name for this function: SU is the result obtained by Eq. (3) proposed here, i.e. it is an estimate which can be compared to or predict real sampling errors.

Theory

Two new functions, the Sampling Uncertainty SU proposed here, and the Fundamental Sampling Uncertainty FSU [7], allow estimation of the effect of segregation on sampling errors from theoretical or experimental data.

The Sampling Uncertainty SU

The Sampling Uncertainty SU is calculated in a manner parallel to the calculation of the distributional heterogeneity DH_L . The only difference is that the groups for SU are all the potential samples, that can be taken from the lot by a given sampling protocol, while the groups for the distributional heterogeneity are all the potential increments that is needed to sample the whole lot. The difference in the results is that DH_L is characteristic of the lot, but only depends on the size of an increment, thus the other characteristics of the sampling protocol are not included and accordingly sampling errors cannot be predicted. In SU all characteristics of the lot and the sampling protocol are included and sampling error can be predicted (from theoretic data) or estimated (from previous samplings like in variographic analysis), with an accuracy equal to that of the input data.

This treatment will start with a situation such as a riffle splitter where the lot is 3-dimensional (X, Y, Z), but one dimension Y is sampled in its entirety. Assume that the concentration in the X-direction along the input tray perpendicular to the chutes are known for all x_{max} positions.

To explain the concept of the “potential samples”, look at the simplest example, a vertical sample with increments, taken from top to bottom of the lot, as shown in Fig. 1. The increments could be taken at all positions in the horizontal direction as indicated by the white arrow in the figure.

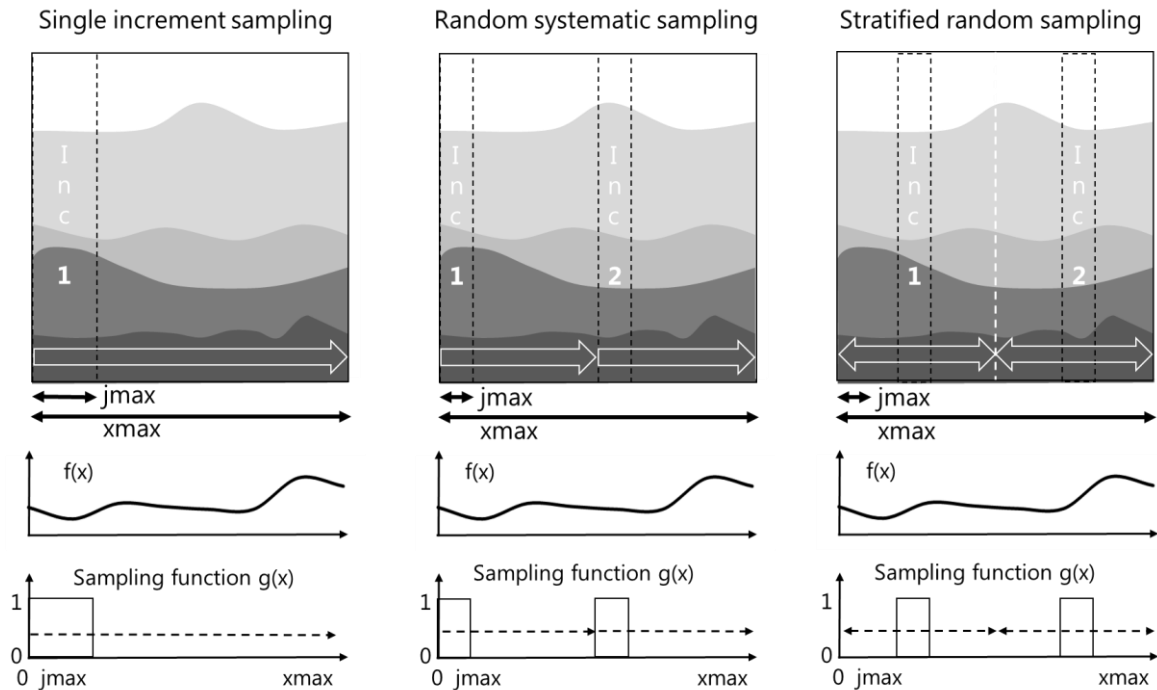


Figure 1. Sampling with 2 increments of width j_{max} taken from a lot of width x_{max} . $f(x)$ is the concentration as function of position and $g(x)$ is the sampling function.

The single increment sample consists of one increment that could be taken at any position within the lot. The 2 increments in the random systematic sample are synchronized, so the distance between them will always be constant. For stratified random sampling the 2 increments could be taken at any position within half of the lot. For random sampling all increments can be taken from all parts of the lot as long as they do not overlap.

