Heterogeneities in Samples of Contaminated Soil

Björn Gustavsson
Sammanfattning
Many factors are important during sampling of contaminated soil. One of these is the sample sizes used. By estimation of the Heterogeneity Invariant (HI) it is possible to balance the sample size to one uncertainty contribution that is attached to sampling and sample handling. This is called the Fundamental error. Large overestimation of HI leads to larger samples and increased cost for sample handling. Large underestimation of HI leads to too small samples and to a larger uncertainty contribution, and possible skewed samples.

Some methods to estimate HI is described and discussed from the perspective of contaminated soil sampling. Contaminated soil is a widely used concept, it is quite different challenges to sample if the contaminant is e.g. metallic particles, in-evaporated solutions or oils. None of the discussed methods is without any limitation.

Field portable X-ray spectroscopy fluorescence is (XRF) is a popular instrument to analyse for metals in contaminated soils. It can provide quick and cheap analysis. The most prepared samples are dried, ground finely and put into Mylar thin film XRF sample cups. The sample volume is about 5-7 cm³, but the actually measured volume is only a fraction thereof. In the, likely, case of segregation in the sample volume this can lead to a biased measurement.

Mechanisms for segregation in the XRF sample cup are discussed. Further suggestions are made to reduce the segregation. Despite precautions to reduce the effect of segregation it is difficult to eliminate it.

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SUMMARY

Many things are of importance during sampling of contaminated soil. One of these is the sample sizes used. By estimation of the Heterogeneity Invariant (HI) it is possible to balance the sample size to one uncertainty contribution that is attached to sampling and sample handling. This is called the fundamental error. Large overestimation of HI leads to larger samples and increased cost for sample handling. Large underestimation of HI leads to too small samples and to a larger uncertainty contribution, and possible skewed samples.

Some methods to estimate HI is described and discussed from the perspective of contaminated soil sampling. Contaminated soil is a widely used concept; it is quite different challenges to sample if the contaminant is e.g. metallic particles, in-evaporated solutions or oils. None of the discussed methods is without any limitation.

Field portable X-ray spectroscopy fluorescence is (XRF) is a popular instrument to analyse for metals in contaminated soils. It can provide quick and cheap analysis. The most prepared samples are dried, ground finely and put into Mylar thin film XRF sample cups. The sample volume is about 5-7 cm³, but the actually measured volume is only a fraction thereof. In the, likely, case of segregation in the sample volume this can lead to a biased measurement.

Mechanisms for segregation in the XRF sample cup are discussed. Further suggestions are made to reduce the segregation. Despite precautions to reduce the effect of segregation it cannot be trusted to be eliminated. There is always a risk for biased measurements for measurements in XRF sample cups.
SAMMANFATTNING

Många faktorer är viktiga när man tar prover av förorenad jord. En av dessa är provstorleken. Efter bestämning av konstanten ”Heterogeneity Invariant” (HI) kan man hitta en balans mellan provstorleken och ett av de osäkerhetsbidrag som sker vid provtagning och provhantering. Detta osäkerhetsbidrag är det fundamentala felet. Stor överskattning av HI leder till större prover och med det följer ökad provhantering och ökad kostnad. Stor underskattning av HI leder till för små prover och stort osäkerhetsbidrag, samt i värsta fall systematiska fel.

Några olika metoder för att uppskatta HI beskrivs och diskuteras utifrån från perspektivet provtagning i förorenad jord. Förörenad jord är i sig ett vitt begrepp och det bjuder lite olika utmaningar att prova om föroreningen t.ex. är partikulär metall, intorkad lösning eller olja. Ingen av de diskuterade metoderna är helt utan begränsningar.

Fältutrustning för röntgen fluorescens spektrometri (XRF) används ofta för undersökning av metaller i förorenad jord. Det kan ge snabba och billiga analyser. De mest bearbetade proverna är torkade, malda och placerade i provkoppar. Provkopparna har ”fönster” av en tunn Mylar-film. Provvolumen är 5-7 cm³, men volymen som verkliga mäts av instrumentet är endast en bräckdel av denna volym. Vid de, troliga, fall segregering uppstår i provvolumen kan detta leda till systematiska fel.

Mekanismer för segregering i XRF provkoppar diskuteras. Vidare föreslås metoder för att, i bästa fall, minska segregeringen.

Trots att åtgärder görs för att minska det systematiska felet kan man inte räkna med att de har elimineras. Det finns alltid en risk för segregering vid mätning i XRF provkoppar.
LIST OF PAPERS

Paper I

Paper II
Gustavsson, B., Maurice, C. and Lagerkvist, A. (submitted) Effect of sample preparation prior to X-Ray Fluorescence spectroscopy analysis of contaminated soil. Submitted to: *Chemometrics and Intelligent Laboratory Systems*

Paper III

Paper IV

Paper V
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1. INTRODUCTION

Soil pollution is a common problem, in Sweden, about 83,000 sites has been identified as contaminated. It is estimated that 1,500 of those will be classified in risk class 1 “very high risk” and about 15,000 in risk class 2 “high risk” (Österlund, 2007). The risk classification is done according to the Swedish MIFO-model (SEPA, 2002).

The remediation projects financed by government subsidies costs on the average 40 MSEK, and the 20 largest are estimated to cost 100-150 MSEK (Österlund, 2007).

To under estimate or over estimate contaminants of a contaminated site can lead to environmental risks and unpredicted costs. Frequently the amount of contaminant is underestimated; it is not unusual that the amount of contaminant shows to be twice the expected (Nordlinder, 2007).

This work focuses on “small scale” heterogeneities regarding each single sample and discusses some aspects of these. Much of the discussion relates to the Theory of Sampling.

If samples are not accurate and reproducible any further analysis and evaluation is futile. Definitions of these terms are given by Gy (2004).

Theory of sampling (TOS) systematizes all the different contributions of uncertainties and bias from a sampling procedure. A bias is introduced when the sampling and sample handling alters the sample to not have the same properties as the lot from where it was obtained. The global error estimate (GEE) can be split up into components (figure 1). Each sample preparation step can introduce sampling errors and GEE is the sum of all sampling errors from all sample preparation steps.

The ”small scale” heterogeneities in the context of TOS concerns the fundamental sampling error (FSE) and the grouping and segregation error (GSE) for correct sampling and sub sampling. For incorrect sampling and sub sampling also the incorrect delimitation error (IDE), the incorrect extraction error (IEE) and the incorrect preparation error (IPE) add to the materialisation error (MSE) (figure 1).

Theory of sampling (TOS) is known under various names like “Pierre Gy sampling theory” (after its founder Dr Pierre Gy), “sampling theory”, “sampling theory and practice - STP”. Other sampling theories exist, but TOS is referred to as being the most comprehensive (Gerlach and Nocerino, 2003; Minkkinen, 2004; Peterssen, et al., 2005; Pitard, 1993).
Figure 1. A family tree for the different sampling errors of TOS, after (Gy, 2004; Minkkinen, 2004). The stars mark the main issues discussed in this work.
2. RESEARCH QUESTIONS

Within a material there is always a variety of particle properties. This variety gives a sampling error that can never be avoided, thereof its name; fundamental sampling error (FSE). Calculations of FSE, or rather its component the heterogeneity invariant (HI) are critical when constructing a sampling protocol. For example this entity is used when estimating an optimal sampling mass (Pitard, 1993) p388. HI is a heterogeneity constant with the unit of mass. It is invariant for a given material during many types of material handling, but will be altered by, e.g. particle size reduction. Knowledge about HI gives information about the relation between sample mass and fundamental error for the given matrix (soil). The larger samples the smaller the fundamental error, to half the error requires a fourfold sample size. Sample masses smaller than HI have variances of FSE larger than 100 %. Several equations exists to estimate the HI and hence the FSE. The different methods might have limitations if applied to contaminated soil.

Question 1
What limitations have different HI estimation methods in contaminated soil applications?

Intimately linked to FE is the GSE. GSE occurs due to material segregation. Many materials tend to segregate due to different material properties between particles, like particle size or particle density. For samples where the analysis is done on the entire analysis sample, like total decomposition, correct sub sampling procedures can be performed (Gerlach and Nocerino, 2003; Petersen, et al., 2004).

However, during measurements with field portable X-ray fluorescence spectroscopy analyzer (XRF) on a sample a principally other procedure is followed. The last sub sampling occurs during measurement on a fixed sample by the instrument.

For free flowing particulates (like dried soil) segregation occurs easily due to many mechanisms. If segregation has occurred during the filling of the Mylar thin film window XRF sample cup (XRF cup), there can be a biased measurement.

Question 2
How can small volume and fine particulate sample in an XRF cup, give a biased measurement?

If segregation mechanisms are known, the knowledge might also be used to suggest prohibitive measures.

Question 3
How can the effect of the bias be reduced prior to measurements in XRF cups?

Materials and methods used as well as primary results are presented in the appended papers. If not presented elsewhere, such information is included under the relevant discussion topic.
3. DISCUSSION

Inside a soil to be sampled there are particles with different properties. These differences can for instance be their size, shape, weight, density, contamination level, and tendency to aggregate with other particles etc. The best of sampling procedures reaches a limit that cannot be passed. This is called the fundamental sampling error (FSE). Although FSE cannot be eliminated, it can be reduced for many sample types.

Investigation of heterogeneities within a material is important, and required to make proper sampling protocols. Estimation of HI is one part, and useful for decision on optimal sample sizes.

TOS was developed for the needs of the mining industry and some of the methods used to determine HI are simplified and adapted to conditions of relevance for that application area. Thus the validity for other situations may be limited. The use and limitations of some different methods to determine HI are discussed in the perspective of contaminated soil sampling.

Statistically significant concentration variations have been observed within prepared 5-7 cm$^3$ fine soil amoles in XRF cups (Paper II). The procedure of filling the XRF cup with the sample is discussed from a TOS perspective.

Further the relevant sampling errors that may occur during a XRF measurement is discussed. The filling of and the measurement on the sample in a XRF cup concerns the materialisation sampling error (MSE) (figure 1). The material in the cups tends to be segregating and methods to reduce the segregation are discussed.

3.1. Heterogeneity invariant estimation

3.1.1. HI estimates from a Brownfield investigation

HI estimates calculated on experimental data from a Brownfield investigation (Paper I) is presented in table 1. The estimates vary over about six orders of magnitude, with the largest being 1, 200 g.
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Table 1. HI determinations [g] based on contaminated site data (Paper 1). The largest HI values are marked with bold text and the smallest underlined. Analysis is performed with XRF (X-Ray Fluorescence Spectroscopy) and ICP (Inductively Coupled Plasma).

<table>
<thead>
<tr>
<th>ID</th>
<th>XRF Cu max</th>
<th>XRF Cu min</th>
<th>XRF Pb max</th>
<th>XRF Pb min</th>
<th>XRF Zn max</th>
<th>XRF Zn min</th>
<th>ICP Cu</th>
<th>ICP Pb</th>
<th>ICP Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.2 10^3</td>
<td>5.8</td>
<td>1.1 10^3</td>
<td>2.0</td>
<td>3.2</td>
<td>4.3</td>
<td>3.8</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.2 10^1</td>
<td>3.2 10^1</td>
<td>6.4 10^1</td>
<td>7.0 10^1</td>
<td>2.4 10^1</td>
<td>7.7 10^1</td>
<td>3.0 10^1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2.0 10^1</td>
<td>3.0 10^1</td>
<td>7.7</td>
<td>8.4</td>
<td>9.4 10^1</td>
<td>1.1</td>
<td>3.9 10^1</td>
<td>3.1 10^1</td>
<td>3.4</td>
</tr>
<tr>
<td>D</td>
<td>1.4 10^3</td>
<td>1.4 10^1</td>
<td>3.4 10^1</td>
<td>3.7 10^1</td>
<td>7.6</td>
<td>9.4</td>
<td>1.4 10^3</td>
<td>2.4 10^1</td>
<td>9.4</td>
</tr>
<tr>
<td>E</td>
<td>2.8 10^0</td>
<td>3.3 10^0</td>
<td>4.7 10^3</td>
<td>5.5 10^3</td>
<td>1.2 10^3</td>
<td>1.3 10^3</td>
<td>2.1 10^3</td>
<td>3.5 10^1</td>
<td>1.2 10^1</td>
</tr>
<tr>
<td>F</td>
<td>4.4 10^2</td>
<td>5.1 10^2</td>
<td>1.6 10^5</td>
<td>1.6 10^5</td>
<td>1.2 10^5</td>
<td>1.1 10^5</td>
<td>4.0 10^2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>3.5 5.3</td>
<td>4.3</td>
<td>4.5</td>
<td>9.1 10^3</td>
<td>1.1</td>
<td>3.6</td>
<td>4.5</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>8.2 1.3 10^1</td>
<td>1.4 10^1</td>
<td>1.5 10^1</td>
<td>4.3</td>
<td>4.6</td>
<td>8.2</td>
<td>1.3 10^1</td>
<td>5.0</td>
<td></td>
</tr>
</tbody>
</table>

If the accepted contribution of the fundamental error on the primary sampling error is 10% the sample sizes need to be 1/(0.1)^2 = 100 times larger than the HI presented in table 1. The largest sample would be sample F, based on ICP (Inductively Coupled Plasma) measurement of copper, which equals 1.2 10^3 - 100 g = 120 kg.

Pitard (1993) p 385, mentions that environmental samples can require sample masses of a 100 kg or even some tonne. If the sample size required can not be accommodated within the budget of an investigation he states “If a very large sample is necessary, it is better to be aware of it, and it should be mentioned in the sampling log as a critical issue.”

Despite this comment, sample sizes of 120 kg is about two orders of magnitudes larger than what is usually taken from contaminated soils. To sample and prepare such large samples would increase the work and cost of investigation.

It can therefore be justified to discuss if different methods to estimate HI are suitable for contaminated soil.

Note that the HI can differ with orders of magnitudes between elements in the same sample, as is clearly visible in sample C (table 1). The largest HI will then be determining.

3.1.2. Gy-equation

The Gy-equation can be used to estimate the variance of the fundamental error, or its order of magnitude.

When deriving equation 1 the assumption is made, that the particles size class affects the critical content (contaminant) in a negligible way (Pitard, 1993) p158. This assumption may be relevant for ores. For a contaminated soil this might not be a valid assumption since the contaminants often are attached on the surface of particles, and finer particles size classes have higher specific surface area.
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\[ s^2_{FSE} = \left( \frac{1}{M_E} - \frac{1}{M_L} \right) \cdot HI = \left( \frac{1}{M_E} - \frac{1}{M_L} \right) \cdot c \cdot \beta \cdot f \cdot g \cdot d_{95} \]

Equation 1

Legend for equation 1:
- \( s^2_{FSE} \): variance of the fundamental error
- \( M_E \): extracted sample mass [g]
- \( M_L \): mass of the lot (original material) from where the samples are extracted [g]
- \( HI \): heterogeneity invariant [g]
- \( c \): constitution factor [g/cm³]
- \( \beta \): liberation factor [-]
- \( f \): particle shape factor [-]
- \( g \): the particle size range factor [-]
- \( d_{95} \): upper particle diameter (95th percentile) [cm]

The constitution factor, \( c \), is defined as in equation 2 (Minkkinen, 2004). This factor represents the maximum degree of heterogeneity that the contaminant can represent and occurs if the contaminant is completely liberated (Pitard, 1993) p 161. A complete liberation means the contaminant occurs as separate particles that are not attached to or included in the matrix (soil) particles. The constitution factor grows enormously when the concentration is decreasing, (Paper I) fig 1.

\[ c = \left( \frac{1 - \frac{a_L}{a}}{\frac{a_L}{a}} \right) \cdot \rho_c + \left( 1 - \frac{a_L}{a} \right) \cdot \rho_m \]

Equation 2

Legend for equation 2:
- \( a_L \): mass proportion of the contaminant (critical component) in the entire lot [-]
- \( a \): mass proportion of the contaminant (critical component) in the critical particles [-]
- \( \rho_c \): contaminant (critical component) density [g/cm³]
- \( \rho_m \): soil (matrix) density [g/cm³]

Equation 1 gives the relation between \( s^2_{FSE} \), sample mass and upper particle size. This can be used for construction of nomogrammes which supports the design of sampling protocols sampling (Gerlach and Nocerino, 2003; Gustavsson, 2004; Mason, 1992; Pitard, 1993).

The better the factors are determined the better the estimate of HI will be, but within reasonable economical limits this may not always be possible to make reliable determinations of the factors. In those cases default values can be used (Peterssen, et al., 2005). It is hard or impossible to determine some of the factors for contaminated soil applications. The factors in equation 1 and 2 are discussed below:
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3.1.2.1. The constitution factor, \( c \), and its components \( a_\ell \), \( \alpha \), \( \rho_c \), \( \rho_m \)

For situations where equation 2 is valid the mass proportion (concentration) of the contaminant in the entire lot, \( a_\ell \), is important. It has a large effect on the constitution factor, \( c \), and thus on HI. The constitution factor grows enormously when \( a_\ell \) is lower than 1 g/kg, (Paper I), fig 1. All Swedish limit values for soil contaminants are in the range 1 to 10\(^{-8}\) g/kg (SEPA, 1996).

The factors \( \alpha \) and \( \rho_c \) requires knowledge of what form the contaminant occurs in, not only total concentration. Principally it is assumed to only occur in one type.

The constitution factor is derived for samples with two physical constituents, the critical component (contaminant) and the matrix (soil). Further, it is assumed these are fully liberated \( i.e. \) contaminant particles do not occur as inclusions in the matrix (soil) particles. If the contaminant is not fully liberated, this is compensated by the liberation factor, \( \beta \). For samples with a more complex distribution the product \( c\beta \) needs to be replaced, and calculations become more difficult (equation 3) (Pitard, 1993) p 161. The latter case may be valid for contaminated soils. As a case in point CCA may be used: The CCA contaminant occurs in soils in a wide range of forms, and is bound to a variety of mineral surfaces and organic matter (Kumpiene, et al., 2006).

\[
c \cdot \beta = \sum D \rho_D \left( a_D - a_\ell \right)^2 \frac{M_{LD}}{M_L}
\]

**Equation 3**

Legend for equation 3:

- **D**: index of density fractions
- **\( \rho_D \)**: the density of a given density class D [g/cm\(^3\)]
- **\( a_D \)**: the mass proportion of contaminant in one density fraction [-]
- **\( M_{LD} \)**: the mass of one density fraction [g]

3.1.2.2. Liberation factor, \( \beta \)

When extracting valuable minerals from rock materials, the starting point is often a rock material with grains of valuable minerals buried in it. If the material is crushed to fine enough particles these mineral grains will be liberated from the rest of the material. The liberation factor ranges from a complete separation of the components where \( \beta = 1 \), to a hypothetical complete homogenous matrix where \( \beta = 0 \) (Gy, 1998). Four methods to determine the liberation factor are discussed below:

- The first method assumes that all particle size classes have roughly the same contaminant content, \( i.e. \) concentration of pollutants (Pitard, 1993), which makes it less relevant for contaminated soils where contaminants can be distributed quite differently in different particle size classes.

- The second method assumes that grinding will liberate the contaminant. The latter case may be valid for some contaminants in soils. If it is valid equation 4 can be used (Pitard, 2004).
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\[ \beta = \left( \frac{d_0}{d} \right)^b \]  

Equation 4

Legend for equation 4:
- \(d_0\): the liberation size of the mineral particles, [cm]
- \(d\): actual diameter, [cm]
- \(b\): parameter, [-]

The parameter \(b\) is often put to 0.5, but this value is debated to be 1.5, 3 or might need to be determined for each specific sampling situation (Francois-Bongarcon, 1998; Minkkinen, 2007b; Pitard, 2004).

- As a third method tabulated values can be used (Gerlach and Nocerino, 2003; Smith, 2001; Pitard, 1993). The matrix (soil) is to be classified in classes like “homogenous” or “almost homogenous”. This involves a judgement, and therefore an uncertainty.

- The forth method is to give \(\beta\) a value of 1, in order not to under-estimate the heterogeneity; “When unsure, it is best to set \(\beta = 1\)” (Gy, 1998).

The value of \(\beta\) affects the required sample size in a linear fashion. For example; if a material is almost homogenous and should have a \(\beta\) of 0.05 but the sampler sets \(\beta\) to 1, in order to be on the safe side, the consequence will be that a 20 times larger sample must be taken.

For particulate contaminants like metals on a scrap yard (paper I, paper II), ore transhipment stations (paper II) or lead shoots the liberation factor may be calculated and have a meaning. At least if the particles remain particulate.

For non particulate contaminants, like oils, the liberation factor may not be valid.

For complex mixtures where the contaminant occurs in various forms (section 3.1.2.1.) it is not obvious how to determine the liberation factor.

In both these latter cases the product \(c \cdot \beta\) needs to be replaced with the term determined by equation 3.

3.1.2.3. Particle shape factor: \(f\)

The form factor relates the volume of the particles to cubes with the same diameter.

The quickest method to determine the particle shape factor is to have a look at the material in a microscope (Pitard, 1993), p159. If the soil particles are almost spherical, the particle shape factor can be set to 0.5. (Gerlach and Nocerino, 2003) states: “The majority of particulate samples have shape factors from 0.3 to 0.5. Typical hazardous waste samples particles are roughly spherical and have shape factors close to 0.5”

(Gerlach and Nocerino, 2003) writes that; ” If there are several types of shapes present, then the shape factor should be selected for the particle types that contain the analyte of interest, since those particles are expected to contribute more toward the sample uncertainty than any of the other particle types.” Thus it is difficult to set the value of \(f\) if the particles have a variety of shapes, which may well be the case for contaminated soils.

Björn Gustavsson, Waste Science and Technology, LTU, 2007
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Soil should not be extra complicated to investigate form factor of. Possibly the form factor is different for various particle size classes.

3.1.2.4. Particle size range factor, $g$, and particle size, $d_{95}$
These factors are derived from sieving data. For dry, free flowing, contaminated soils, there should not be any particular problems. If the contaminant is sticky like oil, sieving may be difficult.

3.1.2.5. Pros and cons with the Gy equation applied to contaminated soils
Advantages with the Gy equation applied to contaminated soils:
+ Show pedagogically the connections between several sample properties.
+ Can be used for constructing sampling nomographs that can be used as support for constructing sampling protocols.

Limitations with the Gy equation applied to contaminated soil:
- It is based on the assumption that particle size classes is of little importance for concentration of critical components (contaminants), which is not likely true for contaminated soils.
- Several of the factors needed in the calculations may be difficult to determine in contaminated soil scenarios. And the use of default values might lead to suboptimal sampling designs.
- If the contaminant is distributed in several different components the product $c \cdot \beta$ may be invalidated and should be replaced by a more complex term.

3.1.3. Sieves analysis method
Data from sieves analysis can be used to calculate HI, and consequently the fundamental error, for different particle size classes in a sample. The evaluation is done according to equation 5, assuming that the critical particle size proportion is smaller that 0.25 (Pitard, 1993) p 334.

\[
H_{I_{Lc}} = \left( \frac{1}{M_{E}} - \frac{1}{M_{L}} \right) \cdot f \cdot \rho \cdot \left[ \frac{1}{a_{Lc}} - 2 \cdot d_{FLc} + g \cdot d_{c_5} \right] 
\]

Equation 5

Legend for equation 5:
$H_{I_{Lc}}$ heterogeneity invariant for particle size class of interest [g]
$\rho$ density of the material [g/cm$^3$]
$a_{Lc}$ the proportion of the critical particle size class in the lot [-]
d$_{FLc}$ average fragment size of the critical particle class [cm]

With this method a separate $H_{I_{Lc}}$ can be calculated for each separate particle size class. This should not be assumed similar to HI for the contaminant of interest. It is not possible to use a HI value for one property determined in one matrix (soil) for other matrices (soils) or let the value calculated for one property also represent other properties in the same matrix (soil) (Pitard, 1993).
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The sieves analysis method is suitable as a first step in an iterative process for gaining better understanding of a matrix (soil). A rough determination of the HI which is required to represent at least all particle size classes can be done already on site during a brown field investigation, and without the use of other analyses. This makes it a valuable tool when quick results and decision are asked for (Paper V).

Advantages:
+ No additional analyses are required.
+ Can be used in an early stage of an investigation since basically only a sieves analysis is required to design samples at least representing all particle size classes of interest.

Disadvantages:
- No sensitivity to contaminant concentration.
- Even if the sample is large enough to represent all particle size classes, it might not be large enough to represent the property of interest, like contaminants in the soil. HI for one property in a material is not necessarily the same as for another property in the same material.

3.1.4. Simplified equation

Equation 5 can be simplified by assuming that \( a_{LC} < 0.25 \) since \( g \cdot d_{95}^3 \) can then be excluded as being negligible (Pitard, 1993). Further if \( f = 0.5 \) (Back, 2003; Ramsey and Suggs, 2001) and \( a_{LC} = 0.05 \) (Back, 2003) then equation 6 can be used.

The limitations of equation 6 was described by (Ramsey and Suggs, 2001): "The equation below is only for non-calibrated materials (materials which are not at all the same size; e.g. soil) in which the analyte of interest does not exist as a few discrete “nuggets.” The equation also assumes that the material is generally rounded in shape”

\[
s^2_{FSE} = \left( \frac{1}{M_E} - \frac{1}{M_L} \right) \cdot HI = \left( \frac{1}{M_E} - \frac{1}{M_L} \right) \cdot K \cdot \rho \cdot d_{95}^3
\]

Equation 6

Legend for equation 6:
K a constant set to 9 or 10 [-]

The constant K is set to 10 by (Ramsey and Suggs, 2001) and to 9 (Back, 2003) respectively. Back (2003) derives the constant to 9 by setting \( f = 0.5, \ a_{LC} = 0.05 \), and assume \( g \cdot d_{95}^3 \) is negligible in equation 5. No explanation is given to the constant 10 by Ramsey and Suggs (2001), but a similar derivation may be assumed.

