

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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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 workshop an area were 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 [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.

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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 soil obtained for ICP analysis has the mass of 0.5 g.

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)

Sample	M_E (g)	Depth (cm)	XRF (ppm)						ICP (ppm)		
			Cu		Pb		Zn		Cu	Pb	Zn
			Maximum	Minimum	Maximum	Minimum	Maximum	Minimum			
A (L ₁)	312.2	50	4,110	875	1,980	1,010	3,570	2,180	2,090	3,020	1,390
B (L ₁)	581.8	0	412	282	178	162	297	267	338	149	239
C (L ₁)	543.1	25	693,000	205,000	1,490	1,360	7,550	6,220	575,000	367	2,070
D (L ₂)	1,021.6	50	658	647	333	309	936	757	642	485	759
E (L ₂)	991.1	100	321	270	241	209	611	559	432	321	613
F (S)	435.8	80	–	–	25.4	22.3	45.4	45.4	7.55	<10	18.0
G (S)	846.7	0	2,540	1,660	2,620	2,540	7,760	6,660	2,510	2,500	5,020
H (S)	858.6	50	–	–	57.6	47.8	51.7	45.4	24.3	31.3	40.6
I (L ₂)	532.7	100	1,100	709	814	764	1,650	1,540	1,100	899	1,430

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]:

$$S_{FE} = \sqrt{\left(\frac{1}{M_E} - \frac{1}{M_L}\right) d_{95}^3 c \beta f g} \quad (1)$$

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_{95} the mesh sieve size where 5% of the material is retained (cm), c the mineralogical factor (g/cm^3), β the liberation factor, f the particle shape factor and g is the particle size range factor or granulometric factor. The mineralogical factor, c , is described in Eq. (2) [12,15]:

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

In Eq. (2) the denotations are: a_L is the mass proportion of the contaminant in the lot to be sampled, α the contaminant proportion in the critical particles, ρ_c the contaminant density (g/cm^3) and ρ_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]:

$$S_{GSE} = \sqrt{S_{FE}^2 YZ} \quad (3)$$

In Eq. (3), the 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]:

$$S_{TE} = \sqrt{\sum S_{\text{sampling error, sampling step}}^2} \quad (4)$$

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].

$$S_{OE} = \sqrt{S_{TE}^2 + S_{AE}^2} \quad (5)$$

Table 2
Presenting correct sample geometry in different sampling dimensions

Sampling dimension	Example	Correct sample geometry
3D	Pile	A sphere inside the lot
2D	Flatted pile, soil strata	A cylinder, perpetual to the plane, through the entire thickness of the strata
1D	Elongated pile, conveyor belt	Cut off with two parallel planes, e.g. a scope with flat bottom and parallel walls
0D	Quite similar units, like truckloads or shovel loads	Randomly chosen units; preferable stratified randomised

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

Lead NIST 2709			Zinc NIST 2709			Copper NIST 2710		
<i>m</i> (ppm)	S.D. (ppm)	R.S.D. (%)	<i>m</i> (ppm)	S.D. (ppm)	R.S.D. (%)	<i>m</i> (ppm)	S.D. (ppm)	R.S.D. (%)
24	2.88	12	87.5	8.14	9.3	101	21.9	21.7
24.9	4.52	18.2	82.8	9.21	11.1			
24	5.1	21.2	74.6	11.9	16			
Pooled result		17.6			12.5			

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

R.S.D. Pb (%)	11.3
R.S.D. Zn (%)	8.32
R.S.D. Cu (%)	10.7

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 ($M_{E1} = 312.2$ g, $M_{L1} = \infty$ g, $d_{95} = 0.2$ cm, $\beta = 1$, $f = 0.5$, $g = 0.25$, $a_L = 3020 \times 10^{-6}$, $\alpha = 1$, $\rho_c = 11.4$, and $\rho_m = 2.65$ g/cm³):

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

$$S_{FE}^2 = \left(\frac{1}{312.2} - \frac{1}{\infty}\right) \times 0.2^3 \times 3750 \times 1 \times 0.5 \times 0.25 = 0.0120, \quad S_{FE1} = 11.0\%$$

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 ($M_{E2} = 0.5$ g and $M_{L2} = 312.2$ g):

$$S_{FE2}^2 = \left(\frac{1}{0.5} - \frac{1}{312.2}\right) \times 0.2^3 \times 3750 \times 1 \times 0.5 \times 0.25 = 7.50 S_{FE2} = 274\%$$

Table 5

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

Sample	S _{FE1} (%)								
	XRF						ICP-AES		
	Cu		Pb		Zn		Cu	Pb	Zn
	High	Low	High	Low	High	Low			
A	8.33	18.1	13.6	19	7.98	10.2	11.7	11	12.8
B	19.3	23.4	33.2	34.7	20.3	21.5	21.3	36.3	22.7
C	0.194	0.74	11.9	12.4	4.15	4.58	0.269	23.9	7.96
D	11.5	11.6	18.3	19	8.63	9.6	11.7	15.2	9.59
E	16.8	18.3	21.8	23.5	10.9	11.3	14.5	18.9	10.8
F	–	–	101	108	60.1	60.1	165	162	95.4
G	6.44	7.97	7.15	7.27	3.28	3.54	6.48	7.32	4.08
H	–	–	48	52.7	40.1	42.8	65.5	65.1	45.3
I	12.4	15.4	16.2	16.7	9	9.32	12.4	15.4	9.67

The values used for β , f , g and ρ_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 α 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. β 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 and 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 $S(GSE)$ 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 increment extraction error during field sampling. No values will be estimated.