The concentration a_i in a potential samples starting at index i can be obtained as a simple sum:

$$\text{Potential samples:} \quad a_i = \frac{1}{ni \cdot j_{max}} \sum_{l=1}^{l=ni} \sum_{j=1}^{j_{max}} a_{i+j-1+(l-1)h} \quad \text{for } i = 1 \text{ to } h \quad (1)$$

- i : Start position of the first increment
- j_{max} : Width of one increment, $j_{max} = x_{max}/(ratio \cdot ni)$
- ni : Number of increments
- h : Distance between increments $h = x_{max}/ni$
- $ratio$: Sampling ratio, M_{Sample}/M_{Lot}

For systematic sampling, only h terms are needed, because the results will repeat themselves in a cyclic manner for indices $l > h$. This mathematical sampling is equivalent to circular convolution integration, i.e. the output (the sampled concentrations) is equal to the input (the lot concentrations) convoluted with the sampling function, $a(x) = f(x) \cdot g(x)$. Single increment sampling is equivalent to box-car averaging. For stratified random sampling and random sampling, it is slightly more complicated, and this will be treated below.

The position of a sample is indicated by the index for the first element in the sample, so a potential increment could start in all positions $i = 1$ to $x_{\max}$. If the increment starts close to the upper limit of the lot, the increment will extend beyond the lot, and in this case the concentrations to be sampled are taken from the start of the lot. This operation is necessary in order for the sampling to obey the fundamental sampling principles, that every fragment in the lot must have the same non-zero probability of ending up in the final sample. This also means that the results are independent of the phase of the concentration profile, see Supplemental material S2 in [14].

For stratified random and random sampling, sums similar to Eq. (1) could be set up but the number of terms would be extremely high for more than a few increments. Instead, a Monte Carlo method is proposed, where the positions of the increments are generated by random numbers. Taking 4000 samples, the results will be accurate to $\pm 3\%$.

To estimate SU, all the potential concentrations a_i from the mathematical sampling for a given sampling method are used in Eq. (3).

The heterogeneity is derived from the heterogeneity of one group.

$$\text{Heterogeneity of one group: } h_i = \left(\frac{a_i - a_L}{a_L} \right) \cdot \frac{M_i}{\bar{M}_i} \quad (2)$$

The Sampling Uncertainty is simply the standard deviation of all potential groups (samples) in the lot:

$$\text{SU: } s_{SU} = \sqrt{\frac{1}{N_i} \sum \left[\left(\frac{a_i - a_L}{a_L} \right) \cdot \frac{M_i}{\bar{M}_i} \right]^2} \quad (3)$$

In the rest of this paper the weighting of the terms with the masses of the individual groups is neglected. Although it is correct in the spirit of Gy to apply this weighting, it is rarely done in practice, because 1) the mass of the increments are often quite similar, and 2) the increments are rarely actually weighted individually. It would be trivial to include this correction if needed.

Here two things are of the utmost importance:

First: The groups are defined as the groups of potential samples for a specific sampling method. Thus the groups for random systematic sampling, stratified random sampling, random sampling and single increment sampling are different.

Second: The variations in a_i may not include variations caused by the constitutional heterogeneity, i.e. when the input are theoretical data without effects of fragment properties other than concentrations. In this case SU is equal to GSE alone. When, on the other hand, a_i are experimental results from sampling experiments, such as data for variographic analysis, SU contains FSE, GSE and all long range errors. In the latter case SU is an estimate of the Minimum Practical Error.

The Fundamental Sampling Uncertainty FSU [7]

The concentrations within an increment in Fig.1 are not randomly distributed as indicated by the colours in the figure (could be low density fragments at top and high density fragments at the bottom). In this case sampling error due to constitutional heterogeneity (that fragments are different) are not equal to FSE, because FSE is the sampling error when all fragments are randomly distributed within the lot. However, the sampling error due to constitutional heterogeneity can be estimated by the Fundamental Sampling Uncertainty FSU proposed in [7] when the distribution of the fragments is known as function of position. FSU is simply the concentration weighted average of FSE for separate parts of all increments in the sample.

In conclusion: From a table of concentrations of fragments or analyts as function of position the sampling errors due to constitutional, distributional and long range heterogeneities can be estimated by the proposed sampling uncertainties SU and FSU. SU and FSU are proposed as standard uncertainties [8] to distinguish them from the traditional sampling errors.

Workbooks in Excel for estimation of sampling uncertainties SU and FSU are available in Svensmark [14].

Results and discussion

Validation of the SU-method: comparison to variographic analysis

SU can be used to predict the sampling uncertainty for 1-dimensional sampling. Examples are given, where the predictions using SU are compared to the prediction obtained from the auxiliary functions obtained by numeric double integration of the 1-dimensional variogram according to Gy [1, 2, 9]. For point selection, i.e. when the mass of the sample is neglectable relative to the mass of the lot the results are correct by the factor $1/\sqrt{1-N_i/x_{\max}}$.

