Licentiate Thesis

Estimating and Reducing Errors in Soil Sampling

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Sammanfattning

Contaminated sites are sampled and analysed to assess their remediation need. In the process the question arises if the results of the analysis represents the site they are taken from properly.

Sampling and preparation is known to induce errors. Results from the analysis of soil samples may be expected to include errors. For a heterogeneous material like soil, much of the overall errors may be associated with the sampling and sample handling. To improve the reliability of the results, the sampling and preparation procedure need to be evaluated and improved.

This thesis focus on how to estimate and reduce sampling errors.

According to the Theory of Sampling (TOS), also known as Pierre Gy’s Sampling Theory, the total sampling error is a sum of seven different errors. The theory describes how to calculate the uncertainty of some errors. It also describes how to reduce the errors.

A case study were used for calculating the sampling error and make comparisons with the analytical error. Ways to reduce sampling errors are presented and discussed as application of TOS on the sampling of contaminated soil.

The errors can be reduced by means like: -Grinding or milling the samples. -Increase the sample size. -Taking several small increments to compose a sample. -Avoiding bias during sub-sampling through selection of equipment.

Nyckelord

Theory of Sampling, Pierre Gy Sampling Theory, soil, sampling, error, uncertainty, sub-sampling, contaminated soil, sample splitting, XRF, sample preparation, waste

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Summary

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Sampling and preparation is known to induce errors. Results from the analysis of soil samples may be expected to include errors. For a heterogeneous material like soil, a large extent of the overall error may be associated with the sampling and sample handling. To improve the reliability of the results, the sampling and preparation procedure needs to be evaluated and improved.

This thesis focuses on how to estimate and reduce sampling errors.

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The errors can be reduced by means such as:
-Grinding or milling the samples.
-Increasing the sample size.
-Taking several small increments to compose a sample.
-Avoiding bias during sub-sampling through careful selection of equipment.

Sammanfattning

Områden med förorenad jord provtas och analyseras för att bedöma behovet av marksanering. Under processen uppstår frågan om resultatet av analysen representerar jordvolymen de tagits ifrån.

Provtagning och provhantering inducerar fel. Resultatet från analyserna av jordproverna kan antas inkludera fel. För ett heterogent material som jord, kan mycket av det övergripande felet förknippas med provtagningen och provhanteringen. För att förbättra resultatens pålitlighet behöver provtagnings- och provhanteringsproceduren utvärderas och förbättras.

Detta arbete fokuserar på att bedöma och reducera provtagningsfelen.

Enligt teorin för provtagning (Theory of Sampling- TOS) även känd som Pierre Gy’s provtagningsteori, är det totala provtagningsfelet en summa av sju olika fel. Teorin beskriver hur man kan beräkna osäkerheterna för några av felen. Den beskriver även hur man kan minska felen.

En fallstudie användes för att beräkna provtagningsfelen och jämföra dem med det analytiska felet. Olika sätt att minska felen presenteras och diskuteras som en applikation av TOS för provtagning av förorenad jord.

Felen kan reduceras på sätt som:
-Mala eller mortla proverna.
-Öka provstorleken.
-Ta många små delprover för att komponera ihop ett prov.
-Undvika att skevhet uppstår i provet under provklyvning genom noggrant val av utrustning.

Table of Contents

Appendices

Paper I
Review of Soil Sampling Issues
Björn Gustavsson, Anders Lagerkvist (2004)

Paper II
Uncertainty in Soil Sampling-A Case Study
Björn Gustavsson, Karin Luthbom, Anders Lagerkvist (2004)

Paper III
Sample Preparation Prior to XRF Analysis
Björn Gustavsson, Anders Lagerkvist (2004)

1 Introduction

According to the Swedish Environmental Agency an approximation of the number of potentially contaminated sites in Sweden runs up to about 40,000. The funding for remediation from the Swedish Government alone amounts to 300-400 MSEK annually for the period 2003-2006 (Naturvårdsverket, 2003).

To decide if a site is in need of treatment an investigation of the site is needed. The investigation will consist of sampling, analysis of the samples and evaluation of the data. The planning should include how many samples to take, where to take the samples on the site, what method to use for obtaining the samples, how large a sample is needed, how to store and transport the sample, how to prepare the sample, how to sub-sample prior to analysis, how to analyse the sample, how to handle the data, how to interpret the data and how to make decision about the site.