As a simplification it is easier to use but is less flexible. Derived from equation 5, the “sieve analysis method” the resulting HI can only be assumed to represent the particles, not any contaminants they might contain.

Advantages:
+ Easy to use since few input variables are needed.

Disadvantages:
- No sensitivity to contaminant concentration.
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- Even if the sample is large enough to represent all particle size classes, it might not be large enough to represent the property of interest, like contaminants in the soil.
- Risks to be over simplified with a limited usage.
- Can give erratic results if the limitations/ restrictions are not known and respected.

3.1.5. The size-density fractionation method

The variance of the fundamental error can be estimated by separation of a sample in both particle size classes and density classes for determination. Two similar equations have been suggested for particle size-particle density fractionating; equation 7 (Pitard, 2004), (Pitard, 1993) p157 and equation 8 (Lyman, 1998).

This method requires the fragments to be picked one by one and at random to eliminate any sampling error except the FSE, which is to be determined. If the fragments are too small to analyse individually, particles can be combined until the formed groups are large enough for analysis. Still, the single fragments of the groups have to be picked individually. Each fragment or group must be analysed in their whole to avoid any sub sampling error.

\[
S^2_{FSE} = \left( \frac{1}{M_E} - \frac{1}{M_L} \right) \cdot HI = \left( \frac{1}{M_E} - \frac{1}{M_L} \right) \cdot \sum S \sum D \rho_D \left( a_{SD} - a_L \right)^2 \cdot MLSD \cdot M_L \quad \text{Equation 7}
\]

Legend for equation 7:
- \( S \): index of size fractions
- \( V_S \): the average volume of one fragment in a given size fraction \( S \) \( [\text{cm}^3] \)
- \( a_{SD} \): the contaminant (critical content) of one size-density fraction \([-]\)
- \( MLSD \): the mass of one size-density fraction \([\text{g}]\)

\[
S^2_{FSE} = \left( \frac{1}{M_E} - \frac{1}{M_L} \right) \cdot HI = \left( \frac{1}{M_E} - \frac{1}{M_L} \right) \cdot \sum S \sum D m_S m_{SD} \rho_{SD} \left( a_{SD} - a_L \right)^2 \quad \text{Equation 8}
\]

Legend for equation 8:
- \( m_S \): mass fraction of material in the \( S \)’th size class \([-]\)
- \( m_{SD} \): mass fraction of the material of the \( S \)’th size class within the \( D \)’th density class \([-]\)
- \( \rho_{SD} \): density of a particle in the \( S \)’th size class within the \( D \)’th density class \([\text{g/cm}^3]\)

Equations 7 and 8 differ in the weighting for particle classes. For equation 7 this is performed as the quotient \( MLSD/M_L \) and for equation 8 it is done by the \( m_S \) and \( m_{SD} \) terms.

Pitard (2004) comments on equation 7 to be “…a reference formula. It is complete, and carries no assumptions”. It should therefore give reliable results, supposing that good laboratory work has been performed. Backdrafts with the method is that it is “…cumbersome, requires sophisticated mineral processing equipment, and it is very expensive.” (Pitard, 2004).
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If using the method on soils it is important to not over/under represent any particle size class in the random picking of particles, since this might bias the group's composition compared to the lot to be sampled.

One principle for density separation is flotation in various liquids with different density. Density separation based on flotation in liquids can alter the contaminants by solving, extraction or leaching.

Advantages:
+ The equations are not based on any assumptions that might limit the application.
+ Correctly performed it will yield reliable results.

Disadvantages:
- Cumbersome
- Expensive
- Requires special equipments.
- Density separation by flotation can alter the contaminant composition.

3.1.6. SIS waste standard equation

The SIS waste standard equation is of large relevance for contaminated soil, at least in Sweden. The standard is referred to when presenting criteria's of reception for wastes at landfill sites (SEPA, 2007). As such it could be used after excavation remediation of contaminated sites (Paper I, Paper II, Paper V), or after a treatment step as control (Paper III, Paper IV)

\[ s_{FSE}^2 = \left( \frac{1}{M_e} - \frac{1}{M_L} \right)^2 \quad HI = \left( \frac{1}{M_e} - \frac{1}{M_L} \right) \cdot \frac{(1-p)}{p} \cdot \rho \cdot \frac{\pi}{6} \cdot g \cdot d_{50} \]  

Equation 9

Legend for equation 9:
p the mass fraction with a specific critical property (contaminant) [-]
\( \pi/6 \) form factor for a sphere [-]

If equation 9 is used strictly as described in the standard it has some limitations.
- All particles are assumed to be spherical (\( f = \pi/6 = 0.524 \) compare to equation 1). This may often be a valid assumption, but not always.
- Both critical component (contaminant) and matrix (soil) particles are assumed to have the same density. This may be an optimistic assumption in many scenarios.
- According to the standard a default value of \( p = 0.02 \) can be used on e.g. soils (SIS, 2007). The term \((1-p)/p\) then become 49. But e.g. for values of \( p = 1000 \cdot 10^{-6} \) (1000 ppm) and \( 10 \cdot 10^{-6} \) (10 ppm) the term becomes 999 and 99999 respectively. This leads to an underestimation of HI by orders of magnitudes for the concentration region of Swedish guidelines for contaminated soil that are at 1000 ppm and below (SEPA, 1996).

Derived from the binomial distribution the variable \( p \) is a number fraction, but usually concentrations are given as mass fractions (Minkkinen, 2007b). If the number fraction is not known e.g. equation 1 might be easier to use.

Björn Gustavsson, Waste Science and Technology, LTU, 2007
If equation 9 is put under other strict assumptions it will become identical to equation 1 (Minkkinen, 2007a, 2007b). These assumptions are:
- \( p = \frac{a_r}{a} \)
- \( \beta = 1 \); total liberation.
- \( f = \frac{\pi}{6} = 0.524 \); spherical particles.
- \( g = 1 \), all particles are of same size.

But for many contaminated soil scenarios (and for other wastes) these assumptions may not be valid (see section 3.1.2.1.).

Using the SIS- waste standard method, without modification is concluded inferior due to its restrictions.

Disadvantages of by the book-usage of equation 9:
- Limited to spherical particles.
- Limited to totally liberated contaminatees.
- Assumes same density of contaminant and matrix (soil).
- For contaminated soils the variable p may be difficult determine.

3.1.7. The two tiered variance comparison and experimental HI determination method

A two tiered variance comparison was presented by Pitard (1993) 385. The method Pitard describes for environmental applications is a simplification, with fewer samples, of a method to investigate unevenly distributed, low level contaminants in pure materials.

In this procedure two series of samples are taken from the lot investigated, and their respective variances are compared. The sample sizes (masses) of the two series differ at least with a factor of ten. At least nine samples of each size should be taken.

If the variances are similar the sample sizes are concluded to not be of big importance at the tested scale. If they differ much the sample size is of importance at the tested scale. Possibly a larger sample size should be tested, or an optimal sample size found. Grouping and segregation can be explanations. In a two step mixing trial 1% iron particles were added to soil (Paper III, Paper IV). After first mixing step, the variances were \( 4.1 \times 10^{-5} \) and \( 1.4 \times 10^{-5} \) respectively (\( n = 10 \)) for sample sizes of 100 and 10 dl. Similar data after second mixing step were \( 3.1 \times 10^{-6} \) and \( 2.3 \times 10^{-6} \) respectively (\( n = 10 \)). The differences had decreased from a factor 2.9 to 1.3 indicating that the impact of grouping and segregation had decreased. In fact, after first mixing step iron was found in clustered inclusions in the soil (fig 2b in Paper IV).

Instead of using larger sample size an alternative approach is proposed by Minkkinen (2007a). The result from the two tiered variance comparison can be used for an F-test:
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Significant \( \Rightarrow F_{(n_L-1,n_S-1)} < F = \frac{s^2_L \cdot M_{EL}}{s^2_S \cdot M_{ES}} < F_{(n_L-1,n_S-1)} \Rightarrow \) Non significant \hspace{1cm} Equation 10

Legend for equation 10:
- \( F_{(n_L-1,n_S-1)} \) tabulated F-value with \( (n_L-1, n_S-1) \) degrees of freedom [-]
- \( n_L \) number of large samples
- \( n_S \) number of small samples
- \( F \) calculated F-value [-]
- \( s^2_S \) variance of small sized samples [-]
- \( s^2_L \) variance of large sized samples [-]
- \( M_{ES} \) average mass of extracted sample, small size series [g]
- \( M_{EL} \) average mass of extracted sample, large size series [g]

If the F-test shows significance, this means the contaminant has a markedly uneven distribution in the sampled lot. In such cases the normal distribution is not valid. Instead a semivariogram should be used to estimate the sampling variance. A stratified random or stratified systematic sampling should be performed, and evaluated by 1-D semivariogram or semivariogram of geostatistics.

If the F-test does not show significant differences the FSE model to plan sampling can be assumed applicable. The data from the two tiered variance comparison can be used to estimate the HI, for example by Equation 11.

\[
HI = M_{ES} \cdot (s^2_S - s^2_{AE}) \hspace{1cm} \text{Equation 11}
\]

Legend for equation 11:
- \( s^2_{AE} \) variance of analytical error [-]

With data from sieving analysis, the heterogeneity invariant can be modified according to equation 12.

\[
HI = C \cdot d^{3/4} \hspace{1cm} \text{Equation 12}
\]

Legend for equation 12:
- \( C \) sampling constant of TOS [g/cm³]

Evaluation of data from two tiered variance comparisons (Paper IV) reveal statistical significant differences \( (p = 0.05) \). This indicates that the tested materials are segregated. Further it indicates that the FSE model alone may not be suitable for size determination, due to too large concentration fluctuations.

One risk with the method is one may incorporate residual errors from other sampling errors (Pitard, 2004).

Advantages:
- since the method not considers material properties it may be applied on a wide variety of applications, like oil contaminants.
Disadvantages:
- The method may risk involving some residual variances from other sampling errors, resulting in a overestimated HI.
- The procedure may be considered too costly for some projects, due to the number of samples and large sample sizes.

3.2. Primary samples and analytical samples

Once HI is determined for a material it can be used as support for design of a sampling protocol. Beside the choice of the primary sample size, it is used for the design of a comminution and sub sampling procedures. A practical graphic interpretation is the use of nomograms (Gerlach and Nocerino, 2003; Gustavsson, 2004; Mason, 1992; Pitard, 1993). Note that HI is altered by the comminution of the sample. Anyhow, if the sample is comminuted and subsampled correctly the reproducibility will be controlled and bias will be avoided (Gerlach and Nocerino, 2003; Petersen, et al., 2004).

One scenario where the last sub-sample is not the same as the actual analyse sample is during measurements with field portable X-ray fluorescence spectroscopy (XRF). Not even for the most well prepared samples i.e. in XRF sample cups. This is a situation where a bias may be introduced into the sampling procedure and measurement. Bias is problematic since its size and direction is hard to determine and it may vary over time (Pitard, 1993), p382. There is no reason to believe the bias should be constant even between two consequently prepared samples.

3.3. Bias in a prepared XRF sample cup

3.3.1. Equiprobabilistic rule

In all sampling and sub sampling procedures all particles or groups of particles should have the same chance of being selected. This is known as the equiprobabilistic rule.

The XRF sample cup is a cylinder (ø 25 mm, h 28 mm) with one end covered with a thin Mylar X-ray film (6 μm thick). A sample volume of 4 - 7 cm³ is filled into the cup, a filter-plate is put on its top. On the filter a flexible fibrous material is put before a snap lid is mounted. The design causes the sample to be pressed towards the Mylar film and remain fixed (within reasonable limits).

The XRF sample cups are put into a NITON test platform with the mylar film positioned upwards. The NITON XRF 700 is fixed directly onto the XRF sample cup’s Mylar film window ensuring the shortest possible path between the radiation source and the sample (Paper II), (Niton Corporation, 1998).

Scenario 1

When a prepared XRF cup is analysed only the (near) surface of the sample is exposed to the primary X-ray radiation to excite the fluorescence radiation. Basically the XRF instrument emits X-rays into the surface which excites the electrons. When the electrons relax they emit secondary radiation which is detected by the instrument and the signal intensity at different wavelengths is used to calculate the concentration of various components. The X-ray
radiation is most intense at the surface and becomes less intense with increasing penetration depth. Only a few millimetres depth from the surface is actually radiated (Paper II). The particles at the bottom of the XRF cup have no chance to actually be included in the analytical sample. Thus the equiprobabilistic rule can not be obeyed, unless the sample cup can be filled with a stable random mixture.

Scenario 2
In scenario 2 the procedure of filling the XRF cup is considered. The XRF sample cup is filled with many increments smaller than the radiated volume. Further these are distributed in a random order. Since all particles then have the same chance to be included in the measured volume of the sample the equiprobabilistic rule may be considered fulfilled. The measurement itself is the same as scenario 1.

The relevant sampling errors (figure 1) are listed and discussed below, in order to elucidate what impact they have, and how they can be influenced.

3.3.2. Fundamental error (FSE)
The FSE occurs during all sampling and sub sampling procedures. The variance of FSE can be reduced in two ways, either by taking larger samples or by reducing the particle size of the material to be sampled.
The analyse sample mass cannot be manipulated for XRF measurements. But, the sample can be ground to a finer particle size distribution before filled into the sample cup.

3.3.3. The grouping and segregation error (GSE)
The GSE is caused by an uneven distribution of particles with different properties within the lot, on the scale of sample sizes. These properties can be particle size, particle density, etc. An obvious example is the iron clusters in the intermediate mixture of iron and CCA contaminated soil (Paper III, Paper IV).

The variance of the grouping and segregation error is expressed by equation 13. In practice this product has never been successfully calculated (Pitard, 1993), and can be considered as conceptual.

\[ s^2_{GSE} = s^2_{FSE} \cdot Y \cdot Z \]  

Equation 13

Legend for equation 13:
- \( s^2_{GSE} \) the variance of the grouping and segregation error,
- Y grouping factor
- Z segregation factor

There are three ways to reduce the GSE; reducing the fundamental error, reducing the grouping factor Y or reducing the segregation factor Z. The two latter are discussed below.
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3.3.3.1. Reducing the grouping factor Y of GSE
The grouping factor, Y, is characterising the size of the increments. It is dimensionless and ranges from nil to eternity, $Y \geq 0$. The most extreme case is $Y = 0$, when a single fragment is the entire increment (Gy, 1998).

To reduce the grouping factor as many small increments as possible should be taken to be combined into the sample.

If, as an alternative approach, the sub sampling is considered to happen during the filling of the XRF cup, the cup should be filled with as many and as small increments as possible.

3.3.3.2. Reducing segregation factor Z of GSE
The segregation factor, Z, can hypothetically be reduced by a homogenisation processes. But, homogenisation processes can actually themselves induce segregation mechanisms which risk to bias a sample (Mason, 1992; Ramsey and Suggs, 2001; Shefsky, 1997). Even if homogenisation has been successful, segregation may occur during the filling of the XRF cup.

If the mixing is done in the XRF cup, segregation may still occur. One example of this was reported by (Korpelainen, et al., 2002) where two different minerals were mixed in sample cups. These mixtures showed a vertical segregation.

To evaluate the mixing quality within a XRF sample cup would require several samples to be taken (Paper III, Paper IV). Further it requires the analysis of the samples to be performed with another method than XRF since the volumes would then be too small. The sampling itself from the XRF sample cup risks to disturb the system if performed on the dry particulate volume due to settlements and problems similar to those discussed in section 3.4.1.2. If a low viscous glue can be added, without causing disturbing turbulence, the sample could be sliced and analysed, for example by scanning microscope methods in analogy with the methods described by Korpelainen et al (2002). Turning the sample to a paste (material properties allowing) by water addition of water could be another path to sub-sampling with limited alteration of the particulate distribution in the sample cup. Another potential method would be to dry freeze the sample and cut it into suitable pieces.

It should be possible to reduce the grouping factor by homogenisation, but that may be futile or counteracted by segregation mechanisms. Homogenisation should not be relied on as the sole means to reduce the GSE.

3.3.4. Segregation mechanisms

Segregation between particles can occur due to differences in various particle properties. The most important properties for segregation are in falling order particle size, density, shape resilience, where size is the “by far the most important and almost always this is the most serious cause of segregation” (Harnby, et al., 1985). Other properties of importance can be surface roughness, forces of attraction and friction (Harnby, et al., 1985).

Segregation occurs when some movement is induced to the bulk of particles, like vibration, mixing or transportation.
Some mechanisms of particle segregation are:

- **Percolation/Sifting**: Finer particles fall between larger particles. If the material is falling at a pile the finer particles will sift into the pile and the coarser will fall off, accumulating at the base (Paul, et al., 2004; Pitard, 1993; Weinekötter and Gericke, 2000).

- **Floating**: Finer particles fall between larger particles. Due to movements in the bulk, e.g. vibration, larger and/or denser particles compacts the finer and/or lighter. The larger and/or denser particles will then eventually be found on top of the bulk (Harnby, et al., 1985; Weinekötter and Gericke, 2000).

- **Agglomeration**: Finer particles in close contact stick together in agglomerates by various strong inter particle forces, like liquid bridges or electrostatics (Weinekötter and Gericke, 2000).

- **Trajectory segregation**: If particles has a horizontal speed (like on a conveyor belt) and comes to a free fall, the heavier and larger particles will be less impacted by air friction and fall longer (Harnby, et al., 1985; Paul, et al., 2004; Pitard, 1993; Weinekötter and Gericke, 2000).

- **"Chute density segregation"**: Denser particles will have higher friction and lower speed if falling through a chute to a discharge point, making the less dense particles fall longer from the discharge point (Pitard, 1993).

- **"Chute friction rate segregation"**: Similar to chute density segregation but caused by different friction of particles with similar density. Causes of different friction can be different shape (Pitard, 1993).

- **Fragment shape heterogeneity segregation**: If particles are poured on a pile without horizontal speed particles with low friction are likely to fall of to the base of the pile, and high friction particles are accumulated in the core of the pile. If the particles have an initial speed, the low friction particles will tend to mainly fall off in the direction of the horizontal movement (Pitard, 1993).

- **Air streams and turbulence**: Fine particles can be blown away by air streams or turbulence. Lower particulate flow speed avoid some of the turbulence problems (Paul, et al., 2004; Pitard, 1993).

- **Fluidisation**: If a particular material is pulled into a vessel very fine particles can be floating in the air (or other gas) for a long time (Paul, et al., 2004).

- **Electrostatic**: If some particle classes stick to the walls of containers or on the equipment these particles segregates.

Segregation occurs in fine particulate materials. Materials with particles larger than 75 μm segregates easily, and with materials with particles in the range 10 - 75 μm the tendencies for segregation is reduced, but may still be detected (Harnby, et al., 1985).

Examples of observed and identified segregation mechanisms:
- When emptying large scale mixers on asphalt surfaces (Paper III, Paper IV) the soil mixture forms piles. A percolation/sifting segregation can be observed when larger lumps of soil aggregates fall of the heaps to the periphery.
- In iron-soil mixtures aggregation segregation can be observed when larger lumps of soil segregates fall of the heaps to the periphery.
- For dry and fine particulate samples electrostatic forces can be problematic when particles attach to plastic bags, sample containers, tools et c. (Paper I, Paper II).

Other segregations mechanisms may have occurred, despite not being observed.
Segregation mechanisms may bias the sample if they alter the proportion of e.g. particle size classes, and different particle size classes have different properties of interest.

The elimination of coarser particle size classes through sieving was altering the average metal content, statistically significant in four out of 16 tests (Paper II). These data are shown in figure 2 to show the average concentration progress after one and two sieving steps. The values from XRF prep are normalised to highest value per sample and element. Finer particle classes have a higher specific surface than coarser particle size classes. Therefore often the finer particle size classes are considered to be more contaminated, due to larger surface available for sorption. Such findings have also been reported for XRF analysis of particulate size classes in contaminated soil (Hartyáni, et al., 2000). It is concluded to be a problem if the samples are handled unconscious (USEPA, 1996).

![Figure 2](image-url)

**Figure 2.** Normalised changes in concentration due to passing sieves of 2.00 and 0.25 mm. Based on data from (Paper II).

3.3.5. Incorrect delimitation error (IDE)

The soil volume in the XRF sample cup has roughly the same extension in all three space directions. From a TOS view this is a 3-D sampling situation. As such two conditions must be fulfilled: a) The sub sample should have the geometry of a sphere. This gives isotropic sub sample geometry and will not favour any sample direction. b) It should be possible to place the sphere randomly within the volume of the lot.

Neither is fulfilled due to the construction of the XRF. In the used XRF (NITON 700), the sample is radiated at 30° to the plane of the sample surface (Paper II). Varying data have been presented with regard to the penetration depth. (Kalnicky and Singhvi, 2001) have reported it to be 2 mm, (Andersson, 2004) reports 3-5 mm, (USEPA, 1998) a penetration depth of 25 mm is given. (Hewitt, 1995) reports a penetration depth of 4.8 and 40 mm in a
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quarts matrix, using Cd-109 and Am-241 as radiation source respectively. The penetration depth is dependent on matrix, radiation source intensity and wave length of radiation, and possibly more factors. Since the instrument design only allows measurements on the surface of a bulk IDE will always occur during XRF measurements.

3.3.6. The incorrect extraction error (IEE)

For XRF cups the isotropic geometry is a sphere (section 3.3.5.). Particles with the mass centre inside the sphere should be included in the sample, all others excluded. Deviations give rise to IEE.

The measuring principle of XRF on sample cups (neither in bags or in-situ) gives no possibility to manipulate the sample geometry.

During XRF-measurement IEE will always occur.

3.3.7. Incorrect preparation error (IPE)

During preparation several IPE can occur (Paper I).

During filling of the XRF cup IPE might occur, like loss of particles due to dusting, sticking to tools et cetera.

During measurement in a prepared XRF cup it is not easy to realise if any IPE occurs. This is not necessarily meaning no IPE occurs.

Incorrect Preparation errors might occur during filling of the XRF cup.

3.3.8. Sampling weighting error (SWE)

Sampling weighting error occurs if the increments are of various sizes.

3.3.9. Summary of sampling errors in XRF cup preparation

The errors relevant to filling a XRF sample cup discussed above is summarised in table 2 and commented.
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Table 2. Conclusions of the sampling error applied to XRF cup measurements.

<table>
<thead>
<tr>
<th>Error</th>
<th>Factor</th>
<th>Not considered relevant</th>
<th>Unsolvable</th>
<th>Solvable reducible</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSE</td>
<td>sample mass</td>
<td>X</td>
<td></td>
<td></td>
<td>is fixed in sample cup</td>
</tr>
<tr>
<td>FSE</td>
<td>particle size</td>
<td>X</td>
<td>X</td>
<td></td>
<td>grind particles further</td>
</tr>
<tr>
<td>GSE</td>
<td>FSE</td>
<td>X</td>
<td></td>
<td></td>
<td>see FSE</td>
</tr>
<tr>
<td>GSE</td>
<td>segregation factor</td>
<td>X</td>
<td></td>
<td></td>
<td>mixing reduces the segregation factor, but…</td>
</tr>
<tr>
<td>GSE</td>
<td>segregation factor</td>
<td>X</td>
<td>X</td>
<td></td>
<td>…mixing cannot be trusted to stay stable</td>
</tr>
<tr>
<td>GSE</td>
<td>grouping factor</td>
<td>X</td>
<td></td>
<td></td>
<td>many small increments when filling the XRF cup</td>
</tr>
<tr>
<td>GSE</td>
<td>grouping factor</td>
<td>X</td>
<td></td>
<td></td>
<td>reduce the possibilities for segregation to occur during filling of the XRF cup</td>
</tr>
<tr>
<td>IDE</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td>never correct</td>
</tr>
<tr>
<td>IEE</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td>never correct</td>
</tr>
<tr>
<td>IPE</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td>avoid</td>
</tr>
<tr>
<td>PSE1</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSE2</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WE</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td>use equal increment sizes</td>
</tr>
<tr>
<td>TAE</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From table 2 it can be concluded that the following means can be used:
- Reducing the particle size.
- Filling the XRF cup with many small increments.
- Reducing the risk for segregation mechanisms while filling the cup.
- Using equal sized increments to build up the sample in the cup.
3.4. Potential solutions to reduce segregation in XRF cups

The procedure is divided into extraction phase and filling phase.

3.4.1. Extraction methods of sample from mortar or similar

3.4.1.1. Extraction by pouring

If particles are poured from a sample container several segregation mechanisms can occur, namely trajectory segregation, chute density segregation and chute friction rate segregation. As result property gradients in the pouring direction can develop (fig 3).

![Figure 3](image)

**Figure 3.** Pouring particles into a heap (in an XRF cup) can give a gradient in the direction of pouring. The arrow indicates the gradient.

3.4.1.2. Extraction with spoon

A quick and simple method to extract the increments is to use a spoon, spatula *et cetera*. Preferable many and small increments are to be extracted. This would have the benefits that the method would be quick, easy and without need of special equipment.

However, extracting increments with a spoon or similar can cause a similar type of segregation as the *percolation/sifting mechanism*, because coarser particles are more likely to fall off the tool (fig 4). This means that fines may be overrepresented in the first increments and with larger particles in the last increment. As a result a trend is created. Both IDE and IEE occur.
Advantages:
+ Easy and quick extraction to perform.
+ No "special equipment" is required.

Disadvantages:
- May cause an artificial trend of size distribution over the sample increments.