In order to produce results similar to variogram integration, the calculations in SU must be somewhat modified. The variogram only considers variations up to half the maximum length of the input, thus the SU cannot be done in all input points at a time, but must be done for half the input points at a time, shifting the range until the whole length has been covered.

Unfortunately an exact comparison is not possible, mainly because of the limitations of variographic analysis. The limitations are 1) the data must be approximately stationary, i.e. the mean and the standard deviation may not change as a function of position, 2) cyclic variations are levelled out, and 3) predictions for systematic sampling are too low for nugget effects around zero [10], and 4) the weighting of the data is not uniform, the centre sample in the variogram contributes twice as much to the results as the first and the last point. There are also limitations for SU in comparison to variograms: When the result should be valid for half the length of the data (as in variograms) it is not possible to use weights identical to the weights in the variograms, see Supplementary material S3 in [14].

For SU this limitation is only present for the comparison to variograms. In normal use, when SU is calculated for a specific length of data, the weights are uniform along the whole length obeying the fundamental sampling principles.

SU vs variograms for a simple case – influence of trend in data: This example is with a relatively smooth increasing variogram. The data were taken from Pitard [2] page 119 and the variogram and the predictions from the variogram were identical to the results in [2] within rounding errors. For stratified random and random sampling the predictions from SU are essentially identical to the results of traditional variogram integration Fig. 2. There are tiny differences, but it must be remembered that the method of calculation of the estimates (SU vs variogram+ integration) is completely different.

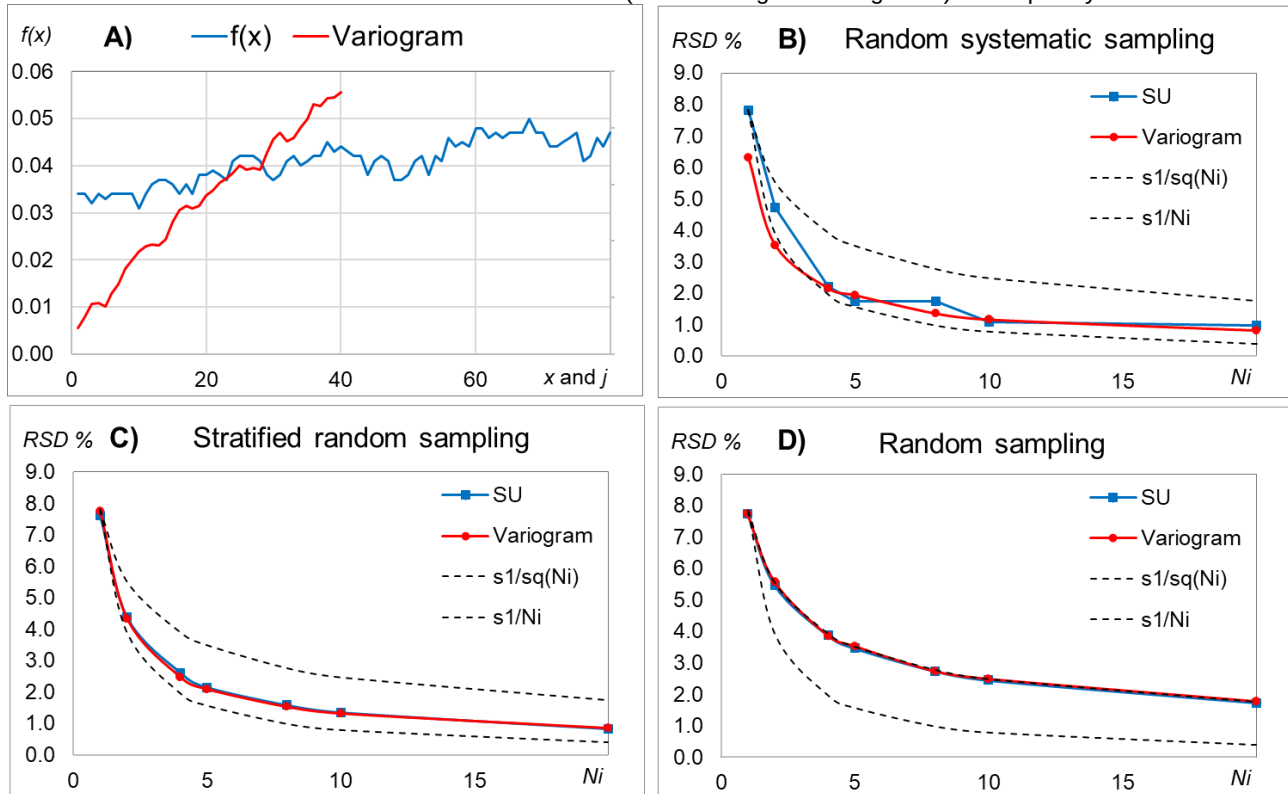


Figure 2. Influence of trends in data for predictions of sampling uncertainty ($RSD\%$) for variogram integration and for SU estimation. A) Concentrations, $f(x)$, and variogram. Data from Pitard [2]. B) to D). Predicted $RSD\%$ from SU and variogram integration. The black dotted lines indicate the position for a $RSD\%$ proportional to $1/\sqrt{Ni}$ and $1/Ni$.