Uncertainties will arise when obtaining samples in field, preparing them in laboratories and analysing them. Different procedures give rise to varying errors. Using data for decision-making that does not truly represent the site could be fatal. Misclassification of soil could lead to unnecessary costs or to risks to human health and the environment.

A sampling theory was developed in the 1950's, the Theory of Sampling (TOS). TOS deals with sampling of particulate matters. The theory can be used to calculate the sampling uncertainties. Compared to the overall sum of analytical and total sampling error, the analytical error is frequently less than 2% (Mason, 1992), or only a fraction, often negligibly small (Crumbling, 2002). The theory can further be used to control, reduce or eliminate components of the sampling uncertainties.

Applied to soil sampling, the sampling theory has been used to investigate the importance of the analytical error in comparison to the overall error, *i.e.* the sum of total sampling error and the analytical error. The theory has also been used for suggesting how to reduce the sampling errors for soil sampling.

Applying the TOS to data from a field study, this study focuses on two issues in sampling and analysis of contaminated soils:

- What introduces the largest error, the analysis or the sample handling?
- What can be done to reduce the sampling error?

2 Materials and Methods

Eight samples from a site investigation were chosen, with a variety of contaminant levels. The samples were dried, sieved through a 2.0 mm mesh sieve and homogenised by kneading for five minutes in plastic bags. With three measurements for each bagged sample, metals were measured by XRF (X-ray Fluorescence spectroscopy). Confirmatory analysis was made with ICP-AES (Inductively Coupled Plasma-optical emission). Lead, Zinc and Copper were chosen for evaluation. The highest and the lowest readings from the XRF were chosen for evaluation along with the ICP-AES analysis. Data was taken from Gustavsson*, et al* (2004 b) where a more thorough method description may be found.

To estimate the sampling error, the Theory of Sampling (TOS) was used. The Theory of Sampling is also known as Pierre Gy's Sampling Theory. In TOS the total sampling error is divided into seven sampling errors. A more thorough description of TOS and how it is applied to soil sampling may be found *i.e.* in the literature study by Gustavsson and Lagerkvist (2004 a). Hereafter "correct" means 'correct in accordance with the Theory of Sampling'. For the field sampling and the sub-sampling in the laboratory the fundamental error (FE) and the grouping and segregation error (GSE) were found to be applicable (Gustavsson*, et al.*, 2004 b).
The sum of the total sampling errors (TE) may be expressed as in equation 1, and is the sum of all sampling errors for all sample preparation steps.

$$s(TE) = \sqrt{\sum \sigma^2_{samplingerror,samplingstep}} \qquad \text{Equation 1.}$$

By measuring seven replicates on standard reference material the analytical error (AE) was calculated as the relative standard deviation. The analytical errors for the ICP-AES analysis were calculated by recalculation of information from the laboratory (Gustavsson*, et al.*, 2004 b).

3 Result and Discussion

3.1 The distribution of uncertainty over different sample handling steps.

In order to improve the uncertainties of data from soil sampling the weakest part has to be identified. Compared to the overall sum of analytical and total sampling error, the analytical error is frequently less than 2% (Mason, 1992), or only a fraction, often negligibly small (Crumbling, 2002).

Using the data from a case study of soil sampling, the analytical uncertainty contributes to approximately 6% of the overall uncertainty (Back, 2003). In that case study the fundamental error and the grouping and segregation error from the primary field sampling are not included; if they were, the contribution from the analytical uncertainty would decrease.

The analytical errors from the case study were compared to the total analytical error for the samples. The size of the analytical error was compared to the size of the sampling error for the same sample, figure 1.