Figure 4. Courser particles are more likely to fall off a spoon or spatula than fines due to similar mechanisms as in forming of piles.

3.4.1.3. Correct extraction and delimitation
Take many and small increments with correct delimitation and extraction. Correct delimitation and extraction of the increments will not cause any change of particle size distribution like the spoon/spatula extraction method (section 3.4.1.2.). Techniques from correct sub sampling can be applied (Gerlach and Nocerino, 2003; Petersen, et al., 2004).

Since the increments to be put in the XRF cup might cause inherent segregation (section 3.4.1.2.) it is important that the increments can be extracted at random to break any correlation between them.

Advantages:
+ Correct delimitation and extraction of the increments will not cause any change of particle size distribution like the spoon-grab sampling method above.
+ Random choice of increments reduce the risk with correlation between increments.

Disadvantages:
- Time consuming

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3.4.2. Filling XRF cup

3.4.2.1. Filling XRF cup with spoon loads
The constructed “heap” on the bottom of the XRF cup will segregate horizontally; the coarser will fall of to the periphery of the heap and the core will be overrepresented with fines according to the percolation/ shifting mechanism (fig 4).

Advantages:
+ Quick and easy.

Disadvantages:
- The coarser fragments fall of the sides to the base of the heaps.

![Figure 5](image.png)

**Figure 5.** Pouring particles on a heap without horizontal speed causes a “circular gradient” from the centre and outwards.

3.4.2.2. Filling XRF cup by pouring
The segregation caused by pouring is similar to filling with spoon loads, possibly with the addition of a higher horizontal speed. The horizontal speed can induce the mechanisms namely trajectory segregation, chute density segregation and chute friction rate segregation (fig 3, fig 5).
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Advantages:
+ Quick and easy.

Disadvantages:
- The coarser fragments fall of the sides to the base of the heaps.
- Can also have horizontal segregation due to horizontal speed.

3.4.2.3. *Filling with dry frozen aggregates*

The increments are frozen into aggregates which are added randomly to the XRF cup. If small aggregates of fine particulate matter is put into the XRF cup one by one at random and gently piled close to each other, many segregation mechanisms might be avoided or reduced. Further trends in the sample are broken.

The delimitation and extraction of the increments are of course critical. The method of freezing is another critical aspect. To freeze by adding some liquid gas is an option as long as the gas does not interact with the material. When the aggregates thaw, the voids between them will fill up through to erosion and some segregation may occur.

Advantages:
+ Potentially reduces (or even eliminates) segregation mechanisms during the filling of the XRF sample cup.
+ The random filling of the increments breaking up trends in the sample.

Disadvantages:
- A freezing step is added to the operational procedure.
- The sample preparation takes more time.
- When the aggregates thaw, voids between them will be filled through erosion and some segregation may occur.

3.4.2.4. *Filling with aid of vertical channels*

By dividing the XRF cup into sections with walls between, the horizontal segregation is to be reduced. Further, the procedure allows filling increment by increment in a randomised order into the XRF cup, to fulfil the equiprobabilistic rule. The walls of the channels may attract the particles by electrostatic forces causing selective particle loss, when they are withdrawn.

Advantages:
+ Less horizontal segregation of the type “falling of a heap”.
+ Can be handled in a way that obeys the equiprobabilistic rule, for groups of particles.

Disadvantages:
- Possibly loss of fines due to electrostatic forces during withdrawal of the channels.
- Time consuming.
- *Within* each channel some horizontal segregation risks to occur.
3.5. Perspective

The significance and impact of the discussed questions; HI estimation methods and potential improvement or XRF cup filling procedures is unknown. This is in the nature of the problems.

To evaluate a precision improvement, data from improved methods need to be compared to other methods. This cannot be done in advance.

To evaluate the reduction in bias (like segregation in XRF cups) measurements should be made on a system where the concentrations are known, like a standard reference material. But not even this is fool proof, segregation could occur in the standard reference material as well. Further the standard reference material might behave in another way then the “usual” samples. Anyhow, if a bias is estimated it is only useful to show that bias occurs. A bias may not be assumed to be constant, but varies from time to time. Therefore it is better to put the effort towards avoiding bias rather than to calculate it (Pitard, 1993).

The fundamental error is unique among the sampling error of TOS in the respect it can be estimated in advance of the sampling, if HI is known (see section 5.2.). With its knowledge in advance suggestions can be made to sampling and sub sampling protocols, i.e. how to grind (if suitable for the contaminant) and sub sample to reduce the contribution from FSE (Gerlach and Nocerino, 2003; Gustavsson, 2004; Mason, 1992). If FSE is small compared to other sampling errors its reduction might give negligible effect on GEE until the larger errors are reduced. Further FSE estimation alone gives no reliable errors estimate (Paper I), this requires other methods.

The sum of MSE and TAE can be calculated for the material sampled in the 1-D trajectory and evaluated with semi-variogram (Petersen and Esbensen, 2005). The semi-variograms of Geostatistics gives likely similar results.

With nested sampling designs (Minkkinen, 2004; Nordtest, 2007) the sampling variance can be split into components, like:
- spatial distribution (or temporal)
- sampling error
- analytical error

Theoretically, if all bias is (assumed) avoided and $s^2_{\text{FSE}}$ is calculated, the GSE component could be estimated. But it is argued by Pitard that this is usually wishful thinking, usually there is some residual variances left from the other sampling errors (Pitard, 1993).
4. CONCLUSIONS

Determination of the heterogeneity invariant (HI) is an important step in the design of sampling protocols according to the theory of sampling (TOS). It is used to balance the fundamental error against the sample size. Or, expressed another way; balance an uncertainty contribution against a cost. The better HI estimates the better decisions can be made. An overestimation with a factor of 20 may lead to 20 times larger sample with increased cost as result. The same magnitude of underestimation gives an uncertainty contribution from the fundamental error which is 4.5 times higher.

Several methods for HI determination are presented in the literature. The applicability and limits of the different methods for contaminated soils are summarised below:

- The Gy-formula can only be applied when the contaminants are particulate.
- The usefulness of the Gy-formula is limited when the contaminants are not particulate, since some factors used in the formula may be hard or impossible to determine. Tabulated classification of sample properties and their respective values may be used, but may introduce uncertainty due to subjective judgement.
- The size – density fractionating method can be applied if the soil and contaminants can be split in both density and size classes.
- The usefulness of the density-particle size-method is limited by the high cost, cumbersomeness and the need of special equipment. Further density separation by flotation in various liquids may carry the risk of altering the contaminants.
- The size – density fractionating method can be applied, to get a quick first idea of HI for all particle size classes (given that the material can be sieved).
- The usefulness of the sieves analysis method is limited to determination of HI for specific particle size classes, which is not necessarily the same as HI for the contaminants of interest.
- The simplified method is based on and simplifies the sieves analysis method.
- The usefulness of the simplified method is limited due to its restrictions caused by the simplifications e.g. not considering concentration of contaminant.
- The SIS waste equation can be applied when the contaminant is totally liberated spherical contaminant particles, with same density as the soil (matrix) particles, in a known mass fraction.
- The usefulness of the SIS waste equation is limited to the scenario described above. Further the variable p, (mass fraction of particles with specific properties) is hard to determine for contaminated soil. To use a default value of p as suggested gives severe miss interpretations of HI in low concentration ranges.
- The two tiered variance comparison can be applied in a very broad variety of samples.
- The usefulness of the two tiered variance comparison may be limited by requirements of 20 samples to be taken and analysed, this may in some projects considered to be too many. Further, residual variances may interfere, resulting in an overestimation of HI.

If a method should be developed, more suitable for contaminated soil, a starting point may be to use the size-density method for a wide range of soils, contaminants, contaminant types, soil types et cetera. For the samples where the contaminants are not particulate it may be possible that the density is of minor importance. This may open up for developing other equations for relating sample size to fundamental error.
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The phenomenon of HI variations merit further studies due to its large importance for the sample protocol design. Among factors that may be important are: the spatial scale of the samples, different sites, soils and contaminants.

To avoid bias all particles must have the same chance to be in the analytical sample (equiprobabilistic rule). With portable X-Ray fluorescence spectroscopy (XRF) measurements in Mylar thin film XRF sample cup special attention must be paid during the filling of the XRF cup.

The applicable measures to reduce the correct sampling errors (CSE) during XRF cup filling are:
- particle size reduction.
- to fill the XRF cup by as small and as many increments as possible.
- avoid segregation of the samples during filling of the XRF cup.

Field portable X-ray fluorescence spectroscopy analyser (XRF) measurements always induce incorrect delimitation error (IDE) and incorrect extraction errors (IEE). These can not be eliminated. However, their effect can be reduced by the same means as the reduction of the segregation effects in the XRF cups.

Segregation mechanisms are likely to occur in the process of filling a XRF cup. These induce biased measurements as result. To reduce the effects of the segregation mechanisms one can:
- Avoid: Extraction with spoon/ spatula, which can favour finer particles.
- Avoid: Extraction by pouring the sample out of a container, which can induce horizontal segregation.
- Recommended: Extraction of increments by following principles for correct sub sampling according to TOS. Increments can e.g. be extracted by incremental sampling.
- Recommended: Transfer the increments in a randomised order, thereby breaking possible correlations between the increments due to trends in the sample volume.
- Avoid: Filling the XRF cup by pouring or adding by spoon/ spatula risk to create heaps with fines in the core and the coarser on the base of the heap.
- Suggestion: Filling the XRF cup with dry frozen aggregates of particles to avoid/ reduce segregation.
- Suggestion: To reduce vertical segregation in XRF cups, fill the sample increments through a system with vertically channels.

If fundamental error is small compared to other sampling errors its reduction might give little effect on the global error estimate. Further, only fundamental error estimation alone gives no reliable errors estimate.

Estimation of a bias (like segregation in an XRF cup) requires some effort. But such estimation is of little value since a bias never can be trusted. A bias is not constant from time to time. Bias prevention is a better spent effort.
### 5. LISTS OF SYMBOLS AND ABBREVIATIONS

**Table 3.** Description of the components in equations.

<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_i$</td>
<td>concentration in fragment or group i</td>
<td>[g/g]</td>
</tr>
<tr>
<td>$a_D$</td>
<td>the mass proportion of critical component (contaminant) in one density fraction</td>
<td>[-]</td>
</tr>
<tr>
<td>$a_L$</td>
<td>mass proportion of the critical component (contaminant) in the entire lot</td>
<td>[-]</td>
</tr>
<tr>
<td>$a_{L_{i}}$</td>
<td>the proportion of the critical particle size class in the lot</td>
<td>[-]</td>
</tr>
<tr>
<td>$a_{SD}$</td>
<td>the critical content (contaminant) of one size-density fraction</td>
<td>[-]</td>
</tr>
<tr>
<td>$b$</td>
<td>parameter</td>
<td>[-]</td>
</tr>
<tr>
<td>$c$</td>
<td>constitution factor</td>
<td>[g/cm$^3$]</td>
</tr>
<tr>
<td>$C$</td>
<td>sampling constant of TOS</td>
<td>[g/cm$^3$]</td>
</tr>
<tr>
<td>$d$</td>
<td>actual diameter</td>
<td>[cm]</td>
</tr>
<tr>
<td>$D$</td>
<td>index of density fractions</td>
<td>[-]</td>
</tr>
<tr>
<td>$d_0$</td>
<td>is liberation size of the mineral particles,</td>
<td>[cm]</td>
</tr>
<tr>
<td>$d_{95}$</td>
<td>upper particle diameter (95th percentile)</td>
<td>[cm]</td>
</tr>
<tr>
<td>$d_{FLC}$</td>
<td>average fragment size of the critical particle class.</td>
<td>[cm]</td>
</tr>
<tr>
<td>$f$</td>
<td>particle shape variable</td>
<td>[-]</td>
</tr>
<tr>
<td>$F$</td>
<td>calculated F-value</td>
<td>[-]</td>
</tr>
<tr>
<td>$F_{(nL-1, nS-1)}$</td>
<td>tabulated F-value with (nL-1, nS-1) degrees of freedom</td>
<td>[-]</td>
</tr>
<tr>
<td>$g$</td>
<td>the particle size range factor</td>
<td>[-]</td>
</tr>
<tr>
<td>$H_{I}$</td>
<td>heterogeneity invariant</td>
<td>[g]</td>
</tr>
<tr>
<td>$H_{I_{L_{C}}}$</td>
<td>heterogeneity invariant for particle size class of interest</td>
<td>[g]</td>
</tr>
<tr>
<td>$i$</td>
<td>index for fragments or groups</td>
<td>[-]</td>
</tr>
<tr>
<td>$K$</td>
<td>a constant set to 9 or 10</td>
<td>[-]</td>
</tr>
<tr>
<td>$M_{E}$</td>
<td>extracted sample mass</td>
<td>[g]</td>
</tr>
<tr>
<td>$M_{EL}$</td>
<td>average mass of extracted sample, large size series</td>
<td>[g]</td>
</tr>
<tr>
<td>$M_{ES}$</td>
<td>average mass of extracted sample, small size series</td>
<td>[g]</td>
</tr>
<tr>
<td>$M_{i}$</td>
<td>mass of fragment or group i</td>
<td>[g]</td>
</tr>
<tr>
<td>$M_{L}$</td>
<td>mass of the lot to be sampled</td>
<td>[g]</td>
</tr>
<tr>
<td>$M_{LD}$</td>
<td>the mass of one density fraction</td>
<td>[g]</td>
</tr>
<tr>
<td>$M_{LSD}$</td>
<td>the mass of one size-density fraction</td>
<td>[g]</td>
</tr>
<tr>
<td>$m_{S}$</td>
<td>mass fraction of material in the S’th size class</td>
<td>[-]</td>
</tr>
<tr>
<td>$m_{SD}$</td>
<td>mass fraction of material in the S’th size class with in the D’th density class</td>
<td>[-]</td>
</tr>
<tr>
<td>$n_{L}$</td>
<td>number of small sized samples</td>
<td>[-]</td>
</tr>
<tr>
<td>$n_{S}$</td>
<td>number of large sized samples</td>
<td>[-]</td>
</tr>
<tr>
<td>$p$</td>
<td>the mass fraction with a specific critical property (contaminant).</td>
<td>[-]</td>
</tr>
<tr>
<td>$S$</td>
<td>index of size fractions</td>
<td>[-]</td>
</tr>
<tr>
<td>$s_{AE}^2$</td>
<td>variance of analytical error</td>
<td>[-]</td>
</tr>
<tr>
<td>$s_{FE}^2$</td>
<td>variance of the fundamental error</td>
<td>[-]</td>
</tr>
<tr>
<td>$s_{GSE}^2$</td>
<td>the variance of the grouping and segregation error,</td>
<td>[-]</td>
</tr>
<tr>
<td>$s_{L}^2$</td>
<td>variance of large sized samples</td>
<td>[-]</td>
</tr>
<tr>
<td>$s_{S}^2$</td>
<td>variance of small sized samples</td>
<td>[-]</td>
</tr>
<tr>
<td>$V_{S}$</td>
<td>the average volume of one fragment in a given size fraction S</td>
<td>[cm$^3$]</td>
</tr>
<tr>
<td>$Y$</td>
<td>grouping factor</td>
<td>[-]</td>
</tr>
<tr>
<td>$Z$</td>
<td>segregation factor</td>
<td>[-]</td>
</tr>
</tbody>
</table>
Heterogeneities in samples of contaminated soil

Continuation of table 3.

<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>mass proportion of the critical component (contaminant) in the critical particles</td>
<td>[-]</td>
</tr>
<tr>
<td>$\beta$</td>
<td>liberation factor</td>
<td>[-]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density of the material</td>
<td>[g/cm$^3$]</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>critical component (contaminant) density</td>
<td>[g/cm$^3$]</td>
</tr>
<tr>
<td>$\rho_D$</td>
<td>the density of a given density class D</td>
<td>[g/cm$^3$]</td>
</tr>
<tr>
<td>$\rho_{SD}$</td>
<td>density of a particle in the S’th size class within the D’th density class</td>
<td>[g/cm$^3$]</td>
</tr>
<tr>
<td>$\rho_m$</td>
<td>soil (matrix) density</td>
<td>[g/cm$^3$]</td>
</tr>
</tbody>
</table>
Heterogeneities in samples of contaminated soil

Table 4. List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AE</td>
<td>analytical error</td>
</tr>
<tr>
<td>CSE</td>
<td>correct sampling error</td>
</tr>
<tr>
<td>CCA</td>
<td>chromated copper arsenate</td>
</tr>
<tr>
<td>0,1,2,3-D</td>
<td>0,1,2,3-dimension</td>
</tr>
<tr>
<td>FSE</td>
<td>fundamental sampling error</td>
</tr>
<tr>
<td>GEE</td>
<td>global error estimate</td>
</tr>
<tr>
<td>GSE</td>
<td>grouping and segregation error</td>
</tr>
<tr>
<td>HI</td>
<td>heterogeneity invariant</td>
</tr>
<tr>
<td>IDE</td>
<td>incorrect delimitation error</td>
</tr>
<tr>
<td>IEE</td>
<td>incorrect extraction error</td>
</tr>
<tr>
<td>IPE</td>
<td>incorrect preparation error</td>
</tr>
<tr>
<td>ISE</td>
<td>incorrect sampling error</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organisation for Standardization</td>
</tr>
<tr>
<td>ME</td>
<td>materialisation error</td>
</tr>
<tr>
<td>MIFO</td>
<td>metodik för inventering av förorenade områden (methods for inventory of contaminated sites)</td>
</tr>
<tr>
<td>MSE</td>
<td>materialisation sampling error</td>
</tr>
<tr>
<td>PSE</td>
<td>point selection error</td>
</tr>
<tr>
<td>SEPA</td>
<td>Swedish Environmental Protection Agency</td>
</tr>
<tr>
<td>SEK</td>
<td>Swedish krona (currency)</td>
</tr>
<tr>
<td>SIS</td>
<td>Swedish Standards Institute</td>
</tr>
<tr>
<td>TOS</td>
<td>theory of sampling</td>
</tr>
<tr>
<td>TSE</td>
<td>total sampling error</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States environmental protection agency</td>
</tr>
<tr>
<td>SWE</td>
<td>weighting error</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence spectroscopy</td>
</tr>
</tbody>
</table>
6. ACKNOWLEDGEMENTS

It’s been a long journey. But it’s been my journey.

But, to make my Doctoral Thesis I needed help from many persons and organisations:

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- Ragn-Sells AB
- Luleå University of Technology
- Interreg IIIA Nord

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I am very thankful to my beloved wife Anna-Maria for all her love, and her patience with my long working hours.

Finally I wish to thank my son Alfred for being himself. And for giving me some perspective; having a fancy title belongs just to the carrier, but having him belongs to life.

Luleå 2007-10-29
Björn Gustavsson
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Paper 1
Comparison of analytical error and sampling error for contaminated soil

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Abstract

Investigation of soil from contaminated sites requires several sample handling steps that, most likely, will induce uncertainties in the sample. The theory of sampling describes seven sampling errors that can be calculated, estimated or discussed in order to get an idea of the size of the sampling uncertainties. With the aim of comparing the size of the analytical error to the total sampling error, these seven errors were applied, estimated and discussed, to a case study of a contaminated site. The manageable errors were summarized, showing a range of three orders of magnitudes between the examples. The comparisons show that the quotient between the total sampling error and the analytical error is larger than 20 in most calculation examples. Exceptions were samples taken in hot spots, where some components of the total sampling error get small and the analytical error gets large in comparison. Low concentration of contaminant, small extracted sample size and large particles in the sample contribute to the extent of uncertainty.

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Keywords: Soil contamination; Sampling error; Metal; Uncertainty; X-ray fluorescence

1. Introduction

In order to investigate the need for remediation, sampling and analysis of soil from Notviken workshop, northern Sweden, were performed.

Any analysis of contaminated soil introduces an uncertainty. The sample handling of the contaminated soil also introduces an uncertainty. This might be significantly larger compared to the analytical uncertainty.

The aim of this paper is to evaluate and to compare the uncertainty introduced by analytical procedures to the uncertainty introduced by sample handling.

1.1. Research question

How large is the analytical error compared to the total sampling error in the case study in Notviken?

1.2. Description of the contaminated site

The site at Notviken is an area where trains have been serviced. A summary of the land use includes railway tracks, landfills, scrap yards and workshop buildings. The area has had a history of industrial activities since the beginning of the 20th century. Studies from areas with similar activities indicate that pollutants like metals, oils, wood preservatives, pesticides and PAHs can be expected\cite{1}. Previous investigations revealed increased levels of arsenic, lead, nickel and zinc in samples from groundwater.

The area is filled with varying materials, ranging from natural material to slag. The depth of the filling ranges was between 10 and 50 cm. The quaternary deposits below the fillings are mainly till (sand-silt), and river sediments, possible glaciofluvial, are also occasionally found. The river (or glaciofluvial) sediments may have covered the till surface, but have been partly eroded. Below the till, glacial clay with an unknown depth can be found.

A residential area is located 150 m east of the workshop area. The Luleå Rivers flows directly south of the workshop area, and there is a forest to the north and the west.
2. Materials and method

2.1. Samples

2.1.1. Sampling

Nine samples, marked A to I, were taken from two landfills and a scrap yard within the workshop area. An excavator dug trial pits for soil sampling. Samples were generally taken at the depths of 0, 50 and 100 cm. A trowel was used to obtain the samples from the walls in the trial pit. From each sampling depth, a sample was composed of four increments, except for sample C. Sample C is a grab sample from an obvious hotspot of copper where the soil was green.

2.1.2. Sample preparation

The sample preparation consisted of weighing, mixing by kneading for 5 min in the plastic bags, drying at temperatures over 100°C and sieving through a 2.00 mm polyamide sieve. The two fractions were weighed. A second mixing was performed on the fraction passing the sieve, before metal measurements. Metals were analysed by X-ray fluorescence spectroscopy (XRF). The XRF used was a NITON 700 XL with a cadmium isotope as radiation source. The measurements were performed with the samples in the plastic bags, with three measurements on different locations on each sample. Each measurement was performed for approximately 120 nominal seconds [2,3].

2.1.3. Description of the samples

Nine samples were chosen from the entire site investigation, having a spread of contaminant levels and sampling depths and taken from various places inside the workshop area. The samples were sent to a laboratory for confirmatory analysis by inductively coupled plasma optical emission spectroscopy (ICP-AES). The sample mass and its measured level of contaminant is presented in Table 1. For XRF three measurements were made on each sample and the highest and lowest were used for further calculations. The evaluated elements are copper, lead and zinc. The XRF measures on 0.3 g of the soil sample [4].

(The table is not transcribed here but would contain columns for sample names, sample mass, depth, and measured contaminant concentrations.

2.2. Analytical error

2.2.1. XRF

Using a standard reference sample to make seven repeated measurements and calculate a relative standard deviation is considered to be a measure of precision [2].

The standard reference materials used are sediments from The National Institute of Standards and Technology (NIST); highly contaminant NIST 2710, medium contaminant NIST 2711 and low contaminant NIST 2709. XRF sample cups were used during measurements of the standard reference materials.

The Niton 700 is calibrated by Niton Company when the isotope is changed. This was done shortly before the measurements were performed. When starting up the XRF, an internal calibration check is performed automatically. As extra control, well-known reference samples should be measured. Any error induced by the calibration has not been taken into consideration in this work.

2.2.2. ICP-AES

The laboratory reports its analysis with measurement uncertainty approximately similar to a 95% confidence interval. This corresponds to two standard deviations.

2.3. Sampling error: theory of sampling

Since the early 1950s a theory for correct sampling has been developed. The theory is known as Pierre Gy sampling theory or theory of sampling (TOS). The theory defines seven sampling errors described below in the light of this case study.

Accumulating all sampling errors, for all sampling steps, yields the total sampling error (TE). Adding the analytical error to the total sampling error gives the overall error (OE).

The term correct means hereafter correct according to TOS.

2.3.1. Fundamental error

The heterogeneity inside the lot to be sampled gives rise to the fundamental error. The fundamental error can be reduced but never eliminated.

