Validation of X-Ray Fluorescence Spectrometer Technique to Determine Heavy Metal Concentrations in Soil Samples

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Keywords: *heavy metals, soil, pollution, X-Ray fluorescent spectrometer, inductively coupled plasma – mass spectrometer, validation.*

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Jessica Briffa [α], Renald Blundell [σ], Emmanuel Sinagra [ρ] & Joseph Grech [ω]

Abstract- Heavy metal soil pollution had increased in recent years and this has produced adverse effects to human wellbeing's health by being uptaken in the food chain. A potential threat of heavy metal pollution was suspected at the Government Farm in Għammieri. This is due to heavy traffic and fireworks causing concern to the farmers who cultivate fruit and vegetables in these fields. Soil sampling with an instrument that can give rapid results was needed to analyse the data and give the real-time in-situ mapping of heavy metal pollution in the soil. Comparison between an X-Ray Fluorescent (XRF) spectrometer and an Inductively Coupled Plasma – Mass Spectrometer (ICP-MS), both of which are conventional analytical techniques, was performed to measure the heavy metals in the soil by using laboratory and field work. This was performed to make sure that the XRF that was being used, would give accurate results before testing larger sample size. The XRF used was situated at the Department of Chemistry, at the University of Malta, whilst the ICP-MS was situated in Germany, at an accredited laboratory. Five samples were collected from around the whole field, where each sample was split into 2 identical batches. Heavy metal concentrations were determined using the XRF by sample cup method and results were validated using the ICP-MS using aqua regi digestion. To identify heavy metals without processing the sample, XRF is the preferred method due to direct analysis of the sample and less analysis time. XRF analysis produced quantitative results which correlated with high linearity when compared to the accredited ICP-MS data using the Spearman correlation coefficient ($R2 = 0.811$).A strong positive relationship close to 1 for arsenic ($R2 = 0.646$) copper ($R2 = 0.888$), cadmium ($R2 = 0.202$), lead ($R2 =0.837$), nickel ($R2 = 0.513$) and zinc ($R2 = 0.699$) was observed, whilst no relationship of $R2=0$ for chromium and mercury. When using the binomial test, all the ρ-values exceeded the 0.05 level of significance, signifying that the mean XRF score is comparable and positively related to the ICP-MS data. The analysis showed that the ICP-MS validated the XRF results for heavy metal soil measurements and implies. that XRF is quicker and reliable to use when measuring heavy metals in soil compared to traditional methods.

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I. Introduction

Environmental pollutants and contaminants are chemicals found at a higher level than in any sector of the environment [1–4]. Industrialization has grown at an increased rate over the last few years. Thus, the request for utilization of the Earth's natural resources has increased at a careless rate, which has aggravated the Earth's problem regarding environmental pollution [5]. The environment has been critically polluted by several pollutants including inorganic ions, organometallic compounds, organic pollutants, radioactive isotopes, nanoparticles and gaseous pollutants .[2,4]

Heavy metals are defined due to their high density or high atomic weight. Currently the word 'heavy metal' is used to explain metallic chemical elements together with metalloids that are toxic to both the environment and to humans. Some light metals and metalloids are toxic, such as including arsenic, aluminium and selenium, though not all heavy metals are toxic such as gold[6–9].

Heavy metals have been present in the Earth's crust since the Earth's formation. Heavy metal use has increased exponentially and has resulted in a surge of metallic substances in both aquatic and terrestrial environments[5]. Anthropogenic activity is the prime cause of heavy metal pollution, primarily due to mining of the metals, smelting, foundries, and other metal-based industries, leaching of metals from a variety of sources like landfills, excretion, waste dumps, livestock manure, automobiles, roadworks, and runoffs. The secondary cause of heavy metal pollution is agriculture including pesticides, fertilizers, insecticides, and more. Natural activity is another source which can increase heavy metal pollution including volcanic activity, metal evaporation from land and water, metal corrosion, soil erosion and geological weathering. Unintended pollution of heavy metals is also possible these include shipwrecks, oil spills and fires. Intended pollution can take the form of waste disposable like industrial effluents and sewage disposal, and intended application of

biocides like vector controls. The movement of heavy metals in the Earth's spheres depends on temperature, direction and movement of surface waters, speed of wind and circulation of air mases. Other factors include partition coefficient, vapour pressure, polarity and molecular stability [1,2,4–6,10–12].