Predictions for random systematic sampling show some significant differences: SU has small deviations up and down from a smooth line. The reason for this behaviour is that SU is very sensitive to (even small) cyclic variations, as discussed later. The results from the variogram seem to be too low for small Ni . The reason for this is that the data are not stationary, as there is an increasing trend in the data.

Also note that the prediction from variograms for the uncertainty for taking a single increment ($Ni = 1$), is different for random systematic sampling ($RSD\% = 6.3$) and stratified random sampling or random sampling ($RSD\% = 7.7$ and 7.7). But how can a single increment taken at a random position within the lot have a different uncertainty depending on the sampling method? Random systematic sampling is started at a random position within the first box, and with only one box this would be identical to stratified random or random sampling. To prove that the trend in the data is responsible for this discrepancy, the data has been corrected to remove the trend, i.e. $\text{slope}(f(x)) = 0$, see Fig.3.

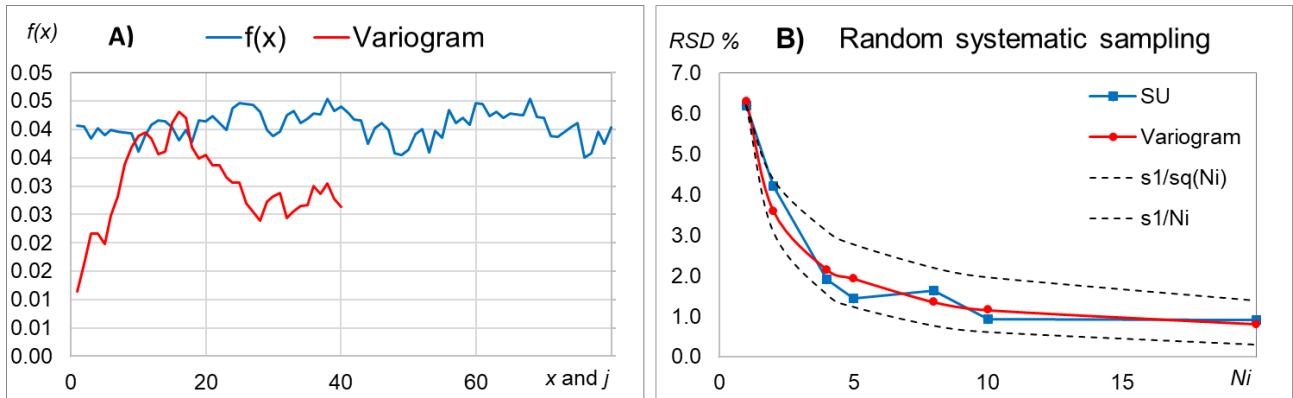


Figure 3. Data without trends ($\text{Slope}(f(x)) = 0$). Predictions of sampling uncertainty (RSD %) for variogram integration and for SU estimation.

Now RSD % for a single increment is the same for all methods and protocols. Note, that RSD % for random systematic sampling from variograms is identical in the two cases (Fig. 2 & 3), i.e. variogram integration neglects linear trends in data. This is easy to understand because for a linear trend the mean integral w_j will have twice the value of the mean double integral $w'_{j/2}$, and the variance for systematic sampling is predicted by $\text{Var}(\text{syst}) = 2w'_{j/2} - w_j$ [1, 2, 9], see Supplementary material S4 in [14]. The predictions for stratified random sampling are based on the double integral w'_j alone, and will thus include the effect of any trend like SU. For random systematic sampling, the predictions from SU are seen to oscillate around the line from variograms because of small cyclic variations.

So both SU and variogram seem to give correct results for stratified random and random sampling in the case of a linear trend, whereas only SU gives reliable predictions for random systematic sampling.

SU vs variograms for data with cyclic variations: In this example of length $x_{\max} = 96$, there is a cyclic variation with a period of $j = 6$, as shown by the variogram Fig. 4 A.