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

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

Sample	S _{FE2} (%)								
	XRF						ICP		
	Cu		Pb		Zn		Cu	Pb	Zn
	High	Low	High	Low	High	Low			
A	269	583	437	613	257	330	292	274	320
B	850	1,030	1,460	1,530	894	944	728	1,240	772
C	8.24	31.5	504	528	176	195	8.87	788	262
D	673	679	1,070	1,110	504	560	528	685	433
E	964	1,050	1,260	1,350	624	652	644	842	482
F	–	–	3,870	4,130	2,290	2,290	4,870	4,770	2,810
G	342	424	380	386	174	188	267	301	168
H	–	–	2,570	2,820	2,150	2,290	2,710	2,700	1,870
I	520	648	683	705	379	393	403	503	315

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

$$S_{FE1} = 11.0\%, \quad S_{GSE1} = 11.0\%, \quad S_{FE2} = 274\%,$$

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

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

$$S_{TE} = 388\%$$

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

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

$$s_{OE} = 388\%$$

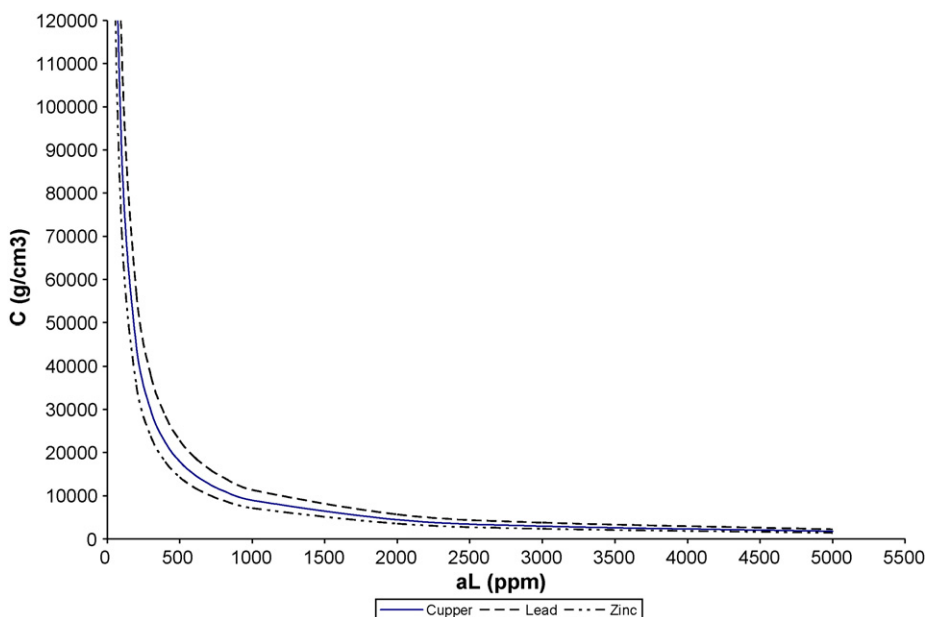


Fig. 1. The mineralogical factor, c, as a function of the contaminant level in ppm.

Table 7
Total sampling error given as S_{TE} (%)

Sample	S_{TE} (%)								
	XRF						ICP		
	Cu		Pb		Zn		Cu	Pb	Zn
	High	Low	High	Low	High	Low			
A	380	826	619	867	364	467	413	388	453
B	1,200	1,460	2,070	2,160	1,270	1,340	1,030	1,750	1,090
C	11.7	44.5	713	747	250	275	12.6	1,110	371
D	953	960	1,510	1,570	713	793	747	969	613
E	1,360	1,490	1,780	1,910	882	922	911	1,190	682
F	–	–	5,470	5,840	3,240	3,240	6,890	6,750	3,980
G	484	599	537	546	246	266	377	426	238
H	–	–	3,630	3,990	3,030	3,240	3,840	3,820	2,650
I	736	917	966	997	536	555	570	712	446

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

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

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

Sample	S_{OE} (%)								
	XRF						ICP		
	Cu		Pb		Zn		Cu	Pb	Zn
	High	Low	High	Low	High	Low			
A	381	826	619	867	364	467	414	388	453
B	1,200	1,460	2,070	2,160	1,270	1,340	1,030	1,750	1,090
C	24.6	49.5	714	747	250	276	16.5	1,110	371
D	953	961	1,510	1,570	713	793	747	969	613
E	1,360	1,490	1,780	1,910	882	922	911	1,190	682
F	–	–	5,470	5,840	3,240	3,240	6,890	6,750	3,980
G	484	600	538	546	246	266	377	426	238
H	–	–	3,630	3,990	3,030	3,240	3,840	3,820	2,650
I	737	917	966	997	537	555	570	712	446

The largest effect of the results in Table 9 is due to the concentration of the contaminant. The larger the contaminant level, the lower the fundamental error and thus the larger the 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 9
The quotient between the total sampling error and the analytical error

Sample	S_{TE}/S_{AE}								
	XRF						ICP		
	Cu		Pb		Zn		Cu	Pb	Zn
	High	Low	High	Low	High	Low			
A	17.5	38	35.1	49.3	29.1	37.3	38.6	34.3	54.4
B	55.4	67.1	117	123	101	107	96.2	155	131
C	0.537	2.05	40.5	42.4	20	22	1.17	98.6	44.6
D	43.9	44.3	85.8	89.1	57	63.4	69.8	85.8	73.7
E	62.8	68.5	101	108	70.6	73.8	85.1	105	82
F	–	–	311	332	259	259	644	598	479
G	22.3	27.6	30.5	31	19.7	21.3	35.2	37.7	28.6
H	–	–	206	227	243	259	359	338	319
I	33.9	42.3	54.9	56.6	42.9	44.4	53.3	63	53.7

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 β 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 see what they reveal.

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

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