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Lead Determination and Heterogeneity Analysis in Soil from a Former Firing Range

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Abstract. Public places can have an unknown past of pollutants deposition. The exposition to such contaminants can create environmental and health issues. The characterization of a former firing range in Athens, Greece will allow its monitoring and encourage its remediation. This study is focused on Pb contamination in the site due to its presence in ammunition. A dense sampling design with 91 location (10 m apart) was used to determine the spatial distribution of the element in the surface soil of the study area. Duplicates samples were also collected one meter apart from 8 random locations to estimate the heterogeneity of the site. Elemental concentrations were measured using a portable XRF device after simple sample homogenization in the field. Robust Analysis of Variance showed that the contributions to the total variance were 11% from sampling, 1% analytical, and 88% geochemical; reflecting the suitability of the technique. Moreover, the extended random uncertainty relative to the mean concentration was 91.5%; confirming the high heterogeneity of the site. Statistical analysis defined a very high contamination in the area yielding to suggest the need for more in-depth analysis of other contaminants and possible health risks.

1. Introduction

Bullet cores typically used in firing ranges are made mainly of Pb, which is a known pollutant with many effects on human health. Firing ranges, on the other hand, have shown high concentrations of different trace elements across the globe [1]–[3]. A threat to human health might be created when such firing ranges become restored and available for public use.

Characterizing a site allows to determine the extent and distribution of a suspected contamination in order to define its features e.g. concentration values, spatial distribution, heterogeneity. A proper characterization requires a sampling design that covers the study area as much as possible [4]. Likewise, the spatial heterogeneity of a contaminant in the soil allows to suggest its natural or anthropogenic nature through analyzing the uncertainty of measurements i.e. elements with low variability tend to have natural background concentrations. This can be achieved by estimating the uncertainty empirically from sampling using randomized replicated experiments [5].

A recent technique used for measuring metals in soils and sediments is portable X-ray fluorescence (XRF). This technique has the advantages of scrutinizing the measurements immediately, good detection limits, lower costs of analysis, and keeping an intact sample [6]. Approaches using portable XRF have been applied to soils, sediments, pollution variability, and elemental contamination through cities, among others [7]–[10]. This way, characterizing Pb using portable XRF appears as feasible and necessary.

In this paper, a case study is presented on a former firing range in Athens, Greece. The main focus is the analysis of Pb due to its presence in ammunition. The main objective of this work is to present the spatial distribution of the heavy metal and discuss its heterogeneity characteristics in order to propose its nature. To reach this aim, data from site investigation at an urban park in Athens is used. This type of preliminary site studies are of great help to perform subsequent environmental site assessments.

2. Methodology

2.1. Site Description

The study area is a public place located in the Skopeftirio Park of the Municipality of Kesariani, in Athens, Greece (see Figure 1). The area of the park is ~0.7 km^2, which is mainly covered by coniferous trees and grass. The history of the park began in the 1940's when it was used an execution place and years later when it was used for military purposes. During the 1980's, the same area was used as a shooting range for recreation. Nowadays, it is a historical monument of the city and many people gather around the area for leisure. Along the years, some areas have been modified and others, such as the one here studied, remain intact.

2.2. Instrumentation

Experiments were performed using reagent-grade chemicals and deionized water. Certified reference materials (CRMs) were obtained from NIST® and AccuStandards®. Blank samples consisted of clean silica sand. Portable XRF analysis was carried out using an Olympus Delta Premium 6000 device.

2.3. Sampling

The study area consists of ~0.9 ha. International regulations suggest that such extension can be characterized using a minimum of 10 samples [11]–[14]. However, international guidelines include the preparation of the sample and the use of an analytical technique to define the concentrations of the trace elements. This way, the present study follows a sampling design through a regular grid with 10 m square size, reaching 91 sampling points (see Figure 1).