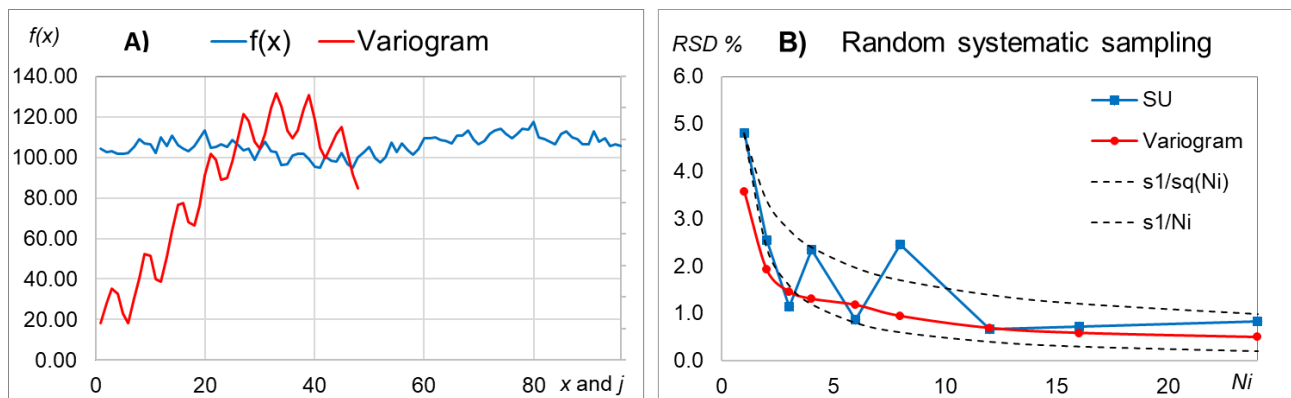


Figure 4. Influence of cyclic variations for predictions of sampling uncertainty (RSD %) for variogram integration and for SU estimation.

It is seen that there are differences in the predictions for random systematic sampling, even though a common trend is seen. The numeric double integration of the variogram is intended to remove noise, but unfortunately it also levels out cyclic variations. It is well known, from sampling theory for (electric) signals, that sampling with a period equal to that of the signal (or any whole multiple of it), will give a maximum variation of the mean ($j = 6$ or 12 corresponding to $N = 8$ or 4), exactly as seen in the SU predictions.

For stratified random sampling and random sampling, the two methods are again essentially identical as expected (data not shown). Supplementary material S5 in [14] shows an example with a pure sine wave variation. So SU will give a correct prediction for all sampling methods even in the case of cyclic variations.

SU vs variograms low nugget effects and for other cases

In the first case the nugget effect is zero, and the results from variogram is too low for random systematic sampling, Fig. 5.

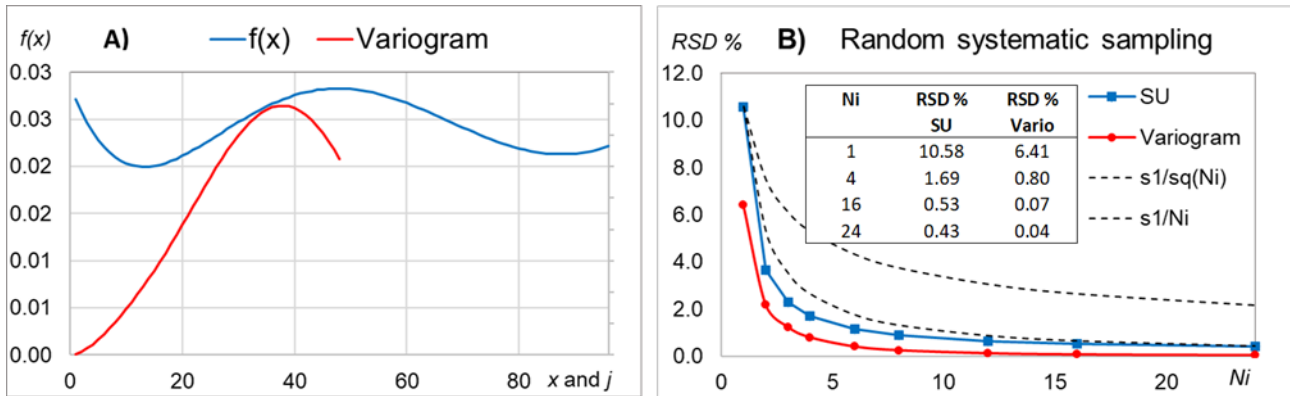


Figure 5. Influence of a low nugget effect for predictions of sampling uncertainty (RSD %) for variogram integration and for SU estimation.

For random systematic sampling the difference increases dramatically with decreasing lags, Fig 5 B. So what is the correct sampling uncertainty for $j = 2$, $Ni = 24$: 0.04 % or 0.43 %? Heikka and Minnkenen [10] have shown that the variogram integration underestimates the uncertainty for short lags, supporting that variographic integration can give estimates that are too low for random systematic sampling. Actually, the estimation of the nugget effect in variograms may be a problem as shown in [11]. If random noise is added, this difference levels out, see Supplementary materials S6 in [14] where this problem is discussed further.

Examples for data with variation in standard deviation as function of position is given in Supplementary material S7 in [14].

Summary for SU vs variograms: The conclusion of the comparison of SU and variograms is that SU gives similar or better results compared to variograms. Also all differences between the SU and variogram results can easily be accounted for by the properties of variogram integration and the different weightings as explained at the beginning of these sections.

