Heavy Metals in Maltese Agricultural Soil

"submitted in partial fulfilment
of the requirements of the
Master of Science in Biochemistry"

Jessica Briffa
2020

EU funds for Malta | 2014 2020

The research work disclosed in this publication is partially funded by the Endeavour Scholarship Scheme (Malta). Scholarships are part-financed by the European Union - European Social Fund (ESF) - Operational Programme II –Cohesion Policy 2014-2020 "*Investing in human capital to create more opportunities and promote the well-being of society*".

European Union –European Structural and Investment Funds
Operational Programme II –Cohesion Policy 2014-2020
"Investing in human capital to create more opportunities and promote the well-being of society."
Scholarships are part financed by the European Union - European Social Funds (ESF)
Co-financing rate: 80% EU Funds; 20% National Funds

Acknowledgement

I wish to express my sincere appreciation to my supervisor, Professor Renald Blundell, for the motivation to start this course, the encouragement and help, throughout the course. My heartfelt gratitude goes to my co-supervisor Professor Emmanuel Sinagra, for his advice and support, throughout these two years.

I would like to thank Mr Joseph Grech for helping me understand how to use and interpret the X-Ray Fluorescence spectrometer and for his help and patience throughout the research journey.

Special thanks go to the individuals who provided me with the soils to analyse since, without their help, this study would not have been possible. Thanks go to the Department of Agriculture for their support, primarily to conduct the pilot study.

Last but not least, I would like to express my thanks and gratefulness to my mother, father, brother, sister-in-law, and Florin, who have been so supportive during these years and have been there for me throughout it all. I would not have managed without them. Thanks go to my friends Nicolette Sammut, Stephanie Smith and Maria Calleja for their continuous support and motivation throughout this journey.

Abstract

Soil pollution has increased over the last few decades due to anthropogenic sources. Heavy metal pollution has been of great concern since it has been noted that these contaminants have entered our food chain. High concentration of heavy metals can adversely affect the health of the public wellbeing. The aim of the study was to evaluate whether i) heavy metals found in soil are present in high amounts; ii) heavy metals found in soil are present differently across Malta and Gozo; iii) there are soil limits regulating heavy metals. The soil samples were analysed with an X-Ray Fluorescence Spectrometer using the sample cup method. The method of analyses was validated by comparing it to the results obtained in an external laboratory. The samples were analysed to determine the concentration of heavy metals, namely aluminium, vanadium, chromium, cobalt, manganese, nickel, copper, zinc, molybdenum, arsenic, silver, cadmium, selenium, mercury and lead in soil. Samples were collected from five districts in Malta and from Gozo. A total of 103 samples were collected and analysed, out of which two samples were collected from organic farms and used as controls. Samples were analysed in triplicate and an average was calculated. Most of the soil samples tested showed that the heavy metals found in the soil were observed to be present at higher concentrations in the South-Eastern District and the Southern Harbour. Concentrations of the heavy metals tested were mapped out according to district and localities. The highest concentration of aluminium was found in the Western District at 38106.00 mg/kg. The highest concentration of lead was observed in the Southern Harbour and was statistically significantly (ρ-value<0.05) different from the rest of the districts with a concentration of 249.51 mg/kg. Other metals that were found at their highest concentrations in the Southern Harbour, were copper at 95.15 mg/kg and zinc at 251.33 mg/kg. The heavy metals vanadium at 64.25 mg/kg, chromium at 45.93 mg/kg, manganese at 586.67 mg/kg, nickel at 21.90 mg/kg and selenium at 15.51 mg/kg, to be observed at their highest concentrations in the South-Eastern District when compared to the other districts. The highest concentrations of molybdenum at 12.09 mg/kg, arsenic at 7.93 mg/kg and cadmium at 30.10 mg/kg were observed in the Northern District. Cobalt was seen with the highest concentration in the Gozo and Comino District, at 15.83 mg/kg. The Finland and Dutch standards were used to compare the results observed. Lead was found to exceed the threshold limits of the Finland standard which is 60 mg/kg and the Dutch standard which is 85 mg/kg. Cadmium was observed to exceed the threshold value of the Finland standard which is 1 mg/kg and the Dutch standard which is 0.8 mg/kg. The Finland standard concentration of arsenic is 1 mg/kg, which was much lower than the concentration observed in the Northern District. Zinc was found to exceed the threshold limits of the Finland standard which is 200 mg/kg and the Dutch standard value which is 50 mg/kg. The lower concentration of heavy metals observed in organic farms may be attributed to the lack of chemical use whereby instead biodiversity is applied to aid in pest and weed reduction. There is a need for the implementation of methods to address the high concentrations of heavy metals. Such methods which can be applied include phytoremediation, intercropping and organic farming.

Table of Contents

List of Tables

List of Figures

List of Abbreviations

ATP	Adenosine Triphosphate
ATSDR	Agency for Toxic Substances and Disease Registry
COPD	Chronic Obstructive Pulmonary Disease
DDT	Dichlorodiphenyltrichloroethane
DNA	Deoxyribonucleic acid
EDXRF	Energy dispersive X-ray fluorescence
EU	European Union
GPS	Global positioning system
HCHs	Hexachlorocyclohexanes
HDL	High-Density Lipoproteins
IAEA	International Atomic Energy Agency
IARC	International Agency of Research on Cancer
ICP-MS	Inductively coupled plasma mass spectrometry
ICAO	International Civil Aviation Organization
IPPC	Integrated Pollution Prevention and Control
ISRIC	International Soil Reference and Information Centre
LAU1	Local administrative units, level 1
NSO	National Statistics Office
NUTS	Nomenclature of Territorial Units for Statistics
PAHs	Polycyclic Aromatic Hydrocarbons
PBBs	Polybrominated Biphenyls
PCBs	Polychlorinated Biphenyls
PCDDs	Polychlorinated Dibenzidioxins
PCDFs	Polychlorinated Dibenzoflurans
PCPs	Personal Care Products
PM	Particulate Matter
PPCPs	Pharmaceuticals and Personal Care Products
ppm	Parts per million
RNA	Ribonucleic acid
TCDD	2,3,7,8-Tetrachlorodibenzo-p-dioxin
U.S.	United States
UNDP	United Nations Development Programme
UNEP	United Nations Environment Programme
WHO	World Health Organisation
XRF	X-ray fluorescence

Chapter 1: Introduction

1.1 Soil Formation and Composition

Soil formation is a time-consuming progressive process and is a precious natural resource. It is known as pedogenesis and is dependent on a combination of processes occurring at the top of the soil, which includes physical, anthropogenic, chemical and biological processes. Soil is composed of weathered rocks which are the mineral particles, together with water, air and organic matter, all of which are easily affected by anthropogenic activity. The minerals present in the soil, which are derived from the weathered rocks, experience changes where secondary minerals are formed together with other sporadically water-soluble compounds. These elements are translocated from one region of soil to another through animal activity and by water (Environment & Resources Authority, 2016a). All the translocation and transformation of the minerals throughout the soil causes distinct soil horizons (Environment & Resources Authority, 2016a; Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

The physical properties of soil consist of six characteristics which include the colour, texture, consistency, structure, horizonation and bulk density, while the soil chemical properties consist of two characteristics, namely the soil's pH and its cation exchange capacity.

Soil horizons are developed during soil genesis, which produces different layers that vary in colour and texture compared to the layer above and below. The soil colour depends on three properties which comprise of the amount of iron oxide found in the soil, the amount of organic matter and the amount of moisture present. The texture depends upon the quantities of the soil "separates" which consist of sand, clay and silt. Sand and silt do not play any role in the soil since they do not partake in the mineral or water retention. Clay is the only separate that contributes to the soil, by attracting water and ions due to its surface charge. Soil structure can be defined as the aggregation of the soil separates into discrete structural units known as “peds”, which can be found in repeating patterns. Pores can be present between the structural units where air and water can pass. The structural shape in the soil horizon describes the type of soil structure, and the proportion of soil weight compared to the volume describes the bulk density of the soil. The last characteristic of soil is consistency. Consistency depends on the moisture content present in the soil. It describes the effortlessness of crushing an individual ped. Soil consistency can be divided into three types and is described as moist soil, wet soil or dry soil (Brady, 1990).

Soils are essential for agricultural purposes as they are the medium through which crops are grown. Natural causes such as heavy storms and winds may lead to soil erosion and can sometimes displace the amounts of soil. Soil erosion displaces mainly the top horizon of the soil, but sometimes the whole profile is compromised causing issues when coming to food security, biodiversity and climate change desertification (Environment & Resources Authority, 2016a; Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Malta and its sister islands Gozo and Comino, have a total area of 316 km^2 of land (NSO, 2019). Between the islands there is 41% of agricultural land, where Gozo and Comino have 46.9% of agricultural land and Malta has 35.2% (NSO, 2019). Forage plants are the popular component in arable land in both Malta and Gozo, followed by vegetables and fallow land. Vineyards, citrus, fruit and berry plantations and olive plantations are found to be the top permanent crops (NSO, 2019). Farming land is found scattered all over the islands, and each area has a different type of soil with different characteristics and different elements.

The Maltese Islands have different types of soils regardless of the archipelago’s small territorial extent. D.M. Lang was the first person to create a map of Malta’s soil in 1956-1957

(Sammut, 2005). He established that the different soils result from local geology, are extremely calcareous and are chemically closely correlated (Sammut, 2005).