Deliberate soil pollution occurs through wastewater irrigation, the use of pesticides and fertilisers, animal manures, leaded paint, mine tailing, spillage of petroleum distillates, sewage sludge, coal combustion residues and waste dumping. Non-deliberate pollution can occur through the flooding or rivers and seas bringing sewage and contaminated waters to the land. This is in addition to accidents entailing vehicles conveying toxic chemicals. Microbial or chemical degradation cannot occur to heavy metals since they are non-degradable and thus remain in the soil for a very long time [1,2,4,13–16].

The ecosystem is in danger due to heavy metals entering the food chain. Their properties also affect the biodegradability of organic pollutants which causes them to become less degradable and consequently causing a twofold effect of polluting the environment. Heavy metals present in the soil cause all the biospheres to be at risk and are taken up through direct ingestions of the heavy metal or ingestions through food or water that contains the heavy metal after absorbing it. Uptake of the heavy metal may be affected by the soil property like pH, porosity, colour and natural chemistry [1,2,4,13–16].

Elements or chemicals which are not usually present, exist at higher level concentrations and cause damage to organisms, are termed as "soil pollutants". Modern technology such as agrochemical use, together with industrialisation, has caused several contaminants to be present in soil [17].

Soil contamination can be a deliberate action, such as using animal manure, fertilizers, wastewater irrigation, waste dumping, mine tailing, pesticides, sewage sludge and much more [1,2,13,15,16,18]. Watering agricultural land with untreated sewage and wastewater is one of the main complications of adding pollutants to the soil [15,18]. Some pollutants remain in the soil since they are non-biodegradable, thus they would not be able to undergo degradation even if it is chemical or microbial [2].

The soil's sorptive capacity is affected by the heavy metals' bioavailability. Metal can only be up taken in the ionic form by plants and soil biota. Due to the metal's affinity, they adsorb to surfaces of humus, calcium carbonate salts, iron and manganese hydrous oxides, together with clay minerals. Other metals can form complex compounds by having an affinity with organic molecules. A factor that affects the sorption process is pH, the less acidic the soil, the higher the sorption, whilst the higher the soil acidity, the more it is desorbed and released [17].

One of the ways to analyse the presence and concentration of heavy metals is through XRF spectrometry. Element analysis is recognised through the excitement of individual atoms through an external energy source, which goes on to release X-ray photons that emit energy or wavelength which is distinctive for each element. The energy released sets of several photons are used to identify and quantify the element present. Both solids and liquids can be analysed by the XRF, to analyse major and trace elements. Elements are identified under certain conditions through the release of distinctive radiation from the atom's inner electronic shells. Emitted quanta of radiation release X-ray photons which have specific energies, thus allowing for the atom's source to be identified. Since only the inner electron shells are involved during the X-ray emissions, the chemical bond is not taken into consideration. Samples have to be homogenous and refined to get good results when using powder form. Powder form has to be refined, as more than 50 μm in particle size can show errors of 50%. This is due to the variation of the extent of the X-ray penetration with energy [19,20].

II. Method and Materials

Five soil samples were collected from the fields of the Government Farm in Għammieri. A detailed map showing the location of the samples is given in figure 1. Each sample gathered comprised of a mixture of soil from five sites; the four corners of the plot together with the centre. The soil samples were placed in sterilized labelled plastic containers (A-E) and taken to the laboratory. The soil samples were air-dried at ambient temperature after being placed in plastic trays for 48 hours. These were then homogenised and sieved using a 45 μm mesh to remove any plant matter or stones that were present in the sample. Each of the five samples was then separated into two identical batches so that five were used for the XRF and the other identical five will be sent to be tested by the ICP-MS.

One set containing five samples was oven-dried for 24 hours at ~110°C using watch glasses. The process was carried out meticulously so that sample cross-contamination, as well as external contamination would not occur. The soil samples were then sieved again to make it more homogenous and finer and were then stored in sterilized plastic containers containing desiccators until further use.