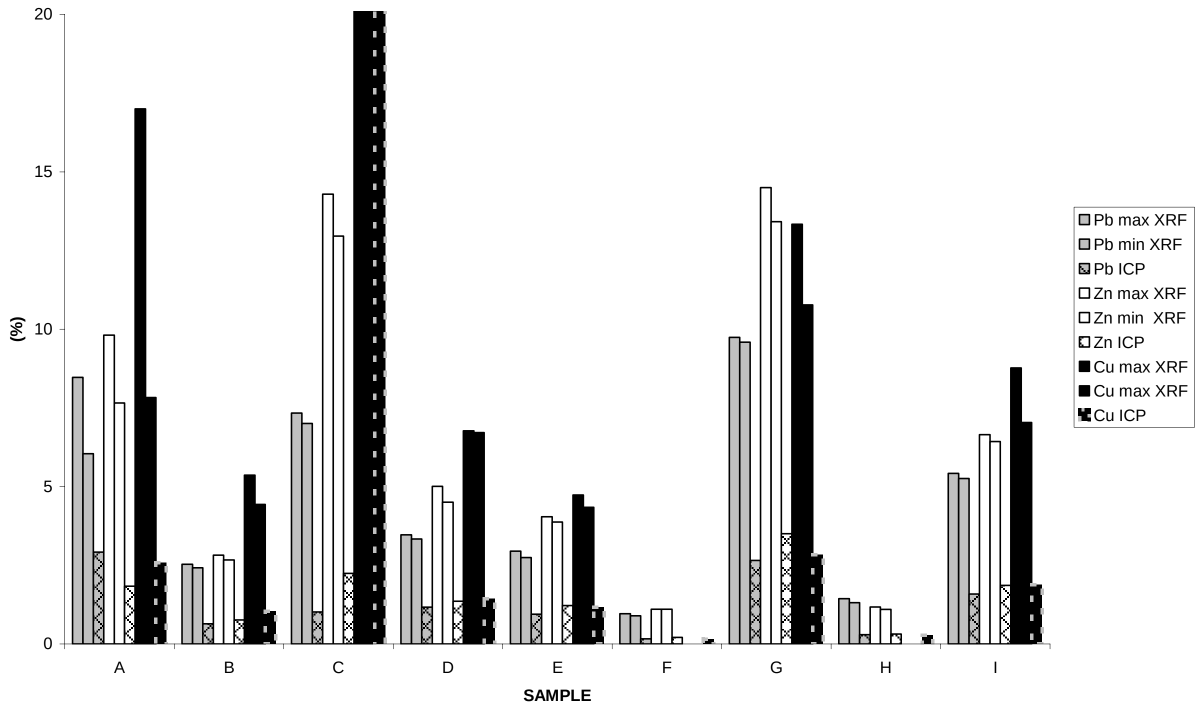

Figure 1. The analytical error compared to the total sampling error, expressed in percent. For sample C the bars for copper are cut off. The levels of Cu max XRF, Cu min XRF and Cu ICP are 553%, 145% and 85.2% respectively. In samples F and H no copper was detected with XRF.

Sample C, copper; have the highest analytical error compared to the total sampling error. 553%, 145% and 85.2%. The samples above 10% analytical error compared to the total sampling errors are sampled in hotspots. Due to the elevated contaminant levels in the hotspot-samples, the fundamental errors are relatively small compared to the analytical error. Except from the hot spot samples, the analytical error is less than 10% of the total sampling error.

These examples indicate that the sampling and sample handling procedure may introduce large errors that exceed the analytical error by far. This is what could be expected according to Mason (1992) and Crumbling (2002).

3.2 Methods of reducing the sampling errors.

In order to reduce the sampling errors, the total sampling error has to be divided into its components. According to the TOS the total sampling error is the sum of seven different errors for all sampling preparation steps.

Long-range heterogeneity fluctuation error deals with the spatial variability in the soil on the site.
This is dealt with in geostatistics and will not be further discussed.

Periodic heterogeneity fluctuation error deals with concentration fluctuations in the soil over time, such as seasonal changes (Back, 2003). Back (2003) states, “For many contamination problems it can be neglected, e.g. for sites contaminated by non-volatile heavy metals under stable chemical conditions and no leaching, because no changes are expected."

A scenario for leaching of soil contaminants in Northern Scandinavia would be no leaching during the freezing period, large leaching during spring thawing and snow melting and varied leaching during summer and autumn depending on the amount of rainfall.

If samples are frozen for storage and later thawed, an effort should be made to attain the same equilibrium afterwards (SIS, 2003). If soil samples are taken during the freezing season, a similar effort should be made.

This error will not be further discussed.

How to reduce each of the remaining contributing errors will be discussed bellow.