Maltese soil has a distinctive pattern that is very intricate. A single field may contain different soil types, and the nearby agricultural land may have a different type. Different soil types have come about due to three prime human factors which are intertwined and are (i) urbanisation; (ii) excavated soil transportation from construction sites (*Fertile Soil (Preservation) Act*, 1973); and (iii) the replenishment of shallow or eroded soils or soil that has been subjected to human interference (Sammut, 2005).

The archipelago’s soils are slightly-moderately alkaline, and two-thirds of the island’s soils are problematic to work since they have a high clay content which may amount up to 48%. On the other hand, these soils have a higher water filtration capacity and a greater nutrient retention capacity (*Malta Environment & Planning Authority state of the environment report*, 2005).

A map was drawn up to show the different types of soils due to the different types of rock present which influences the soil’s minerals. Most of the land can be seen to be globigerina limestone (Figure 1).

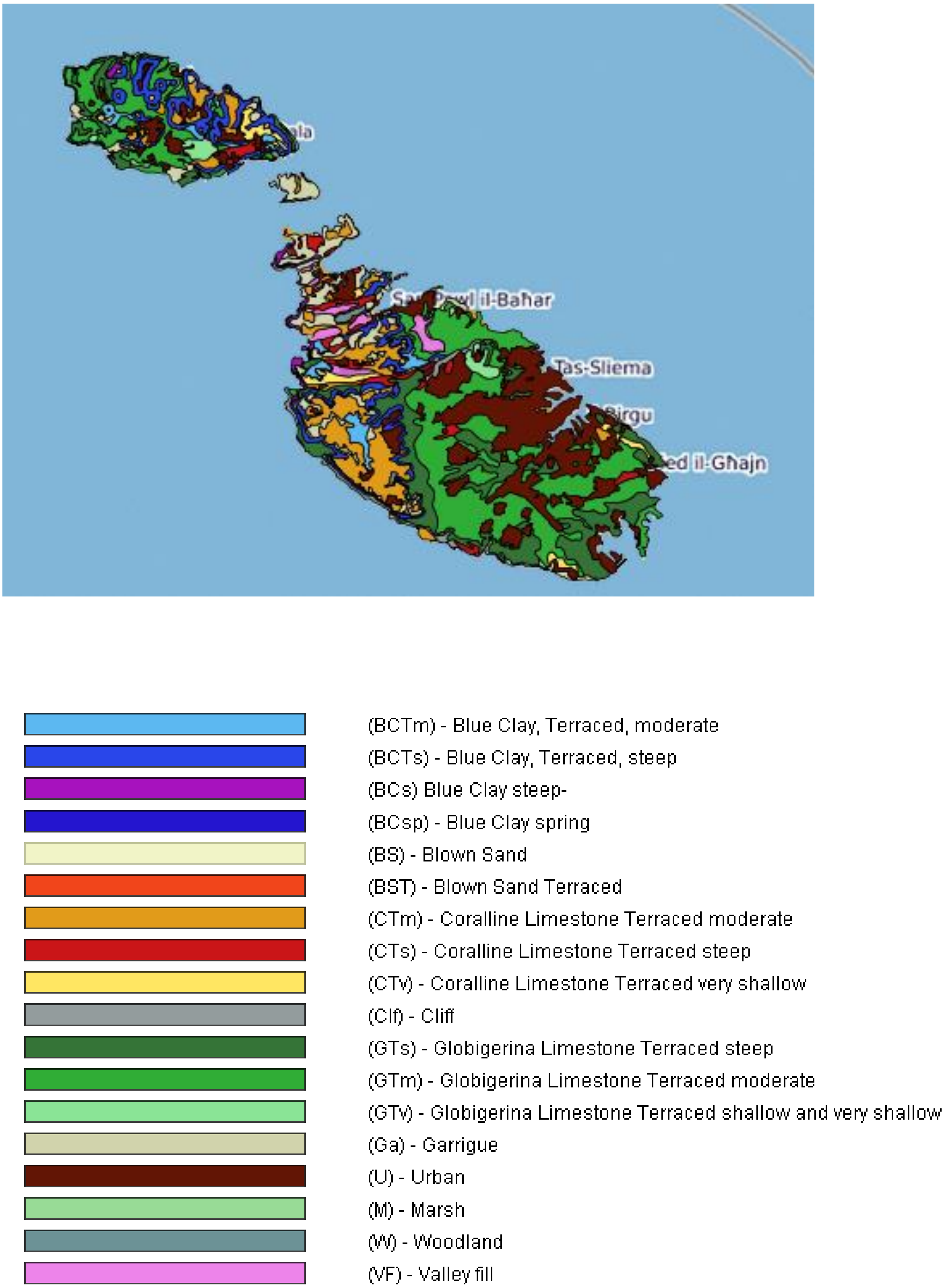


Figure 1: Different Soils which can be found in Malta, Gozo and Comino (MALSIS, 2004).

A variety of soil biophysical functions include several properties such as nutrient cycling, water dynamics, and filtering plus buffering, physical support and physical stability to the plants' system as well as human structures, habitat for organisms and biodiversity promotion. For soil to deliver its functions, the condition of the soil's properties has to be taken into account (Hatfield, Sauer and Cruse, 2017).

Soil function has led to a degradation of the soil, due to agricultural practices that are being used today to increase the amount of crop yield being grown. The soil has degraded due to wind and tillage, erosion due to overwatering, salinization and sodification, organic carbon reduction, the decline in soil biodiversity and most of all through soil contamination (MacEwan, Dahlhaus and Fawcett, 2012; Baishya, 2015). There are three types of soil degradation which are known as physical, chemical and biological (Baishya, 2015).

Physical degradation is caused by tillage and heavy machinery which leads to a restriction in root growth, limits the amount of water and air kept by the soil, and structural deterioration of the soil (Baishya, 2015).

The main culprits of chemical degradation are fertilizers, pesticides and the quality and management of water used. These factors lead to a reduction in water availability in the soil, structural deterioration of soil, environmental pollution and toxic salt effects (Baishya, 2015).

Biological degradation is caused by reduced biodiversity and organic matter depletion affecting the carbon cycling in the soil, which has an impact on the physical degradation of soil and nutrient and water regulation processes (Baishya, 2015).

1.2 Soil Pollution

The term “soil pollution” refers to the presence of an element or chemical that is found in soils that do not have the element or chemical usually present, or found at a higher concentration level than usual, which can cause adverse effects on any organism. Since soil pollution is not something that can be seen by the naked eye, it makes it even more dangerous. A variety of contaminants are continually being evolved as a result of agrochemical use and industrialisation (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Soil contamination and soil pollution have sometimes been used interchangeably, though they do not have the same meaning. Soil contamination is used when describing the concentration of a substance or chemical which is present at a higher concentration than it would have been found typically and does not cause any harm. On the other hand, soil pollution refers to the presence of substances or chemicals that are not usually found naturally and are present at a high concentration which will cause adverse effects to an organism (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). Determining a threshold may vary from country to country. When taking heavy metals and metalloids into consideration, other factors have to be seen, such as the rate of weathering of rocks which may release a more significant number of heavy metals into the soil. Other factors such as threshold values, screening values, target values, acceptable concentrations, intervention values and many more can affect the threshold value between countries (Carlon, 2007; Jennings, 2013; Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Industrialisation, has had a significant impact on the utilisation of earth’s natural resources over the last hundred years, which has aggravated environmental pollution, together with agriculture and livestock, mining and wars. The environment has been polluted by a variety of contaminants such as organic and inorganic ions, radioactive isotopes, organometallic compounds, nanoparticles and also gaseous pollutants (Bundschuh *et al.*, 2012; C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012; Gautam *et al.*, 2016; Rodriguez-Eugenio, McLaughlin and Pennock, 2018). Unfortunately, Malta's soils have been contaminated through a variety of factors such as industrial waste dumps; quarries; lead shot; car and plane exhaust emission; acid rain; agriculture chemicals such as pesticides, snail and rat poison; and manure application. Soils also have been eroded through salt, water and the addition of nutrients (Sammut, 2005; MacEwan, Dahlhaus and Fawcett, 2012).

All these contaminations have added compounds and elements to the soil that are not naturally found and which can cause harm to the vegetation growing, along with the end-user of the product. Such elements are heavy metals. Zinc has been found in excess at 200 mg/kg in 7% of Maltese soils. Lead concentration was found in 25% of the soils with values of more than 100 mg/kg. 3% of the soils have been seen to have copper which exceeded 100mg/kg (*Malta Environment & Planning Authority state of the environment report*, 2005).

Soil pollution has been recognised as the third most significant risk to soil functions in Eurasia and Europe and is an alarming problem. It is found to be the fourth and fifth risk to soil functions in North Africa and Asia respectively, seventh and eighth in Northwest Pacific and North American while ninth in sub-Saharan Africa together with Latin America (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

In the 1990s, the International Soil Reference and Information Centre (ISRIC) together with the United Nations Environment Programme (UNEP), had done a global estimation of the total amount of soil that was polluted which amounted to an average of 22 million hectares (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). The amount of soil polluted was then thought to be an underestimation of the real amount of soil pollution. Some countries have investigated their soil pollution, which has brought about informative data.