Table 1

Sample mass (g) and metal concentrations (ppm)

<table>
<thead>
<tr>
<th>Sample</th>
<th>M (g)</th>
<th>Depth (cm)</th>
<th>XRF (ppm)</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>ICP (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu</td>
<td>Max</td>
<td>Min</td>
<td>Max</td>
<td>Min</td>
</tr>
<tr>
<td>A (L1)</td>
<td>312.2</td>
<td>50</td>
<td>4.110</td>
<td>875</td>
<td>1,980</td>
<td>1,010</td>
<td>3,570</td>
</tr>
<tr>
<td>B (L1)</td>
<td>581.8</td>
<td>0</td>
<td>412</td>
<td>282</td>
<td>178</td>
<td>162</td>
<td>297</td>
</tr>
<tr>
<td>C (L1)</td>
<td>543.1</td>
<td>25</td>
<td>6,930,000</td>
<td>205,000</td>
<td>1,490</td>
<td>1,360</td>
<td>7,550</td>
</tr>
<tr>
<td>D (L2)</td>
<td>1,021.6</td>
<td>50</td>
<td>658</td>
<td>647</td>
<td>333</td>
<td>309</td>
<td>936</td>
</tr>
<tr>
<td>E (L2)</td>
<td>991.1</td>
<td>100</td>
<td>321</td>
<td>270</td>
<td>241</td>
<td>209</td>
<td>611</td>
</tr>
<tr>
<td>F (S)</td>
<td>435.8</td>
<td>80</td>
<td>–</td>
<td>–</td>
<td>25.4</td>
<td>22.3</td>
<td>45.4</td>
</tr>
<tr>
<td>G (S)</td>
<td>846.7</td>
<td>0</td>
<td>2,540</td>
<td>1,660</td>
<td>2,620</td>
<td>2,540</td>
<td>7,760</td>
</tr>
<tr>
<td>H (S)</td>
<td>858.6</td>
<td>50</td>
<td>–</td>
<td>–</td>
<td>57.6</td>
<td>47.8</td>
<td>51.7</td>
</tr>
<tr>
<td>I (L2)</td>
<td>532.7</td>
<td>100</td>
<td>1,100</td>
<td>709</td>
<td>814</td>
<td>764</td>
<td>1,650</td>
</tr>
</tbody>
</table>

L1: landfill 1, L2: landfill 2, S: scrap yard.
Eq. (1) shows how to calculate, or estimate, the standard deviation of the fundamental error, $S_{FE}$, where $S_{FE}$ is dimensionless [5–14]:

$$S_{FE} = \sqrt{\frac{1}{M_E} - \frac{1}{M_L}} d_{50}(g)$$

(1)

In Eq. (1) the denotations are: $M_E$ is the extracted sample mass (g), $M_L$ the mass of the lot to be sampled (g), $d_{50}$ the mesh sieve size where 5% of the material is retained (cm), $c$ the mineralogical factor ($g/cm^3$), $\beta$ the liberation factor, $f$ the particle shape factor and $g$ is the particle size range factor or granometric factor. The mineralogical factor, $c$, is described in Eq. (2) [12,15]:

$$c = \frac{1 - (a_c/\alpha)^2}{a_c/\alpha} \rho_c + \left(1 - \frac{a_c}{\alpha}\right) \rho_m$$

(2)

In Eq. (2) the denotations are: $a_c$ is the mass proportion of the contaminant in the lot to be sampled, $\alpha$ the contaminant proportion in the critical particles, $\rho_c$ the contaminant density ($g/cm^3$) and $\rho_m$ is the soil density ($g/cm^3$).

2.3.2. Grouping and segregation error

Grouping and segregation error is a non-random segregation of the sample elements. Often it is due to gravity. The standard deviation of the segregation and grouping error, $S_{GSE}$, can be calculated by Eq. (3) [5–11]:

$$S_{GSE} = \sqrt{S_{FE}^2 YZ}$$

(3)

In Eq. (3), $Y$ is the grouping parameter and $Z$ is the segregation parameter. The product $S_{FE}^2 YZ$ would be extremely difficult to estimate and it is never done [14].

2.3.3. Long-range heterogeneity error

This error deals with trends in the lot to be sampled, spatial or temporal. When investigating a contaminated site, the spatial distribution of the contaminant, and its uncertainty, might be of most interest. This is dealt with geostatistics [5,7,11].

2.3.4. Periodic heterogeneity error

This error handles periodic variations in the lot to be sampled. These can be both spatial and temporal. The spatial case would be dealt with by geostatistics if the sample pattern is dense enough.

As for the temporal aspect in northern Sweden, where the site is located, this error should include seasonal changes over the year; freezing–thawing and raining–snowing. This could give a periodic behaviour of leaching and transportation of pollutants [5,7,11].

2.3.5. Incremental delimitation error

It is important for sampling that all particles in the lot have the same chance to be included in the sample. The correct geometry for a sample to be obtained is dependent on the extension of the lot in space (or time). Table 2 summarizes different situations. If the sample geometry is violated, the incremental delimitation error occurs [5–11,13,14].

When performing primary soil sampling on site, a correct delimitation is practically impossible to achieve, since a correct delimitation in two- or three-dimensional lots is an unsolvable problem. These samples are, anyway, sampled every day in environmental sampling. These data should be looked on with carefulness [14].

2.3.6. Increment extraction error

If the defined sample is not taken correctly, an extraction error occurs. The extraction is said to be correct, if the particles with their mass centre inside the defined sample volume get into the sample and the others are excluded from the sample [5].

A main problem is the equipment used. But even if the correct equipment is used, it has to be correctly used [5–11,13,14].

2.3.7. Preparation error

These errors are due to the human factor when designing a sampling and sample handling protocols, during sampling and sample handling, when designing, constructing tools, etc. Examples are losses, contamination, physical or chemical alteration, fraud and sabotage [5–11,13,14].

2.4. Total sampling error

The sum of the total sampling errors can be expressed as in Eq. (4) [5–11,13,14]. To use this equation the errors need to be statistically independent, otherwise the co-variance has to be included [16]:

$$S_{TE} = \sqrt{\sum S_{error}^2}$$

(4)

2.5. Overall error

The overall error, the sum of the total sampling error and the analytical error, can be expressed by Eq. (5) [5–11,13,14]:

$$S_{OE} = \sqrt{S_{TE}^2 + S_{AE}^2}$$

(5)

Table 2 presents correct sample geometry in different sampling dimensions

<table>
<thead>
<tr>
<th>Sampling dimension</th>
<th>Example</th>
<th>Correct sample geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D</td>
<td>Pile</td>
<td>A sphere inside the lot</td>
</tr>
<tr>
<td>2D</td>
<td>Flattened pile, soil strata</td>
<td>A cylinder, perpetual to the plane, through the entire thickness of the strata</td>
</tr>
<tr>
<td>1D</td>
<td>Longitudinal pile, conveyor belt</td>
<td>Cut off with two parallel planes, e.g. a scope with flat bottom and parallel walls</td>
</tr>
<tr>
<td>0D</td>
<td>Quite similar units, like truckloads or shovel loads</td>
<td>Randomly chosen units, preferable stratified randomised</td>
</tr>
</tbody>
</table>
Table 3
Mean concentrations, m (ppm); standard deviation, S.D. (ppm); and relative standard deviation, R.S.D. (%) from seven replicated XRF measurements of standard reference material from NIST.

<table>
<thead>
<tr>
<th></th>
<th>Lead NIST 2709</th>
<th></th>
<th>Zinc NIST 2709</th>
<th></th>
<th>Copper NIST 2710</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m (ppm)</td>
<td>S.D. (ppm)</td>
<td>R.S.D. (%)</td>
<td>m (ppm)</td>
<td>S.D. (ppm)</td>
</tr>
<tr>
<td>NIST 2709</td>
<td>24</td>
<td>2.88</td>
<td>12</td>
<td>87.5</td>
<td>8.14</td>
</tr>
<tr>
<td>NIST 2710</td>
<td>24.9</td>
<td>4.52</td>
<td>18.2</td>
<td>82.8</td>
<td>9.21</td>
</tr>
<tr>
<td>Pooled</td>
<td>24</td>
<td>5.1</td>
<td>21.2</td>
<td>74.6</td>
<td>11.9</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Analytical error

3.1.1. XRF

Table 3 shows the results from seven measurement campaigns carried out to estimate precision.

By pooling the results from NIST 2709, the analytical error for lead is 17.6%, and for zinc 12.5%. The analytical error for copper is chosen from a measurement campaign on NIST 2711, and is 21.7%. The results chosen are the largest analytical error for each element.

3.1.2. ICP-AES

The result of the calculated analytical error is presented in Table 4.

The relative standard deviation is very similar within analysis of the same element, despite the level of contaminant ranges over some orders of magnitudes.

Table 4
Relative standard deviation (%) from ICP-AES analysis

<table>
<thead>
<tr>
<th></th>
<th>R.S.D. Pb (%)</th>
<th>R.S.D. Zn (%)</th>
<th>R.S.D. Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11.3</td>
<td>8.32</td>
<td>10.7</td>
</tr>
</tbody>
</table>

3.2. Sampling errors

3.2.1. Fundamental error

The calculation of the fundamental error for sample A, lead measured by ICP-AES, is shown below for the case of field sampling (\(M_{E1} = 312.2 \text{ g}, M_{L1} = \infty \text{ g}, d_{95} = 0.2 \text{ cm}, \beta = 1, f = 0.5, \varphi = 0.25, a = 3020 \times 10^{-6}, \alpha = 1, \rho_{c} = 11.4, \text{ and } \rho_{m} = 2.65 \text{ g/cm}^3\)):

\[
c = \left(1 - \frac{3020 \times 10^{-6}}{1}\right)^{2} \times 11.4 + \left(1 - \frac{3020 \times 10^{-6}}{1}\right) \times 2.65 = 3750 \text{ g/cm}^3,
\]

\[
S_{FE1}^2 = \left(\frac{1}{312.2} - \frac{1}{\infty}\right) \times 0.23 \times 3750 \times 1 \times 0.5 \times 0.25 = 0.0120, \quad S_{FE1} = 11.0\% 
\]

Sample A, lead measured by ICP-AES, is shown below for the case of sub-sampling. The sample extracted from the field has now become the lot to be sampled (\(M_{E2} = 0.5 \text{ g} \text{ and } M_{L2} = 312.2 \text{ g}\)):

\[
S_{FE2}^2 = \left(\frac{1}{0.5} - \frac{1}{312.2}\right) \times 0.23 \times 3750 \times 1 \times 0.5 \times 0.25 = 7.50 S_{FE2} = 274\%
\]

Table 5
Dimensionless standard deviation (%) of the fundamental error calculated for the field sampling

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu High</th>
<th>Cu Low</th>
<th>Pb High</th>
<th>Pb Low</th>
<th>Zn High</th>
<th>Zn Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8.35</td>
<td>18.1</td>
<td>13.6</td>
<td>19</td>
<td>7.98</td>
<td>10.2</td>
</tr>
<tr>
<td>B</td>
<td>19.3</td>
<td>23.4</td>
<td>33.2</td>
<td>34.7</td>
<td>20.3</td>
<td>21.5</td>
</tr>
<tr>
<td>C</td>
<td>0.194</td>
<td>0.74</td>
<td>11.9</td>
<td>12.4</td>
<td>4.15</td>
<td>4.58</td>
</tr>
<tr>
<td>D</td>
<td>11.5</td>
<td>11.6</td>
<td>18.3</td>
<td>19</td>
<td>8.63</td>
<td>9.6</td>
</tr>
<tr>
<td>E</td>
<td>16.8</td>
<td>18.3</td>
<td>21.8</td>
<td>23.5</td>
<td>10.9</td>
<td>11.3</td>
</tr>
<tr>
<td>F</td>
<td>–</td>
<td>–</td>
<td>101</td>
<td>108</td>
<td>60.1</td>
<td>60.1</td>
</tr>
<tr>
<td>G</td>
<td>6.44</td>
<td>7.97</td>
<td>7.15</td>
<td>7.27</td>
<td>3.28</td>
<td>3.54</td>
</tr>
<tr>
<td>H</td>
<td>–</td>
<td>–</td>
<td>48</td>
<td>52.7</td>
<td>40.1</td>
<td>42.8</td>
</tr>
<tr>
<td>I</td>
<td>12.4</td>
<td>15.4</td>
<td>16.2</td>
<td>16.7</td>
<td>9</td>
<td>9.32</td>
</tr>
</tbody>
</table>

3.2. Sampling errors

3.2.1. Fundamental error

The calculation of the fundamental error for sample A, lead measured by ICP-AES, is shown below for the case of field sampling (\(M_{E1} = 312.2 \text{ g}, M_{L1} = \infty \text{ g}, d_{95} = 0.2 \text{ cm}, \beta = 1, f = 0.5, \varphi = 0.25, a = 3020 \times 10^{-6}, \alpha = 1, \rho_{c} = 11.4, \text{ and } \rho_{m} = 2.65 \text{ g/cm}^3\)):

\[
c = \left(1 - \frac{3020 \times 10^{-6}}{1}\right)^{2} \times 11.4 + \left(1 - \frac{3020 \times 10^{-6}}{1}\right) \times 2.65 = 3750 \text{ g/cm}^3,
\]

\[
S_{FE1}^2 = \left(\frac{1}{312.2} - \frac{1}{\infty}\right) \times 0.23 \times 3750 \times 1 \times 0.5 \times 0.25 = 0.0120, \quad S_{FE1} = 11.0\% 
\]

Sample A, lead measured by ICP-AES, is shown below for the case of sub-sampling. The sample extracted from the field has now become the lot to be sampled (\(M_{E2} = 0.5 \text{ g} \text{ and } M_{L2} = 312.2 \text{ g}\)):

\[
S_{FE2}^2 = \left(\frac{1}{0.5} - \frac{1}{312.2}\right) \times 0.23 \times 3750 \times 1 \times 0.5 \times 0.25 = 7.50 S_{FE2} = 274\%
\]
The values used for $\beta, f, g$ and $\rho_m$ are found tabulated and described “for most cases” [7,11,15]. Gy [8] states “When unsure, it is best to set $\beta = 1$”, which is the case in a very heterogeneous material [7,11]. The value of $\alpha$ is an assumption of a pure metal, which might be a simplification. This is a simplified procedure to solve the equations. To determine these variables for a given sample is complicated, but might give other results. If e.g. $\beta$ were set to 0.5, the result would be multiplied with its square root $=0.7$.

The results of all the calculations of standard deviation of fundamental error for field sampling are presented in Table 5 and the standard deviation of the fundamental error of sub-sampling are presented in Table 6. In Table 5 especially Table 6 some of the fundamental errors are larger than the analytical error.

Large particles and small sample size contribute to large variance of the fundamental error (see Eq. (1)). Low concentration of the contaminant gives high variation of the fundamental error. This is demonstrated in Fig. 1 where the mineralogical factor is plotted versus the level of contaminant. The variance of the fundamental error is directly proportional to the mineralogical factor. The lower the contaminant level is, the larger the mineralogical factor is, and the larger the variance of the fundamental error will be.

3.2.2. Grouping and segregation error

The Grouping and Segregation error is not explicitly demonstrated in any table, but is included in the total sampling error. Pitard [14] claims that the product $Z \times Y$ is approximately 1 in many cases, but it can be larger. During field sampling the soil was observed visually to be very segregated. It is reasonable to believe that this product is larger, but it is unknown. To make it possible to calculate any value for $\Delta(GSE)$ this product is set to be 1, but a sensitivity analysis is performed to assess the impact of this simplification, see Section 3.3.

3.2.3. Long range heterogeneity error

By modelling a variogram, it may be possible to get a measure of how a variable varies over the surface. In the case study, no spatial autocorrelation between the samples could be found, and all variance is random. All pair-comparisons among the data set were over lag intervals and longer than the range of a spatial dependence [17].

3.2.4. Periodic heterogeneity

This error is assumed to be small and is not to be taken into consideration.

3.2.5. Incremental delimitation error

If the soil samples taken at certain depth were said to represent a soil stratum of 10-cm thickness, the ideal sample geometry would be a cylinder through the 10 cm plane. The shape of the field sample delimitation is irregular and it is not possible to estimate if the bias is positive or negative. Neither will any value of this error be estimated for the sub-sampling.

Samples B and G are taken from upper 10 cm at the surface. The hole after the sampling had the approximately shape of a reversed soil heap. Compared to a cylinder the uppermost particles had more chances to be included than the lower particles in the “cylinder”. Activities at the site have produced metal particles, which can be expected to be more present closer to the surface. This will bias the sample positively.

The samples analysed with ICP-AES is sub-sampled by a riffle splitter by the laboratory. This procedure, if performed in a correct way with correct equipment that meets the requirements for a 1D lot, will not introduce an incremental delimitation error.

A risk with mixing is that the process can actually increase segregation and thus bias the sample [4,11]. Citing Back [5], “...Myers (1997) warns that homogenisation of heterogeneous material is often wishful thinking and may instead promote segregation, e.g. by the gravity force.”

Most likely the effect of this error is segregation in the sample-bag despite, or due to, kneading. This segregation would mean that the finer particles and the denser particles are underrepresented in the volume measured. If these were more highly contaminated, the sample would be biased negatively.

3.2.6. Incremental extraction error

It is not possible to estimate if the bias will be positive or negative due to incremental extraction error during field sampling.

A correct procedure for riffle splitting prior to ICP-AES analysis reduces or eliminates this error during sub-sampling.

For a physically obtained sample the particles are inside or outside the sample. To avoid this error the included particles should be inside the sample geometry that the sampling dimension requires. When measuring soil with XRF the particles get measured to various degrees, since the radiation intensity decreases with the depth of the bulk. Therefore, the XRF measured samples can never be said to avoid the incremental extraction error.

A trowel with rounded bottom was used for sample extraction from the walls of the trial pit. This tool gives no chance to correct increment extraction. The particles situated in the upper part of the sample to be extracted have smaller chances to remain in the sample than the particles situated in the lower parts due to the fall-off. A selection due to particle size might also occur.

3.2.7. Preparation errors

During the entire site investigation the following preparation errors showed to be of concern.

Some samples lost some of the finest particles due to dusting during sample handling. If the finer particles contain the highest pollutant level a negative bias would be the result for these samples.

Sample sticks to tools due to electrostatic forces, despite precautions. This is not considered a large error.

Some samples were dropped due to breaking sample bags. Double sample bags are recommended [18].

The system used for labelling the samples was not sufficient, causing some confusion. The sample ID consisted of too much information. To give each sample a unique code, as short as possible, might minimise this risk when reading and writing the
code several times during the sample preparation steps with a large number of samples. Samples were dried at temperatures over 100 °C, and this made measurements of volatile species of mercury, arsenic and lead useless. Drying at lower temperatures would be a solution.

### 3.3. Total sampling error

The results of the calculations of total sampling error are presented in Table 7. The calculation of the standard deviation for the total sampling error for sample A, lead measured by ICP-AES is shown as

\[ S_{FE1} = 11.0\% \], \[ S_{GSE1} = 11.0\% \], \[ S_{FE2} = 274\% \],

\[ S_{GSE2} = 274\% \], \[ S_{TE} (%) = \sqrt{S_{FE1}^2 + S_{GSE1}^2 + S_{FE2}^2 + S_{GSE2}^2} \],

\[ S_{TE} = \sqrt{11.0^2 + 11.0^2 + 274^2 + 274^2} = 387.8\% \],

\[ S_{TE} = 388\% \]

If the product \( Z \times Y \) would be set to 10, 100, 1000 and 10 000 for the primary sampling the total sampling error would increase on average 0.14, 1.5, 14 and 100%, respectively. If the product \( Z \times Y \) would be set to 10, 100, 1000 and 10 000 for the sub-sampling the total sampling error would increase on average 130, 610, 2100, and 7000%, respectively. If the sub-sampling technique should manage to totally eliminate the grouping and segregation error, this would decrease the total sampling error on average with 29%, for these specific samples.

### 3.4. Overall error

The results of the calculations of overall error are presented in Table 8. The calculation of total sampling error for sample A, lead measured by ICP-AES is shown as follows

\[ s_{OE} = \sqrt{S_{TE}^2 + S_{AE}^2} \], \[ s_{OE} = \sqrt{387.8^2 + 17.6^2} = 388.2 \],

\[ s_{OE} = 388\% \]

---

Table 6
Dimensionless standard deviation (%) of the fundamental error calculated for the sub-sampling

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XRF</td>
<td>ICP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>A</td>
<td>269</td>
<td>583</td>
<td>437</td>
<td>613</td>
<td>257</td>
<td>330</td>
</tr>
<tr>
<td>B</td>
<td>850</td>
<td>1,030</td>
<td>1,460</td>
<td>1,530</td>
<td>894</td>
<td>944</td>
</tr>
<tr>
<td>C</td>
<td>8.24</td>
<td>31.5</td>
<td>504</td>
<td>528</td>
<td>176</td>
<td>195</td>
</tr>
<tr>
<td>D</td>
<td>1,070</td>
<td>1,110</td>
<td>504</td>
<td>560</td>
<td>528</td>
<td>685</td>
</tr>
<tr>
<td>E</td>
<td>964</td>
<td>1,050</td>
<td>1,260</td>
<td>1,350</td>
<td>624</td>
<td>652</td>
</tr>
<tr>
<td>F</td>
<td>342</td>
<td>424</td>
<td>380</td>
<td>386</td>
<td>174</td>
<td>188</td>
</tr>
<tr>
<td>G</td>
<td>–</td>
<td>–</td>
<td>2,570</td>
<td>2,820</td>
<td>2,150</td>
<td>2,290</td>
</tr>
<tr>
<td>H</td>
<td>520</td>
<td>648</td>
<td>683</td>
<td>705</td>
<td>379</td>
<td>393</td>
</tr>
</tbody>
</table>

---

Fig. 1. The mineralogical factor, \( c \), as a function of the contaminant level in ppm.
Table 7
Total sampling error given as $S_{TE}$ (%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (XRF)</th>
<th>Pb (XRF)</th>
<th>Zn (XRF)</th>
<th>Cu (ICP)</th>
<th>Pb (ICP)</th>
<th>Zn (ICP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
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<tr>
<td>A</td>
<td>380</td>
<td>826</td>
<td>619</td>
<td>867</td>
<td>364</td>
<td>467</td>
</tr>
<tr>
<td>B</td>
<td>1,200</td>
<td>1,460</td>
<td>2,070</td>
<td>2,160</td>
<td>1,270</td>
<td>1,340</td>
</tr>
<tr>
<td>C</td>
<td>11.7</td>
<td>44.5</td>
<td>713</td>
<td>747</td>
<td>250</td>
<td>275</td>
</tr>
<tr>
<td>D</td>
<td>953</td>
<td>960</td>
<td>1,510</td>
<td>1,570</td>
<td>713</td>
<td>793</td>
</tr>
<tr>
<td>E</td>
<td>1,360</td>
<td>1,490</td>
<td>1,780</td>
<td>1,910</td>
<td>882</td>
<td>922</td>
</tr>
<tr>
<td>F</td>
<td>484</td>
<td>599</td>
<td>537</td>
<td>546</td>
<td>246</td>
<td>266</td>
</tr>
<tr>
<td>G</td>
<td>–</td>
<td>–</td>
<td>3,630</td>
<td>3,990</td>
<td>3,030</td>
<td>3,240</td>
</tr>
<tr>
<td>H</td>
<td>–</td>
<td>–</td>
<td>3,630</td>
<td>3,990</td>
<td>3,030</td>
<td>3,240</td>
</tr>
<tr>
<td>I</td>
<td>736</td>
<td>917</td>
<td>966</td>
<td>997</td>
<td>536</td>
<td>555</td>
</tr>
</tbody>
</table>

A low contaminant level gives a large contribution to the fundamental error. This affects the total sampling error as the sum of all sampling errors.

Copper in sample C is extremely high, giving a low uncertainty, and samples F and H having low contaminant levels have high uncertainties.

The fundamental error deals with heterogeneity due to composition and the grouping and segregation error deals with heterogeneity due to local distribution. Both these errors concern different aspects of the sample and are considered statistically independent.

3.5. Comparing total sampling error to analytical error

The total sampling error is compared to analytical error as a quotient, which is presented in Table 9. The calculation example of the quotient for sample A, lead measured by ICP is shown as follows:

$$\frac{S_{TE}}{S_{AE}} = 388 \div 11.3 = 34.3$$

The largest effect of the results in Table 9 is due to the concentration of the contaminant. The larger contaminant level, the lower the fundamental error and thus the larger proportion the analytical error will have. This effect is shown in Fig. 1, or can be seen by comparing Table 9 to Table 1.

The samples with a quotient of approximately 20 or less in Table 9 are from samples with high contaminant levels. The samples with high contaminant levels do not necessarily mean that the proportion will be 20 or less. Both the sample size (both primary and sub-sample for analysis) and the analytical error for the element and analysis method affect the results.

Using data from Back [6] the analytical error is 6% compared to the total sampling error. Mason [11] states that the analytical error is often less than 2% compared to the data variation. According to Crumbling [19] the analytical error is small or negligible compared to the overall data uncertainty.

Note that the samples evaluated were sieved through a 2 mm sieve prior to analysis, thus altering the sample. This might have biased the sample high (giving higher concentration level), since the smaller particle size fraction is considered to have a higher contaminant level. It has also affected the estimated variance of

Table 8
The overall error as $S_{OE}$ (%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (XRF)</th>
<th>Pb (XRF)</th>
<th>Zn (XRF)</th>
<th>Cu (ICP)</th>
<th>Pb (ICP)</th>
<th>Zn (ICP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>A</td>
<td>381</td>
<td>826</td>
<td>619</td>
<td>867</td>
<td>364</td>
<td>467</td>
</tr>
<tr>
<td>B</td>
<td>1,200</td>
<td>1,460</td>
<td>2,070</td>
<td>2,160</td>
<td>1,270</td>
<td>1,340</td>
</tr>
<tr>
<td>C</td>
<td>24.6</td>
<td>49.5</td>
<td>714</td>
<td>747</td>
<td>250</td>
<td>275</td>
</tr>
<tr>
<td>D</td>
<td>953</td>
<td>961</td>
<td>1,510</td>
<td>1,570</td>
<td>713</td>
<td>793</td>
</tr>
<tr>
<td>E</td>
<td>1,360</td>
<td>1,490</td>
<td>1,780</td>
<td>1,910</td>
<td>882</td>
<td>922</td>
</tr>
<tr>
<td>F</td>
<td>484</td>
<td>600</td>
<td>538</td>
<td>546</td>
<td>246</td>
<td>266</td>
</tr>
<tr>
<td>G</td>
<td>–</td>
<td>–</td>
<td>3,630</td>
<td>3,990</td>
<td>3,030</td>
<td>3,240</td>
</tr>
<tr>
<td>H</td>
<td>–</td>
<td>–</td>
<td>3,630</td>
<td>3,990</td>
<td>3,030</td>
<td>3,240</td>
</tr>
<tr>
<td>I</td>
<td>737</td>
<td>917</td>
<td>966</td>
<td>997</td>
<td>537</td>
<td>555</td>
</tr>
</tbody>
</table>
the fundamental error from the field sampling by smaller sample mass and smaller particle size.

The volumes of soil included in the sample measured by XRF are probably overestimated, and this would underestimate the fundamental error.

