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Trace element soil contamination at a former shooting range in Athens, Greece

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ABSTRACT

This study was focused on the determination of lead, zinc and nickel in a former shooting range in Athens, Greece. In order to propose a hybrid methodology, two analytical techniques were complimented, namely inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF). Analysis by ICP-MS was carried out over a minimum of locations following international sampling guidelines whereas analysis by XRF was carried out using a portable device and over a denser sampling design. After analyzing certified reference materials, the reliability of both techniques was Pb > Zn > Ni. Linear correlation analysis between techniques suggests that at least some degree of homogenization must be carried out in the field to achieve reliable results with XRF. Characterization maps were built using data from both techniques. A comparison of areas of concern led to the conclusion that the proposed hybrid methodology allows a highly efficient delineation of the contamination and that additional improvement in the characterization can be reached by correcting the XRF data by calibration against ICP-MS measurements.

1. Introduction

Contaminated soils from shooting range areas have been reported to have high concentrations of metals and metalloids such as lead, copper, antimony, mercury and zinc mainly from ammunition (Okkenhaug et al., 2016; Strømseng et al., 2009). As a result of urban growth and city development, old shooting ranges can become public areas like parks and squares, which could pose an emerging threat in health quality for the population that will use such facilities in the future (Filippelli et al., 2012). Governments around the world have set limits of metal concentrations in soil and sediments for residential and industrial areas, since the adverse effects of several metals and other elements on the environment and human health are well known (Ajmone-Marsan and Biasioli, 2010; Paulette et al., 2015; Sanjeevani et al., 2015). In particular, when inhaled or ingested, Pb is known to cause renal, cardiovascular, and neurological complications; Zn has been reported to cause anemia and digestive diseases; and Ni has been reported as a human carcinogen (ATSDR, 2015; OSHA, 2014; USEPA, 2000). As part of ammunition used in shooting ranges, bullet cores contain mainly Pb; and cartridges and cases comprise Zn and Ni (Ackermann et al., 2009).

The assessment of a site through its characterization determines contamination levels and remediation needs (Sorvari, 2011). The choice of the sampling design to be used is based on the extent of the site, its previous use, the natural concentration of a given contaminant in the site, and the overall purpose of finding the degree of contamination of the site (for instance, to comply with authorities' determinations) (Argyraki et al., 1997; CCME, 1993; Davidson and Williams, 2009; Victoria, 2009; NSW EPA, 1995; SEMARNAT, 2006, 2004; Theocharopoulos et al., 2001; USEPA, 1991).

Traditional methods demand the use of ex situ analytical techniques (i.e. samples must be collected, transported to the laboratory, prepared, and analyzed following an established analytical protocol). According to international organizations, one validated technique for defining concentrations of metals in soil is inductively coupled plasma mass spectrometry (ICP-MS) (OSHA, 2014; USEPA, 2014a). The advantages of applying such a conventional technique include the high accuracy and precision of the measurements, very low detection limits, and well-documented quality control processes. On the other hand, the disadvantages include a time-consuming and demanding process, the

Abbreviations: XRF, X-ray fluorescence; ICP-MS, inductively coupled plasma mass spectrometry; CRM, certified reference material; BS, basic sampling design; ES, extended sampling design; PS, primary soil samples; SS, secondary soil samples; TS, tertiary soil samples; RPD, relative percent difference; RSD, relative standard deviation

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destruction of the sample, the high cost per analyzed sample, and the fact that a sample taken may not be representative of the whole site (Myers, 1997; Paulette et al., 2015; Ramsey and Boon, 2012; Salmanzadeh et al., 2016; USEPA, 2015).

Sites presumably contaminated are not frequently characterized or studied because such processes demand both financial and time investment, and because regulations usually dictate the acceptable levels of metal concentrations of a site but do not define when to assess public spaces such as parks or roads, and hence these remain intact. Although there is still a perception that in situ techniques are less reliable than the ones made ex situ (Ramsey and Boon, 2012), alternative methods for soil characterization appear as a tempting option to obtain data faster in order to determine the extent of the contamination and consequent remediation decisions.

X-ray fluorescence is an alternative analytical technique that can be used in situ for the elemental characterization of contaminated sites. Its principle of operation is based on the energy released by the interactions between electrons and radiation. Portable X-ray fluorescence (PXRF) devices have been used lately in fresh soil and sediments to measure metal concentrations (Lee et al., 2016; Mejía-Piña et al., 2016; Peinado et al., 2010; Ramsey and Boon, 2012; Suh et al., 2016), to assess contaminant variability (Paulette et al., 2015), to map the distribution of elements across cities (Clark and Knudsen, 2013; Sun et al., 2017; Weindorf et al., 2013), and also for other purposes (Brunetti et al., 2016; Guimarães et al., 2016). The advantages of a portable device include the ability to take non-destructive measurements in situ and see the reading immediately, lower costs per sample, and the option to make an adaptive sampling design (Argyraki et al., 1997; Ramsey and Boon, 2012). An approach using PXRF constitutes a high-throughput technique for screening areas with expected contamination.

