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HETEROGENEITY IN HEAVY METAL CONCENTRATIONS IN THE SOIL OF A FIRING RANGE AREA AT KESARIANI, ATHENS, GREECE

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Abstract

Heterogeneity in metal concentrations is a typical characteristic of contaminated sampling targets, with consequences in the estimation of measurement uncertainty and the spatial delineation of contamination. Heterogeneity of contamination is site specific and is linked to the type and origin of the contaminants. In this paper we present a case study on a completed firing range, at Skopeftirio Park in Kesariani, Athens, Greece. The study focused on two heavy metals in the soil with contrasting properties. Lead, an element with high concentrations due to the previous land use of the park and Cr, an element with concentrations close to the natural background at this site. Forty nine top soils samples (0-10cm) were collected from an area of 0.7 km^2 *by using a 40m x 40m grid. Duplicate samples were collected from 8 randomly selected sampling sites, 5 m away from the original sampling location and were analyzed in duplicate for the estimation of measurement uncertainly. Elemental concentrations were measured by AAS after an aqua- regia acid attack. Robust analysis of variance applied on duplicate measurements separated the total variability of the results into three components, representing the analytical, sampling and geochemical variances for the two elements in soil. It was shown that the combined sampling and analytical variance for the Pb has a high proportion in the total (53.5%) reflecting the extreme small-scale spatial variation of Pb contamination. For Cr, the proportion is lower (17%) indicating a more homogeneous distribution of elemental concentrations.*

Key words: *geochemical sampling, measurement uncertainty, heterogeneity, ANOVA, contaminated soil, heavy metals.*

1. Introduction

Sampling is an integral part of the measurement process in geochemistry. However, only recently appropriate attention has been given to this process in terms of the errors and uncertainty that it generates. Uncertainty of measurement, according to metrological terminology is defined as a parameter, associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand (ISO, 1993). The idea of devising methods for the estimation of sampling uncertainty analogous to the methods already in use for the estimation of analytical uncertainty has been suggested (Ramsey, 1994; Thompson and Ramsey, 1995). The analogy is limited by three important differences from analytical practice (Ramsey and Thompson, 2007) namely: (i) the heterogeneity of sampling targets plays a role during assessment of sampling uncertainty, while this (ideally) does not play a role during assessment of analytical uncertainty, (ii) practical difficulties obstruct the estimation of sampling bias, (iii) analytical variations can be observed directly, but sampling variation cannot be observed directly because there will always be interfering analytical variations.

However, through recent research, methodology has been developed for estimating uncertainty from sampling empirically by using techniques based on randomized replicated experiments. In such techniques, the utilization of analysis of variance, often abbreviated as ANOVA, has a central role. In the instance of contaminated land investigations, where the objective of the measurement is defined in terms of contaminant concentration in the sampling target and not simply in the laboratory sample, the act of taking a sample introduces uncertainty in the reported result. Possible sources of error and uncertainty during sampling operations may include cross-contamination and imperfect stabilization of samples resulting in bias or additional variability, but the most significant source of uncertainty is heterogeneity of the sampling target and its effects, such as random variability and selection bias. Furthermore, studies of environmental systems have shown that effects caused by heterogeneity often outweigh between-sampling operator and between-sampling protocol differences in concentration results (Ramsey and Argyraki, 1997) and uncertainty on the measurements is greatly affected by the heterogeneity of contamination, which in turn is linked to the type and origin of the contaminants. It has been shown that the higher the heterogeneity of contamination the higher the levels of the estimated measurement uncertainty (Taylor et al., 2005). Work on contaminated land with different characteristics also confirmed that heterogeneity is site specific.

In this paper we present a case study on a completed firing range, at the Skopeftirio Park in Kesariani, Athens, Greece. The study focused on two heavy metals in soil with contrasting properties. Lead, an element with high concentrations in surface soil due to the previous land use of the park as shooting range and chromium, an element with concentrations close to the natural background which is controlled by local geology. The objective of this work is to present an application of analysis of variance (ANOVA) technique to sampling uncertainty estimation and to discuss the heterogeneity in heavy metal concentrations in soil with reference to sampling quality as well as fitness for purpose of the used sampling protocol.

2. Site description

The study area is situated in the Skopeftirio Park of the Municipality of Kesariani, about 3km east of Athens centre. The Skopeftirio Park has a total area of 0.7 km^2 of almost flat topography. The vegetation within the park includes coniferous trees and grass areas. Park amenities include playgrounds and a gun-shooting club which is fenced and isolated from the rest of the park area. The park has a long history mostly related to the 2nd World War when it was used as an execution place by the Nazis. The area has been also used for military purposes over the years. Recently it has been declared as a historical monument of modern Greece by the Ministry of Culture. After the 50's, different parts of the park have been used as shooting ranges for recreational purposes. Some of these areas have been remediated while others are left in their original state. The previous use of the later is evidenced by small spherical lead shots lying on the ground. Lead shots remaining on the surface soil are eroded over time, releasing Pb into the soil (Petrakaki, 2009).