3.2.1 Fundamental error, FE

For soil samples there might be heterogeneity in particle size, particle shape, particle weight, density of particles, contamination levels, a tendency to aggregate with other particles, and numerous other properties inside the lot to be sampled. Therefore sampling will always generate a fundamental error. This error is generally large for particles compared to gases and liquids (Smith, 2001)

The fundamental error can never be cancelled out. This is what will remain if a sample is taken in an error free manner (witch is an unattainable limit). This is the only error that is not dependent on the sampling method (Mason, 1992).

Equation 2 shows how to calculate, or estimate, the variance of the fundamental error, s^2(FE).

$$s^2(FE) = \left(\frac{1}{M_E} - \frac{1}{M_L} \right) \cdot d_{95}^3 \cdot c \cdot \beta \cdot f \cdot g \qquad \text{Equation 2}$$

In equation 2 the mineralogical factor, c, is defined as in equation 3 (Minkkinen, 2004).

$$c = \frac{\left(1 - \frac{a_L}{\alpha}\right)^2}{\frac{a_L}{\alpha}} \cdot \rho_c + \left(1 - \frac{a_L}{\alpha}\right) \cdot \rho_m \qquad \text{Equation 3.}$$

Table 2. Description of the components of equation 2 and 3.

components	dimension	description
M_E	[g]	extracted sample weight
M_L	[g]	weight of the lot to be sampled/ sub sampled
d_{95}	[cm]	size of a mesh sieve where 5% of the material is retained
c	[g/cm^3]	mineralogical factor
β	[dim.less]	liberation factor
f	[dim.less]	particle shape factor
g	[dim.less]	the particle size range factor
ρ_m	[g/cm^3]	contaminant density
a_L	[dim less]	average mass proportion of the contaminant in the lot to be sampled
α	[dim less]	massproportion of the contaminant in the critical particles
ρ_g	[g/cm^3]	density of the soil material

Values of β, f and g can be calculated or found tabulated (Gerlach and Nocerino, 2003), (Mason, 1992), (Minkkinen, 1986) and (Smith, 2001). The contaminant is assumed to be pure metal particles; α=1.

The fundamental error can be reduced in two ways. The first way is to increase the size of the sample weight, M_E. The second way to minimisation is to decrease the determining particle size of the sample; d_{95}.

For simplification $k = c \cdot \beta \cdot f \cdot g$ is here seen as a constant determined by the properties of each sample. If the extracted sample weight M_E is much smaller than the weight of the lot that we sample from, M_L, then $1/M_L$ can be excluded from the bracket in equation 4. This gives equation 4.

$$s^2(FE) = \frac{1}{M_E} \cdot d_{95}^3 \cdot k \qquad \text{Equation 4}$$

Logaritmation of equation 4 gives equation 5.

$$\log(s^2(FE)) = -\log M_E + 3 \cdot \log d_{95} + \log k \qquad \text{Equation 5.}$$

By plotting $\log(s^2(FE))$ versus $\log M_E$ for a given diameter, d_{95}, a line is created in a nomogram. A nomogram is a diagram used instead of making calculations. By repeating the process for other diameters, d_{95}, more lines can be plotted (Gerlach and Nocerino, 2003). The nomogram can be used to estimate how the fundamental error for a sample depends on particle size and sample size. Figure 1 shows an example of such a diagram. Data for point A in figure 1: M_E=582g, d_{95}=0,2cm, ρ_m=7,14g/cm^3, a_L=297ppm Zinc, ρ_g=2,65g/cm3, β=1, f=0,5, g=0,25 (Aylward and Findlay, 1974), (Gerlach and Nocerino, 2003), (Mason, 1992), (Minkkinen, 1986).

Only 0.5 g soil is required when analysing with ICP. If the sub-sampling is performed without any prior grinding, this is represented by the route A-B in the diagram.

Taking a larger primary sample would decrease the fundamental error in the direction of the route A-C, assuming that the particle distribution was not affected.

Milling the sample to pass a 0.125 mm sieve is represented by the route A-D in the diagram.