However, low-income countries have not reported any data till this time which does not reflect the real data of soil pollution across the world (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). In the European Economic Area, together with West Balkans, around three million possibly polluted sites are present (Van Liedekerke *et al.*, 2014). The Chinese Environmental Protection Ministry has also acknowledged that 16.1% of the Chinese soils exceed the general pollution limits, along with 19% of agricultural soils where confirmed as polluted. Australia has confirmed that they have an estimation of 80,000 contaminated sites (Department of Environment and Conservation, 2010; CCID, 2015). The United States (U.S.) of America has confirmed that they have more than 1,300 contaminated soils (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Numerous countries, have implemented or are in the process of implementing national regulations to safeguard their soils, thus preventing pollution and tackling significant problems of contamination. One of the main topics discussed during the Estonian Presidency, in the second half of 2017 of the Council of the European Union, was soil. Soil was discussed concerning food production and its vital role (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Soil pollution can be caused by a single identifiable source, called point-source pollution, such as industrial effluent and shipwrecks. On the other hand, soil pollution can be caused by mostly dispersed and detached sources of pollution, called non-point source pollution or diffuse pollution such as urban runoffs (Li, 2014; Tarazona, 2014).

1.2.1 Point Source Pollution

Point-source pollution is mainly caused through anthropogenic activities which release pollutants into the soil, and the source is identified effortlessly. It is quite widespread in urban areas. Activities which lead to point-source pollution comprises of factory sites, uncontrolled landfills, waste disposal, and extreme use of agrochemicals, mining and smelting which are conducted using inadequate environmental guidelines. These usually are a source of heavy metal contamination in many parts all over the world (Mackay *et al.*, 2013; Lu *et al.*, 2015; Strzebońska, Jarosz-Krzemińska and Adamiec, 2017). Oil spills are a source of aromatic hydrocarbon pollution, together with toxic metal. Examples of oil spills around the world are the Greenland oil tanks, whereby these tanks used small amounts of oil daily, which caused an exceeded release of aromatic hydrocarbons and toxic metal compared to the Danish environmental quality criteria (Fritt-Rasmussen *et al.*, 2012). In Tehran, there was an accidental leakage of oil from the oil refinery storage tanks, which caused a release in aliphatic hydrocarbons (Pourang and Noori, 2014; Bayat *et al.*, 2016). Old landfills sometimes had waste disposed of which were not controlled or not disposed of properly, including but not limited to batteries, medicines and radioactive waste (Karnchanawong and Limpiteeprakan, 2009; Baderna *et al.*, 2011; Swati *et al.*, 2014). High concentrations of polycyclic aromatic hydrocarbons, heavy metals and other elements, are found at high concentrations in the soils that are near roads due to road dust, traffic emission, domestic emission, industrial emission, weathering of pavements and building surface and so on (Wei and Yang, 2010; Hua Zhang *et al.*, 2015; Kumar, Kothiyal and Saruchi, 2016; Kim *et al.*, 2017). Sewage sludge and wastewater not disposed of properly are also classified as point-source pollutants (Marttinen, Kettunen and Rintala, 2003; Tikilili and Nkhalambayausi-Chirwa, 2011; Kalmykova *et al.*, 2013)

1.2.2 Diffuse Pollution

Before pollutants are transferred directly to the soil such as point-source pollution, diffuse pollution transpires. Where released, transformation and dilution of the pollutants transpire in other media (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). Diffuse pollution may be harder to track, analyse and restrict its spatial extent, as it comprises of the transfer of pollutants through the air-soil-water systems. Thus a sophisticated analysis is needed involving these three systems (release, transformation and dilution) to sufficiently evaluate the type of pollution (Geissen *et al.*, 2015).

Source of diffuse pollution are (i) uninhibited waste disposal and contaminated sewages expelled in and near catchments; (ii) nuclear power activities; (iii) weapons activities; (iv) sewage sludge application on lands; (v) flooding; (vi) soil erosion; (vii) tenacious organic pollutants; and (viii) agricultural use of fertilizers, manure and pesticides, which add heavy metals, higher concentrations of nutrients and agrochemicals. Human health is severely impacted by diffuse pollution and additionally impacts the environment. Severity of the effect and extent of the impaction, are largely not known (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). The soils' top layer is enriched by many pollutants due to atmospheric deposition from both natural and anthropogenic pollution (Steinnes *et al.*, 1997; Blaser *et al.*, 2000; Steinnes, Berg and Uggerud, 2011).

Due to the Chernobyl bomb in 1986, radionuclides are present at a high concentration in the northern hemisphere compared to background levels, and the radionuclides will be present for many centuries. Since there are different sources of pollution, new methods are needed to measure and monitor the atmospheric deposition processes together with the degree of diffuse pollution (Fesenko *et al.*, 2007). After the immediate effect of the atomic bombs of Hiroshima and Nagasaki, which included the plutonium in the bomb to undergo fission, an enormous amount of energy have been released. The energy released created a blinding flash together with temperatures growing to 10 million degrees Celsius. The electromagnetic radiation then formed a fireball where the wind created from the blast, destroyed everything in its wake. The extreme temperatures from the radiation burnt everything. The detonation created a radioactive dust which descended into the surrounding area. Currents of wind and water carried the radioactive dust further out from the explosion which then contaminated more soils, water and the entire food chain. Radionuclides have been present ever since the Chernobyl accident, atomic bombs and testing of nuclear weapons by the military have occurred (The Committee for the Compilation of Materials on Damage Caused by the Atomic Bombs in Hiroshima and Nagasaki, 1981).

1.3 Source of Pollution

As previously stated, there are two types of pollution sources; natural and anthropogenic sources.

1.3.1 Natural Source of Pollution

Soil pollution should take into consideration the baseline of the soil depending on the pedo-geochemical fraction together with the dynamics of the environment which formed that particular soil (Horckmans *et al.*, 2005; Paye, Mello and Melo, 2012; Rodriguez-Eugenio, McLaughlin and Pennock, 2018). Baseline values, at any given point in the superficial environments, indicates the value of the genuine content of the element. Background values show the geogenic natural content of the element (Salminen and Gregorauskiene, 2000; Reimann, Filzmoser and Garrett, 2005). Concentrations of heavy metals in soils, depending on the natural difference in the trace metal concentration in the parent rock, can differ from two to three orders of magnitude (National Research Council, 1977). Many parent rocks are natural sources of several heavy metals together with other elements including radionuclides. The volcanic rock contain arsenic, thus weathering of volcanic rock increases the amount of arsenic (Albanese *et al.*, 2007).

Volcanic eruptions, forest fires, meteorites and dust storms are natural events that cause natural pollution where several toxic elements such as polycyclic aromatic hydrocarbons and heavy metals are discharged into the environment. Volcanic soil samples had been tested around the world, showing that they had high concentrations of heavy metals especially mercury, together with elements such as chromium, arsenic, nickel, zinc and copper. This was seen when testing soils on the islands of Réunion and Hawaii, where volcanoes are found. The elements were present due to the erosion of the parent material which had these elements as part of its natural geochemical origin. Findings of these elements in high amounts proved that volcanic eruptions cause a higher amount of the element, in both the atmosphere and the surrounding soils (Varekamp and Buseck, 1986; Dœlsch, Saint Macary and Van de Kerchove, 2006; Peña-Rodríguez *et al.*, 2012; Fiałkiewicz-Kozieł *et al.*, 2016). Polycyclic aromatic hydrocarbons can be found in the soil through cosmic dust from meteorites that had landed in the area, (Basile, Middleditch and Oró, 1984; Wing and Bada, 1991) or through diagenetic alteration developments of waxes found in the organic matter of soil (Trendel *et al.*, 1989).

1.3.2 Anthropogenic Source of Pollution

Anthropogenic activity in recent years has increased and resulted in soil pollution all over the world. Anthropogenic pollution can be caused intentionally such as the use of herbicides, use of untreated wastewater for irrigation, fertilizer; or sewage sludge land application. It can also be caused unintentionally by oil spills and landfill leaching (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Anthropogenic sources of soil pollution include livestock and agriculture; sewage and waste production and disposal; industrial activity; infrastructure, transport and urbanisation; fireworks; mining and warfare.

The major part of Malta's industrialisation covers the Southern Harbour, Northern Harbour and South-Eastern District (Figure 2). Ports, airports, construction sites and waste sites are labelled on the map. Firework factories and hard stone quarries can be found dispersed mainly around Malta, with the highest concentration of activity around the whole island, though concentrated in South-Eastern, Western and Northern District (Figure 3).