If the value of $\beta$ would have been set to 0.5, the conclusions would have been similar.

4. Conclusions

The level of contaminant highly affects the mineralogical factor in the low level range. Due to direct dependency the variance of the fundamental error is also strongly affected by high contaminant level increases.

Except for samples taken in the hotspots, the quotient between the total sampling error and the analytical error is larger than 20. In several examples the quotient was larger than 100. The grab-sample taken in the hotspot (sample C) has smaller fundamental error for copper, and therefore the analytical error gets relatively large. It is therefore interesting to note that there is a difference with a factor of approximately 3.4 between the largest and the lowest measurements of the sample. This could be an indication that some of the assumptions, about the variables, made in this study are not entirely correct.

It would be valuable to investigate how large an effect it would have, if the values now assumed or found tabulated would be determined.

The approach in this investigation has been to investigate error for error and then summarise them. There could be other approaches that might give more accurate results, and it would be interesting to apply these to this data and se what they reveal.

It is clear that the sampling errors deserve serious attention if one wants to reduce the uncertainties of soil characterisation.

Acknowledgements

Thanks to our co-operation partners, AB Bothniaconsult and Jernhusen AB. Thanks to colleagues at the Division of Waste Science & Technology for help during sample preparation. Thanks to Kim Esbensen for input on the grouping and segregation error. The financial support has been provided by the European Union Structural Funds and New Objective 1, North Sweden Soil Remediation Centre (MCN), contract no. 113-12534-00, and by Jernhusen AB.

References


Paper II
Effect of Sample Preparation Prior to X-Ray Florence Spectroscopy Analysis of Contaminated Soil

Björn Gustavsson, Christian Maurice, Anders Lagervist

Abstract

The metal content of contaminated soil can be analyzed by XRF (X-Ray Fluorescence Spectroscopy) in situ, in sample bags or in XRF sample cups. In situ analyses are the quickest to perform, but sample preparation can result in more reliable results. The step by step effect of several sample preparation operations was investigated according to response (mean value of repeated analyses of a sample) and variance (variance of repeated analyses of a sample). The investigated sample preparation operations included drying and sieving. Comparisons were made between analysis in situ and in sample bags, and between analysis on samples in bags and in XRF sample cups. Further, the variability (physical distribution of the metal of interest within a sample) in XRF sample cups was investigated.

Generally, the variance decreased with sample preparation (which is one of its purposes). To extract a finer fraction of the sample by sieving can give varying results, both regarding response and variance. The smallest variances were achieved with the samples placed in the XRF sample cups, and with fine particulate samples. There was noticeable variability even within these well prepared samples.

Keywords:
sample preparation, contaminated soil, sieving, bias, XRF

1 Introduction

In Sweden, the number of contaminated sites is estimated to be 83,000 [1]. During site investigation, and especially during a remediation project, many samples are needed to assess the contaminant levels. For metal determination, samples can be sent to a commercial laboratory for ICP-analysis (Inductively Coupled Plasma). A quicker and cheaper alternative for metal analysis is using a portable XRF (X-Ray Fluorescence Spectroscopy) in the field. Thus, XRF is commonly used in brown-field work in Sweden, especially during the remediation phase when quick answers are needed. The XRF analyses can be performed in three modes: directly on the soil (in situ), on sample bags filled with soil samples, or after placement in XRF sample cups following thorough sample preparation [2].

At courses on the use of XRF and sample preparation it is thought that drying and grinding the sample prior to placing samples into XRF samples cups will improve the reliability of the measurements. Despite this fact, the XRF operators often say they would prefer to use
minimal sample preparation prior to measuring, typically three measurements on a sample in a bag. The minimal sample preparation intends to save time and money. Sometimes several samples are chosen for confirmatory analysis on a laboratory with another method, like ICP [3]. A minimal or non-existent sample preparation might have a price in less reliability of the measurement.

Several studies have investigated the effects of: variance improvement by comparing in-situ to intrusive measurement [4], drying on response [5-8], sieving on response [5, 7, 8] and variance [8], particle size classes on response [9-11], combination of drying and grinding on variance [4], the correlation between XRF and laboratory methods [5, 6, 8, 12, 13], homogenization [4, 9, 14], measuring time [4, 6, 11] and detection limits [4, 6, 11, 15].

The scope and contribution of this investigation is to step by step evaluate the effect of some sample preparation operations. The evaluation pertains to both precision (standard deviation) and response (mean value) for the investigated samples.

The sample preparation operations addressed in this paper include: soil excavation and transfer to sample bags; drying; sieving; and placement in XRF sample cups. The variability within a single XRF sample cup was also investigated. The sample preparation of operations grinding, mixing and sub-sampling were not investigated.

2 Materials and methods

2.1 Samples

Four soil samples were taken from different contaminated sites in Northern Sweden. The elements copper and lead were used in the evaluation. The following sites were sampled:
A; A former wood impregnation plant.
B; A scrap yard.
C; A former wood impregnation plant.
D; An ore trans-shipment station.
For reference, a standard reference material from National Institute of Standard and Technology was used; NIST 2710, (sample N).

2.2 XRF (X-Ray Fluorescence Spectroscopy)

With XRF (X-Ray Fluorescence spectroscopy) rapid multi-element measurement readings of solid samples is possible. A radiation source (an isotope or a Roentgen tube) excites electrons in the solid sample. When the electrons relax they emit secondary radiation, specific for each element. The relative intensity is interpreted as concentrations.

The XRF used was a NITON 700, with a cadmium isotope as excitation source. For operator protection the isotope is encapsulated in the instrument, with a fixed angle of measurement. To perform analyses a radiation proof shutter must be opened. This shutter is operated by pushing a plunger situated beside the reading window on the underside of the instrument.
When measuring in situ and with samples in bags, a test guard is needed for support. The test guard gives mechanical protection against contamination and damage of the instrument [2].

The XRF sample cups used have a window of thin Mylar X-ray film (6 μm), towards which the sample is pressed. This window is positioned upwards during measurements, fixed in direct contact with the XRF. With this configuration the distance and material between the instrument and sample is minimized, ensuring a strong signal. A typical sample volume of a XRF sample cup is 4 - 7 cm³. Each sample configuration was analyzed 12 times, although some of the readings failed. The nominal observation time was two minutes each.

2.3 Sample preparation operations

The samples were prepared with several sample preparation operations described below:

In situ  
The soil was loosened and scraped into a pile that was flattened. The analyses were performed directly on the soil heap with the XRF [2, 4]. Only sample B were analyzed in situ.

Untreated  
With samples in bags, the instrument is put directly on to the bag [2]. The test-guard was used and each measurement was performed on different locations.

Drying  
Drying 115°C over night for sample A, C and D, 105°C during two hours for sample D [2, 4] (analysis performed on bags).

Sieving <2mm  
The samples were sieved through a 2.00 mm sieve (analysis performed on bags).

Sieving <0.25 mm  
The samples were sieved through a 0.25 mm sieve (analyses performed on bags).

XRF sample cup  
A sub-sample from each <0.25 mm sample was put into XRF sample cups for analyze [2, 4]. Sub samplings were performed by grab sampling.

XRF sample cup; rotated  
The bulk testing platform that follows the NITON 700 has a receptacle for the XRF sample cup. Once the cup is placed in the receptacle it can only be rotated around its own vertical axis. Between each measurement the XRF sample cup was rotated 30° clockwise.

2.4 Statistics

For statistical evaluation Statgrapichs 5.1 from Statistical Graphics Corporation was used. Student’s t-test and F-test were used to investigate significant differences in means and standard deviations respectively. The tests were evaluated at 95% confidence level.
3 Results and discussion

The results are presented in table 1. The responses (the means) and the variances (displayed as relative standard deviations) are presented with the results from the t-tests and the F-tests at 95% significance level. A bold value indicates a significant change compared to the value over it; or in other words, indicates that the sample preparation operation has induced a statistically significant change compared to the previous step.

Table 1. Results of the measurements after various sample preparation steps. n = number of successful measurements, Conc = arithmetic average in ppm, RSD = Relative standard deviation in percent. Significant differences between averages (t-test) and standard deviations (F-test) are marked by using bold figures. The tests are performed with 95% confidence level. The t-tests and the F-tests are done between the same row and the row above with one exception; # = comparisons between “sample cup” and “remixed sample cup”.

<table>
<thead>
<tr>
<th>Sample A</th>
<th>Cu</th>
<th>n</th>
<th>Conc (ppm)</th>
<th>RSD (%)</th>
<th>Pb</th>
<th>n</th>
<th>Conc (ppm)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>12</td>
<td>4210</td>
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<td>5</td>
<td>17.5</td>
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</tr>
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<td>5560</td>
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<td>18.5</td>
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<td></td>
</tr>
<tr>
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<td>5540</td>
<td>9</td>
<td>6</td>
<td>19.3</td>
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<td></td>
<td></td>
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<td>8</td>
<td>17</td>
<td>8</td>
<td></td>
<td></td>
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<tr>
<td>Sample B</td>
<td>Cu</td>
<td>n</td>
<td>Conc (ppm)</td>
<td>RSD (%)</td>
<td>Pb</td>
<td>n</td>
<td>Conc (ppm)</td>
<td>RSD (%)</td>
</tr>
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<td>12</td>
<td>2890</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>sample cup</td>
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<td>2910</td>
<td>6</td>
<td>12</td>
<td>3510</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample C</td>
<td>Cu</td>
<td>n</td>
<td>Conc (ppm)</td>
<td>RSD (%)</td>
<td>Pb</td>
<td>n</td>
<td>Conc (ppm)</td>
<td>RSD (%)</td>
</tr>
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<td></td>
</tr>
<tr>
<td>Sample D</td>
<td>Cu</td>
<td>n</td>
<td>Conc (ppm)</td>
<td>RSD (%)</td>
<td>Pb</td>
<td>n</td>
<td>Conc (ppm)</td>
<td>RSD (%)</td>
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<td>1990</td>
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<td></td>
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<td>306</td>
<td>9</td>
<td>12</td>
<td>2590</td>
<td>2</td>
<td></td>
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<tr>
<td>sample cup</td>
<td>12</td>
<td>234</td>
<td>6</td>
<td>12</td>
<td>2350</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample N</td>
<td>Cu</td>
<td>n</td>
<td>Conc (ppm)</td>
<td>RSD (%)</td>
<td>Pb</td>
<td>n</td>
<td>Conc (ppm)</td>
<td>RSD (%)</td>
</tr>
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<td>12</td>
<td>5500</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The data presented below are derived from table 1 to illustrate the changes in response and variance. The data presented within brackets are the percent changes compared to the previous step. For example; copper in sample A for untreated and dried sample averages 4210 and 5560 ppm respectively. This gives $\frac{5560}{4210} = 1.32$ and that is presented as (+32%).

In table 2 the dry content of the samples are presented together with the weight proportions passing the sieves.

### Table 2. Presentation of dry content (in percent) and weight fractions (in percent) of the sample passing a 2.00 and a 0.25 mm sieve.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dry content %</th>
<th>Weight proportion to pass 2.00 mm sieve (%)</th>
<th>Weight proportion passing the 0.25 mm sieve (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>92.3</td>
<td>100</td>
<td>92</td>
</tr>
<tr>
<td>B</td>
<td>99.5</td>
<td>70</td>
<td>32</td>
</tr>
<tr>
<td>C</td>
<td>94.1</td>
<td>94</td>
<td>50</td>
</tr>
<tr>
<td>D</td>
<td>98.8</td>
<td>86</td>
<td>54</td>
</tr>
</tbody>
</table>

3.1 **Comparison of in situ and in bag analyses**

Bagging the samples was expected to lower the response about 5-10% according to the manufacturer of the XRF [2]. In our case no significant difference in average response could be observed between the bagged sample and the *in situ* soil.

However, the variance was significantly reduced by bagging *i.e.* 52% and 59% for copper and lead respectively.

This indicate that the sampling and sample handling lead to a homogenization.

*In-situ* measurements are reported to have lower precision than measurements in sample cups. The reported data are averaged standard deviations from several samples, with five and ten replicates *in-situ* and intrusive respectively [4]. However, insufficient details were given about the statistics calculation.

3.2 **Drying**

The response might change after drying if the sample contains much water. Water in the sample can shield the Roentgen radiation. The size of this effect depends on several factors such as the matrix properties, the radiation source, and the elements observed.

The drying itself is not expected to affect the variance.

A shielding effect of water was observed on response in two cases, for copper in sample A (+32%) and for lead in sample D (+10%). Both samples showed significantly increased response after drying. For the other two samples only smaller differences were observed.

The variance of copper observations on sample A increased (+71%) while for sample B the variance decreased for both copper (-53%) and lead (-59%). During the drying operation the samples were poured on plates for drying, and after drying they were put back sample bags. This may give a homogenization effect as indicated by copper in sample A, but it can also
Induce segregation due to varying particle sizes and densities as indicated by lead in sample B [16, 17].

The effects of moisture content are different depending on the element of interest and the sample composition [11]. Dry samples have been reported to generally have higher response than undried/wet samples. Dried samples were compared to the natural level of moisture [5, 7] and to different moisture content [6, 8].

In conclusion we observe that the drying can increase the responses, but not in all cases.

### 3.3 Sieving

The fraction finer than 2 mm is per definition the soil material [2, 9, 14, 18-23]. To measure on a material finer than 0.25 mm is recommended by the instrument supplier (even more recommended is finer than 0.125 mm) [2]. According to Hartyáni, et al. [24] the finer soil particles contain more contaminant due to a higher specific surface, where contaminants could be adsorbed. A change to higher responses could therefore be expected after eliminating the coarser fractions by sieving. A finer particle size distribution reduces the variance by reducing both matrix effects and sample heterogeneity [2, 4, 9, 14, 25, 26] (analyses on bags).

When handling samples with various particle sizes, several mechanisms tend to favor segregation by particle size, e.g. percolation and floating which both eventually put the largest particles on top of the bulk [16, 17]. The bulk of a porous medium consisting of mainly large particles contain large pores. A significant portion of the XRF radiation has to pass a longer distance before hitting the solid surface, which decreases the response. This effect may also give a larger variation between measurements on different positions on the sample, especially when measuring in situ or in sample bags.

Significantly increased responses were observed; lead in sample B when passing the 2.00 mm sieve (+8%), for both copper and lead in sample B when passing the 0.25 mm sieve (+15% and +21% respectively) and for lead in sample D when passing a 0.25 mm sieve (+18%). This confirms the hypothesis that finer fractions contain higher levels of these metals. It can also be due to less particle size segregation when the sample only contains finer particle size fractions; with coarser particles on top the result would be a lower response.

In general lead responses are reported to increase after passing a 2.00 mm and a 0.25 mm sieve [5].

Significant changes of the variance were observed only in sample D. The variance increased for both copper and lead when passing the 2.00 mm sieve (+106% and +134% respectively) but on the other hand it decreased for after passing the 0.25 mm sieve (-68% and -86% respectively). The change of the variance in sample D when passing the both sieves could be due to either of two processes, or a combination thereof:

A lead ore product was transshipped at site D. All particles were finer than 0.250 mm, and most finer than 0.125 mm [27].
A hypothesis is that the lead product occurs agglomerated in the soil. Before the 2.00 mm sieving the relatively heavy lead agglomerates easily settles between the coarser particles. That results in a low response, since the radiation only reaches the upper few millimeters of the sample. After 2.00 mm sieving the agglomerates are intact, but have less tendency to segregate in the below 2 mm fraction which is reflected by the higher response. The agglomerates cause an uneven distribution of lead in the bulk soil, yielding a high variance. During the 0.25 mm sieving, these agglomerates are broken up, resulting in a lower variance. The higher lead response is due to a concentration effect. Copper has a similar behavior, indication that both copper and lead is present in the agglomerates.

Sample B and D are likely to contain metal fragments due to the previous industrial activities at the sites. Sample A and C are on the other hand more likely to contain adsorbed and/or precipitated salts from the wood impregnation liquids. In the metal fragment cases the fragments might be of another particle size distribution than the soil itself, and therefore sample B and D are more affected by the sieving than sample A and C. Sieving the samples without grinding the coarser fraction can alter the responses, and thus risks to bias the samples. Based on these results, the common practice of sieving soil through a 2 mm sieve before further sample preparation and analyses may be questioned (see section 2.3.4.).

During investigations with XRF others found that sieving through a 2.00 mm sieve increased the response [5, 7] or gave no particular change to response or precision [8]. To pass a 0.25 mm sieve increased response [5], [8] and precision [8]. Dividing the samples into different particle size classes showed increased response for finer particles in many of the investigated samples, but not without exceptions [6]. A critique to the latter investigation is that no compensation for air pockets in the coarser fractions was made. The air pockets induce shielding and scattering which decreases response as a result. Analyzing different particle size fractions can show a varied distribution of both elements and minerals within the same sample [10, 24] or sometimes larger response with higher particle size fraction [14].

To see to what extent the finer particles are to be expected to be most contaminated it could be interesting to investigate how the particle size classes correlates with the level of contamination. The sub-sampling procedure is critical to avoid bias in the sampling procedure.

With that knowledge it would be possible to better know what traps a contaminated soil sample preparation can offer, and how to avoid them. Or, with a more provocative point of view, how can a sample be manipulated into a desired bias? Perhaps within the limits of an accepted standard?

### 3.4 Analyzing on samples in bag versus XRF sample cup

Analyzing through sample bags is expected to give 5-10% lower response than analyzing in XRF sample cup [2]. The changed configuration can be expected to increase the response due to decreased distance and less material for the radiation to pass [4]. The Mylar X-Ray plastic film is 6 μm thick compared to approximately 0.1 mm in the plastic bag; several orders of magnitudes.

When comparing analyses in sample bags with analyses in XRF sample cups both increased and decreased responses were observed. Increased responses were observed for copper and lead in sample B (+47% and +36% respectively). Decreased responses were observed for both copper and lead in sample A (-17% and -64% respectively) and for both copper and lead in
sample D (-24% and -9% respectively). The change in response are likely due to unrepresentative sub sampling which can severely bias the samples [25, 26, 28-30].

The variance was significantly decreased in for both copper and lead in sample A (-74% and -64% respectively) and for both copper and lead in sample D (-37% and -9% respectively). Compared to samples in a bag the sample in a XRF sample cup has a smaller volume and less possibility for relocation within the sample volume since the bulk of the XRF sample cup is relatively fixed. With the samples in bags each measurement were done on a different location of the bag, and the probability for a specific particle (or group of particles) to be repeatedly measured are lower than for the case of using XRF sample cups.

To put sub samples into XRF sample cups gave significant changes in responses, both increasing and decreasing. This is most likely due to unrepresentative sub sampling.

A decreased variation might be a consequence of decreasing the sample volume, and minimizing the possibilities to rearrange the sample.

3.5 Variability in each XRF sample cup

The response is decreased in a statistically significant way for copper in sample B (-3%), when the XRF sample cup is rotated 30º clockwise in the plane between each analyze instead of being fixed between the measurements. This indicates that copper has an uneven physical distribution in the volume of the rotated XRF sample cup.

No significant effect was observed for the sample N, neither on response nor variance.

Compared with the fixed XRF sample cup, the remixing of a sample in the XRF sample cup between analyses shows a statistically increased variance, indicating that the physical distribution of lead and copper in the XRF sample cup can be segregated. This is observed for both copper and lead in sample B (+185% and +40% respectively).

How the XRF is positioned relative to the XRF sample cup during analyze seem to be of importance for a soil volume of < 9 cm$^3$, for particles smaller than 0.25 mm. Most likely, the XRF-position on a larger sample in a bag with larger particles will have an even larger effect. Variability can be expected at any scale. Even in a few cubic centimeters with a fine particle size distribution. This implies that care must be taken during the entire sample handling and preparation since if this is critical in this case, it is critical also in all preceding steps. It also implies that the preparation of the XRF sample cups can be of importance for the results.

Even after a thorough preparation of a sample, the very last step risks to bias the sample or induce uncertainties. One possible explanation of these changes could be settlement of finer particles giving a bias to the observations [11]. Particle segregation has been observed among in particles as fine as 10 μm [31]. It would therefore be relevant to develop methods to minimize the risk of particulate segregation when filling XRF sample cups.
Effect of Sample Preparation Prior to X-Ray Florescence Spectroscopy  
Analysis of Contaminated Soil

4 Conclusions

All sample handling steps studied are found to have an impact on either the response or the variance of the measurements, or both, for some of the studied samples. The handling may increase or decrease both response and variance. In several cases a suspected reason is segregation of particles in the samples. The observations for the different sample preparation operations are:

- The variance is lowered, in comparison to in situ measurement, by bagging the sample.
- Drying increased the response, and gave contradicting results on the variance; both increasing and decreasing.
- After sieving the finer fraction had higher response than the entire sample had before sieving. The variance can both increase and decrease for a sample after passing through sieves.
- Incorrect sub-sampling induced a bias for the samples in XRF sample cups compared to the samples in sample bags. A correct sub-sampling is important.

All evaluated sample preparation steps had effect on response and variance for at least some sample. However, sample C was not affected in a statistically significant way by any of the evaluated sample preparation steps. Thus, it is not predictable how the sample preparation will affect the response and so it is important that all samples are treated in the same way.

5 Acknowledgements

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Effect of Sample Preparation Prior to X-Ray Florescence Spectroscopy Analysis of Contaminated Soil


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Effect of Sample Preparation Prior to X-Ray Floreescence Spectroscopy Analysis of Contaminated Soil


Paper III
EVALUATION OF PARTICULATE IRON AND SOIL MIXES

Björn Gustavsson, Sofia Lidelöw, Christian Maurice, Anders Lagerkvist

ABSTRACT

A large number of soil pollution cases exists in Sweden. Both from the perspective of resource conservation and environmental protection an in situ treatment through the addition of stabilizing agents may be an attractive method. However, the success of success soil amendment depends to a large extent on the extent to which the additive can be well distributed in the soil. Thus the evaluation of mixing procedures becomes important for ensuring a good treatment effect without over-spending on mixing operations. A series of evaluations have been done on the addition and mixing of elemental iron in soils polluted with Copper, Chrome and Arsenic (CCA). Large differences have been observed between different mixing methods, additions and solids. It is concluded that for larger soil remediation projects an optimisation of the mixing method is called for. Several methods to perform such evaluations are discussed.

KEYWORDS
Mixing, soil, iron, sample size, mixing time, evaluation

1. INTRODUCTION

In Sweden, there is an estimated 83,000 contaminated sites (Österlund, 2007), many of which include contamination with trace elements. In view of the large number of sites needing treatment, conventional remediation practices such as excavation and landfill disposal are too costly.

The use of chromated copper arsenate (CCA) preservatives has caused widespread soil contamination at wood impregnation sites. During the remediation of Tvaråns såg, Sweden, 13,017 ton soil were excavated containing 4.1 ton arsenic (Sandström, et al., 2004).

At sites that are not severely contaminated, the application of a treatment that chemically stabilises trace elements in the soil could be a viable option (Kumpiene, 2005; Mench, et al., 2000). After treatment the soil could be left in-situ, disposed of more safely at a landfill, or reused e.g. as filling material.

By mixing the contaminated soil with an additive (ameliorant) that can adsorb, co-precipitate, or complex the targeted elements the mobility and bioavailability of the soil contaminants can be significantly reduced. Because iron oxides can effectively sorb both cations and anions in soil, iron-rich ameliorants have been suggested for the remediation of combined metal-As contaminated soil (Hartley, et al., 2004; Kumpiene, et al., 2006; Mench, et al., 2003; Warren,
et al., 2003). For example, laboratory tests have shown the addition of 1% iron grit to reduce the leaching of As by 60-70% from As-contaminated canal dredgings (Hartley, et al., 2004) and to decrease the leaching of As and Zn by 99%, Cu by 93%, and Cr by 57% from a chromated copper arsenate (CCA)-contaminated soil (Kumpiene, et al., 2006).

A good mixing of the soil and ameliorant is essential for the method to succeed and the evaluation of it is important from an economic as well as environmental risk assessment perspective. For large scale applications, optimising the mixing is crucial to minimise costs since solid-solid mixing of large volumes is both energy- and time-consuming. For example, a 75 kW electrical engine in a vertical mixing wagon only manages 4 - 5 tonnes of a soil-iron mixture in one batch. Each mixture follows its own function of mix quality versus mixing effort. This function needs to be determined for each situation and is dependent on e.g. the properties of the materials to be mixed and the amount of material supplied to the mixer in one batch. After a certain mixing effort no improvement will be achieved by further mixing.

In situ applications of soil ameliorants are usually undertaken using traditional agricultural equipment such as ploughs and harrows. However, if treatments are applied ex-situ, prior to reusing the soil or placing it in a landfill, other types of equipment can be used that are able to improve the soil and/ or "refine" it, e.g. by dividing it into fractions of different quality classes that can be used for different purposes.

In this study, two large-scale mixing experiments were performed:

- In the first experiment, a two-step mixing procedure was applied using first a screener crushed (SC) attached to a front loader, then a rotating single skin trommel (RT). The mixing quality achieved after each mixing step was investigated.
- In the second experiment, a vertical mixing wagon (MW) was applied. The mixing quality and the dependency of mixing quality on the mixing time were evaluated.

The mixture quality can be evaluated using several different indices or statistical measures. Hence, it is also investigated whether different means of evaluating the mix quality achieved in the experiments give consistent results.

1.1. Research questions

Different ways to evaluate the quality of iron and soil mixes are discussed on the basis of experiments using different mixing methods, additives and soils.
2. MATERIAL AND METHODS

The experimental procedures are showed in figure 1 and explained in detail below.