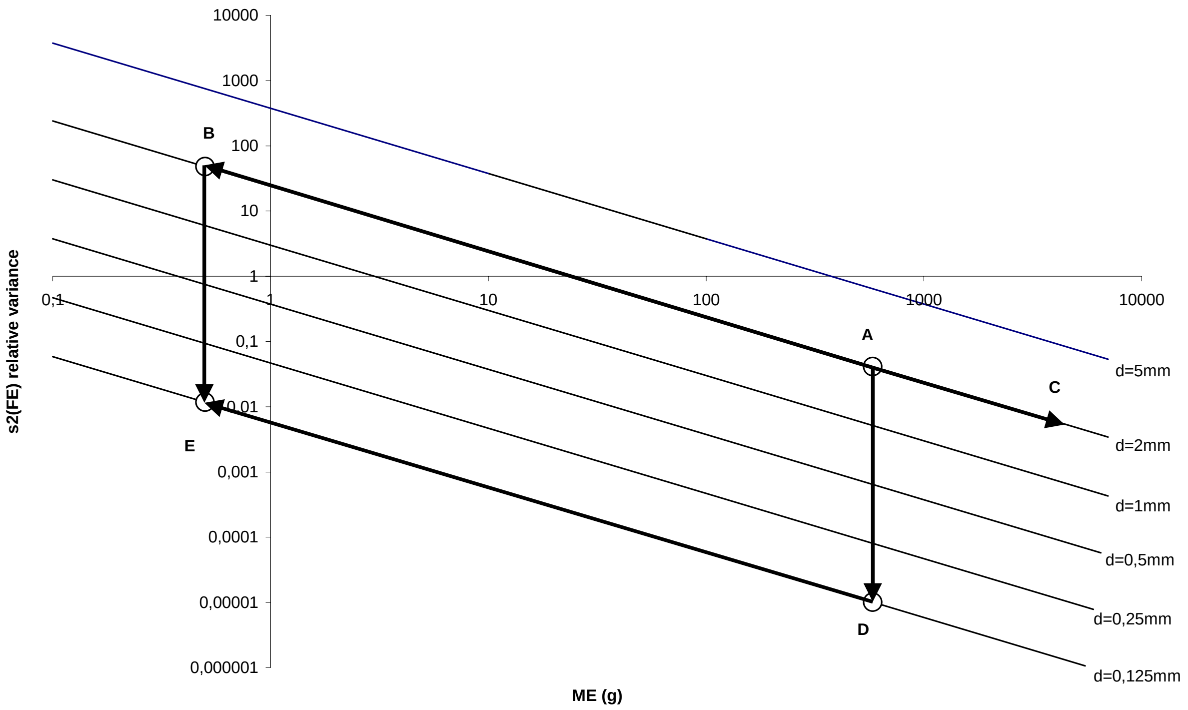

Figure 2. The dependence of the fundamental error on sample size and particle and particle diameter. Data from (Gustavsson*, et al.*, 2004 b)

It is during sub-sampling, not during grinding, that the fundamental error occurs. Sub-sample 0.5 g for analysis with or without grinding the sample first yields fundamental errors differing with orders of magnitudes. To first grind the sample to 0.125 mm particle size (A-D) and then sub-sample the 0.5 g to analyse (D-E) results in a fundamental error of 10.8 % (RSD%). Sub-sampling 0.5 g without grinding (A-B) produces a fundamental error of 693% (RSD%). For practical reasons grinding a large sample to 0.125 mm diameter particle size may be unsuitable. Therefore grinding and sub-sampling can be done stepwise in a suitable way. Note that the errors of each sub-sampling accumulate. Despite the fact that the fundamental error adds up, there will most likely be combinations leading to a smaller fundamental error than would just sub-sampling without grinding.

Minimising the variation of the fundamental error "…should be the prime objective of any sampling process" (Gy, 1998).

3.2.2 Grouping and segregation error, GSE

The variation of GSE may be reduced by obtaining several small increments to compose the sample. In primary field sampling these should be taken on a small scale, close to the selected sampling point. The more increments, the more the variance of the GSE is reduced (Pitard, 1993).

The relation between FE and GSE may be expressed as in equation 6 (Gerlach and Nocerino, 2003) and (Back, 2003) after (Myers, 1997).

$$s^2(\mathrm{GSE}) = \frac{s^2(\mathrm{FE})}{\mathrm{N}} \qquad \text{Equation 6.}$$

In equation 6 s^2(GSE) is the variance of the grouping and segregation error, s^2(FE) is the variance of the fundamental error and N is the number of increments.