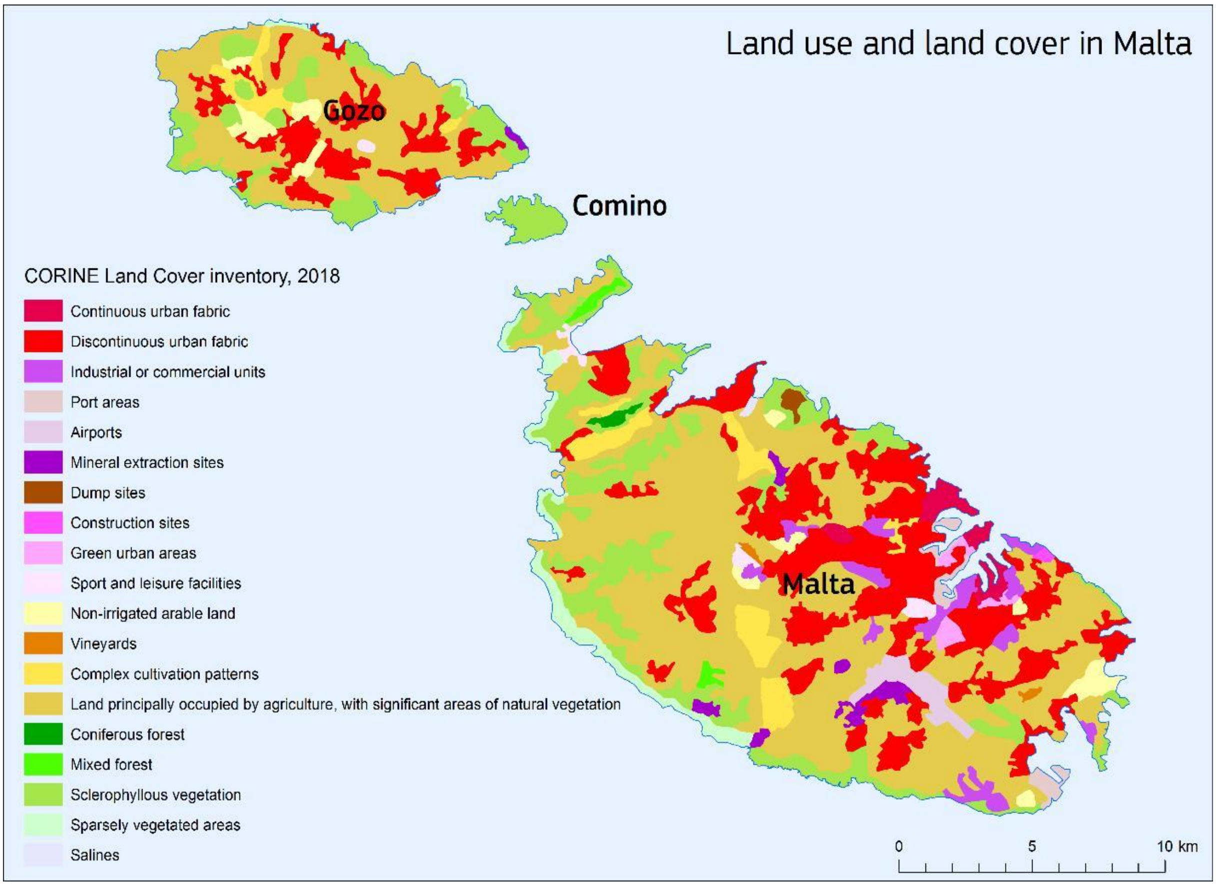


Figure 2: Land Use and Cover of Malta, Gozo and Comino (European Commission, 2019).

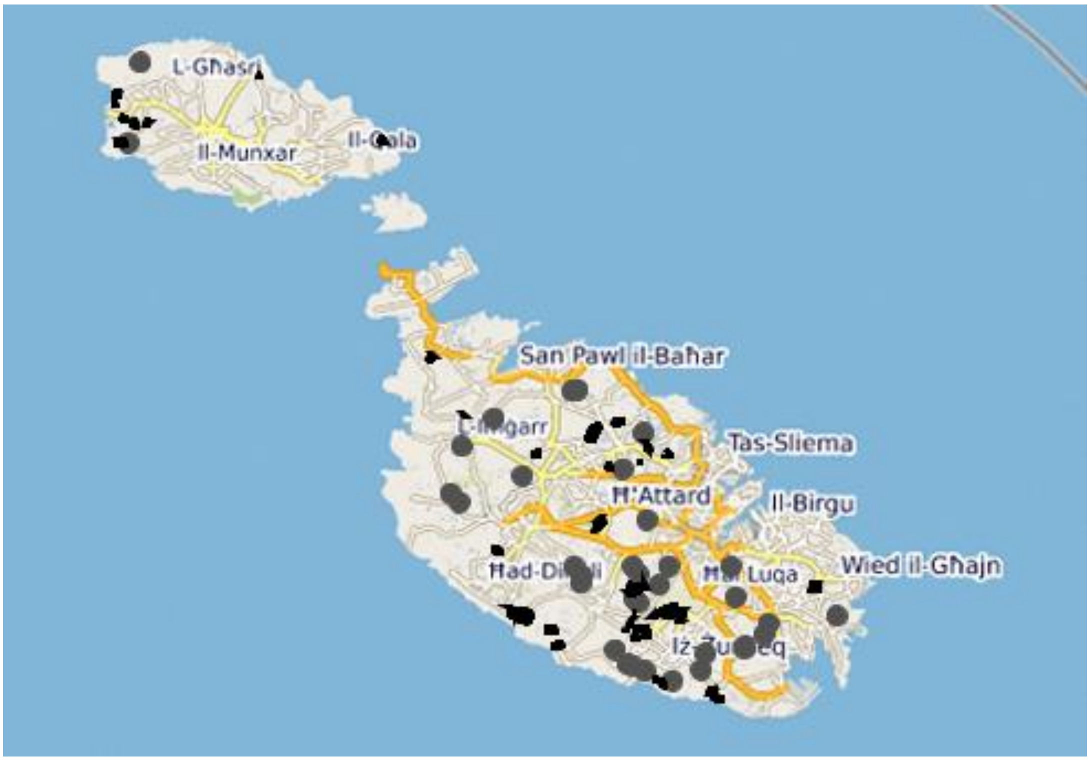


Figure 3: Locations of fireworks factories (grey spots) and mineral and stone quarries *(black shading)* (European Commission, 2019)

1.3.2.1 *Livestock and Agriculture Soil Pollution*

The causes of soil pollution through agriculture and livestock activity can be associated to the use of pesticides and herbicides, livestock wastes, amendments with solid waste, using untreated wastewater or poor quality water for crop irrigation, and over fertilisation (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Most farmers add fertilizers and manure to the soils in excessive amount, thus providing too much nitrogen and phosphorous to the soil (Kanter, 2018). This was seen in the application of fertilizers in the North China Plain, which had increased drastically, particularly in the greenhouse vegetable production systems. Northeast China has also mismanaged fertilizers in agriculture, which has contributed to environmental damage from diffuse pollution, thus causing alarm, both nationally and internationally (Ju *et al.*, 2007).

Excess fertilizer in the soil can result in the heavy metal build-up, an increase of soil salinity, and accumulation of nitrogen which is a potential hazard to humans and water eutrophication. Green gas emissions may cause the extra nitrogen found in the soil to be lost to the atmosphere, while eutrophication of nearby water sources may be the cause of an excess of phosphorous. Apart from the diffuse pollution of nitrogen and phosphorous caused by fertilizers, fertilizers are also a source of heavy metals and natural radionuclides. These metals and radionuclides are mercury, cadmium, arsenic, lead, nickel, copper, 238 uranium, 232 thallium and 210 polonium. This shows that fertilisers should not be added in excess (Stewart *et al.*, 2005; Savci, 2012).

Waste of livestock production is another cause of point source pollution if not disposed of correctly. Animal manure has increased in its use as it is considered as an essential source of nutrients for the soil and plants. Even though it is of importance to agriculture, there is evidence that the use of animal manure may increase heavy metals, veterinary antibiotic residues and pathogens into the soil which may cause antimicrobial-resistant bacteria to increase in soils. (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). The microorganisms present in the urine and faeces, can be non-pathogenic or pathogenic to both humans and animals. Microorganisms that are found in the soil will also be negatively affected by livestock waste. Medicines given to the livestock is then excreted. These have tendencies to be lipolytic which do not degrade quickly, thus causing the medical substance to remain in the manure, which will later be used as fertilizer and thus end up in the soil. (Halling-Sørensen *et al.*, 1998; Haibo Zhang *et al.*, 2015; Manyi-Loh *et al.*, 2016). In Liaoning China, pigs and poultry are given feed with a high amount of zinc and copper. On testing soil treated with manure, it was found that there was an increased amount of copper and zinc in the soil, due to these metals being added to the poultry and pig feeds. Apart from copper and zinc, arsenic can be present in poultry health products which will then be excreted in their manure (Jiang, Dong and Zhao, 2011; Wuana and Okieimen, 2011).

Pesticides have been used for a long time to preserve the crops and to have a large crop yield. The word “pesticides” includes a range of compounds. (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). Pesticides and their transformation products can be grouped into hydrophobic, bioaccumulative and persistent groups, which are firmly bound to the soil such as lindane, endrin and organochlorine Dichlorodiphenyltrichloroethane (DDT). Most of these are banned but can still be found in the soils. They can also be grouped into polar pesticides which include herbicides, fungicides, carbamates and a few organophosphorus insecticide transformation products (Aktar, Sengupta and Chowdhury, 2009).