Recent studies have used PXRF for assessing soil contamination by trace elements based on international intervention levels and have produced a spatial representation of the results (Paulette et al., 2015; Peinado et al., 2010; Weindorf et al., 2013). Nonetheless, these works do not show a validation of the measurements taken using site-specific calibration standards. Therefore, in this work, the performance of an alternative in situ analysis by X-ray fluorescence is compared with an established method based on ICP-MS when characterizing a shooting range that became a public space, for Pb, Zn, and Ni. Both are later supplemented to define a hybrid characterization, which seeks to better delineate the contamination distribution of a trace element by combining the measurement of many samples in a rapid manner and a few samples with high accuracy.

2. Methodology

2.1. Study area description

The study area is situated in the Skopeftirio Park of the Municipality of Kesariani, about 3 km east of Athens center. The park has a total area of 0.7 km^2 of almost flat topography. The vegetation includes coniferous trees and grass areas. Recreational 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 World War II 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 50s and until the 80s different parts of the park have been used as shooting ranges for recreational purposes. Some of these areas have been remediated while others, such as the area used for the experiments of the present study, are left in their original state. The previous use of the latter 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 (Argyraki and Petrakaki, 2010; Petrakaki, 2009). Geologically, the area belongs to the Athens Unit which lithologically is comprised of solid, white, platform carbonates as well as some pelagic clastic sediments including bodies of mafic and ultramafic rocks and volcano-sedimentary tuffs (Papanicolaou et al., 2004). Field work for this study was fulfilled in the first trimester of 2016.

2.2. Reagents and instrumentation

All experiments were performed using reagent-grade chemicals and deionized water. Hydrochloric acid, nitric acid, and standard stock solutions used were obtained from Sigma-Aldrich. Certified reference materials (CRMs) were obtained from NIST® and AccuStandards®. Blank samples consisted of clean silica sand. PXRF analysis was carried out using an Olympus Delta Premium 6000 device (4W X-ray tube). Instrumental analysis was performed by ICP-MS using a Thermo Fisher X Series 2 instrument.

2.3. Sampling design

The collection of a statistically valid data set can be reached by following a systematic sampling design. Given the size of the study area, the number of sampling locations suggested by international regulations range between 10 and 20 (CCME, 1993; CDPHE, 2012; Davidson and Williams, 2009; Victoria, 2009; NSW EPA, 1995; SEMARNAT, 2006; Theocharopoulos et al., 2001). For the ICP-MS analysis, a basic sampling (BS) design was developed by generating a regular geometric pattern to locate sampling points at regular intervals. Systematic sampling was held through a square grid superimposed onto the study area (Fig. 1a). The square size was calculated using Eq. (1), where C is the square side length, A is the surface of the study area, and n is the number of sampling points planned (SEMARNAT, 2006). The square grid resulted in a 30 m spacing, as the study area is ~0.9 ha and 13 sampling points were proposed. The BS design shows a balance between the number of sample locations suggested by regulations and an efficient spatial distribution.

$$C = (A/n)\text{^}(1/2) \quad (1)$$

A higher number of sampling locations was covered by the PXRF analysis, using an extended sampling (ES) design that encompasses the aforementioned BS design. Systematic sampling was held through a square grid superimposed onto the study area with a grid spacing of 10 m in order to increase the number of locations in a uniform manner from 13 to 91 (Fig. 1b).

2.4. Analysis by PXRF

The PXRF measurements were calibrated daily using certified samples and under USEPA recommendations (2007). Measurements of CRMs were performed as first and last tasks of the day. CRMs used for calibration were NIST® 2710 (highly elevated trace element concentrations), NIST® 2711a (moderately elevated concentrations), AccuStandards® CRM025-050 (moderately elevated concentrations), and AccuStandards® CRM023-050 (medium concentrations). Readings with a time of 90 s were obtained to quantify main target elements in surface soil (i.e. Pb, Zn and Ni).

In the first instance, primary soil (PS) samples were analyzed without removal or preparation. Surface debris and vegetation were cleared away from each location in order to position the nose of the PXRF analyzer against the surface soil. A Prolene® thin-film was placed on top of the surface to obtain readings from each sampling location.

Secondary soil (SS) samples were collected by using a spatula to dig through superficial soil with ~20 cm radius and ~20 cm depth. Soil vegetation, gravel and debris were removed. A soil sample of ~400 g was removed for analysis and future reference. These samples were placed in zip-locked 500 ml polypropylene bags, labeled according to the ES design, and subsequently placed in a pail and mixed thoroughly by stirring and by rotating the pail at 45 degrees. Shaking of the