Geologically, the area belongs to the Athens Unit which lithologically comprises solid, white, platform carbonates as well as some pelagic clastic sediments including bodies of basic and ultrabasic rocks and volcano-sedimentary tuffs (Papanikolaou et al., 2004). These basic and ultrabasic rocks are naturally enriched in Cr and contribute to the geochemical fingerprint in the park soil with respect to the concentrations of this metal.

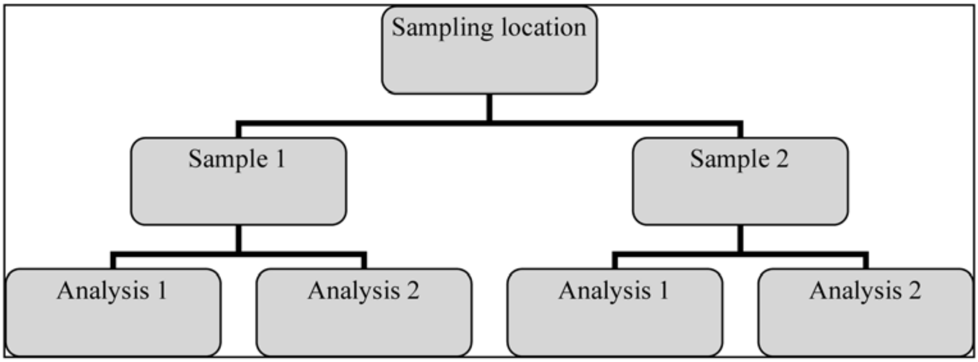

Fig. 1: Schematic balanced design of sampling and analytical duplicates.

3. Methods

3.1. General

When investigating a single sampling target of contaminated land, by applying duplication on sampling and analysis, ANOVA can be applied to the measurement of a parameter on the duplicated samples for estimating the random component of uncertainty (Ramsey and Ellison, 2007). Although a higher level of replication can be used, duplication is the most effective form of replication in sampling studies. Research has shown that a minimum of eight duplicates is required to provide sufficiently reliable estimates of uncertainty (Lyn et al., 2007). The experimental design of this method is the balanced two-stage nested design (Fig. 1).

Based on this, two independent estimates of the population variance can be made, the between sample variance estimate, $s^2_{sampling}$ and the within sample (between analysis) variance estimate, $s^2_{analytical}$. The sum of these represents the measurement variance, s^2_{meas}:

$$s^2_{meas} = s^2_{sampling} + s^2_{analytical}$$

and the standard uncertainty (u) can be estimated as:

$$u = s_{meas} = \sqrt{(s^2_{sampling} + s^2_{analytical})}$$

Subsequently, the estimate of the total variance in the sampling target is given by:

$$s^2_{\mathrm{total}} = s^2_{geochemical} + s^2_{sampling} + s^2_{analytical}$$

where:

$s^2_{\mathrm{geochemical}}$ = the variance estimate between sampling locations

It should be noted here that because classical ANOVA is a parametric statistical method, it relies on the assumptions of normality of the distribution of the studied parameter and homoscedasticity of the variances. The obtained variance estimates become less reliable when these assumptions do not hold. The first assumption is not met in many instances, particularly in the case of environmental contaminants where analyte concentrations often display log-normal distributions. Furthermore, in order for homoscedasticity to hold, ANOVA assumes no change of the variance within the concentration range. Thus, the estimation of uncertainty by this method is only applicable close to the mean value of the sample's concentration but does not apply in instances of wide range of concentration where a change in measurement precision with concentration is expected. To overcome the problems with non-normally distributed data the use of robust statistics has been suggested (AMC, 1989; Ramsey, 1998). Robust ANOVA treats outlying values by down-weighting them rather than rejecting them.

Fig. 2: Map of Skopeftirio Park at Kesariani in Athens, showing the sampling points [open circles] of surface soil.

3.2. Sampling and chemical analysis

Forty nine top soil samples (0-10cm) were collected from the study area based on a 40m x 40m regular grid. The exact sampling points were located using a GPS (Fig. 2). A hand auger was used to collect a three-fold composite sample over a 1m^2 area at each sampling point. The sampling precision was estimated by taking sampling duplicates at 5m distance away from the initial sampling point in random direction, in order to reproduce variability accurately so that a realistic estimate of the sampling repeatability variance could be made. A total number of 8 sampling duplicates were also collected.