In conclusion, SU is a valid method for estimation of sampling uncertainty for 1-dimensional sampling.

SU for 1-dimensional data

Contrary to variographic analysis SU can be used to estimate the sampling uncertainty for 1-dimensional data obeying the fundamental sampling principles, i.e. all points will have the same weight (probability) to be sampled. Extensive examples are given in Supplementary materials S8 and S9).

SU can be used to investigate the effect of the sampling method and the number of increments for all cases that can be represented by 1-dimensional data. Even if the effect of these (sampling method and number of increments) are well known in theory, it is only possible to judge the magnitude of the differences from quantitative data: is random systematic sampling better than stratified random sampling, how much is 32 increments better than 8 increments, etc.- that depends very much on the actual case as shown by the examples given.

SU for 2-dimensional sampling

Just one example will be discussed, a square Japanese slab cake [12]. The lot is a 120 x 120 grid and samples are taken in 1, 4, 9, 16 and 25 boxes as shown in Fig. 6 I).

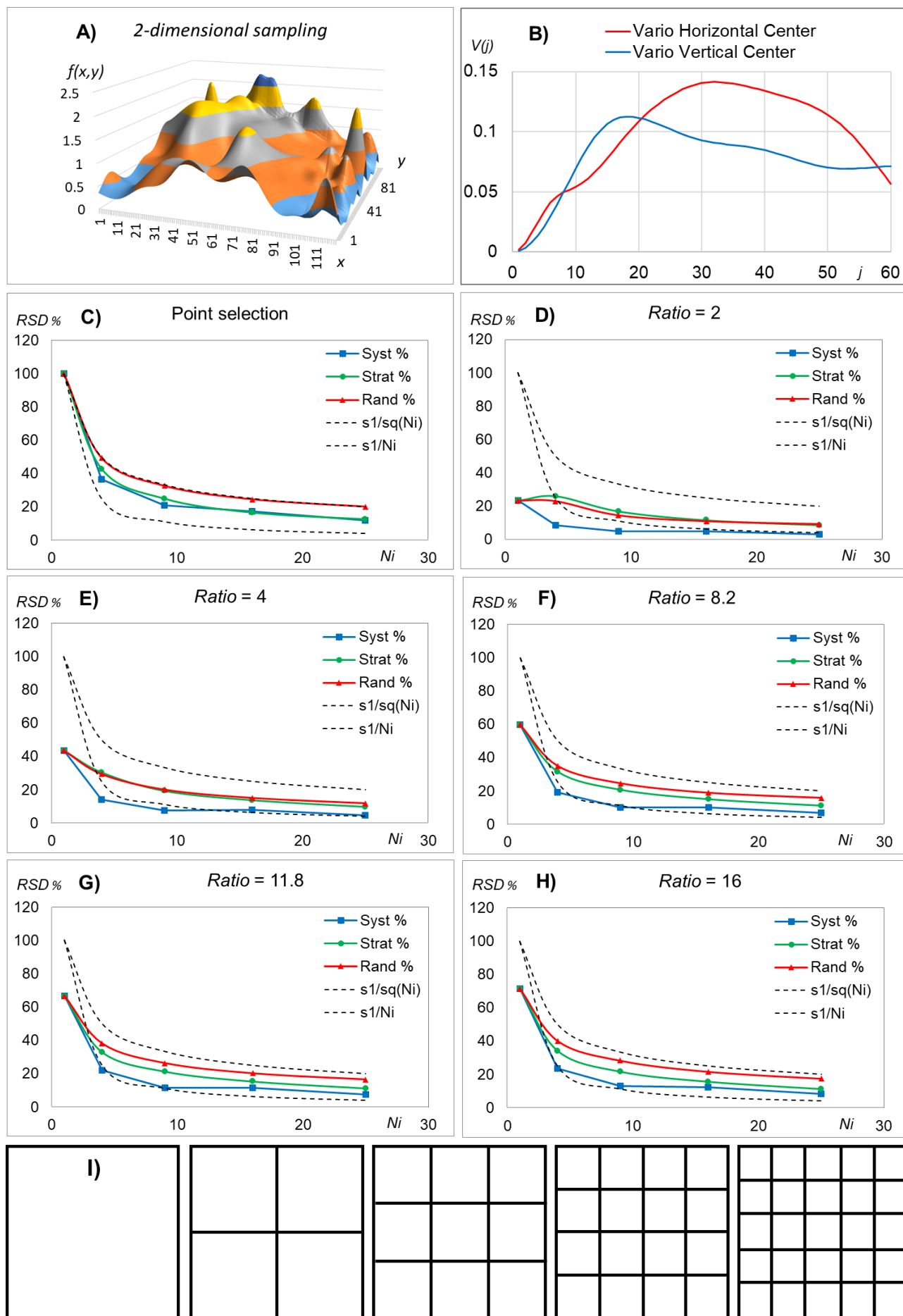


Figure 6. SU for 2-D sampling. A) Concentrations; B) Variogram at the centre in two directions; C) Predicted RSD % for 1 to 25 increments for point selection; D) to H) Predicted RSD % for sampling ratios from 2 to 16; and I) Sampling strata for 1 to 25 increments. The dotted lines start at 100 % of the standard deviation of the lot, and all RSD % are shown in % of standard deviation of the lot.