Concentrations of arsenic, lead, cadmium, chromium, copper, nickel, mercury, thallium and zinc were determined using the S2 Ranger Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer situated at the laboratory of the Department of Chemistry, at the University of Malta. The XRF spectrometer was calibrated before each batch of the sample was placed in the instrument. A copper disc calibration was analysed first, followed by a quality check. Each sample

was prepared using the sample cup preparation. The sample cup was assembled using a 3.6 μm SpectroMembrane® Mylar® Thin-film. Each round consisted of around fourteen samples, where an average of 12 minutes was taken for each sample to be analysed. Each of the five samples was tested three times ensuring that the EDXRF was calibrated and provided reliable results. The data produced was semi-quantitative, and the elemental concentrations were then established by using a fitting method supplied by Bruker.

The second batch was tested at an accredited lab situated in Germany, using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The laboratory used was accredited according to DIN EN ISO/IEC 17025:2005 notification under the Deutsche Akkreditierungsstelle (DAkkS), the national accreditation body of the Federal Republic of Germany for testing. The standard ISO/IEC 17025:2005 stipulates, in both English and German, the general prerequisites for the competence to perform tests and/or calibrations, carried out using standard methods, laboratory-developed methods and non-standard methods[21]. The laboratory was (D-PL-14081-01-00) accredited. DIN EN 13657: 2003-01 standard was used for the aqua regia digestion which is the 'characterisation of waste - digestion for subsequent determination of aqua regia soluble portion of elements in waste'[22].

Statistical analysis was determined using the software package IBM® SPSS® Statistics 26 by comparing the results obtained by the two equipment. The data were compared by using the binomial test to calculate the ρ-value and its level of significance, and the Spearman correlation coefficient test which measured the strength of the relationship.

III. Results and Discussion

The five samples were analysed using both the XRF and ICP-MS. The quantification of the XRF data was attained by using the automatic Bruker S2 Ranger XFlash® technology which was equipped with an X-ray tube anode made of Palladium. Using tube voltages of 10 kV, 20 kV, 40 kV and 50 kV, for 180 seconds, at each voltage with a helium atmosphere, a current of 2 mA, and having a silicon drift detector. The elements detected in the soil samples were expressed as oxides. Calcium carbonate was used as a matrix to calculate the heavy metal oxides, while using the instrument's software, Spectra EDX Launcher, to read the data.

The XRF method provided a simultaneous result of 44 elements, though only As, Pb, Cd, Cu, Ni and Zn were used to compare the results with the same elements as those given in the ICP-MS report. Table 1 shows the comparison of the mean values between the XRF and the ICP-MS which were used to statistically test the data. The binomial test confirmed that the XRF data

are positively related to the ICP-MS as all the ρ-values exceeded the 0.05 level of significance as seen in table 2. The Spearman correlation coefficient used to compare the relationship can be seen in figures 2-5 where figure 2 and 3 display a strong positive relationship close to 1 for arsenic ($R^2 = 0.646$) copper ($R^2 = 0.888$), cadmium ($R^2 = 0.202$), lead ($R^2 = 0.837$), nickel ($R^2 = 0.513$) and zinc ($R^2 = 0.699$), whilst figure 4 displays no relationship of 0 for chromium and mercury. The overall correlation was a strong positive relationship where $R^2 = 0.811$.

The results indicated that the XRF and ICP-MS are comparable and that the XRF produces good results when compared to an accredited instrument. The ICP-MS when compared to the XRF can be seen to be a very reliable instrument that can accomplish limits of detections at many orders of degree lower. Although it has excellent accuracy, the ICP-MS has a disadvantage that the sample needs to be in a liquid form when being tested, thus requiring acid digestion and long preparation times, when comparing it to the other instrument. The ICP-MS also has a higher cost including the consumables. On the other hand, the XRF spectrometer is cheaper to use, easier, and uses a rapid technique when comparing it to other methods of analysis. It has the advantage of reading both the solid and liquid form [23].