Test portions of all soil samples weighing 0.250 g each were prepared for chemical analysis by AAS in order to measure the concentrations of Pb and Cr. Analytical duplicates were prepared for each sampling duplicate, for the estimation of sampling and analytical precision. Reagent blanks and three certified soil reference materials were analysed at random positions between the sample test portions for the estimation of analytical bias.

4. Results and discussion

The statistical interpretation of analytical measurements focused on the study of two elements with contrasting properties at this site; Pb and Cr. These elements were selected so that comparisons of the results of the applied sampling methodology could be made. The statistical interpretation of the data was made after applying the quality control procedures discussed below. The frequency distribution for the mean Pb concentration at each sampling point show a positive skew and approaches a log-normal distribution. The concentration of Pb is generally high with an arithmetic mean of ~300μg g^{-1} and a maximum of ~2400μg g^{-1} in the soil. The distribution of Cr is less skewed with a mean of ~140μg g^{-1}. The descriptive statistics for Pb and Cr concentrations in the sampled area are summarised in Table 1.

Table 1. Descriptive statistics for Pb and Cr in µg g^{-1} based on the 49 collected samples.

Statistic	*Pb*	*Cr*
Mean	309	137
Median	114	136
Standard deviation	491	22
Minimum	30	96
Maximum	2394	198

Table 2. Measured concentrations of Pb and Cr (µg g^{-1}) in sampling (S1, S2) and analytical (A1, A2) duplicates.

		Cr		
Sample	S1A1	S1A2	S2A1	S2A2
C6	112	117	128	133
E12	125	132	150	142
G11	134	135	144	143
H19	169	178	166	156
I3	110	114	119	108
K11	128	129	121	125
K15	167	171	162	149
M8	105	109	119	118
		Pb		
C6	564	557	168	198
E12	42	66	78	108
G11	378	347	90	120
H19	1336	1313	1887	2008
I3	78	78	42	54
K11	120	60	84	102
K15	72	78	48	48
M8	48	54	60	54

Sampling and analytical quality control was applied to estimate only the random measurement errors of Pb and Cr. For this purpose a nested design of sample and analytical duplicates was used. Robust analysis of variance was applied to the concentrations measured for the sampling and analytical duplicates (Table 2) so as to estimate separately the geochemical, sampling and analytical variances ($s^2_{geochem}$, s^2_{samp}, s^2_{anal}) respectively. The technique was implemented using the computer program ROBAN. EXE, adapted from a published program (AMC, 1989) and available from the (UK) Royal Society of Chemistry web site.

The total variance is:

$$s^2_{total} = s^2_{geochem} + s^2_{samp} + s^2_{anal}$$

where:

s^2_{total} = the total variance
$s^2_{geochem}$ = the geochemical variance
s^2_{samp} = the sampling variance
s^2_{anal} = the analytical variance

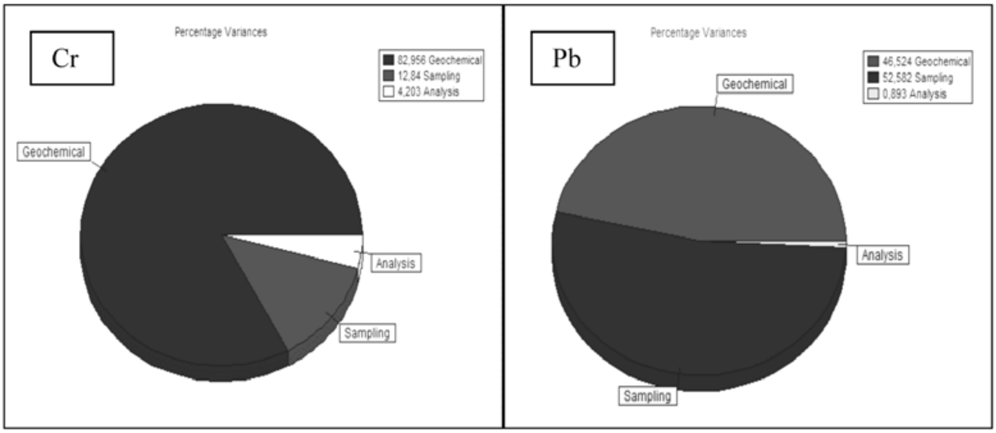

Fig. 3: Relative importance of measurement errors from sampling and analysis and geochemical variability, in the park of Skopeftirio, both expressed as proportions of total variance. Robust ANOVA estimates were used.

The proportions of the variances in the total variance were then calculated and displayed as pie charts (Fig. 3). The pie chart for the Cr variance in soil using the duplicate data shows that the analytical precision is acceptable as it contributes 4% to the overall variance and less than 20% to the measurement variance (Ramsey, 1993). Similarly the combined sampling and analytical precision was also acceptable contributing less than 20% to the overall variance.