Two different granule iron products were used:
- Oxygen scarfing granulate (OSG), a by-product from steel manufacturing (Lidelöw, et al., 2007; Maurice, et al., 2007)
- Steel abrasive (SA) used for blasting (Lidelöw, et al., 2007; Maurice, et al., 2007)

Two different soil materials were used:
- CCA contaminated soil from Forsmo, Sweden (CCA) (Lidelöw, et al., 2007; Maurice, et al., 2007)
- Excavation residues (ER) with similar, sandy properties as many wood impregnation sites.

Three types of mixes were prepared:
- About 10 tonnes of CCA soil with planned 1% SA addition
- About 10 tonnes of CCA soil with planned 15% OSG addition
- Four batches of 4 - 5 ton of ER soil with planned 5% OSG addition.

Three different mixing procedures were used:
- Elongated piles of CCA soil were prepared. The iron material was spread on top of the heaps. A front loader attached screen crusher (SC) were used for mixing the materials. The materials were passed through the screen several passages, (figure 2).
- As a second mixing step after the SC the mix was run one passage through a single skin rotating trommel (RT), (figure 3a).
With a front loader ER soil were filled in a vertical mixing wagon (MW), followed of the OSG product on top (figure 3 b). Mixing times tested were 3, 5 and 10 minutes.

Figure 2. Mixing with front loader attached screener crusher (SC). a) elongated heap of soil with added iron product on top picked up by SC and b) mixed by passing the rotating screens. photos: Jan-Olov Andersson

Sampling of the soil mixtures (CCA and ER) was performed by flattening heaps of soil on an asphalted surface (figure 4). The heap was divided into ten strata and within each stratum sample locations were randomly selected. Further sampling, sample preparation and analyses were performed in slightly different ways for the two soil materials since the mixing experiments were conducted at different times and locations.

Figure 3. a) A view of the single skin rotating trommel (RT), photo Sofia Lidelöw b) The two vertical mixing screws in the vertical mixing wagon (MW), photo Jan-Olov Andersson.

For the CCA-soil, sample volumes of 1, 10 and 100 dl were taken. Each sample consisted of a single cylinder cut through the entire thickness of the heap. The samples were dried, sieved through a 2 mm sieve, sub sampled using first a riffle splitter, then a rotating paper cone riffle splitter. The final sub-samples were milled to pass a 0.125 mm sieve, then put in a XRF (X-ray fluorescence spectroscopy) sample cup and measured with a NITON XRF 700 for iron content. The fraction larger than 2 mm was analysed using magnetic separation. A weighted sum of iron content was calculated for both particle size fractions. No correction was made for background iron content.

For ER, sample volumes of about 50 dl were taken. A plastic cylinder was pressed through the depth of the material. Typically 5-7 cores were taken close to each other within one
EVALUATION OF PARTICULATE IRON AND SOIL MIXES

stratum and were combined until a 50 dl bucket was filled. Samples were dried, agglomerates were crushed, sieved through a 6 mm sieve and sub-sampled using a riffle splitter until sub-samples of about 100 g were obtained. The iron particles were separated with an electromagnet and weighted for iron proportion calculation.

Figure 4. a) Flattening of soil heap prior to sampling, photo Jan-Olov Andersson b) Principal sketch over stratified randomised soil sampling with two sample sizes on a flatted heap.

Different statistical methods were used to evaluate the mixing quality:

- \( s; \) Standard deviation (Weinekötter and Gericke, 2000)
- \( \text{RSD}; \) Relative standard deviation (Paul, et al., 2004)
- \( s^2; \) Variance (Weinekötter and Gericke, 2000)
- \( I_L; \) the Lacy index (Coulson, et al., 1991; Harnby, et al., 1985)
- \( I_S; \) the intensity of segregation index (Paul, et al., 2004).
- \( I_{PTW}; \) the Pole-Taylor-Wall index (Harnby, et al., 1985).
- \( s^2_0; \) theoretical variance of worst mix quality (Coulson, et al., 1991; Paul, et al., 2004; Weinekötter and Gericke, 2000).

Table 1. Overview of the sampling series

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Fe (%) (target)</th>
<th>Fe type</th>
<th>Soil</th>
<th>Mixing method</th>
<th>Sample volume (dl)</th>
<th>Time in MW (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5</td>
<td>OSG</td>
<td>ER</td>
<td>SC</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>OSG</td>
<td>ER</td>
<td>MW</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>OSG</td>
<td>ER</td>
<td>MW</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>D</td>
<td>5</td>
<td>OSG</td>
<td>ER</td>
<td>MW</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>SA</td>
<td>CCA</td>
<td>SC</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>G</td>
<td>1</td>
<td>SA</td>
<td>CCA</td>
<td>SC</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>1</td>
<td>SA</td>
<td>CCA</td>
<td>SC</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>J</td>
<td>1</td>
<td>SA</td>
<td>CCA</td>
<td>RT</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>1</td>
<td>SA</td>
<td>CCA</td>
<td>RT</td>
<td>100</td>
<td>-</td>
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<tr>
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<td>15</td>
<td>OSG</td>
<td>CCA</td>
<td>SC</td>
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<td>OSG</td>
<td>CCA</td>
<td>RT</td>
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<td>-</td>
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<tr>
<td>O</td>
<td>15</td>
<td>OSG</td>
<td>CCA</td>
<td>RT</td>
<td>10</td>
<td>-</td>
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RESULTS

The resulting measures of mixing quality achieved in the different experiments are presented in table 2 and figure 5.

Table 2. Resulting quality index values.

<table>
<thead>
<tr>
<th></th>
<th>$S^2$</th>
<th>S</th>
<th>RSD</th>
<th>$S^2_{S}$</th>
<th>$S^2_{R}$</th>
<th>Lacy index</th>
<th>Intensity of segregation</th>
<th>Pole-Taylor-Wall index</th>
<th>Average iron content (%)</th>
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<td>1.0·10^{-3}</td>
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<td>2.9·10^{-5}</td>
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<td>10</td>
<td></td>
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<tr>
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<td>8.5·10^{-2}</td>
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<td>1.4·10^{-3}</td>
<td>3.1</td>
<td>9.4</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5. Mixing quality data plotted versus mixtures. The value for Intensity of segregation for treatment N can not be seen in the diagram (negative value).
Typically the individual measures varies over about one order of magnitude for all observations. One exception is the Lacy index ($I_L$) which only shows a small variation close to 1. Another exception is the best case mixture ($s^2_{\text{R}}$) that shows a larger variation for two data series and also differing trends than other indices. The entire dataset ranges over ten orders of magnitude. Mixture quality data from different mixtures should not be compared to each other, neither should data for different sample sizes.

3. DISCUSSION

3.1. Consistency between mixing quality measures

When regarding all the different mixture quality measures (figure 5) there are apparent inconsistencies. One reason for this is that different data are considered when calculating the indices. The basic statistical functions such as average, variance ($s^2$), standard deviation ($s$) and relative standard deviation (RSD) only considers concentration data, while the designated mixing indices also considers material properties such as the sample mass, particles size distributions and densities of the materials. So, if these factors are held constant the mixture quality measures are consistent, see mixtures A-B-C-D (figure 5). The Lacy index deviates from the general pattern. It only varies less than one per mille. It has earlier been criticized for being too insensitive (Harnby, et al., 1985). The index calculation includes subtraction between numbers differing in orders of magnitude, and resulting in minute variations.

The mixing indices $I_S$ and $I_{\text{ITW}}$ require more effort to calculate than the ordinary statistics of $s^2$, $s$ and RSD. But on the other hand they may give information on how much the mixing quality can be further improved. This is due to their inclusion of a comparison between the achieved and a best case mix quality. This is useful when selecting mixing procedures and optimising operations. However, the ideal mixing quality may be not be achievable in practice.

3.2. Mixing quality dependency on mixing methods

The combination of a rotating trommel (RT) and a screener crusher (SC) yields a clearly better mixing result than that of SC alone. As presented in table 3, the observed variances were 6 and 13 times lower for the combined treatment as compared to the SC alone.

Table 3. Comparison of mixing results, expressed as variance, between different mixers. The mixers are: 1) screener crusher (SC); 2) a combination of SC and single skin rotation trommel (RT); and 3) a vertical mixing wagon (MW).

<table>
<thead>
<tr>
<th></th>
<th>SC sample $s^2$</th>
<th>RT sample $s^2$</th>
<th>MW sample $s^2$</th>
<th>Quotient</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>$1.4 \times 10^{-5}$</td>
<td>$2.3 \times 10^{-6}$</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>H</td>
<td>$4.1 \times 10^{-5}$</td>
<td>$3.1 \times 10^{-6}$</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>A</td>
<td>$2.6 \times 10^{-4}$</td>
<td></td>
<td>B $2.9 \times 10^{-5}$</td>
<td>11</td>
</tr>
</tbody>
</table>

The improvement from using RT after SC was also visible in the field; after the SC mixing there were still visible iron aggregates within the material which were later broken up and smeared out in the RT. But SC can still be a useful pre mixing method to quickly distribute the iron particles in the soil as groups or aggregates. A large scale convection mixing occurs. The second step mixing might then be performed quicker.
Using the mixing wagon (MW) gave a better mixing result than using the screener crusher at all treatment times. In this comparison the variance improved with a factor of 11. The Rotating trommel and the Mixing wagon can not be compared directly since different mixtures were used. The screener crusher is clearly the poorest performing of the three tested mixing methods.

3.3. Mixing quality dependency on treatment time

A descending, nonlinear trend is found when evaluating the mixing quality versus mixing time. Figure 6 illustrates the improvement of achieved mix quality ($s^2$) approaching the ideal mixing quality ($s^2_R$). In practice this state might never be reached, a steady state between mixing and segregation mechanisms might occur with lower mixing quality. From the available data it is not possible to predict if a longer mixing time than the applied would have improved the mixing quality. However a mixing time exceeding 10 minutes would be unpractical. The uncertainty of the trends are due to the fact that the average iron content for the 10 minutes mixing time was higher (8.9%) than for the 3 and 5 minutes mixing times (7.4%). However the variance is clearly decreasing with increased treatment time over the investigated range.

![Figure 6](image)

Figure 6. Development of mixing quality with mixing time.

3.4. The achievement of a good enough mixing quality

Given that the required mixing quality is known, the corresponding mixing time in a batch mixer can be experimentally determined (fig 6).

When deciding the number of samples that must be taken to evaluate the mix quality, cost and precision need to be balanced. The variance of the measurements can be used as a
measure of mix quality, but it is in itself uncertain. To calculate the confidence interval of the variance, it is multiplied with a factor (table 4). The factor is determined by the degrees of freedom (number of samples -1) divided by the $\chi^2$ value for the actual degrees of freedom and confidence level. The calculations assumes normal distributions (Weinekötter and Gericke, 1995, 2000). Initially the confidence interval decreases much by increasing the number of samples, but more than 30 samples gives only minor decreases and that may be the point where statistic quality and cost balances. The 95% confidence interval for the variance is still 60% larger than the estimated variance at that point.

Table 4. Number of samples and corresponding factor to determine 95% confidence interval of the variance.

<table>
<thead>
<tr>
<th>number of samples</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>factor</td>
<td>5.6</td>
<td>2.7</td>
<td>1.9</td>
<td>1.6</td>
<td>1.5</td>
<td>1.4</td>
<td>1.3</td>
</tr>
</tbody>
</table>

In order to make a meaningful statement of the mix quality the sample mass need to be included in the assessment.

As example, for batch G, with sample masses on average 1481 g, the estimated variance of iron content is $1.4 \cdot 10^{-5}$. With 95 % probability the variance is lower than $2.7 \cdot s^2 = 2.7 \cdot 1.4 \cdot 10^{-5} = 3.78 \cdot 10^{-5}$.

When sampling a poor mixture, the results will probably not follow a normal distribution. A material with a clustered component, which is large in comparison to sample volumes, will most likely yield skewed results. If skew enough, it may best be described by a Poisson distribution (Pitard, 1993).

The mix quality measure is affected by sample sizes. To small samples in a clustered lot can give a false interpretation of a low level and low degree heterogeneity of a compound, while a larger sample show a larger heterogeneity (Pitard, 1993). Thus, it is possible to get different results depending on the sample size. Further, too small samples can give the false impression of good mixing quality, but too low concentration of the critical component, if the clusters are missed in the samples.

Pitard (1993) concludes that it is the diameter of the largest cluster that will decide the sample size, not the largest individual particles. In our experimental data, this is of special relevance after SC mixing where clusters were found. In the context of mixing, it is better to put the effort on improving the mixture quality. The SC mixture is only an intermediate product. But if the final product is found to be clustered it might not be suitable for its purpose.

Usually it can be expected that larger sample sizes results in lower variances. This is reflected in the calculation of $s^2_R$ by a inverse proportionality to the sample mass. The latter is easily seen in figure 5 for $s^2_R$ for F-G-H and J-K which are series from the same batch, differing in sample volume. The resulting $s^2_R$ differ about one order of magnitude from series to series. Indirectly this affects several of the mixing quality indexes that relate to $s^2_R$. 


For the estimated variance $s^2$ the trend is not like the ideal. A decrease is seen between F-G, but is increasing in the following G-H. For J-K the trend is also increasing with increasing sample size. This can have one or more of following explanations:

The larger samples are to higher degree capturing clusters of iron particles. This hypothesis is strengthened by the fact the average iron content is somewhat larger for higher sample sizes. After the SC treatment clusters were observed, but after the RT they were not. For F and G the distribution is skewed, with a pair of high values each, also strengthening the cluster hypothesis.

"Only" ten samples show to not give to god estimates of the "true" variance; the 95% confidence interval is 2.7 times bigger than the variances themselves. This must leave room for some randomness to occur.

All variances combine. The sampling, sample preparation and analysis contributes with uncertainties (variances) that combines with the variance stemming from the actual mix quality. If unlucky, their contributions are big, but are evaluated as mix quality.

One method to investigate the importance of sample size is to use the two tiered variance comparison, meaning that the variance of two series with different sample masses/volumes are compared. Depending on the relative sizes of the variances conclusions can be drawn about the sample sizes tested and the material, appendix 2, (Gerlach and Nocerino, 2003; Mason, 1992; Pitard, 1993). The two tiered variance comparison gives no decision criteria in itself but has an illustrative function, see figure 7.

**Figure 7.** Variances of series with differing sample volumes plotted against relative difference in variance, related to the smaller series variance ($\frac{(s^2_L - s^2_S)}{s^2_S} \times 100\%$).

The different Fe additions were 1% and 15% respectively. SC denotes mixing with screens cruiser, RT; mixing with screens cruiser and single skin rotating trommel. The sample volumes (in dl) compared were 1/10, 1/100, 10/100.
If a relative difference of +/-20% for the variance is set as acceptable, the only pair that passes the criteria in this dataset is the one with the highest variance in the entire dataset, where both variances are similarly high. The pairs can be classified in four cases (for explanations see appendix 2):

Case #1 : N-O (15% Fe, RT1/10)
Case #3 : F-G (1% Fe, SC 1/10)
Case #4 : G-H (1% Fe, RT10/100), F-H (1% Fe, SC1/100), J-K (1% Fe, RT10/100)

One can note that the same sampled lot can yield different indications, depending on which sample sizes are compared. For the comparisons of 1% Fe additions with SC-treatment, both the 10/100 and 1/100 ratios are classified as case #4 (try larger samples; effects of grouping and segregation is important at the tested scale) while the 1/10 comparison behaves like case #3 (find optimum sample size; large sample finds clustered contaminants, small samples measures back ground levels).

The variation reflects the properties of the material sampled. After the mixing with a screen crusher the mixing was insufficient; egg sized aggregates of iron particles were observed. The aggregates were more or less missed with the smaller sample sizes, but to a larger degree found by the larger sample size. It is the size of the clusters that should be limiting for the sample size instead of the size of individual particles Pitard (1993).

One can also note that when a second mixing step follows (J-K) the variance drops and the sample size is of less importance, for the tested interval.

3.5. Economy versus treatment and assessment

A longer mixing time improves mix quality, but also the cost. This is illustrated by figure 8. In this case, the cost is estimated at 1, 500 SEK/h for a MW, a front loader and an operator. The filling time is 1 minute and time to empty it takes 2 minutes per batch. Each batch contains 5 tonnes of material. The intercept at zero minutes of mixing time and 15 SEK/tonne is the case where the MW is filled and emptied without performing any mixing.

The mix quality must be of enough good quality to be useful for its purpose, otherwise all effort is futile. But it is of value to know what the actually required mix quality is, since the cost increases with longer mixing time. If the volume to treat is “large”, the difference between 5 and 10 minutes mixing will be considerable. In this case it might be worth the effort to find a good enough mixture quality, if it requires a shorter mixing time than expected in the first place. If the volume to treat is “small” it might be a better solution to just make a “long” mixing time to be on the safe side, since the investigation of mix quality requires resources representing a cost.

This cost may be relevant. Based on the experiments described, and excluding transport and material costs, a rough estimate for the sampling, sample preparation and analysis comes to about 2600 SEK/sample (roughly 400 USD).
The mixture quality measures are consistent under similar conditions, i.e. the same type of mixture and same sample size but different mixing times. When several variables are altered the mixing quality measures are less consistent, due to their various relations to material and sample properties. The Lacy index is too insensitive for the tested matrices to be of any use.

Both the Mixing wagon (MW) and the rotating trommel (RT) gave about one order of magnitude better mixing results than that of the screener crusher (SC) for similar or same mixtures. However, using a SC as a premixing step before one of the other treatments can save energy and equipment time.

Extending the treatment time in the MW results in a non-linear improvement of the mixing, with smaller improvement for each additional mixing time unit. The results do not reveal if the best practically mixing quality has been obtained. This would require two mixing times with same achieved mixing quality.

A measure of mixture quality itself gives no information if the mixture is good enough and suitable for its purpose, i.e. some external calibration or past experience is needed for passing judgement.
Taking larger samples did not give the expected decrease of variance. This could be an indication for the formation of fairly large clusters or the critical component (iron) that were under represented in the small and medium size samples.

For large volumes, e.g. several thousands of tonnes, it may be justified to run optimising tests prior to treating the bulk of the material, since the cost saving potential can be considerable. But for smaller volumes the rational choice may be to simply use the longest practical mixing time.

5. ACKNOWLEDGEMENTS

The work was financed by European Union Structural Funds and New Objective 1, North Sweden Soil Remediation Centre (MCN), contract no 113-12534-00, and by the Ragn-Sells waste treatment company. The Ragn-Sells staff at Högbytorp and Dovamyrån helped during the full scale mixing trials. Special thanks to Maria Nyholm, Ulrika Tornerfelt, Martin Tengved and Jan-Olov Andersson (for photos and cost estimations for MW mixing). Desirée Nordmark at Luleå University of Technology (LTU) was of great help during the sampling after the MW mixings. Roger Lindfors, Ulf Nordström and Sanusi Olanrewaju Abdur-Rahman helped with the sample preparation at LTU. Bertil Pålson, LTU, kindly put laboratory resources available. Ralf Weinekötter kindly clarified how to calculate the best case mix quality. Inga Herrman helped with German translation.

REFERENCES


EVALUATION OF PARTICULATE IRON AND SOIL MIXES


APPENDIX 1. DESCRIPTION OF MIXING INDICES

Worst case mix quality is the state when absolutely no mixing has occurred (equation 1).

\[ s_0^2 = p \cdot q = p \cdot (1 - p) \quad \text{Equation 1} \]

In equation 1 p and q are the mass proportion of two components to be mixed.

A theoretical best case mix quality can be calculated (equation 2) (Harnby, et al., 1985; Paul, et al., 2004; Weinėkötter and Gericke, 1995, 2000).

\[ s_R^2 = p^2 \cdot q + p \cdot q \cdot \left( \sum f_i W_i \right) \]  
\[ \text{Equation 2.} \]

Where \( W \) is the mass of the sample taken and \( f_i \) is the “size fraction of one component of average weight \( W_i \) in a particle size range” (Harnby, et al., 1985).

To calculate a sum \( \sum f_i W_i \) for a material, a sieving curve for the material and the densities of particles must be known. For each particle size class an average particle mass is calculated. If the particles can be realistically approximated as spheres, this can be done by calculating spheres with the upper and lower sieve mesh diameter. By multiplying the volumes with the particle density the mass is achieved. By averaging these masses for the particle size class, the particle size class’ average particle mass is calculated. The class average masses should be multiplied with the class mass proportion. Finally these products are added up to calculate the index.

The Lacy index compares how much mixing has occurred with how much mixing could occur (Equation 3). A value of \( I_L \) equal to zero mean total segregation and equal to unity for a mix that is fully randomised. In practice the value for \( I_L \) will be narrower 0,75-1 (Harnby, et al., 1985).

\[ I_L = \frac{(s_0^2 - s^2)(s_0^2 - s_R^2)}{s_0^2 - s_R^2} \quad \text{Equation 3} \]

The intensity of segregation is another index for evaluating the mixing (equation 4) (Paul, et al., 2004).

\[ I_S = \frac{(s^2 - s_R^2)(s_0^2 - s_R^2)}{s_0^2 - s_R^2} \quad \text{Equation 4} \]

For the intensity of segregation index 1 means completely segregated and 0 is randomly mixed. The index ranges in practice mainly between 0,7 and 1.

The Pole, Taylor and Wall-index decreases towards unity while the mixing progresses (equation 5) (Harnby, et al., 1985).

\[ I_{PTW} = S/S_R \quad \text{Equation 5} \]
APPENDIX 2. TWO TIERED VARIANCE ANALYSIS

By taking two series with samples with small and large sample mass, differing at least an order of magnitude the two-tiered variance analysis can be used. When comparing the variances of series with small ($S^2_{ES}$) and large ($S^2_{EL}$) sample sizes, four different cases are described, with different implications (Gerlach and Nocerino, 2003; Mason, 1992; Pitard, 1993):

**Case #1**  $S^2_{ES} \approx S^2_{EL}$: *both large*  Sample weight is not of big importance. Pollution show large scale heterogeneity; spatial trends and/or cycles at the site are likely. Geostatistic evaluation is recommended. Low concentrations and/or larger particles can contribute to large variances. Both sets of data can be used.

**Case #2**  $S^2_{ES} \approx S^2_{EL}$: *both small*  This is a rare case. The material is relatively homogenous on both large and small scale. A potential risk with this case is that the data are measuring the back ground level of contaminant and are missing hotspots and/or agglomerates of contaminant. Both sets of data can be used.

**Case #3**  $S^2_{ES} > S^2_{EL}$  This is the most common case. The sample mass is of importance, effects of e.g. grouping and segregation error are different over the size scales of the samples. Try to find an optimum sample size. Data series from sample sizes smaller than the optimal sample size should be discarded from further work.

**Case #4**  $S^2_{ES} < S^2_{EL}$  This is a rare case. The small samples are only measuring a low background level of the contaminant. The contaminant might exist at high levels but are but are hard to find when the samples are several orders of magnitudes to small. The average concentration can be expected to be much larger in the larger samples since the smaller have a lower chance to sample low frequent clusters of contaminant. Try an even bigger sample size, at least 10 times bigger. If the concentrations are close to critical levels, it can save time to understand the nature of the contaminant distribution. Both the sets of data are based on to small samples, which should be rejected.

**Table A1.** Summary of the four cases in the two tiered variance comparision.

<table>
<thead>
<tr>
<th>Case</th>
<th>$S^2_{ES}$</th>
<th>$S^2_{EL}$</th>
<th>$S^2_{ES}$</th>
<th>$S^2_{EL}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>$S^2_{ES}$</td>
<td>$S^2_{EL}$</td>
<td>$S^2_{ES}$</td>
<td>$S^2_{EL}$</td>
</tr>
<tr>
<td></td>
<td>both large</td>
<td>both small</td>
<td>both large</td>
<td>both small</td>
</tr>
<tr>
<td></td>
<td>not of big importance</td>
<td>not of big importance</td>
<td>important at tested scale</td>
<td>both sizes to small</td>
</tr>
<tr>
<td></td>
<td>large trends / cycles are likely</td>
<td>relatively homogenous at large and small scale</td>
<td>effects of e.g. grouping and segregation is important at investigated scale</td>
<td>$M_{ES}$: background level, $M_{EL}$: clustered contaminant, possibly higher mean values</td>
</tr>
<tr>
<td></td>
<td>geostatistics evaluation is recommended</td>
<td>-</td>
<td>find optimum sample size, $M_{OPT}$</td>
<td>try larger samples, $&gt;10M_{EL}$</td>
</tr>
<tr>
<td></td>
<td>can use both sets</td>
<td>can use both sets</td>
<td>discard $&lt;M_{OPT}$</td>
<td>discard both sets</td>
</tr>
<tr>
<td></td>
<td>a rare case</td>
<td>a rare case</td>
<td>most common</td>
<td>a rare case</td>
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</tbody>
</table>
Paper IV
Techniques for the Stabilization and Assessment of Treated Copper-, Chromium-, and Arsenic-contaminated Soil

Remediation mainly based on excavation and burial of the contaminated soil is impractical with regard to the large numbers of sites identified as being in need of remediation. Therefore, alternative methods are needed for brownfield remediation. This study was conducted to assess a chemical stabilization procedure of CCA-contaminated soil using iron (Fe)-containing blaster sand (BS) or oxygen-scarring granulate (OSG). The stabilization technique was assessed with regard to the feasibility of mixing ameliorants at an industrial scale and the efficiency of the stabilization under different redox conditions. The stability was investigated under natural conditions in 1-m³ lysimeters in a field experiment, and the effect of redox conditions was assessed in a laboratory experiment (10 L). The treatments with high additions of ameliorant (8% and 17%) were more successful in both the laboratory and field experiments, even though there was enough Fe on a stoichiometric basis even at the lowest addition rates (0.1% and 1%). The particle size of the Fe and the mixing influenced the stabilization efficiency. The development of anaerobic conditions, simulated by water saturation, increases the fraction of arsenic (As³⁺) and, consequently, As mobility. The use of high concentrations of OSG under aerobic conditions increased the concentrations of nickel (Ni) and copper (Cu) in the pore water. However, under anaerobic conditions, it decreased the As leaching compared with the untreated soil, and Ni and Cu leaching was not critical. The final destination of the treated soil should govern the amendment choice, that is, an OSG concentration of approximately 10% may be suitable if the soil is to be landfilled under anaerobic conditions. Alternatively, the soil mixed with 5% BS could be kept under aerobic conditions in a landfill cover or in situ at a brownfield site. In addition, the treatment with BS appeared to produce better effects in the long term than treatment with OSG.