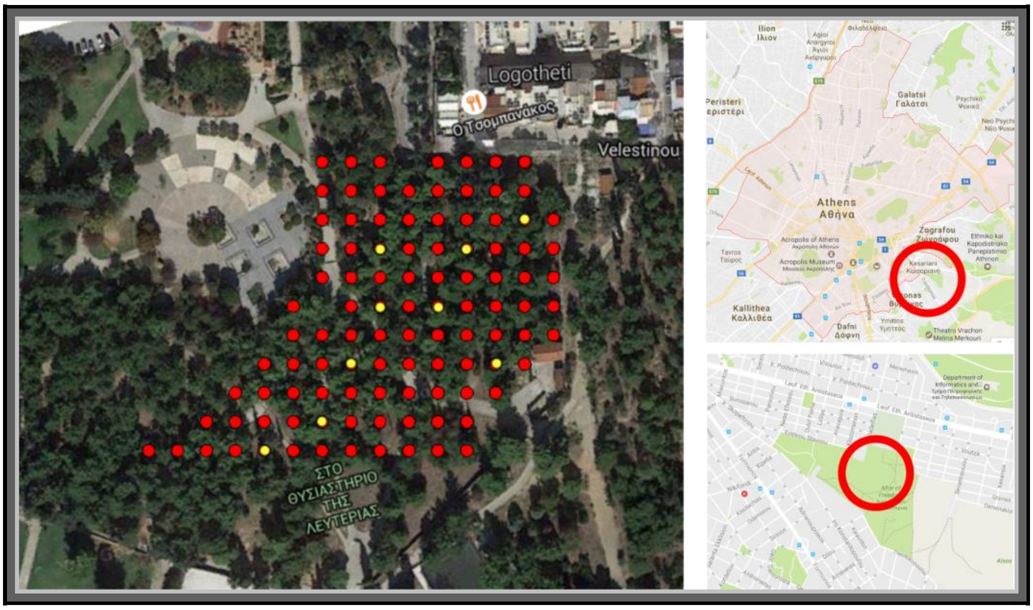

Figure 1. Locations of 91 sampling points for the study area. Sampling locations in red, additional duplicates in yellow. Referenced on the field with a GPS and long measuring tape. Maps data ©2016 Google.

2.4. Analysis by Portable XRF

Reading time for analysis was 90 s to quantify the target element Pb [15]. Calibration of the portable XRF device was held using CRMs: NIST® 2710, NIST® 2711a, AccuStandard® CRM025-050, and

AccuStandard® CRM023-050. CRMs and a blank sample were read repeatedly before and after the analysis of the soil samples every day. Measurements were taken during the first trimester of 2016.
Soil samples were collected with a spatula to dig through superficial soil. Any vegetation, gravel or debris was removed. An amount of ~400 g was placed in a polypropylene bag and labeled according to the sampling design. Each sample was homogenized by stirring and rotating the sample. Finally, a flat layer was formed and the analyzer was placed on top of the bag. All the tools were cleaned with distilled water in between analyzes to avoid contamination.

2.5. Data Analysis
Data obtained was summarized using mean values, medians, and standard deviations. Calculations were performed using Minitab®. Precision for the portable XRF analysis was estimated by measuring CRMs and calculating the relative standard deviation (RSD). Accuracy of the portable XRF analysis was done by reading CRMs repeatedly [15]. Moreover, in order to perform uncertainty analysis, eight duplicates were collected one meter away from random sampling locations (see Figure 2). Robust ANOVA was applied to the duplicated samples and thus the sampling precision, analytical precision, and geochemical precision were estimated using software package ROBAN from the (UK) Royal Society of Chemistry [16]. Finally, the extended random uncertainty relative to the mean concentration was calculated for Pb using equation (1) for 95% confidence, where s_{meas} is the measurement variance and x is the mean.

$$U_r\% = 200\ s_{meas} / x \quad (1)$$

3. Results and Discussion
Measurements of Pb concentrations in soil samples with a portable XRF device yielded the following results: RSD values ranged from 1 to 2% and mean recoveries were ~110%. Quality control procedures were followed in order to perform the statistical interpretation of the data. The frequency distribution for the concentrations followed a log-normal distribution. Pb values are positively skewed and are generally very high with a mean of more than 2,000 ppm, as can be seen in Table 1. A high variability can be readily seen as the standard deviation and coefficient of variation are also very high.

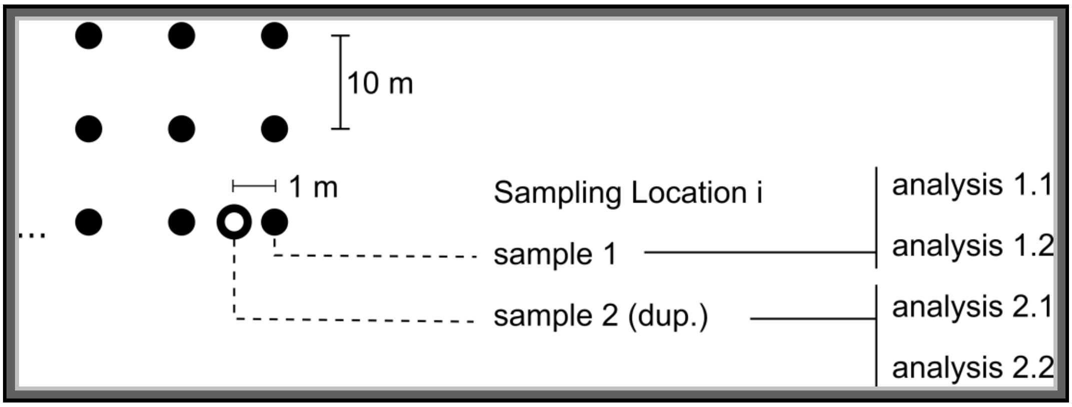

Figure 2. Scheme of duplicate sampling for uncertainty analysis. Modified from Argyraki and Petrakaki [5].