In order to minimise GSE the number of increments, N, should be as large as possible. When composing samples a dilution effect might occur, causing the contaminant of interest to be under the detection limit of the method of analysis (Naturvårdsverket, 1996).

Mason (1992) quotes equation 7 from Skalski and Thomas (1984):

$$N \leq \frac{AL}{MDL} \qquad \text{Equation 7.}$$

In equation 10 N is the maximum number of increments to form the composite samples, AL is the action level and MDL is the minimum detection limit of the method of analysis to be used. If the composite sample has maximum n increments from equation 7, then it will be possible to find hotspots in composite samples, using equation 8 (Myers, 1997).

$$\overline{X}_{\text{contamiant}} < \frac{AL}{N} + LBL \qquad \text{Equation 8.}$$

In equation 11 $\overline{X}_{\text{contamiant}}$ is the average of composite samples, and LBL is the natural background level. Without background level of the contaminant LBL equals zero. If the relation in equation 8 is fulfilled, there is no contaminant in the sample increments above action level.
Composite samples should only be used if the increments included have approximately the same contaminant levels. Whether this is fulfilled may be checked by equation 12 (Naturvårdsverket, 1997).

$$CV = \frac{SD}{\overline{X}_{conta\min ant}} \qquad \text{Equation 9.}$$

In equation 9 SD is the standard deviation of the included increments, if each is analysed by itself and CV is the coefficient of variation, and $\overline{X}_{\text{contaminant}}$ is the average contaminant level of the increments to the composite sample. If the coefficient is less than 1, then the lot to be analysed is considered homogenous enough to make composite samples. If composite samples are to be used on a regular basis in a project, every 10'Th lot to be analysed should be controlled for homogeneity.

3.2.3 Increment delimitation error, DE

The correct sample geometry for different sampling dimensions is presented in table 3; any deviation will induce a delimitation error.

Table 3. Sample geometry in different sampling dimensions (Pitard, 1993), (Smith, 2001).

Sampling dimension	Example	Correct sample geometry
3-D	Pile	a sphere inside the lot
2-D	Flattened pile, soil strata	a cylinder, perpendicular to the plane, through the entire thickness of the strata
1-D	Elongated pile, conveyor belt	a cut-off with two parallel planes, e.g. a scoop with a flat bottom and parallel walls.
0-D	Similar units, like truck-loads or shovel loads	random choice units; preferable stratified randomised

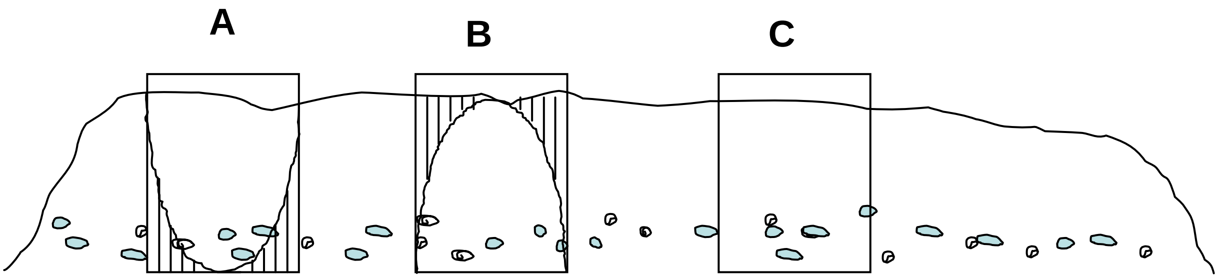

Figure 3. Increment delimitation from a one-dimensional lot. A. A scoop with a rounded bottom induces incorrect increment delimitation. B. A scoop with no sides induces incorrect increment delimitation. C. A scoop with square side walls yields correct increment delimitation (Pitard, 1993).

Primary sampling; obtaining samples from the ground.

Back (2003) found from Pitard (1993) that drilling is likely to produce a vertical segregation and changed particle size distribution. From Myers (1997) he found that most of the sampling devices like augers, triers and thieves used in environmental sampling are incorrect.

(Pitard, 1993) pp 417-418), concludes that the sampling of 3-D and 2-D lots made of particulate material is a practically unsolvable problem. Of course, such lots are sampled every day, especially for environmental sampling; thus the accuracy of sampling must be addressed and looked at with circumspection.