INTRODUCTION

Remediation mainly based on excavation and burial of the contaminated soil is impractical with regard to the large numbers of sites identified as being in need of remediation. Therefore, alternative methods are needed for brownfield remediation. This study was conducted to assess a chemical stabilization procedure of CCA-contaminated soil using iron (Fe)-containing blaster sand (BS) or oxygen-scarring granulate (OSG). The stabilization technique was assessed with regard to the feasibility of mixing ameliorants at an industrial scale and the efficiency of the stabilization under different redox conditions. The stability was investigated under natural conditions in 1-m³ lysimeters in a field experiment, and the effect of redox conditions was assessed in a laboratory experiment (10 L). The treatments with high additions of ameliorant (8% and 17%) were more successful in both the laboratory and field experiments, even though there was enough Fe on a stoichiometric basis even at the lowest addition rates (0.1% and 1%). The particle size of the Fe and the mixing influenced the stabilization efficiency. The development of anaerobic conditions, simulated by water saturation, increases the fraction of arsenic (As³⁺) and, consequently, As mobility. The use of high concentrations of OSG under aerobic conditions increased the concentrations of nickel (Ni) and copper (Cu) in the pore water. However, under anaerobic conditions, it decreased the As leaching compared with the untreated soil, and Ni and Cu leaching was not critical. The final destination of the treated soil should govern the amendment choice, that is, an OSG concentration of approximately 10% may be suitable if the soil is to be landfilled under anaerobic conditions. Alternatively, the soil mixed with 5% BS could be kept under aerobic conditions in a landfill cover or in situ at a brownfield site. In addition, the treatment with BS appeared to produce better effects in the long term than treatment with OSG.

MATERIAL AND METHODS

The soils were collected at 2 former wood impregnation sites in Northern Sweden: Forsmo (soil F) and Robertsfors (soil R) (Table 1). A complete description of the method is presented elsewhere (11, 12).

Soil and Amendment Characterization

The soils collected at 2 former wood impregnation sites in Northern Sweden: Forsmo (soil F) and Robertsfors (soil R) (Table 1). A complete description of the method is presented elsewhere (11, 12).
Two by-products from the steel production industry were used for the stabilization: BS, <1 mm diameter, containing 97% FeO with manganese (Mn) (<1%) as the major impurity, and OSG, <2 mm diameter, containing 79% Fe₂O₃ (28% Fe²⁺ and 69% Fe oxides) with Cr, Mn, Ni, and Cu as the major impurities (11).

Ameliorant Mixing

The field experiments began in June 2005 and 2006, respectively, for soils F and R. The aim was to evaluate the treatment technique on a large scale using BS and OSG. Forty tonnes of soil F, moistened to ~50% of soil water-holding capacity (WHC), and 10 tonnes of soil R, moistened to ~30% of soil WHC, were mixed with or without the Fe products. Three mixtures of each soil were prepared: 1 with 1% BS (by weight), 1 with 8% OSG (by weight), and 1 with no ameliorant. The mixing was undertaken in 2 stages for soil F (Fig. 1) using first a screener crusher (a and b) and then a rotating single-skin trommel (c). Soil R was mixed only with a screener crusher.

To evaluate the mixing processes, samples were taken during the mixing of soil F, both after the screener crusher mixing (step 1) and after the rotating single-skin trommel treatment (step 2). After each mixing stage, heaps of the soil were spread out on an asphalt surface to a depth of 1–2 dm, and 10 soil cylinders were taken through the entire soil depth. The sample locations were distributed using a stratified randomized design (Fig. 2a). The samples were dried, sieved to 2 mm, split into subsamples of ~8 g, crushed to a maximum diameter of 0.125 mm, placed in a sample cup, and analyzed using a portable Niton 700 Series X-ray fluorescence spectroscope (Thermo Fisher Scientific, Waltham, MA).

Stability Under Natural Conditions

Lysimeters were used to simulate natural conditions. About 1.3 tonnes of each soil mixture (unamended, mixed with 1% BS, and mixed with 8% OSG) of both soils were placed in separate lysimeters (6 in total) that were monitored from August 2005 for soil F and August 2006 for soil R. The lysimeters were watered weekly with 40 L of water during 3 summer months (July, August, and September). Each lysimeter was equipped with 3 MacroRhizon soil moisture samplers (Eijkelkamp, Giesbeek, The Netherlands). Soil pore water samples were taken monthly, between July and October, and their contents of trace elements and Fe were analyzed as described below.

Stability Under Reduced Conditions

In order to simulate long-term events under a variety of conditions, small containers were used in a laboratory experiment. Soil F was first split by fractional shoveling (13). For each soil-Fe mixture, ~40 kg of soil was homogenized in a concrete mixer for 15 min and, while rotating, mixed with a defined amount of Fe material: 1%, 7%, or 15% (by weight) OSG or either 0.1% or 1% (by weight) BS. Control samples, without amendments, were homogenized according to the same procedure.

Mixed and homogenized samples were moistened with distilled water to 50% of the water-holding capacity (WHC) and distributed in 15-L containers (13 kg of soil in each), which were loosely covered to reduce evaporation. The water content was kept constant for 2 wk and monitored by weighing the containers. The amount of water in the containers was then adjusted: half of the samples were fully saturated with water.
(100% WHC) and the other half kept at 50% WHC, referred to as saturated and unsaturated samples, respectively. Three Rhizon soil moisture samplers were installed in each container.

Assessing Treatment Efficiency by Pore Water Analysis and Leaching

Four months later, samples of soil pore water were extracted and stored at −20°C prior to analysis. The stability of the treatment was assessed as follows:

- Trace element content of pore water was analyzed by an inductively coupled plasma optical emission spectrometer (11).
- $\text{As}^{III}$ and $\text{As}^{V}$ in the pore water (11) were separated, identified, and quantified by ion chromatography followed by inductively coupled plasma mass spectrometry.
- The basal cytotoxicity of the pore water was assessed by assaying the growth inhibition of L929 cells using a neutral red incorporation (14) with some modification (11). We seeded 96-well microplates (Becton Dickinson Labware, Franklin Lakes, NJ) with 2500 cells per well and 10% fetal calf serum as the growth medium. After filtration to achieve sterility (0.22 μm; Millipore, Billerica, MA), 6 replicates of soil pore water were tested in a dilution series at 50% (by volume) mixtures for 72 h before spectrophotometrically determining the optical density at 540 nm after the addition of neutral red.

- Batch leaching tests of the treated soil in which soil was mixed with water acidified to pH 4 with 1 M HNO$_3$ at L/S 10 and agitated for 24 h using an end-over-end tumbler. The samples were filtered through a 0.45-μm nitrocellulose membrane filter and immediately analyzed for trace elements by inductively coupled plasma optical emission spectrometer.

RESULTS AND DISCUSSION

Mixing Quality

Incorporation of the ameliorant into the soil is essential for the method to succeed. In situ applications are usually undertaken with traditional agricultural equipment, such as ploughs and harrows. However, if treatments are applied off-site, prior to reusing the soil or placing it in a landfill, other types of equipment can be used that are able to improve the soil and/or refine it, by dividing it into fractions of different quality classes that can be used for different purposes.

The primary goal of the field experiment was to assess how well the Fe was distributed through the bulk soil. One measure of the mixing quality is the standard deviation of the average amendment concentration (15). Data from 10-dL samples of the 1% Fe mix were evaluated. The standard deviation of the Fe content after mixing steps 1 and 2 had decreased significantly ($\sigma < 0.05$), correlating well with our visual assessment; after step 1 large clumps of Fe particles were observed (Fig. 2b), but they had disappeared after step 2. Arsenic showed the same tendency, but the difference was not statistically significant ($z > 0.05$). Data are summarized in Table 2.

Step 1 has a convective mixing effect, distributing the Fe particles through the bulk soil as small clusters, whereas step 2 breaks up the aggregations and spreads them more evenly through the bulk soil, corresponding to diffusive mixing. Step 2 alone would probably have been less efficient than the combined process, especially because segregation effects in tumbling mixers have been reported (15).

Trace Element Stabilization Under Saturated and Unsaturated Conditions

Both Fe and As are redox-sensitive elements, so their mobility is enhanced under anaerobic conditions (16–18). Therefore, our efforts focused on assessing the behavior of the treated soil under artificially created anaerobic conditions, that is, waterlogged soil. Even if waterlogging is unlikely to occur in a landfill, this allowed us to simulate the anaerobic conditions that develop due to the degradation of organic matter. Further, many former wood impregnation sites are situated close to rivers, and waterlogging may occur during floods.

In the unamended saturated samples of both soils, the As content of the pore water increased over time (Fig. 3). The arsenic concentration was 1–2 orders of magnitude higher in saturated than in unsaturated samples. Iron oxide is unstable in reduced environments, and both Fe and As occurred as reduced soluble species, that is, $\text{Fe}^{II}$ and $\text{As}^{III}$. The soil amended with 17% OSG had arsenic concentrations 1–2 orders of magnitude lower than the control soil without ameliorants, indicating that a greater amount of Fe had a positive effect on As retention. A possible explanation for this finding is that some of the Fe oxide had not dissolved and adsorbed As. The Fe content in the pore water was about 0.6 g L$^{-1}$ in all saturated samples (Fig. 4), whereas there was about 250 g OSG per liter of pore water, indicating that a large amount of the Fe was still available for adsorption.

Figure 4 shows pore water concentrations of redox-sensitive trace elements after the experiment had been running for 3 mo. The data show that water saturation, that is, the development of

<table>
<thead>
<tr>
<th>Treatment step</th>
<th>Number of samples</th>
<th>Average concentration (mg kg$^{-1}$)</th>
<th>SD (mg kg$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Fe</td>
<td>Fe</td>
</tr>
<tr>
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<td>10</td>
<td>21 900</td>
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<td>23 900</td>
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Figure 2. (a) Randomized soil sampling locations (b) and examples of soil samples after the first mixing stage. Photo: S. Lidelöw

Table 2. Means and SD of iron (Fe) and arsenic (As) concentrations in the soil samples (10 dL soil mixed with 1% Fe) collected after mixing by the screener crusher (step 1) and the rotating single skin trommel (step 2).
anaerobic conditions in the saturated soil, had a clear effect on the concentrations. The concentrations of Fe and Mn were several orders of magnitude higher in the saturated soils. Under unsaturated aerobic conditions, the As concentration decreased with increasing Fe concentration. However, the high OSG additions (17%) resulted in order of magnitude increases in Ni and Cu leaching compared with the untreated soil (to 0.8 mg L$^{-1}$ and 0.16 mg L$^{-1}$, respectively). Leaching of Cr was very low with both 1% Fe and 17% OSG. Chromium is seldom a problem in such applications because its mobility is low (11). Leaching of zinc was not affected by any of the treatments.

Under anaerobic conditions, 17% OSG reduced arsenic leaching by 2 orders of magnitude compared with the unamended saturated soil. Nickel and Cu leaching was very low because these elements are less soluble under anaerobic conditions. The effect of BS was weaker than expected (3, 4) (Fig. 4), because metallic iron (Fe$^0$) was found to reduce arsenic leaching very efficiently in previous tests. Uneven mixing may explain the poor reduction in As concentration of the soil pore water, because, stochiometrically, 0.1 % Fe should have been sufficient. In addition, the BS particles were larger in this study than in previous ones, so less surface area was available for adsorption (19).

Oxygen-scarfing granulate seems to have potential as an ameliorant, even though 4 to 8 times more of the material than BS is required to achieve an equivalent effect. Amendment with 17% OSG decreased the mobility of As even when conditions were anaerobic, although stabilization was most efficient under aerobic conditions. Under aerobic conditions, the unwanted leaching of Ni and Cu could be a limiting factor, although these elements present no problems under anaerobic conditions. The utility of L929 cells for assaying harmful levels of various metals (including As) in aqueous solutions has been demonstrated (20). The cytotoxicity decreased from almost 100% in the untreated soil to less than 10% (within the range of biological variation of the cells used in the bioassay in the absence of pore water) in the soil amended with 1% and 17%.

An exponential correlation ($R^2 = 85\%$) between cytotoxicity and the concentration of As$^{III}$ in the pore water was found. As$^{III}$ is more toxic than As$^{V}$ both with regard to acute toxicity (20) and genotoxicity (21). In the laboratory test, the concentration of As$^{III}$ decreased with increasing ameliorant concentrations (Fig. 5).

It should be noted that several factors may complicate the investigation of As speciation in soil (22, 23). Air intruding during sampling and the analysis of samples with low redox potentials may easily affect detected As levels, because (inter alia) Fe has a high propensity to oxidize and rapidly precipitate with As that may be bound to it. This may account for at least some of the large range of As$^{III}$ concentrations (spanning 2 orders of magnitude) recorded in the control triplicates. In support of this hypothesis, a brown precipitate was observed during the pore water sampling and sample preparation for speciation analysis, which was assumed to be precipitated Fe oxide onto which As adsorbs. The total As$^{III}$ concentration was probably underestimated. However, the mere presence of As$^{III}$ is indicative of anaerobic conditions and illustrates the risk that As migration and toxicity may occur in anaerobic conditions that develop in landfills.

**Future Management of the Soil**

The laboratory experiments showed that the development of anaerobic conditions adversely affected the results of the treatments with respect to As mobility. Other trace elements present in the ameliorant may cause problems with increasing amendment concentrations. However, laboratory tests do not take into account large-scale effects, such as mixing, development of gradients, and climatic influences.

Arsenic (because of its toxicity) and dissolved Ni derived from the OSG were identified in the laboratory experiment as the most critical elements for the success of the treatment. Future management guidelines are presented in Fig. 6 shows the pore water concentrations of As and Ni in the lysimeters with each of the 3 mixture of soils F and R: unamended, with 1% BS, and with 8% OSG.
For soil F, the As concentration in the pore water was lowest in the samples treated with 8% OSG, although the As concentration increased by almost an order of magnitude in these samples during the winter. The addition of 1% BS reduced As leaching by (on average) 70% and the levels of leached As after this treatment remained relatively stable over time. In soil R, the additions had little effect on As mobility; the concentration was initially halved but returned to levels close to those of the untreated soil towards the end of the sampling period. Oxygen-scarfing granulate seems to lose its adsorptive capacity more rapidly in soil R than in soil F because the treatment efficiency of the OSG was significantly lowered after only 3 mo. This may be, at least partly, because the oxidation of Fe can limit its adsorptive capacity and the higher content of organic matter in soil R may enhance the development of anaerobic conditions. Further, soil R reportedly has a higher fraction than soil F of AsIII, which has a lower affinity to Fe than AsV (24).

For both soils, the highest Ni leaching was observed with the 8% OSG amendment (Fig. 6). The Ni concentration was higher in soil F than in soil R for both untreated and treated soils. This is probably an effect of the pore water pH being lower in soil F (5.3–6.3) than in soil R (6.8–7.5) (11), because Ni solubility is closely linked to pH.

The lysimeters model the upper layer of the soil profile, which could be the surface of a stabilized site or a landfill cover, where treated soil could be used in the protection layer. For such applications, metallic Fe, such as BS, may be recommended to avoid addition of other trace elements, such as Ni, to the soil. However, the addition of an ameliorant at more than 1% may be necessary to enhance the stabilization, because the effects observed in the lysimeters were weaker than expected.

As in the laboratory experiment, increased Cu leaching from soil F was observed after treatment with the OSG. In soil R, however, Cu leaching decreased by an order of magnitude after addition of OSG. As for Ni, this difference between the soils may be attributed to the differences in their pore water pH. Zinc and Cr leaching from soils F and R decreased by ~80%–90% with additions of either 1% BS or 8% OSG. For soil F, the treatment efficiency was slightly higher for 8% OSG than for 1% BS (11). Excavated soil is classified as waste (25) and, therefore, must be assessed according to waste assessment rules, such as European Union acceptance criteria for landfilling of waste (NFS 23004:10) (26), which are based on the mobile fraction of the elements, measured by batch leaching tests. The results from batch leaching tests of amended and unamended soil from the saturated and unsaturated containers are presented in Figure 7.

The batch leaching tests did not reflect the conditions observed in either the laboratory or the field tests (27). In the leaching test, leached As concentrations were low (<1 mg kg⁻¹) in samples from the saturated buckets with high Fe concentrations (Fig. 7), whereas the As concentration in the pore water was an order of magnitude higher. This may have been due to dissolved Fe and As precipitating during the leaching and subsequent filtration procedures, both of which are performed under aerobic conditions. According to the leaching tests, soil treated with 1% Fe or more fulfills the criteria for disposal in landfill at a site for inert waste, that is, <0.5 mg kg⁻¹ As was leached (26). However, the pore water collected from the same soils contained the highest As concentrations, such as up to 20 mg L⁻¹ As.

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mg L$^{-1}$ for the soil amended with 1% BS. The batch leaching tests do not take into account the effect of reduced conditions and, hence, underestimate As leaching under anaerobic conditions (4, 12, 17, 28). Microorganisms may play an active role in As reduction (18, 29), and this is not taken into account in 1-d-long leaching tests. The relevance of batch leaching tests to assess the behavior of reduce-sensitive elements, such as Fe and As, in the landfill environment is, therefore, questionable (28).

CONCLUDING REMARKS

The treatments with high additions of ameliorant were more successful in both the laboratory and the field experiments, even though there was enough Fe stoichiometrically to bind all As in all mixtures even at the lowest addition rates. This is probably because more soil particles came into contact with Fe particles at the higher concentrations. The results also indicate that increases in Fe particle sizes are likely to reduce the efficiency of the stabilization treatment and corroborate the known importance of mixing in treatments for contaminated soil.

The results presented in this study indicate that the development of anaerobic conditions, simulated by water saturation, increases the fraction of As$^{III}$ and, consequently, As mobility. Furthermore, increasing the amount of ameliorant is not always an acceptable option because it increases, rather than decreases, the concentration of certain trace elements that may cause problems. The use of 17% OSG, for example, had drawbacks, such as increasing the concentrations of Ni in the pore water. The final destination of the treated soil should govern the amendment choice; for example, an OSG concentration of ~10% may be suitable if the soil is to be landfilled under anaerobic conditions. In such cases, lower As leaching was observed compared with the untreated soil, even though the measured concentrations were 2 orders of magnitude higher than in the unsaturated aerobic soil. In addition, Ni and Cu leaching were not critical under anaerobic conditions. Alternatively, the soil could be kept under aerobic conditions, if used as a cover material at landfills or in situ at brownfield sites, for example. In such cases, BS would be a better option than OSG, because Ni and Cu concentrations were not of concern with 1% BS. In addition, the treatment appeared to produce better effects in the long term if BS was used rather than OSG. However, although earlier experiments with 1% Fe$^2+$ have shown high treatment efficiency, full-scale treatment requires higher addition rates because of the difficulty in achieving good levels of mixing when adding small amounts of Fe to the bulk soil.

The toxicity assessment and the speciation of As analysis highlighted the risks associated with the development of anaerobic conditions and the leaching of As$^{III}$ in such environments as landfilling and flooded areas. Further, limitations of the standard leaching tests to simulate the conditions that developed in the saturated soil were demonstrated, and the project showed that placing As-contaminated soil in landfill may have unexpected effects.

FURTHER RESEARCH

Further research should continue to focus on the sustainability of the treatment by investigating the long-term efficiency of OSG under anaerobic conditions and the effect of the soil quality, that is, organic content, on the treatment efficiency. Thorough mixing is essential for the success of any such treatment, and the factors affecting the mixing efficiency should be investigated, for instance, by assessing the effects of other types of mixer and developing indices to describe the degree of mixing. In addition, monitoring should be conducted over longer periods, and toxicity assays could be developed to determine genotoxicity both in vitro and in vivo.
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Paper V
Improving Soil Investigations at Brownfield Sites Using a Flexible Work Strategy and Screening Methods Inspired by the US Environmental Protection Agency’s Triad Approach

Investigations of polluted brownfield sites and sample analyses are expensive, and the resulting data are often of poor quality. Efforts are needed, therefore, to improve the methods used in investigations of brownfield sites to both reduce costs and to enhance the quality of the results. One approach that could be useful for both of these purposes is the triad strategy, developed by the US Environmental Protection Agency, in which managing uncertainty is a central feature. In the investigations reported here, a field study was conducted to identify possible ways in which uncertainties could be managed in practice. One example considered involves optimizing the uncertainty by adjusting the sizes of samples and the efforts expended in analytical work according to the specific aims of the project. In addition, the potential utility of several toxicity assessment methods for screening sites was evaluated. As well as presenting the results of these assessments, in this contribution we discuss ways in which a flexible work strategy and screening methods inspired of the triad philosophy could be incorporated into the Swedish approach to remediate brownfield sites. A tiered approach taking advantage of field and screening methods is proposed to assess brownfield sites focusing on the response and acceptable uncertainty that are required for the task.

INTRODUCTION

Soil clean-up projects are expensive. Their costly components include the associated site investigations and sample analyses, but despite the expense of these investigations, the knowledge they provide about the sites is often limited. Furthermore, remediation costs often increase as projects progress. Efforts should be made, therefore, to improve brownfield investigations in order both to cut their costs and to enhance the quality of the results. One approach that could be used for these purposes is the triad strategy developed by the US Environmental Protection Agency (1, 2). The key aspect of this methodology is managing uncertainty through systematic project planning, dynamic work strategies, and real-time measurement technologies.

The triad approach was developed to improve the quality and reduce the costs of soil remediation. In a triad approach, the remediation project is systematically planned and a conceptual site model is developed to manage uncertainty in such a way as to optimize the remediation. As an outcome of the systematic project planning, the action levels for remediation of the site are established at an early stage, and the sampling strategy can be adapted according to the goals, so that efforts are directed towards samples that are in the uncertainty interval of the action limits. An alternative way to address sites with uncertain background information is to use broad analytical methods that provide a rapid overview of the site, so-called screening methods. Screening methods are of interest for assessing pollution status and improving site investigations, that is, to direct further investigations and to build the conceptual model. A successful triad approach requires rapid, dynamic analytical methods that can be used to screen brownfield sites for pollution. Field methods, such as X-ray fluorescence (XRF) spectroscopy using portable systems, and scanning tests that are sensitive to most, or all, of the pollutant spectrum (and thus provide indications of overall pollution levels), such as toxicity tests, are valuable tools in the triad approach.

One of the subsidiary objectives of the triad approach is to accelerate the project by optimizing decisions before starting to collect samples. Once in the field, one should only have to follow the predetermined routine for decision making. Therefore, the people involved in the dynamic work strategy need to be well trained and experienced or at least aware of the methodology.

In Sweden, soil cleanup projects can be classified into 4 main types according to their sources of funds: i) publicly financed environmental projects; ii) projects financed by a specific sector, such as the oil industry; iii) projects financed by industrial companies based on the requirements from the environmental authorities, and iv) private soil rehabilitation projects prior to house construction. Each type of project has its own agenda. Although oil industry-financed remediation and house construction projects focus on removing the polluted soil to produce a clean area, the publicly financed projects involve 4 independent steps: 2 prioritizing, 1 remediation planning, and 1 cleanup (3).

We believe that the Swedish approach could be improved by employing some of the features of the triad method using real-time and screening measurement techniques to identify the risk-carrying soil fraction and reduce uncertainty. Here, particular attention is paid to toxicity tests and XRF analysis. A study conducted at a marshalling yard is used to exemplify possible ways in which elements of the triad method could be incorporated into the traditional Swedish approach for publicly financed projects (3).

The aims of the project were to:

- Compare the triad and the present Swedish brownfield investigation strategy.
- Discuss how uncertainties regarding the nature and levels of pollution could be estimated and addressed by means of sample size and measurement times.
- Highlight the possibilities of using several toxicity tests, targeting different pollutants in the soil to identify the risk-carrying fraction and to determine their potential as screening methods.
The inflexibility of the plans. Equipment is already available onsite could be lost because of overall costs by taking more samples when expensive sampling makes it difficult or impossible to adapt the project as be very strictly defined in the tender before the project starts, the sampling activities is often lost because different people are transmitted via written reports, and practical experience from the present situation in Sweden, information is mainly Information management and communication are essential. In the stakeholders because the project may change focus rapidly. It must be made. Further, it requires trust between authorities and with respect to the economic aspects, because rapid decisions must be made. The triad system requires active project partners, especially with respect to the economic aspects, because rapid decisions must be made. Further, it requires trust between authorities and the stakeholders because the project may change focus rapidly. Information management and communication are essential. In the present situation in Sweden, information is mainly transmitted via written reports, and practical experience from the sampling activities is often lost because different people are usually involved in the different steps of the project. Further, the sampling documentation can be of poor quality. Another hindrance is that the framework of the projects may be very strictly defined in the tender before the project starts, making it difficult or impossible to adapt the project as information is gathered. For example, opportunities to save overall costs by taking more samples when expensive sampling equipment is already available onsite could be lost because of the inflexibility of the plans.