Table 1. Descriptive statistics for Pb based on 91 samples from the study area.

Statistic	Concentration (ppm)
Mean	2,021
Median	649
Standard Deviation	3,606
Skewness	3.725
Minimum	12.5

Maximum	24,824
CV	1.78
SE	378

The nested and duplicate sampling design (see Figure 2) was used in order to estimate the random measurement error for Pb. Sampling and analytical quality control was also applied. Table 2 shows the concentrations used in Robust Analysis of Variance applied to the Pb sampling and analytical duplicate samples in order to estimate the percentage of the total variance that can be attributed to the geochemical variance, sampling variance, and analytical variance. Such proportions were calculated and displayed in pie charts (see Figure 3). As shown in Table 2, the analytical variance (<1% of total variance) is lower than the maximum reference value of 4%. Similarly, the sampling variance (~11% of total variance) is lower than the reference value of 20% [17]. Both reference values work as a guide for an acceptable spatial interpretation of the element distribution. Finally, it can be noted that the high geochemical variance (~88%) is the main component of the total variance, which in turn will lead to a high degree of uncertainty. In fact, the extended random uncertainty relative to the mean concentration was calculated as 91.5%. This suggests that the nature of the trace element is indeed anthropogenic

It has been thought that Pb is only present in small spots across the study area [5],[18], however, it has been demonstrated that the contamination of the soil is extremely high and widespread. The dispersion of the element in the media, mainly due to erosion, is present in spots bigger than tens of meters wide. A very dense sampling design has been very useful to determine the distribution of a contaminant with such a high heterogeneity. It can also be stated that a very low level of analytical variance indicates that chemical analysis is not a source of error during the process and hence that the portable XRF device appears to be suitable for geochemical analysis in this case.

Table 2. Concentrations (ppm) of Pb according to the duplicate scheme from Figure 2 and results of Robust Analysis of Variance

Sample	Analysis 1.1	Analysis 1.2	Analysis 2.1	Analysis 2.2
C2	23,049	23,034	25,452	25,467
D4	2,445	2,433	1,067	1,069
D7	2,248	2,219	2,316	2,312
F5	8,020	8,097	6,976	6,963
F7	174	169	59	57
H3	1,629	1,641	176	180
H8	21	24.1	200	197
J9	24.7	24.9	301	292
K11	43.9	45.0	25.2	22.2
Robust ANOVA	Between target	Sampling	Analysis	Measurement
Std. deviation	2085.8	747.3	7.5	747.3
% of total var.	88.6	11.3	0.0	11.3

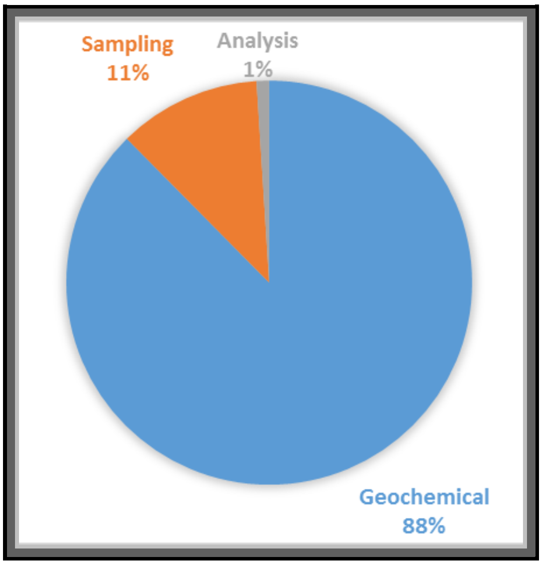

Figure 3. Sampling, analysis, and geochemical proportions of total variance for Pb using Robust ANOVA showing the relative importance of measurement errors.

The concentrations obtained and calculations performed allow to witness a realistic spatial interpretation of Pb across the study area. However, the high level and wide range of concentrations measured suggest that verifying some measurements can be useful. In this instance, the preparation of the sample and subsequent analysis using a traditional analytical technique will allow to compare and contrast the accuracy of the portable XRF technique. Likewise, a human health risk analysis will allow to determine the degree of risk to which the population is exposed by using the public area here studied.

4. Conclusion

A public space from Athens, Greece has been characterized for Pb contamination using a portable XRF device. A 10 m square grid used in this survey proved to be suitable to characterize Pb contamination using a 20% criterion. Robust Analysis of Variance performed over a nested design of sampling and analytical duplicates has allowed the determination of the uncertainty of the contaminant in the field. High Pb concentrations with high spatial heterogeneity have been reported. Results regarding Pb contamination will hopefully yield concerns for further studies.

5. Acknowledgments

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