Obtaining soil samples in field in accordance with the theory of sampling is the subject of ongoing research and future guidance documents (Gerlach and Nocerino, 2003).

An incremental extraction error occurred for the field sampling in the case study. A trowel with rounded bottom was used for sample extraction from the walls of the trial pit. This tool does not allow correct increment extraction.

Secondary sampling; sub-sampling in laboratory.

Sub-sampling should extract a *sub-sample* with the same properties as the lot from where it was obtained. Recommended techniques are, in descending order (Gustavsson and Lagerkvist, 2004 a):
Sectorial splitter
Paper cone sectorial splitter
Incremental sampling
Riffle splitter, ”Riffler”
Alternate shovelling
Fractional shovelling

Some techniques are used although they can yield biased sub-samples. These techniques are not recommended (Gustavsson and Lagerkvist, 2004 a):
Table sampler
Degenerate fractional shovelling
Rolling and quartering
Coning and quartering
V-blender
Vibratory spatula
Grab sampling

No sub-sampling is done in the traditional way when measuring with XRF on sample bags. It must be regarded as a grab sampling situation, anyway. Grab sampling is the most undesired sub-sampling procedure (Gerlach and Nocerino, 2003).

At the commercial laboratory the samples from the case study were sub-sampled with a riffle splitter. With a correct procedure this can avoid the incremental delimitation error. The sample is elongated and cut off with parallel chutes in the riffle splitter.

3.2.3 Increment Extraction Error, EE

An extraction error occurs if the defined sample is not taken correctly. The particles with their mass centre inside the defined sample volume should get into the sample and the others should be excluded from the sample (Back, 2003). A main problem is the equipment used (Smith, 2001) but the handling may also cause errors.

3.2.4 Preparation error, PE

Six categories of preparation errors are listed and described (Gy, 1979), (Pitard, 1993) in table 4.

Table 4. List and examples of preparation errors.

Error by:	Examples:
Contamination	Dusting into sample Contaminated tools Abrasion from tools
Loss	Dusting from sample Sample sticks to tools
Chemical alternation	Oxidation Fixation of CO_2 or H_2O Loss of CO_2 or H_2O
Physical alternation	Changed moisture content Spontaneous size reduction
Unintentional mistakes	Dropping samples Mixing sub-samples from different samples Bad labelling
Fraud or sabotage	- - -

Preparation errors can be controlled if the staff performing the tasks has the proper training, motivation and understanding of the procedures and their significance. The suitability of the used equipment is also important.

4 Conclusions

Samples taken in hotspots have smaller fundamental error than other samples. And in consequence the relative importance of the analytical error is larger.
Except for the samples taken in hotspots, the analytical error is less than 10% compared to the total sampling error. In several examples, the analytical errors were less than a percent, compared to the total sampling error.

The five applied sampling errors from TOS are listed in table 5 with a short description of their reduction options.

Table 5. Possibilities to reduce different sampling errors.

Error	How to reduce the error
Fundamental error	A larger sample can be extracted from the lot
Fundamental error	Particle size reduction
Fundamental error	Grinding the sample prior to sub-sampling; planning the sample preparation protocol with aid of log-log diagram of the fundamental error
Grouping and segregation error	Taking many small increments to compose the sample
Increment delimitation error and Increment Extraction Error	Correct sub sampling, most preferred technique is a sectorial splitter
Preparation errors	Trained and motivated personnel, carefully prepared routines and equipment

Increasing the sample size reduces the fundamental error. This is valid for a field sample as well as a sub-sample.

Decreasing the particle size of the sample by grinding reduces the fundamental error. The grinding should be performed prior to sub-sampling to have any effect. Grinding and sub-sampling can be done in several steps for practical reasons.

By taking several increments to compose the sample, the grouping and segregation error can be reduced. The more increments taken the better in this respect. When obtaining a field sample these increments should be taken close to where the sample was planned.

The sub-sample technique used may affect all the five errors discussed above. The most preferable sub-sampling technique is by means of a sectorial splitter. The advantages of the sectorial splitter are:
-A sectorial splitter allows control of the size of the sub-sample, and therefore contributes to controlling the fundamental error.
-A sectorial sample splitter provides an opportunity to give many small increments to each sub-sample, thus reducing the grouping and segregation error.
-In a sectorial the lot becomes 1-D during transportation, which is a preferred sampling situation.
-A sectorial sample splitter, assuming correct design in accordance with the theory of sampling, yields no incremental delimitation error or delimitation extraction error.
-A sectorial splitter has very little interference with the operator, who will therefore not induce any bias or preparation error.