**THE TRIAD AND THE PRESENT SWEDISH BROWNFIELD INVESTIGATION STRATEGY**

The triad strategy focuses throughout on the final goal, that is, the site remediation, whereas the current Swedish approach to assessing and remediating brownfield sites comprises 4 steps with distinct goals: 2 classification steps, during which sites are inventoried and prioritized; a remediation planning stage; and the remediation project (Table 1). The classification steps are described in detail in the Methodology for Inventory of Polluted Sites, that is, MIFO methodology (3). Using quality criteria, MIFO makes it possible to compare sites from different sectors and identify the sites that should be prioritized for further action.

In both approaches, the project starts with information collection. However, after the contamination suspicions are confirmed and the site is classified as potentially needing remediation, the foci of the 2 approaches diverge. The Swedish methodology has 2 classification steps before any remediation decision is made and planning starts. The triad approach focuses more on the final remediation than the site assessment, including identification of the pollutants to be analyzed, the limit values for specific actions, and the appropriate analytical methods for each identified limit value, keeping in mind at all stages the remediation techniques that may be used.

The Swedish stepwise methodology involves 4 stages, with 4 tenders and better control of the costs for each step. However, the final cost may be unnecessarily high because of these steps. In the triad method, the final cost is unknown at the beginning, and it requires mutual trust between the stakeholders and the contractor that the latter will make the project as cost effective as possible.

The triad system requires active project partners, especially with respect to the economic aspects, because rapid decisions must be made. Further, it requires trust between authorities and the stakeholders because the project may change focus rapidly. Information management and communication are essential. In the present situation in Sweden, information is mainly transmitted via written reports, and practical experience from the sampling activities is often lost because different people are usually involved in the different steps of the project. Further, the sampling documentation can be of poor quality.

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**Table 1. Comparison of Swedish methodology and US Environmental Protection Agency triad approach (1–3).**

<table>
<thead>
<tr>
<th>Swedish methodology</th>
<th>US Environmental Protection Agency triad approach</th>
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<tr>
<td>MIFO 1</td>
<td>Information collection, activity inventory</td>
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<td>Risk evaluation and classification 1</td>
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<td>MIFO 2</td>
<td>Sampling, confirmation of the presence and amount of the pollutant</td>
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<td>Risk evaluation and classification 2</td>
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<td>Remediation</td>
<td>Use of real-time measurement technologies</td>
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<tr>
<td>MIFO – Methodology for Inventory of Polluted Sites.</td>
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The main goal of stepwise MIFO methodology is to prioritize sites where no responsible polluter can be found and society through the EPA must finance the remediation. SPI Miljösaneringsfond AB (SPIMFAB) is a private organization developed by the oil companies in Sweden. The SPIMFAB remediation programs include petrol stations where the activity ceased between 1969 and 1994. The program includes identification, investigation, risk classification, environmental investigations, and, where necessary, remediation. The SPIMFAB approach is closer to the triad approach than to MIFO. Great trust is accorded to the consultant allocated the task by SPIMFAB. When necessary, the consultant can make decisions with respect to required investigations, risk assessments, and remediation techniques. Field instruments, such as photoionization detectors (PIDs), make it possible for the investigator to make rapid decisions onsite. The similarities between the pollution situation at all gasoline stations, such as pollution with well-defined volatile petroleum products, make PIDs a useful tool. However, unlike the triad method, uncertainties in sampling are not considered an issue in SPIMFAB investigations. The experience of the limited number of consultants working with SPIMFAB ensures a common quality level for the investigations. However, the amounts of polluted soil in SPIMFAB projects are often underestimated and the costs rise as a consequence. It is not a problem as long as the project financing is secured by the SPIMFAB fund, but it makes all budget estimations highly uncertain.

Environmental site investigations associated with real estate do not aim to prioritize sites for remediation but to estimate the real estate value. An interview with one of the major housing construction firms in Sweden revealed that great effort is expended on the preliminary investigations, but field instruments are never used, only laboratory analysis. Further, sampling uncertainty is not addressed and is considered a minor problem. The situation described by Woll et al. (2), in which the triad approach is used to calculate more accurate insurance premiums and leads to more profitable brownfield transactions, is not yet recognized in Sweden. The contribution of sampling to the total uncertainty is commonly underestimated, even though there is an increasing awareness in Sweden that sampling is a significant source of uncertainty.

There are similarities between MIFO and the triad system and some of the features of the triad system could simply be applied in the MIFO strategy, especially with regard to use of real-time and screening measurement techniques to identify the risk-carrying soil fraction and to reduce uncertainty.

**CASE STUDY AT THE MARSHALLING YARD**

A study of a 1.6-hectare subarea of the marshalling yard in Boden, Sweden, is used as example to illustrate how site investigation could be improved. Previous studies of marshal-
ling yards have suggested that a broad spectrum of pollutants would be found at the site (4, 5).

On the first day, a total of 44 samples were collected, in order to identify potential polluted spots where a spectrum of pollution could be found (Fig. 1). We used a stratified random design to localize the sampling spot. After removing the upper 5 cm, 5 subsamples of the upper 40 cm were collected at each spot and mixed. During the evening, the collected samples were analyzed using 2 real-time measurement techniques: XRF and the rapid onsite toxicity audit system (ROTAS) (see below). Based on the results, 21 points were further sampled within the area on the second day. After analysis, 11 spots were selected at which a broad spectrum of pollutants was expected to be present at significant concentrations. A 50-cm deep hole was excavated and the soil heap thoughtfully mixed before subsamples were taken so that laboratory techniques could be used to validate the field results.

The tests performed were:

Field assays
- X-ray fluorescence measurements with a portable NITON 700 XRF spectroscope directly through the sample bag (60 and 120 nominal s).
- Rapid onsite toxicity audit system toxicity tests using bioluminescent *Vibrio fischeri*.

Laboratory assays
- Lumitox metabolic inhibition toxicity tests in 96 well plates using bioluminescent *V. fischeri*, adapted from Microtox.
Cell culture toxicity tests based on growth inhibition of the tumor-transformed mouse fibroblast cell line L929. L929 cells were exposed to test solutions in 96 well plates in a 10%, 25%, and 50% (v/v) dilution series. 2500 cells per well were preincubated for 24 hr prior to exposure. For 72 hr, and culture growth was measured using neutral red incorporation (6) adapted to L929 fibroblasts (7).

Laboratory analysis
- Analyses of total metal contents in the soil (Soil2control screening determinations of metal cations using an IRISS emission spectrometer, ALCotrol Laboratories, Rotherham, UK).
- Screening of organic pollutants (Soil2control determinations of volatile organic compounds by headspace/gas chromatography mass spectrometry (GC/MS); petroleum hydrocarbons in the C8-C40 range by EZ Flash GC-FID, and semivolatile organic compounds in soil, water, and products by Time of Flight GC-MS; all by ALCotrol Laboratories).
- Screening of organic pollutants using 2-dimensional GC/MS.

REDUCING AND MANAGING UNCERTAINTY
The total uncertainty related to the response obtained for a single sample is the combination of the uncertainties associated with its collection, preparation, and analysis. Attempts should be made to reduce collection, preparation, and analysis uncertainties. We have chosen 2 examples to illustrate how the total uncertainty could be reduced by managing the collection of the samples and the XRF field analyses, that is, by (i) determining appropriate sample sizes and (ii) optimizing XRF measurements for the requirements of the project. X-ray fluorescence spectroscopy is a real-time measurement technique that is commonly used in Sweden and is suitable for the triad approach.

Representative Sample Size
Heterogeneity of soil occurs at all scales influenced by the particle size distribution of the soil, the mineral composition, and the source of the pollution. This heterogeneity can pose substantial sampling problems because the sampled points may not reflect the distribution of target variables (in this case pollutant levels) and “hot spots” may be missed. Thus, the mean and extreme levels in the samples may be very different from the true levels at the site. The effects of large-scale heterogeneity (trends and cycles) must be addressed by geostatistics. However, the effects of small-scale heterogeneity can be reduced by determining a representative sample size (8), which can, for example, be used to improve assessments of the levels of a given pollutant at the site.

Within the marshalling yard, a 10 x 30 m former gravel-filled storage area was selected for the sample size investigation (Fig. 1). The area was divided into 10 strata from which samples were taken on the basis of a stratified randomized design. Two series of samples were taken, with sample sizes differing by an order of magnitude: small (S) and large (L) samples of 0.1 L and 1 L, respectively (9–11). The samples were dried, passed through a 0.125-mm sieve, and their metal contents were measured in a sample cup 3 times using a portable XRF instrument, with 2-minute nominal count times. Several authors have described the different types of variance relationships between 2 series of small (S1) and large (S2) sample sizes and the implications regarding determination of the optimal sample size (9–11). Variances differing by more than 20% are considered significant in this respect. The variance of the 2 sets of samples was used in our example to determine the appropriate sample size. Data from the 2-tiered variance comparison are summarized in Table 2. No differences in variances are statistically significant for x = 0.05. In our example, the sample sizes for iron, lead, and zinc correspond to a rare case in which S1 < S2 and consequently both sample sizes were too small. The small samples theoretically provide indications solely of the background levels of the contaminants. The contaminants may occur at high levels in some places, but such occurrences are unlikely to be detected if the samples are several orders of magnitude too small. The average concentrations are likely to be much larger in the bigger samples because they are more likely to contain clusters of the contaminant(s). If the concentrations are close to action levels, understanding the nature of the contaminant distribution may save time, and the results show that in this case both sets of samples were too small and that the data obtained from them should be rejected. Samples at least an order of magnitude larger should be taken to determine the optimal sample size. For the copper data S2 < S1, indicating that the smaller samples, at least, are too small and an optimal sample size should be found, S1 > S2 is the most common situation. The sample mass is of importance. Over the range of sample sizes collected, the effects of grouping, segregation errors, and fundamental errors differ. Taking larger samples is generally one way to reduce their effects (9–11), along with attempting to identify an optimum sample size. Data series from samples that are smaller than the optimal size should be rejected for further work. The copper example shows that better estimates of contaminant levels could be obtained by taking larger samples, because this would reduce the confidence intervals. However, the optimal sample size should be identified by increasing the sample size until the variance reaches an asymptotic level.

Two other possible cases are when S1 = S2 and both are either large or small. When S1 = S2 and both are large, the sample weight is not of major importance. The relationship indicates that there are large-scale heterogeneities in the pollution and there are likely to be marked spatial trends and/or cycles at the site. A geostatistical evaluation is recommended in such cases. Low concentrations and/or larger particles can contribute to large variances. Both sets of data can be used in these cases. It is rare for S2 = S1 when both are small. In such cases.
cases, the material is relatively homogenous at both large and small scales. A potential risk is that the data indicate the background level of contaminants and miss hotspots and/or agglomerates of contaminants. Both sets of data can be used.

There is no advice in the literature providing guidance on deciding whether the variances are large or small if the 2 are roughly the same; neither is there guidance on the magnitude at which the variances should be considered equivalent. However, the following could be considered a rough test. If the outcomes correspond to the cases in which \( S_2 \leq S_1 \), the sample sizes used might be appropriate. If the outcome is 1 of the 2 other cases, larger samples should be evaluated, or an optimal sample size should be found using other methods, such as the Visman method (9, 10) and the Gy formula, either mathematically or graphically (4, 8–11). However, Gustavsson et al. (4) found it difficult to determine some of the variables used in the Gy formula and used tabulated values. Pitard (11) presented a modified version of the Gy formula to use on data from sieving analysis to obtain a sample size that, at least, represents all particle size fractions and another even simpler modification, the “rule of thumb” for environmental samples when there is no prior knowledge of the soil.

### Optimizing Real-time Measurement Techniques and Managing the Uncertainty

To improve the precision of XRF measurements (and reduce uncertainty), one can increase the measurement time, increase the number of measurements, or prepare the sample, such as by drying and sieving (12). This study focused on the 2 former factors, investigating ways in which the uncertainty could be reduced in field conditions, that is, analyzing directly through the sampling bag. The soil sample with the highest pollutant content was chosen, and the concentrations of copper and lead were used as examples (Table 3). Two types of uncertainty were identified: i) the instrumental uncertainty, which is related to the instrument itself; and ii) the sample uncertainty, which is related to the sample heterogeneity. The instrumental uncertainty was found to be dependent only on the measurement time, that is, the standard deviation declined from 8.4 to 5.8 when the measurement duration was doubled, and the sample uncertainty could be reduced by increasing the number of measurements.

Increasing the measurement time mainly reduces the instrumental uncertainty, whereas the number of samples mainly affects the sample uncertainty. If the analyzed samples can be classified as clean or polluted according to the remediation goal directly after a few, rapidly collected measurements, there is no need to prolong the analyses. In contrast, if the first results happen to be close to the critical action limit, it may be worthwhile to continue the analysis in order to reduce the uncertainty of regarding the concentrations of target elements in the sample and thus obtain a better indication of whether or not they exceed action levels.

Figure 2 shows the changes in the confidence intervals of the average concentrations of copper and lead in relation to the number of measurements on the same bag. The average, maximum, and minimum confidence intervals are presented. Ten random combinations of a series of 14 measurements and a t-distribution were used to generate the confidence intervals. Large numbers of measurements may be needed to reduce the uncertainty to negligible levels; however, strong reductions were obtained with 6 measurements.

The largest reduction in the uncertainty, that is, the confidence interval, was obtained by increasing the number of measurements. At our site, when the measured concentration is

![Figure 2. Changes in the confidence intervals of the average concentrations of 2 contaminants (copper and lead) in relation to the number of measurements of 1 sample. The average, maximum, and minimum confidence intervals of the measurements are shown. Ten random combinations of a series of 14 measurements were used in a t-distribution to generate the confidence intervals.](http://www.ambio.kva.se)
ASSESSMENT OF THE RISK-CARRYING POLLUTANT FRACTIONS

In our field test, we focused on toxicity measurement methods, because they can provide better indications of the overall pollution status of the soil than the total content of specific pollutants. The total pollutant content of a soil can be divided into the mobile hydrophilic and hydrophobic fractions, the particle-bound fraction, and the immobile fraction. Effects on any recipient are caused by the mobile fractions, and several tests are available to assess their levels, which should be taken into account in the risk assessment to be as precise as possible. Often an extraction step is necessary, the effects on the amounts (and possibly forms of the pollutants) of which should always be considered.

Five approaches were used to investigate the different risk-carrying fractions:

- Hydrophilic pollutants were assessed using water extraction and i) ROTAS assays; ii) Lumitox assays (in which the same bioassay system as in ROTAS was used, but the extraction conditions were more efficient; 10 MPa, 150°C); and iii) L929 assays, in which the more efficient extraction method was used but growth inhibition was the indicator variable.

- Hydrophobic pollutants were assessed with ROTAS using methanol extraction, including methanol dilution necessary to avoid possible toxic methanol effects on the V. fischeri.

- A 2-phase water flea test was used to assess the effect of the particle-bound pollutant fraction.

The results of the different tests were related to the total content of 16 metals, 8 mineral oil constituents, 16 polycyclic aromatic hydrocarbons (PAHs), 7 nitrogen pesticides, 34 organochlorine pesticides, 21 organophosphorous pesticides, 12 chlorophenols, 7 polychlorinated biphenyls, 6 phthalates, and 28 semivolatile and 61 volatile organic compounds.

Three Toxicity Tests for the Hydrophilic Fraction

An attempt was made to validate the 3 toxicity tests by comparing the results they yielded in assays of the same soil samples (Fig 3). The Lumitox and ROTAS methods use the same bioluminescence inhibition bioassay system, but a greater extraction efficiency is obtained thanks to the poly(A)-limiting element (10 MPa, 150°C) in the former. The L929 assays (which provide data on a different aspect of toxicity: growth inhibition [6, 7, 13]) indicated that some of the samples were more toxic, and others less toxic, than the other 2 assays suggested. The concentrations of lead, vanadium, and copper, respectively, exceeded the generic guideline values in samples 8, 10, and 11. A relative luminosity below 50% of the control was considered to indicate toxicity. Sample 8 appears to be the most toxic on the basis of both the Lumitox and L929 tests, which could be related to its high lead content. L929 assays also indicated that samples 10 and 11 are toxic, which may be related to their vanadium and copper contents. The ROTAS system detected toxicity not only in sample 8 but also in samples 1, 6, 7, and 9. Vanadium, nickel, and copper concentrations were close to the generic guideline values for sensitive land use in sample 7, but none of the analyzed metals appeared to be correlated to the toxicity responses in the other samples. The PAH concentration was higher than the guideline value for less sensitive land use in sample 10 and elevated in samples 1, 3, 8, and 11, which may have contributed to the observed responses to those samples. No evidence was found to explain the toxicity recorded in samples 6 and 7. Water extraction was sufficient for water-soluble contaminants in the field ROTAS V. fischeri method. Methanol extraction (ROTAS organics) gave poor results in the field (data not shown).

A multivariate data analysis model was constructed to identify the analysed pollutants that were primarily responsible for the observed toxicity. Figure 4 presents the results of the analysis of all available data from the analyses of the 11 samples.

The evaluation shows a correlation between L-929, Lumitox, and the contents of metals, such as zinc, lead, and arsenic, measured with XRF. A correlation between ROTAS methanol and the organic compounds was also observed. However, the toxicity measured by ROTAS was low. The dilution of the leachate required to use V. fischeri after methanol extraction of the organic pollutants led to a consequent dilution of the pollutant, which explains the low observed toxicity of the PAH.

Soluble and Particle-bound Toxicity

The toxicity tests in the 2 test systems in which V. fischeri is used, ROTAS and Lumitox, were performed on soil extracts, assuming them to be representative of the overall toxicity of the soil (Fig. 2). However, Rydwall (14) introduced a test procedure based on a soil particles which are suspended in growth medium, and showed that chemicals toxic to the water flea (Daphnia magna) may be adsorbed to the suspended soil particles (15) and thus may not be detected if extracts are used in toxicity tests. The assay was used to test 4 PAH- and metal-contaminated soils from former wood preservation sites and gas plants using stock suspensions of the soils prepared by mixing 6-g portions of each soil in 36 mL of Daphnia growth medium. The results are shown in Table 4.

The experiment was set up as a static acute toxicity test, following the essential features of SS028180 ISO 6341-1982: Water quality—Determination of the inhibition of the mobility of D. magna Strauss (Cladocera, Crustacea). Ten juvenile animals were added to a 50-mL glass beaker containing 30 mL of test solution, and 5 replicates per test concentration were used. The exposure time was set to 24 h. EC50 values were calculated using linear regression based on 3-5 different concentrations, each with 5 replicates, to estimate the effective concentration that inhibited the mobility of 50% of the water fleas (16, 17). The calculated EC50 values of the soil suspensions varied between 0.0014% and 42% of the stock suspension (Table 4). Their regression coefficients indicate that there was a significant relationship between the concentration of suspended material and the observed toxic effect. A soil presumed to be "clean" was used as a nontoxic reference.
In addition, the suspension of soil number 11 was centrifuged at 5000 rpm for 15 min. The toxicity of the soil suspension, supernatant, and resuspended pellet (in 30 mL of growth medium) was measured (Table 5). Whereas only 24% of the water fleas were mobile after 24 hr in the 2-phase systems, 100% were mobile in the supernatant and just 15% in the resuspended pellets.

These results suggest that the toxic substances are strongly associated with particles and that toxicity tests of filtered water samples do not adequately measure environmental toxicity.

Toxicity Assessment in a Triad Approach

We believe toxicity analyses could become a useful tool in a triad-inspired approach because they provide valuable information on the effects a polluted soil may have on the recipient, which is an important input to the risk assessment. Furthermore, their screening character would allow a more complete information gathering because they are not pollutant specific and some of them are usable in the field.

Unfortunately, the pollutant concentrations in the soil collected at our test site were not as severe as expected and may have been close to the lower detection limit for use of the methods, which explains the unclear correlation between the tests.

The main advantage of toxicity analyses is that they address the risk-carrying fraction of the pollutant, the one that may have adverse effects on the environment. However, as long as assessments must generate data on total contents, in order to check compliance with official guideline values, the utility of toxicity methods will be limited. Such methods may be used as complementary analysis will be required.

PROPOSALS FOR A TIERED APPROACH TO SCREENING SOIL FOR POLLUTANTS IN THE BROWNFIELD INVESTIGATION

Both chemical and bioanalytical methods can be used to screen polluted areas for organic and inorganic pollutants. In order to reduce the associated costs, we suggest a tiered approach (Fig. 5), in which the representative sample size at the site initially is determined using a cheap analytical method, such as XRF and bioassay. This approach would be mainly applicable in the second step of the MIFO investigation and in the pre-remediation investigation where it would structure and adapt the soil characterization to the need and provide better information to base remediation decisions on a cost-efficient way. As far as privately initiated and financed site investigations are concerned, there are no hindrances to implement the proposed approach. Such projects do not have to follow the MIFO procedure.

Site investigation begins by taking soil samples to determine the representative sample size (1). Next step consists in taking samples that are further screened in the field using bio- or immunoassays both for organic and inorganic pollutants (A) and XRF for inorganics (B). The assays may be either general, like those used in the present study (ROTAS, Lumitox, and L929), or specific, such as class- or compound-specific immunoassays (18–20).

If the bioassays indicate a significant biological effect or a significant degree of pollution (2A), and XRF results do not explain the effect, targeted chemical analyses may be used to screen for likely causative agents, selected on the basis of existing knowledge about earlier activities at the site that may have resulted in soil pollution (3B). If this approach fails, that is, no target analytes are found, a broader screening could be performed (4A). Finally, if that also fails to explain the bioassay results, a broad unprejudiced screening could be undertaken (5A), such as using comprehensive 2-dimensional gas chromatography with mass spectrometric detection (GC-/GC-MS) (21).

– A first XRF measurement is done to assess inorganics (2B). If the uncertainty of the XRF response is too large, prolonged measurement time and measurement replicates could be done to decrease it (3B). If the action appears to be insufficient, a total content analysis using digestion in aqua regia, for example, could be used (4B).

Two-dimensional gas chromatography with mass spectrometric detection is ideally suited to characterizing complex mixtures of organic pollutants, because it combines the unrivaled separation power of GC/GC with the unique identification capabilities of MS. All components are chromatographically separated in 2 dimensions, the first being

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<th>EC50 (%) of stock suspension</th>
<th>R²</th>
<th>EC50 mg/mL L⁻¹</th>
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Table 5. Percent mobile Daphnia after 24 hr (10 juveniles/concentration).

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<tr>
<td>Resuspended pellets</td>
<td>2</td>
<td>15</td>
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The moderate toxicity effect could be valuable; further investigations could focus on the identified pollutants other than mineral oil and PAHs. The absence of a link between the biological effects and pollutant level data may, possibly, be due to the low concentrations and the low bioavailability of the pollutants. Based on this information, the further investigations could focus on the identified pollutants, and the moderate toxicity effect could be valuable input to the risk assessment and the conceptual site model. Further sampling could be focused on the relevant pollutants and make the overall investigation more cost efficient.

CONCLUDING REMARKS

Sampling uncertainty is often not addressed in site investigations; an interesting paradox is that results of laboratory analyses are highly trusted, while the major source of uncertainty, the field sampling, is overlooked. Incorporating more aspects of the triad approach would increase awareness about the real quality of the data collected and improve the quality of conceptual site models. This would also lead to overall financial savings. Field and screening methods have a role to play in the triad approach.

Determining the representative sample size and optimizing the number of measurements are 2 ways of reducing the uncertainty regarding the actual concentration of a pollutant in a soil sample. However, managing uncertainty includes both accepting high uncertainty when low precision is acceptable and reducing the uncertainty (e.g., by taking larger samples or increasing the density of the analysis) when high precision is needed. Determining what constitutes a representative sample size and adapting the duration and number of XRF measurements based on the measured concentrations and the project-specific critical limits are 2 examples of ways in which the uncertainty can be adjusted to an acceptable level. X-ray fluorescence spectroscopy can be used on metal-polluted soil. In our case study, the use of XRF spectroscopy to measure the level of metal (lead and copper) contamination worked well for identifying sample concentrations above the limit for “less sensitive land use.” Other field methods are also available that could be adapted to the project needs, such as PID for oil.

Toxicity assessment is another approach, which examines the effect of the pollutants rather than simply their concentrations. Together with screening analysis, toxicity tests could help to identify problem areas on a site. It is difficult to assess the success of the ROTAS toxicity tests, because the tested soil had rather low levels of contamination. However, the lack of correlation between the results of the toxicity assays and the pollutant content should be addressed. Bio- and immunoassays could become an interesting tool in the sample assessment tiered approach we proposed. However, as long as guidelines are based on total content, the applicability of toxicity tests will be limited, even though it can be argued that risk is more closely linked to the available fraction than the total content of a pollutant.

There are no fundamental contradictions between the Swedish site assessment methodology and triad approach, but the segmented structure of the Swedish methodology may easily hinder the dynamic workflow required by the triad method. The suggested tiered approach for screening soil for pollutants would mainly be applicable in the second step of the MIFO investigation and in the preremediation investigation, where it would provide better information on which to base remediation decisions. As far as privately initiated and financed site investigations are concerned, there are no barriers to implement the proposed approach because such projects do not have to follow the MIFO procedure. However, the lack of requirements from the environmental authorities on uncertainty assessment does not incite consultants to make large efforts on that topic. Successful implementation of a methodology, such as the triad approach, requires all those involved to understand the core of the methodology and be willing to implement it. It is essential for both the systematic project planning and the dynamic workflow. If these requirements are not fulfilled, there is a high risk of reverting to old routines, thus invalidating the new approach. Increasing awareness of uncertainty and
demonstration that methods exist to manage it is one way to encourage problem owners to require uncertainty management in the project they initiate and finance.

References and Notes


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For a complete list of references, see the original publication.
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