For the Pb data, the analytical variance (0.9% over total variance) is well within the 4% limit but the high sampling variance of 52.6% of total, makes the measurement precision to be over the 20% acceptable for spatial interpretation of the concentration estimates. However, the mean concentration results can be interpreted within their stated uncertainties. The apparently high proportion of sampling error, in this case, is due primarily to the relatively low geochemical variance of Pb (46.5% of total variance).

The measurement uncertainty (u_R) caused by random variations (under reproducibility conditions) can be estimated from the combination of the sampling and analytical variance described above giving the measurement variance (s_{meas}) as:

$u_R = s_{meas} = \sqrt{(s^2_{samp} + s^2_{anal})}$

To express the extended random uncertainty (U_R) with a coverage factor k = 2 (for 95% confidence) this gives:

$U_R = k\ u_R = 2s_{meas}$

As uncertainty relative to the mean concentration x becomes:

$Ur\% = 200\ s_{meas}/\ x$

Where x is the estimated mean concentration of the analyte in the site. At this site the relative random uncertainty estimated from the 8 duplicate samples is 15 % and 169% for Cr and Pb respectively. The interpretation of this, assumes that it does not change as a function of concentration. The great difference between the uncertainties estimated for Cr and Pb is attributed to the differences in concentrations between the duplicate samples for each element. Specifically, the within location (sampling) variance for Pb in greater than the between location (geochemical) variance, while the opposite is observed for Cr. This in turn is related to the origin of Cr and Pb in the park soil and the subsequent degree of heterogeneity in heavy metal concentrations in the soil for the same spatial scale.

Lead which is dispersed in soil after the erosion of lead-shots is present within the park area only in few hot-spots, the dimensions of which may be smaller than the 5m distance separating the sampling duplicates. This extreme small-scale spatial variation is characteristic for Pb contamination in the site, contributing to the great magnitude of measurement uncertainty. For Cr, the relative measurement uncertainty is lower indicating a more homogeneous distribution of elemental concentrations. This is explained by the geological origin of this element which is dispersed in soil following the pedological processes influencing the release of the metal and its mobilization from the underlying basic rocks into the soil. Thus, the variability of the element in soil is captured by the 40 m distance separating the sampling locations. It should be noted that the analytical variance is insignificant compared to that of sampling for both Pb and Cr, indicating that chemical analysis is not a major source of error during the measuring process.

The estimates of random uncertainty for the sampling protocol used in the survey allow the assessment of its 'fitness-for-purpose' for this sampling target. 'Fitness-for –purpose' is defined as the property of data, produced by a measurement process that enables a user of the data to make technically correct decisions for a stated purpose (Thompson and Fearn, 1990). For Cr, since the proportion of measurement uncertainty contributes less than the empirical limit of 20% to the total variance, logistical factors, related mostly to the ease of applying the sampling protocol, have the main role in the selection of the most appropriate sampling scheme for the objective of estimating the mean metal concentration in the soil. For the particular field the optimal sampling scheme for this objective appears to be the regular grid because it is fast and simple to set up and should therefore be least prone to location errors. The grid size of 40m is also judged appropriate for delineating the Cr concentrations across the site. On the contrary for Pb, the used sampling protocol is judged as not fit-for-purpose because the magnitude of sampling variance exceeds that of geochemical variance. As a consequence it does not allow the realistic spatial interpretation of the Pb data across the site. In this instance a different sampling protocol has to be applied in order to delineate the element's concentration within the sampled area. Triangular grids are usually performing better when the aim is to delineate contamination hot-spots within an area.

5. Conclusions

This survey demonstrated that it is possible to estimate uncertainty in field sampling by using ANOVA following a nested design of sampling and analytical duplicates on an area of contaminated land. The heterogeneity of the elemental concentration within the sampling target affects the magnitude of precision and makes the sampling variance the dominant factor in the estimation of measurement uncertainty.

The performance of the sampling protocol has been evaluated and compared with criteria based on fitness-for-purpose considerations. The 40m x 40m grid used in this trial proved to be fit-for-purpose for Cr but suspect for Pb, using a fitness-for-purpose criterion of 20%. The main factor affecting the suitability of the sampling protocol is the degree of heterogeneity of the sampling target. A large degree of variation on the estimated mean was observed for Pb, showing the significant role of soil variability on the outcome of analytical measurements on site investigations. Estimates of the uncertainty associated with the sampling protocol could be made. In the instance of Pb, the large sampling precision dominates the total uncertainty. The main reason is the great variability in Pb concentration at the sample target related to its origin from the lead shots. This is contrasted to the more homogeneously distributed Cr concentration in soil related to the local geology.

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