To avoid preparation errors the personnel should be motivated, trained, experienced and well aware of the routines. The laboratory should provide correct equipment, tools and routines.

The studies performed have made it possible to identify relevant areas for further research:

How the samples should be obtained from the ground without violating any aspect of TOS is (most likely) a still unanswered question.

How many resources will the ideal sample preparation demand? How much time will the different preparation steps take? No matter how good the intentions are, the soil sampling projects usually have a limited budget. Sample preparation improves the reliability of the analysis, but also requires resources. The improved reliability will be balanced against the possibly increased cost. A cost model could be developed.

How large sampling uncertainty is usual for soil sampling projects? By using data from several accomplished site investigations an evaluation can be made of the distribution of sampling uncertainties.

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6 References

Aylward, G. H. and Findlay, T. J. V. (1974) *SI chemical data*. pp 136, John Wiley & Sons. Milton, New Zeeland.

Back, P.-E. (2003) On uncertainty and data worth in decision analysis for contaminated soil. Licentiate thesis *Department of Geology*, Chalmers University of Technology, Göteborg. p 130.

Crumbling, D. M. (2002) In search of representativeness: Evolving the environmental data quality model. *Quality Assurance*, vol. 9, pp 179-190.

Gerlach, R. W. and Nocerino, J. M. (2003) Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples. EPA 600-R-03-027, *United States Environmental Protection Agency,*

Gustavsson, B. and Lagerkvist, A. (2004 a) Review of Soil Sampling Issues. *Luleå University of Technology*, Luleå, Sweden.

Gustavsson, B., Luthbom, K. and Lagerkvist, A. (2004 b) Uncertainty in soil sampling - a case study. *Luleå University of Technology,* Luleå, Sweden.

Gy, P. (1998) *Sampling for analytical purposes*. pp 153, John Wiley & Sons. Chichester.

Gy, P. M. (1979) *Sampling of particulate materials – Theory and practice*. pp 431, Elsevier Scientific Publishing Company.

Mason, B. J. (1992) Preparation of Soil Sampling Protocols: Sampling Techniques and Strategies EPA 600/R-92-128.EPA/600/R-92/128, *United States Environmental Protection Agency,* Washington DC, USA.

Minkkinen, P. (1986) Evaluation of the fundamental sampling error in the sampling of particulate solids. *Analytica Chimica Acta*, vol. 196, pp 237-245.

Minkkinen, P. (2004) Practical applications of sampling theory. *Chemometrics and intelligent laboratory systems,* vol.74, pp 85-94

Myers, J. C. (1997) *Geostatistical error management. Quantifying uncertainty for environmental sampling and mapping*. pp 571 pp, Van Nostrand Reinhold. London.

Naturvårdsverket (1996) Rätt datakvalitet; vägledning i kvalitetssäkring vid miljötekniska undersökningar.4667, *Naturvårdsverket,* Stockholm.

Naturvårdsverket (1997) Åtgärdskrav vid efterbehandling. 4807, *Naturvårdsverket,* Stockholm.

Naturvårdsverket (2003) Efterbehandling under utveckling – en utvärdering. *Naturvårdsverket,* Stockholm.

Pitard, F. F. (1993) *Pierre Gy´s sampling theory and sampling practice: heterogeneity, sampling correctness, and statistical process control*. pp 488, CRC Press. London.

SIS (2003) Soil quality-sampling-part 1: Guidance on the design of sampling programmes. SS 10 381-1, SIS - *Standardiseringskommissionen i Sverige, Svensk Standard, Stockholm, Sweden.*

Skalski, J. R. and Thomas, J. M. (1984) Improved field sampling designs and compositing schemes for cost effective detection of migration and spills at commercial low-level radioactive or chemical waste sites. PNL-4935, *Battelle Pacific Norhtwest Laboratory, Richland, WA 99352.*

Smith, P. L. (2001) *A primer to sampling solids, liquids and gases. Based on the seven sampling errors of Pierre Gy.* ASA-SIAM. Philadelphia.