Pesticides are used to prevent, control or eradicate any pest which will hinder the product; they kill off weeds which will interfere with the crop growth, and will also help to reduce disease which can reduce the harvest, which all reduce crop harvest by 40% (Mahmood *et al.*, 2016). Pesticides are used from the beginning of the crop’s growth, until the crop is processed, stored and ready for transport or the market. Synthetic pesticides had a very positive effect and became widespread during the Second World War. After the Second World War, the use of pesticides helped to increase the crop yield and have abundant harvests far beyond the pre-war levels, which was severely needed since people were mainly on fruit and vegetable based diets (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Nevertheless, the overall health risks due to pesticide use are being seen today in humans and the environment, which has shown a negative impact (Popp, Pető and Nagy, 2013; Rodriguez-Eugenio, McLaughlin and Pennock, 2018). Heavy use of pesticides has caused a decline in the microorganism and fungi that are present in the soil, which has caused the soil to degrade. These can be leached and run off so can prove to be more hazardous as they can move to the drinking water supply. Leaching is influenced by the lipophilicity of the pesticide, the organic matter present in the soil and the pH of the soil (Nicholls, 1988). The primary threat of these pesticides is that humans are being exposed to them at a low dose over a lifetime and thus the adverse effects are not seen immediately (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

1.3.2.2 *The Impact of Sewage, Waste Production and Disposal on Soil*

Waste generation has increased as a result of growth in the population and is of concern in underdeveloped countries as there is no means of eliminating the waste properly (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). Proper treatment and disposal methods are not found, or are rare to find in developing and underdeveloped countries. Instead of the sanitary landfills found in developed countries, developing countries have uncontrolled open dumping areas. Furthermore, developing and underdeveloped countries, burn their waste in the open air unlike developed countries which have controlled incinerations (Garfì, Tondelli and Bonoli, 2009). Incineration and municipal waste transfer in landfills are popular ways to manage waste. These two ways of waste management have their adverse effects due to the sources from both domestic and industrial waste, in placing heavy metals, pharmaceutical products, polyaromatic hydrocarbons and other products into the soil which are higher than the background concentrations (Swati *et al.*, 2014). Leaching of these products from the landfills into the groundwater is one of the problems that can cause soil pollution (Wijesekara *et al.*, 2014; Zhan *et al.*, 2014). Ash from incinerators is another pollutant which is ending up in the soil (Wang *et al.*, 2008; Baderna *et al.*, 2011; Fang *et al.*, 2017).

Sewage sludge was being applied to agricultural lands as a fertilizer since it contained organic waste and was a good source of phosphorous and nitrogen. Nevertheless, this posed a problem since it increased the heavy metals in soils which are persistent and can remain there for decades (Alloway and Jackson, 1991; Charlton *et al.*, 2016). The sewage sludge needs to be treated before being added to the soil to remove the pollutants and prevent their accumulation. In the European Union (EU), sewage sludge is regulated. Waste water treatment in EU follow the directive 91/271/EEC, and directive 86/278/EEC on use of sludge in agriculture (European Commission, 2001). Not all countries have implemented the directive 86/278/EEC in the same way. Denmark and Sweden are a few of the countries that have set a lower threshold level of metals in the sludge that will be used in agricultural soil (European Commission, 2001).

Other wastes that have posed problems after being disposed of incorrectly, are lead batteries and electronic waste (Itai *et al.*, 2014; Perkins *et al.*, 2014). Humans were found to have a higher blood level of lead near lead battery recycling plants (Zahran *et al.*, 2013). In Ghana, soils were found to have a high amount of heavy metals together with rare metalloids such as bismuth, indium and antimony, were electronic waste was disposed of (Ho, Sam and Bin Embi, 1998; Labunska *et al.*, 2008).

Treatment plants in Malta and Gozo are Ras il-Ħobż found in Għajnsielem Gozo, iċ-Ċumnija treatment plant in Mellieħa, and Ta' Barkat treatment plant in Xgħajra (Water Services Corporation, 2017). Public sewers which were discontinued together are located in the Ħal-Far industrial estate and in Anchor Bay in Mellieħa. At the same time, another outfall in San Blas Nadur Gozo was also decommissioned. The outfall at Wied il-Mielaħ in Għarb Gozo was decommissioned in June 2011 (The Times of Malta, 2011). Sewers release heavy metals such as arsenic, chromium, copper, selenium, zinc, barium, boron, tin, petroleum hydrocarbon, oil, cyanides, cadmium, lead, nickel and fluorides (Marine Strategy Framework Directive, 2016).

In 2018, a fire broke out at Magħtab waste serve facility sending up a massive cloud of smoke across Malta, where people were advised to stay indoors due to the smoke which might have been hazardous, though no news was ever released of what the fumes contained (Carabott and Macdonald, 2018; Muscat, 2019). In 2017, there was a massive fire which consumed part of the Sant'Antnin recycling plant in Marsaskala and also caused toxic fumes to be released into the atmosphere over the southern part of Malta (The Times of Malta, 2017). Three landfills were used and had to be shut down and rehabilitated, since they were built at a time when leaching of contaminants and their toxicity were not known. These are Qortin in Gozo, Magħtab, and the Marsaskala landfills. Work to address these three landfills took place to restore and rehabilitate them, to address potential impacts on health and to address the environment regarding combustion of wastes, gas production caused by the landfill and leachate emission. None of these sites was in line with the EU Landfill Directive of 1999 (WasteServ Malta, 2004).

Magħtab and Qortin landfills had to be capped to stop any leachate and emission of the gases, together with the combustion of gases. Drainage schemes had to be installed as well as landscaping of the landfill. Rehabilitation of the Magħtab landfill included (i) capping and the formation of slopes; (ii) paved roads; (iii) rubble walls placed along 11 km of length; (iv) construction of 230 planting cells; (v) plantation of indigenous plants and trees together with vegetation covering the slope; (vi) construction of a large water reservoir together with a water culvert, and (vii) the formation of silt ponds together with reed beds so that rainwater would be collected. The area constitutes a large piece of land of around 50 football grounds (WasteServ Malta, 2004).

Qortin landfill was closed in 2004. Capping was done, and the gas emissions were controlled. Waste from the cliff edges was removed, and the height of the mound was limited to have a visually satisfactory landform. Indigenous trees and plants were planted and regularly irrigated. A proposal was prepared to open the rehabilitated landfill to the public.

Marsaskala landfill, on the other hand, had old waste and was not considered hazardous. A simple capping was enough. The Marsaskala landfill was rehabilitated into the Sant'Antin Family Park. This park is made up of eight tumuli of land. It includes a leisure area at a multilevel, picnic area, play area for children, two mazes, a dog park, outdoor gym, rock climbing area, football pitch, relaxation area, olive garden, a play area with equipment for children with special needs, equestrian area and stables, amphitheatre, car parks, Agro Tourism Centre and Wi-Fi access in the park covering a large area. (Axiak, 2004; WasteServ Malta, 2004; European Commission, 2010).

Wied Fulija, situated in the limits of Żurrieq, is another landfill that has been disused. It is to be rehabilitated with 45,000 plants which will be made up mostly of indigenous shrubs. It was used as a landfill in the 1970s and was decommissioned in the 1990s (Martin, 2019). In Xewkija Gozo, there is a transfer station and materials recovery station situated, known as Tal-Kus. This station was built to offer an effective waste management system to Malta and Gozo, and to reduce the amount of transportation to Malta. Municipal solid waste is compacted and then transferred to the mechanical biological treatment in the North of Malta. Organic waste is transferred to the Sant'Antnin plant (WasteServ Malta, 2019).

Recycling of waste has increased in the past years and several countries have implemented strict regulations regarding its disposal and recycling. Plastic pollution has been of great concern since it is found all around us in everyday use, since it is inexpensive, durable, has multipurpose uses and is lightweight. It persists in the environment for decades without degrading, particularly in oceans and landfills (Hahladakis *et al.*, 2018). Microplastics have been found in the soil through the use of sewage sludge and plastic mulches (Wang *et al.*, 2019). Some plastics have been noted to have cancerous properties. Examples of these types of plastics are epoxy resins, polyurethanes, polyacrylonitriles, styrenic copolymers and polyvinyl chlorides. Apart from being carcinogenic, these affect the endocrine functions, have mutagenic. Plastics adsorb polycyclic aromatic hydrocarbons, organic pollutants and heavy metals (Lithner, Larsson and Dave, 2011).

1.3.2.3 *Industrial Activity Pollution*

Industrial polluting activities, according to Directive 96/61/EC regarding the Integrated Pollution Prevention and Control (IPPC) (The Council of the European Union, 1996), and the Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) (*Industrial Emissions (Integrated Pollution Prevention and Control) Regulations*, 2013), is stated to be categorised into six main groups. These groups are (i) the production and the processing of metals; (ii) energy industries; (iii) mineral industries; (iv) waste management; (v) chemical industries and installations; and (vi) the last group involves other activities which include fibre and textile manufacturing, slaughterhouses and many more (García-Pérez *et al.*, 2007). Pollutants from industries are released into the atmosphere, waters and soils. Those that are released into the atmosphere then land onto the soil through acid rain or atmospheric deposition. Waste can be dumped onto the soil or water, polluting both the hydrosphere and lithosphere. Thus such activities can ultimately lead to environmental hazards and illness to humans and other animals. Some waste from particular manufacturing processes causes soil salinization such as soap production, pigment manufacturing and pharmaceuticals (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Chemical pollution in Malta can be caused by several industries. Chemical polluting industries in Malta and Gozo that are still active or have been decommissioned are (Marine Strategy Framework Directive, 2016):

- Marsa Power Station located in Marsa (electrical generation);
- Delimara Power Station in Marsaxlokk (electrical generation);
- Ħas-Saptan fuel storage facility in limits of Għaxaq (oil and fuel terminals);
- Ras Ħanzir in Paola where gas oil is stored (oil and fuel terminals);
- Enemed Co. Ltd in Birżebbuġia, being wholesalers of petroleum and petroleum products (oil and fuel terminals);
- Oil Tanking Malta in Bengħajsal limits of Birżebbuġia (oil and fuel terminals);
- Gasco Energy in Bengħajsal limits of Birżebbuġia (oil and fuel terminals);
- Wied Dalam Installation in the limits of Birżebbuġia (oil and fuel terminals);
- Mediterranean Offshore Bunkering Co. Ltd in Marsa (oil and fuel terminals);
- San Lucian Oil Co. Ltd in Birżebbuġia (oil and fuel terminals);
- LPG Storage Depot, San Lawrenz, Gozo (oil and fuel terminals);
- Easygas LPG Facility, Luqa (oil and fuel terminals).