The ICP-MS is a quantitative instrument and has been increasing in popularity compared to the other instruments. Its detection limits can reach below the single part per trillion of any element, and it can also achieve isotopic analysis. Determination of each element's concentrations in the sample is brought about by relating the counts measured of a definite isotope with an external calibration curve that was formerly created for that specific element [24,25].

The XRF is a semi-quantitative instrument. The data given ascertains the relative element concentrations between the samples though it does not give absolute concentration amounts. The results are calculated by analysing the area under the peak of interest. This proves why the results of both instruments are non-identical and not similar to the elements being tested as seen in Table 1[26].

When comparing the mean concentration of the elements (table 3), to the Government Decree on the Assessment of Soil Contamination and Remediation Needs the threshold limits for soil contamination [27]as seen in table 4, As, Pb and Cd proved to have a higher level than the threshold. These three heavy metals are used in everyday life and cause a number of adverse effects when present in high concentrations as in the study.

Anthropogenic pollution of As could be caused through the preservation of wood, certain insecticide formulations, particular glass manufacturing, doping agent in semiconductors like gallium arsenide which

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was used to alter electric current into laser light; pyrotechnics and the production of bronze. Adverse effects of arsenic to humans can be subdivided into two. Inorganic arsenic toxicity can cause lung irritation, gastro-intestinal system irritation, skin alterations, reduction in production of red blood cells and white blood cells, lung irritation, infertility, miscarriages, brain damage, heart problems, suggestion of increased chances of carcinoma have been stated and damage to the deoxyribonucleic acid (DNA). Organic arsenic toxicity may cause stomach upsets and nerve damage (though it does not affect the DNA and is therefore not carcinogenic) [28–31].

Uses of lead which might have caused pollution are car lead-acid batteries, ammunition and projectiles, cable sheeting, sports equipment, screen sheets on computers for radiation safeguarding, lead crystal glass, roofing in buildings, stained glass windows, canister to hold corrosive liquids, lead piping and diver's weight belt. It has also been used in the past in hair dyes, insecticides and pottery glazes. Human uptake of high concentrations of lead may cause hypertension, still births, miscarriages, premature and low births, sperm damage, peripheral nerve damage, renal impairment, brain damage, pica, signs of encephalopathy, cognitive impairment, haemoglobin synthesis disruption causing iron deficiency and abdominal pain. Children may also suffer adverse effects due to high lead concentration uptake, which causes reduced intelligence, altered brain and CNS development, increase in anti-social behaviour, a reduction in attention span and an educational achievement decline [30,32–35].

Cadmium is used in pesticides, Ni-Cd batteries, phosphate fertilizers, nuclear reactors, pigmentation for glassware, corrosive-resistant plating and as a stabilizer in the production of plastic. The adverse caused in high concentrations affect mainly the kidneys causing nephrotoxicity. Other adverse effects can also be calcium metabolism alterations, bone fractures, osteoporosis, immune system deficiencies, CNS complications, psychological disorders, gastro-intestinal disorders, infertility due to reproductive system failure, DNA impairment, cancer, stated to be genetoxic and ecotoxic in animals, and Itai-Itai disease[30,36,37].

IV. Conclusion

Heavy metal soil pollution has been seen to contaminate agricultural fields due to increase in livestock and agriculture, sewage effluent, industrialisation, infrastructure, transport, urbanisation, fireworks, mining activities and warfare actions[4].Agriculture, industrialisation and fireworks are the probable cause for the farm to be polluted by these heavy metals. The results confirmed that the farm had high heavy metal pollution in As, Cd and Pb since the concentration was more than the threshold given by the Ministry of Environment in Finland. The XRF has been increasing in popularity especially since it is less time consuming, does not need any sample preparation, together with it being less costly. Samples are always 'neat' and do not need any preparation unlike the ICP-MS which needs chemical preparation of the sample. The study proved to validate the XRF and provide results that were similar and statistically significant to the ICP-MS, concluding that the XRF was reliable to test soil samples concerning heavy metals on a larger scale. This would be beneficial if it were to test agricultural soils making it be of use to help prevent heavy metal pollution from ending up being taken up by crops and thus, end up in the food chain.

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