For these data, with smooth variograms, the random systematic sampling gives the lowest uncertainty, whereas stratified random sampling is similar to random sampling for low sampling ratios (*ratio* = 2 and 4) and intermediate between random systematic and random sampling for higher sampling ratios (*ratio* = 8 – 25 and point selection). The effect of the number of increments increases with the sampling ratio. The effect of the number of increments is small for small sampling ratios, but note that the sampling uncertainty for 1 increment is quite low anyway in this case, only 23 % of the standard deviation of the lot for *ratio* = 2. Note that the results for high sampling ratios approaches that for point selection.

The Correct Sampling Uncertainty (CSU)

Combination of the fundamental sampling uncertainty (FSU) [7] and the grouping and segregation error gives the correct sampling uncertainty (CSU), i.e. the sampling uncertainty for correct sampling when both the constitutional and distributional heterogeneity of the lot and the sampling geometry (increment size, number and orientation) is taken into account:

$$\text{CSU: } s_{\text{CSU}} = \sqrt{s_{\text{FSU}}^2 + s_{\text{GSE}}^2} \quad (5)$$

Example of CSU: For one of the runs in the model experiments for the improved Gy's formula [7] the variation was too high for sand. To estimate how much the distributional heterogeneity must be to explain this, different scenarios were simulated and both FSU and SU (equal to GSE in this case) were calculated, and the resulting CSU was compared to the observed total sampling uncertainty. Samples of ~125 g were taken from 1000 g by using a Riffle splitter with 18 chutes 3 times. The mixture contained 50 g sand, 50 g sesame seeds, 700 g barley grains and 200 g steel balls with a diameter of 6 mm. See ref. [7] for further details. The results of estimating FSU, GSE and CSU are given in Table 1 together with the observed experimental results. Since the concentration of fragments changes as function of the position along the input tray, the effect of the constitutional heterogeneity is slightly different from FSE (calculated as if the whole lot were randomly mixed) and must be estimated by FSU.

Table 1: Estimated and observed sampling uncertainty RSD %

	Sand	Sesame	Barley	Steel
FSU	4.0	4.3	3.6	14.1
GSE	8.2	0.0	0.6	0.0
CSU	9.1	4.3	3.6	14.1
OBS	9.1	3.4	3.4	14.1

The distribution of the analytes in the input tray were generated by a random distribution of sand, *mean* = 0.05, *s* = 0.015. The concentration of barley was corrected to give a sum of concentrations equal to one.

The fact that the results fit the experiments nearly exactly does not mean that the distribution is exactly as in the scenario, as many different distributions could all give similar results. What the data and calculations do show is that it is possible to simulate the experiment with a plausible distribution.

This example with a high GSE in a riffle splitter is unusual. Apart from sand in a few experiments in [7] GSE is negligible for proper use of riffle splitters, and good rotary dividers behave similar or even better [13].

How to minimize the Correct Sampling Uncertainty: Results in Svensmark [7] show that it will reduce the fundamental sampling error to separate the lot in a direction parallel to the sampling direction, and results given here show that it will reduce the grouping and segregation error by mixing the lot in a direction perpendicular to the sampling direction. It is true, that the spatial distribution of fragments in most cases are unknown, and that they change with manipulation of the lot, but the message is that it is a very bad idea to try to get a uniform distribution in a direction parallel to the sampling increments (normally this would be in the vertical direction), so segregation according to gravity may in most cases be beneficial, even if mixing horizontally is more important.

Conclusion

The Sampling Uncertainty SU is proposed as a new way of treating correct sampling errors including the grouping and segregation error. SU allows accurate estimation of sampling uncertainty due to distributional heterogeneity and can estimate the effect of the number of increments for the sampling methods random systematic sampling, stratified random sampling, random sampling and single increment sampling. The input for SU is a table of concentrations as a function of position within the lot. For 1-dimensional sampling this is equivalent to the input for variograms, i.e. a series of samples taken in one direction by random systematic sampling. For 2-dimensional sampling the input is a map of concentrations in 2 dimensions. In most cases such experimental concentration maps are not available, but it is often possible to set up realistic theoretical scenarios from prior knowledge or from similar cases.