Oil and fuel terminals release arsenic, chromium, zinc, boron, lead, nickel, petroleum hydrocarbons, oil and fluorides into the atmosphere. Before the Delimara power station was built in Marsaxlokk, there was another power situation which was situated in Marsa, where coal was used as a source of fuel. It had been reported that the coal contained vanadium, nickel and sulphur and had polluted Żabbar, Fgura, Paola, Santa Luċija and Tarxien with ash containing these heavy metals. The fuel was then changed from a 3.5% sulphur content to a

1% sulphur content. Since there was a decrease in sulphur, there was also a decrease in ash which was being transmitted to these localities by the wind (MEPA, 2009). This power station was closed permanently in 2017. The Delimara power station was built and started using heavy fuel oil, which released a high amount of particulate matter which was over the safe amount. PM2.5 and PM10 particulate matters were too high, though authorities had blamed the Sahara dust for the results (Barnes, 2009). The Delimara power station had a big flaw, where no monitors or filters were affixed to it, to reduce the ash and pollution (The Times of Malta, 2009). Absence of filters sent up toxic ash into the surrounding areas. The Delimara power station has been a significant source of pollution where heavy fuel was the source of combustion. Black ash was found all around the area, especially in people's homes. Residents in the surrounding areas were more prone to respiratory problems and asthma. Sulphur dioxide, nitrogen oxides and particulate matters were the primary pollutants being emitted in the atmosphere. In 2011, the highest compound emitted from the power station was carbon dioxide were 821,747,000 kg/year was released, followed by sulphur dioxide and nitrogen oxides. Heavy metals were also released such as nickel, found at 168 kg/year, followed by lead, arsenic, chromium and cadmium (Barnes, 2009; Environmental Software and Services, 2011). Energy generation industries release nitrogen oxide, which have been known to cause inflammatory respiratory responses, such as a higher risk of attacks in asthma and Chronic Obstructive Pulmonary Disease (COPD) patients. In pregnant women, exposure to nitrogen oxides may cause damage to the unborn child. Carbon monoxide is another compound released, which causes hypoxemia leading to nausea and dizziness, headaches, central fatigue, impaired awareness and impaired physical ability. During pregnancy, this may increase the risk to the foetus, and is also an increase in risk to the elderly. Sulphur dioxide also causes respiratory problems to patients who already have asthma or have COPD. Hydrocarbons are carcinogenic and cause central nervous system damage together with nausea and vomiting, while particulate matters increase respiratory mortality and morbidity together with cardiac mortality and morbidity. Other compounds released are copper, zinc, nickel, boron, petroleum hydrocarbon, oils and fluorides (Israel Ministry of Environmental Protection, 2015; Marine Strategy Framework Directive, 2016). In 2017, the power station was changed from heavy fuel oil to natural gas (Grech, 2017). Combustion of natural gas produces a cleaner burning, where negligible amounts of mercury, sulphur and particulate matter are produced. Although nitrogen oxides are produces, they are produced at a lower levels when compared to diesel in motor vehicles. In the United States, electricity powered by natural gas instead of fossil fuels caused a reduction in annual emissions of 1,900 tons of nitrogen oxides, 5,200 tons of particulates, and 3,900 tons of sulphur dioxide, when 10,000 homes where analysed. Emission reductions have translated into benefits for the public health (Tollefson, 2013).

Ship repairs are another source of soil contamination. Malta has a large shipyard situated between Paola and Cospicua, which used to be called Tarzna, and has now been passed on to the Palumbo Company, where dry docking, repair, refitting, maintenance and conversion take place. Processes involved at shipyards which cause pollution include cleaning and de-greasing, painting metallic parts, fibreglass vessel construction, scrapping and operational emissions. Painting involves different types of processes such as the removal of rust, metal oxides together with old paint and grease; cleaned by dissolvent, detergents and steam; sandblasted or treated by stand tools; sandblast and water or hot blasting, or chemically cleaned. When painting a ship, the items used to paint contain zinc oxide, carbon, lead, carbon-tar, aluminium and zinc dust; binding solvent, and alcohol solvents. The hull is painted in protective paint, which is based on copper and tri-butyl-tin, which protects it from sea organisms growing on the hull (Papaioannou, 2004). Ship repairs used to be undertaken on Manuel Island, and the Shipbuilding in Marsa. Compound and elements released through the shipyard trade are chromium, copper, zinc, tin, lead, nickel, cadmium, oils, petroleum hydrocarbons and fluorides (Marine Strategy Framework Directive, 2016).

Cement plants have also shown to cause heavy metal pollution to their surrounding areas (Ogunkunle and Fatoba, 2014). Some of the contaminants that are seen near these plants are nitrogen oxide, which is one of the contributions to a variety of ecological problems such as ground-level ozone, global warming acid rain, visual impairment and water quality deterioration. Children and adults who suffer from lung diseases can be affected as may cause lung tissue damage. Another compound which is found through cement plants is sulphur dioxide which also causes respiratory problems and might also aggravate cardiovascular and respiratory disease in people who are ill, suffer from asthma, emphysema and other disorders. It also is the cause of acid rain. The third compound is carbon monoxide, which can cause hypoxemia, cardiovascular and central nervous system disorders. Ecological wise carbon monoxide also contributes to smog which is also a cause for respiratory disorders (US EPA, 2019b). Apart from these compounds, heavy metals are released into the atmosphere and the surrounding soils such as cadmium, lead and copper (Ogunkunle and Fatoba, 2014). Figure 4 shows the locations of plants which can lead to pollution.

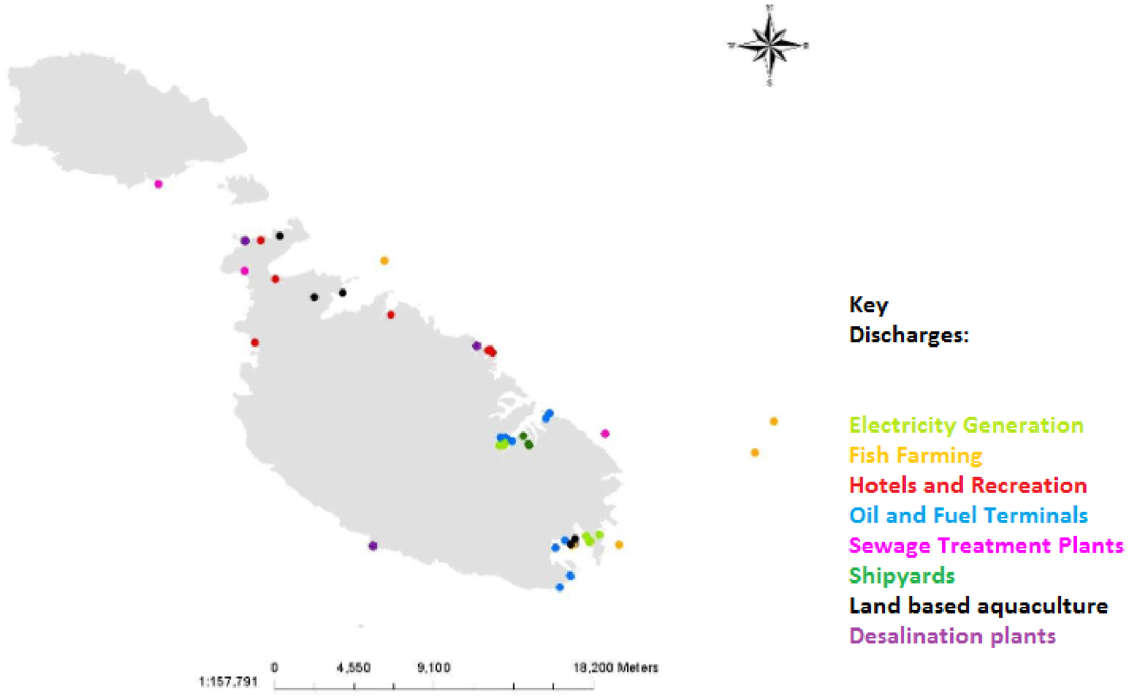


Figure 4: Contamination sites in Malta and Gozo (Marine Strategy Framework Directive, 2016)

1.3.2.4 *Infrastructures, Transport and Urbanisation*

Urbanisation has increased the development of road infrastructures, more housing and in some countries, railways. Land has been taken up and covered by buildings, which is known as soil sealing. Due to urbanisation, more pollutants have entered into the atmosphere and settled on soils (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

In Europe, the chief contributors to atmosphere pollution are agriculture, where ammonia is released; transport, where particulate matter, carbon monoxide and nitrogen oxides are discharged; and power generations, where sulphur dioxide and nitrogen oxides are released. Areas exposed to heavy traffic flow causes high levels of nitrogen oxides and particulate matter. In contrast, ozone is the primary concern for atmospheric pollution in rural areas where there is little pollution through anthropogenic activity (Environment & Resources Authority, 2016b). Road transport in urban areas is the chief contributor to atmosphere pollution in Malta.

The number of vehicles on the roads has risen, and thus traffic associated pollutants have increased. In March 2019, according to the NSO, Malta had 387,775 registered vehicles, an increase of 3.4% from the previous year, in the same quarter (Conneely, 2019). Exhaust from cars releases several pollutants, especially lead, which is found in the form of lead tetraethyl as an anti-knocking agent in petrol, as well as petrol and diesel spills (Kovacic and Somanathan, 2014; Hua Zhang *et al.*, 2015; Venuti, Alfonsi and Cavallo, 2016). Leaded gasoline has been one of the highest soil contaminants where lead is released from vehicles (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). Lead pollution is seen mostly in highly concentrated urban areas and around main roads. Lead and other heavy metals either enter the soil through dry, or wet deposition, or through rainfall and splashes from the cars themselves which may translocate particles onto the soil. Heavy metals released from cars include copper, cadmium, chromium and zinc (Ndiokwere, 1984).

Other types of heavy metal pollution sources may come from tarmac and pavement particles, tyre particles, rust on the cars, rubber and plastic derived compounds and polycyclic aromatic hydrocarbons. Heavy metal pollution is a very worrying situation where crops are grown on agricultural land close to the roads. The particles are absorbed through the leaves and roots and taken up by the crops, which is the end product for grazing animals and humans. Absorption of heavy metals by plants has caused a major health impact to humans and the ecosystem (Ndiokwere, 1984; Birch and Scollen, 2003).

Malta's infrastructure revealed a project in the pipeline to get in line with the EU directives regarding climate change, and in line with the Paris Agreement, to reduce more than 90% of the pollution caused by Ro-Ro ships and cruise liners visiting the Grand Harbour. By switching off their auxiliary engines and using the electrical shore power which will be installed on the quay, Authorities have stated that pollution will decrease. It was stated that there would be a decrease of 92.6% less particulate matter, 93% nitrogen dioxide, and a decrease of 99.6% sulphur dioxide. This Clean Air Project would help to reduce air pollution and will keep up the standard with the EU and national climate change targets in agreement with the Paris Agreement. The targets set are to diminish the carbon footprint of activities that are land-based together with the shipping activities. The obligations on ambient air quality and cleaner air for EU Member States in Directive 2008/50/EC are also met through the contribution of the decrease in emissions caused (The Times of Malta, 2019).

Aircraft engines have been shown to emit pollutants such as nitrogen oxides and Particulate Matter 2.5, especially in ground traffic. Nitrogen oxides released from high-altitude supersonic aircrafts have been observed to damage the stratospheric ozone layer. International standards by the International Civil Aviation Organization (ICAO) have been set and came into effect in 2013. This applies to engines types that were certified after 2013 (Environmental Protection UK, no date).

Households tend to use a lot of detergents and personal care products which end up in the sanitary sewage or on the road. Municipal wastewater that would have generated biosolids, constitute a significant sink for the personal care products (PCPs). If this municipal waste is used to treat the land, then PCPs are introduced into the soil and aquatic environment (Mansouri *et al.*, 2017).

Lead is also a source of soil contamination from lead-based paint. The paint, due to weather conditions and other environmental factors, starts to peel and fragments into small particles, which are powdered into dust and carried along with the wind, landing on soils and waters (Bogden and Louria, 1975; Mielke and Reagan, 1998).

DDT used in mosquito repellents is another soil contaminant used to repel vector-borne diseases like malaria (Mansouri *et al.*, 2017). DDT was found to decrease the population of various microflora, having a massive impact on soils properties (Megharaj *et al.*, 2000).It had been banned as it was found to be detrimental to the environment and has a half-life of 30 years, it was later re-introduced by the World Health Organisation (WHO) for tropical countries in 2006.

1.3.2.5 *Fireworks*

When looking at Malta, one cannot forget the fireworks that are displayed with every feast, especially in the summer months. The display of colours and brightness is due to many elements in the periodic table. It is all about the physical and chemical properties of these elements. Fireworks are made using propellants, oxidizers and colours.

Some of the propellants used in the fireworks are carbon which comes in the form of carbon black, starch or sugar, and comes as a black powder. Sulphur is used as a propellant and fuel for fireworks and is a component of black powder. Phosphorous is used as fuel for fireworks, and one of its properties is that it burns spontaneously in the atmosphere and can cause glow-in-the-dark special effects (Helmenstine, 2020).

Oxidizers such as nitrates, perchlorates or chlorates are used to produce oxygen for burning to occur. Oxidizers can be used to provide oxygen for burning and also colour, depending on which oxide is used. Chlorine is a component of many oxidisers. Metal salts producing a variety of colours usually contain the halogen chlorine. Potassium nitrate, potassium perchlorate and potassium chlorate are also mixtures used to oxidize the fireworks (Helmenstine, 2020).

Colours and effects, are due to several metals and elements. Aluminium is used to produce the white and silvery flames. Antimony in fireworks is used to cause the glitter effect seen. Calcium salts give an orange colour while calcium itself enhances the colours. Blue colours are usually produced through copper compounds. Iron metal creates sparks, though the colour is determined by the heat. Red colour occurs due to the presence of lithium, usually lithium carbonate, and also by strontium salts, which is also used as a stabilizing fireworks mixture. Bright white is brought about the burning of magnesium, which also enhances the global brilliance of the display. Barium produces a green colour and also stabilizes the volatile elements used in the mixture. Golden yellow colours occur due to the presence of sodium. Titanium produces silver sparks and is present as powder or flakes. Zinc generates the smoke effect seen in both the fireworks and in pyrotechnic devices (Helmenstine, 2020). Arsenic is sometimes used to help boost the fireworks blue colour but due to toxicity has been decreased. Sometimes it is still used illicitly. (Sterba, Steinhauser and Grass, 2013).

In a previous dissertation compiled in 2014 by Colette Pace at the University of Malta by the Department of Chemistry and with the assistance of the University of Malta Rector, Alfred Vella, it was shown that the perchlorates used in the fireworks are contaminating Malta’s water sources. Perchlorates and the heavy metals present in fireworks are also found in dust and in the soils, which are then taken up in the food we eat. Perchlorate has been found to interfere with the absorption of iodine by the thyroid gland, which can cause problems since hormone thyroid is essential in metabolism. It regulates heart rate, body temperature and blood pressure. It also controls food conversion rate into energy (Pace, 2014; Vella *et al.*, 2015).

1.3.2.6 *Mining Activities*

Men have been mining for a very long time for metals and minerals such as gold, silver and diamonds. During the process of mining, surrounding areas are heavily contaminated. To release the metal or minerals being mined, a process called smelting is used. Smelting releases many pollutants into the soil. Both the mining process and the smelting process, release a large number of toxic elements and heavy metals into our environment (Ogundele *et al.*, 2017). Unfortunately, they remain in the environment for long periods even after the mines have been closed and are longer in use. When the product is extracted from its ore through chemical and mechanical processes, waste is produced which is known as tailings. Tailings will contain chemicals, inefficient metals, minerals, organics and process water which are unrecoverable, and are discharged to ultimate storage. Tailings are left at the surface, or some industries dispose of it in the empty vaults of unused mines. Recently environmental regulations have been more stringent with disposal and storage of tailings, as they have been one of the sources of heavy metal pollution in the environment. Tailings are usually formed by fine particles, which when kept at the surface are dispersed by wind and water erosion. The tailings can subsequently reach agricultural land (Tailings Info, 2017).

In South Africa, in an area known as the Golden Crescent, gold is mined. Slime dams present there are responsible for pollution plumes. The slime dams cover an area in Wonderfontein of around 25 square kilometres. The tailings seeped into the underground water through rainfall and original moisture. Apart from gold, there is a problem of uranium which was present in the ore that was being mined, and in 2006 it was confirmed that there was a high risk of radioactive pollution in the area (Weissenstein and Sinkala, 2011; Idriss *et al.*, 2016). Mining is known to be one of the causes of release of radioactive elements. Another mode of releasing radioactive elements is through the production of fertilizers using the phosphate rocks, which generated phosphogypsum as a by-product (Bolívar, García-Tenorio and García-León, 1995). Phosphogypsum keeps around 80% of its initial radioactivity, due to the decay products of 238 uranium; 226 radon and 210 polonium (Bolívar, García-Tenorio and García-León, 1995). In Namibia, copper and lead were found in high levels in agricultural land which came from the tailings dam (Mileusnić *et al.*, 2014).

1.3.2.7 *Warfare Actions*

Until a few years ago, wars did not have too much of an impact on the environment. Modern warfare has taken a dramatic turn; it is of significant pollution to the environment affecting pedogenesis with the use of chemical weapons and non-degradable weapons which have had a lasting effect for decades and also for centuries to come (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). Soils can take centuries for a total recovery or a partial recovery. Pollution does not occur during a conflict only but also occurs when military weapons are being tested (Certini, Scalenghe and Woods, 2013). Some of the weapons used that pollute the soils are land mines, radioactive agents, toxic biological agents, discarded chemicals, leftovers of ammunition, and chemical bombs (Kassa, 2002; Kobayashi, 2009; Smičiklas and Šljivić-Ivanović, 2016). The pollution does not occur only when they are used, but also where they are stored and practised with barracks and shooting ranges. Soils in these areas cannot be used as agricultural land due to the high amount of pollution left. The impact of military activity can mean fertility of the soil is decreased and is short term, but it can also mean the complete loss of soil which is irreversible (Certini, Scalenghe and Woods, 2013). Soil damaged through warfare can be divided into three categories: physical, chemical and biological, though intertwining can occur between the groups (Certini, Scalenghe and Woods, 2013).