SU can be used for 1-dimensional sampling and does not suffer from the problems associated with results from variogram integration caused by non-stationarity, cyclic variations and low nugget effects. Real lots do not need to be stationary, and SU will also be correct for non-stationary lots. It is still recommended to calculate the variogram because it gives valuable information about the heterogeneity of the lot, but it is advised to also use SU as a supplement to variogram integration.

SU can also be applied quantitatively to 2-dimensional lots. This is an extension to TOS which only gives quantitative results for 0-D and 1-D sampling. In principles there are no limitations to the number of dimensions that can be used for SU.

SU is very well suited for pedagogical purposes, because all aspects of grouping and segregation and distributional heterogeneity can be simulated with greater accuracy, e.g. to show the benefits of composite sampling by real numbers.

SU allows a quantitative comparison of different sampling schemes and a better-informed selection of the best compromise between precision and 'cost'.

Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Thanks to David Pattison and Giorgio Tomasi for language advices. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Auxiliary materials in [14]

Supplementary materials S1-S9

Workbooks for SU and FSU including 1-dimensional and 2-dimensional sampling, variograms and the discrete Fourier transform.

ORCID iDs

Bo Svensmark: <https://orcid.org/0000-0003-0430-6181>

References

1. P.M. Gy, *Sampling for analytical purposes*, Chichester, England, 1998.
2. Francis F. Pitard, *Pierre Gy's Sampling Theory and Sampling Practice*, 2nd Ed., CRC, 1993.
3. L. Petersen, P. Minkkinen, K.H. Esbensen, *Representative sampling for reliable data analysis: Theory of Sampling*, Chemometrics and Intelligent Laboratory Systems, **77**, 261-277 (2005). <https://doi.org/10.1016/j.chemo-lab.2004.09.014>
4. P. Minkkinen, *Dependence of the variance of lot average on the sampling mode and heterogeneity type of the lot*, in S C Dominy and K H Esbensen, *Proceedings of the 8th World Conference on Sampling and Blending*, 8 – 11 May, 2017, Perth, Australia, The Australian Institute of Mining Metallurgy Publication Series 2/2017, pp. 319-330. ISBN 978 925100 56 3.
5. P.O. Minkkinen and K.H. Esbensen, *Sampling of particulate materials with significant spatial heterogeneity - Theoretical modification of grouping and segregation factors involved with correct sampling errors: Fundamental Sampling Error and Grouping and Segregation Error*, Analytica Chimica Acta, **1049**, 47 – 64 (2019). <https://doi.org/10.1016/j.aca.2018.10.056>
6. B. Geelhoed, M.J.J. Koster-Ammerlaan, G.J.C. Kraaijeveld, P. Bode, D. Dihalu and H. Cheng, *An experimental comparison of Gy's sampling model with a more general model for particulate material sampling*. Fourth World Conference on Sampling & Blending, The Southern African Institute of Mining and Metallurgy, 2009.
7. B. Svensmark, *Extensions to the Theory of Sampling 1. The extended Gy's formula, the segregation paradox and the fundamental sampling uncertainty (FSU)*, Analytica Chimica Acta **1187**, 339127 (2021). <https://doi.org/10.1016/j.aca.2021.339127>
8. *Guide To The Expression Of Uncertainty In Measurement*. ISO, Geneva (1993). (ISBN 92-67-10188-9) (Reprinted 1995: Reissued as ISO Guide 98-3 (2008), also available from <http://www.bipm.org> as JCGM 100:2008)
9. L. Petersen, K.H. Esbensen, *Representative process sampling for reliable data analysis - a tutorial*, Journal of Chemometrics, **19**, 625-647 (2006). <https://doi.org/10.1002/cem.968>
10. R. Heikka) and P. Minkkinen, *Integration of the variogram using spline functions for sampling error estimation*, Chemometrics and Intelligent Laboratory Systems **44**, 205–211 (1998). [https://doi.org/10.1016/S0169-7439\(98\)00187-7](https://doi.org/10.1016/S0169-7439(98)00187-7)
11. R. Heikka and P. Minkkinen, *Comparison of some methods to estimate the limiting value of the variogram, $vh(j)$, for the sampling interval $j=0$ in sampling error estimation*, Analytica Chimica Acta **346**, 277-283 (1997). [https://doi.org/10.1016/S0003-2670\(97\)90063-5](https://doi.org/10.1016/S0003-2670(97)90063-5)
12. P. Gy, *Sampling of heterogeneous and dynamic material systems*, Data Handling in Science and Technology – volume 10, Chapter 22, Elsevier 1992
13. L. Petersen, C.K. Dahl, K.H. Esbensen, *Representative mass reduction in sampling - a critical survey of techniques and hardware*, Chemometr. Intell. Lab. Syst., **74**, 95-114 (2004). <https://doi.org/10.1016/j.aca.2021.339127>
14. B. Svensmark, *Toolbox for analytical chemistry*, www.bosvensmark.dk