Physical damage to soil by military activities is caused by excavations of tunnels and trenches, tanks and troops compacting the soil, sealing of soil due to defensive infrastructures being built, and craters caused by mines and bombs. Involuntary consequences of the influence of chemical and physical properties of the soil can be caused by biological disruptions. On the other hand, biological disruptions can also occur through intentional causes by introducing microorganism, which is lethal to the biosphere (Certini, Scalenghe and Woods, 2013). Anthrax spores are still found today in Gruinard Island, which is found in western Scotland (Szasz, 1995). Chemical damage to soil is caused by radioactive elements, oil, cholinesterase-inhibiting organophosphorus nerve agents which are considered as one of the most dangerous chemical warfare's, heavy metals, explosives containing nitroaromatic compounds which are both toxic and carcinogenic, and more (Certini, Scalenghe and Woods, 2013). Mustard gas is a vesicant chemical warfare that was used during the Second World War. Apart from contaminating the site of storage for around fifty years, it has been seen to affect the soil's microbiota (Watson and Griffin, 1992; Medvedeva *et al.*, 2008).

1.4 Soil Pollutants

As mentioned above, we have seen a variety of pollutants which are contaminating the soils, mostly through anthropogenic activity. Soil pollutants can be systematically divided as stated by Swartjes, into inorganic and organic pollutants. Inorganic pollutants are divided into metal and non-metals. Organic pollutants are divided into chlorinated and non-chlorinated pollutants, where both are sub-divided into alkenes and alphates (Swartjes, 2011).

1.4.1 Inorganic Ions

Inorganic ions include heavy metals and metalloids, together with anions.

1.4.1.1 *Heavy Metals and Metalloids*

The term 'heavy metal' has been endlessly discussed regarding its definition. Heavy metals have been assigned this word, due to their high density or due to their high atomic weight (Duffus, 2002). Metallic chemical elements, such as metalloids, have also been used recently under the word heavy metal. These are toxic to all living thing, including the environment. Some lighter metals and metalloids such as arsenic, aluminium, selenium and antinomy have been labelled as heavy metals due to their toxicity. On the other hand, some heavy metals are not toxic, such as gold (Wang, 2009; Tchounwou *et al.*, 2012).

Heavy metals are common in our everyday life. Examples of heavy metals placed in ascending order, according to their atomic weight, are titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, molybdenum, silver, cadmium, tin, platinum, gold, mercury and lead.

Some of them are essential to plants, humans, and animals at minimum concentrations but are toxic at high concentrations. Toxicity is caused because they are non-biodegradable, thus can accumulate in the tissues and living organisms. Unlike many organic compounds, heavy metals are not subject to metabolic breakdown. (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). When introduced in soil, they have been known to accumulate in the food chain and is thus hazardous to any animal or human that will be taking in the contaminated food.

Heavy metals have originated on the Earth's crust since the beginning (Herawati *et al.*, 2000). Since the use of these metals has been increasing rapidly over the past years, the metallic substances in the environment have amplified in the soil, atmosphere and waters (Gautam *et al.*, 2016). Anthropogenic activity has been the primary cause of heavy metal pollution. Natural causes of heavy metal pollution include volcanic activity, soil erosion, stone weathering, metal corrosion, sediment re-suspension and metal evaporation from waters and soils (Gautam *et al.*, 2016; Masindi and Muedi, 2018). Pollution due to anthropogenic activity can be seen through mining activity, smelting and foundries (Shallari, 1998), leaching of metals from landfills, excretion, waste dumps (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012), poultry and livestock manure (He, Yang and Stoffella, 2005), and an increasing factor is automobile exhaust and roadworks. A secondary source for anthropogenic pollution is in the agricultural field, were a few examples include the use of pesticides, fertilisers, insecticides and manure (He, Yang and Stoffella, 2005).

1.4.1.2 *Anions – Phosphorus and Nitrogen*

Phosphorus and nitrogen are essential elements for all living organisms. They are soil pollutants, not because they are toxic, but because in large amounts they can cause severe damage to the soil and plants. Phosphorus forms part of DNA and RNA and is also used to make up ATP which transports cellular energy. In humans and animals, phosphorous is essential for the formation of bones and teeth. Not enough phosphorus in the soil will cause a decreased amount of crop to grow (Yaron, Dror and Berkowitz, 2012). Nitrogen is a vital element for living organisms and plays an essential role in amino acids which are the backbone of proteins and nucleic acids, thus deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), enzymes, hormones and vitamins (Yaron, Dror and Berkowitz, 2012). Human and animal tissue need protein. Growth, cell substitution and tissue repair require nitrogen while protein as enzymes are needed for the body's metabolic processes. Like humans and animals, nitrogen is also crucial for plants, as it makes up a significant part of chlorophyll. It forms part of the adenosine triphosphate (ATP) which is to transport cellular energy. Plants also need nitrogen as they are the building blocks for nucleic acids to make up DNA so that they can reproduce and grow (Yaron, Dror and Berkowitz, 2012).

Nitrogen can be found as organic and inorganic forms. Nitrogen in its pure form is used by microbes; ammonia, nitrates and amino acids is used by plants; amino acids and nucleic acids used by animals and humans. Agriculture has used nitrate fertilizers extensively over the past years to help the demand for more crops, due to the increase in the population (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Thus nitrogen, phosphorus and potassium were added to the soils. Fertilizers are absorbed during the plant growth and are released when the plant dies and decomposes. The nitrates are released and may enter the groundwater. Increase in nitrates can cause eutrophication, causing phytoplankton and other photosynthetic plants such as algae, to grow rapidly, known as algal blooms. Algal blooms limit the amount of dissolved oxygen, due to the massive growths, which causes problems for other aquatic organisms who need oxygen. At hypoxic levels, animals and plants trapped under the overgrown plants and phytoplankton, tend to asphyxiate. These can cause anaerobic conditions for microorganisms, which produce toxins that are toxic to the aquatic mammals and to the birds that prey on them. Eutrophication causes a loss of biodiversity, loss of aquatic life and dead zones. Increase in nitrates also happens with phosphate present in fertilizers and washing powders. When these anions are added in excess, plants do not grow as they should since chlorophyll production is increased and energy is directed at foliage proliferation instead. Plants get distorted, which leaves them vulnerable to pathogens. Microbial activity is also affected together with soil pH and salinity (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

1.4.2 Organic Pollutants

Organic compounds are molecules containing carbon except for the compounds carbon monoxide and carbon dioxide. Since carbon can chelate, it can form an assortment of complex organic compounds which have stable covalent bonds, producing molecules in the configuration of rings or chains known as carbon skeletons. Carbon can also bond with hydrogen known as hydrocarbons, oxygen and nitrogen (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

Hydrocarbons have low polarity and thus have low water solubility. When carbon molecules have a groups attached to them such as hydroxyl functional group (-OH), a formyl functional group (-HCO) or a nitro functional group (-NO_2), the compounds are inclined to be more polar and more reactive. When seeing the properties of on organic pollutant, the formulae of the compound is essential to know, as it reveals the properties of the compound. Behaviour relies on the compounds molecular size and shape, and what functional group is attached. These properties will determine their toxicity and metabolic rate. Most organic pollutants are anthropogenic compounds. Aromatic hydrocarbons are produced by combustion of organic matter, and have increased exponentially in the past few years due to an increase in human activity (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

1.4.2.1 *Hydrocarbons*

Hydrocarbons are divided into two classes. One contains alkanes, alkynes and alkenes. Alkanes are a saturated hydrocarbon with a carbon-carbon bond; alkenes are an unsaturated hydrocarbon with a carbon-carbon double bond; while alkynes are an unsaturated hydrocarbon with a carbon-carbon triple bond (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). The second category contains aromatic hydrocarbons meaning that it has one or more benzene ring. Benzene rings contain six carbons in the ring which are unsaturated. Hydrocarbons are only composed of carbon and hydrogen, where most hydrocarbons are in liquid or solid states. These properties include low polarity, low water solubility, extremely soluble in oils and the majority of organic solvents (Ma and Zhou, 2011; C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

Aromatic hydrocarbons are more reactive than the other hydrocarbons and are prone to biochemical and chemical alteration. Some polycyclic aromatic hydrocarbons (PAHs) have flat molecules which have three or more benzene rings connected (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). PAHs are persistent and semi-volatile organic pollutants. Solid-phase slow mass-transfer rate and low solubility of these PAHs, encumbers the natural attenuation by microbial processes since availability is limited. The amount of microbial organisms and the diversity of them is also altered by PAHs, as PAHs alters the soil porosity, soil size and the water-holding capacity of the soil (Sakshi, Singh and Haritash, 2019). Subsequently, a large number of PAHs remain and accumulate in the soil for a prolonged time due to their hydrophobic properties and persistence. These properties class most of the polycyclic aromatic hydrocarbons, as persistent organic pollutants which persist in all of the earth's spheres. Those with two to three rings and have a low molecular weight, makes the compound volatile and are present mostly in the atmosphere. Those with a higher molecular weight, and thus having more rings, are found in the atmosphere as particles depending on the temperature at the time (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). They are highly toxic to human and are classed as carcinogenic and mutagenic (Sakshi, Singh and Haritash, 2019).

Petroleum and natural gas are the chief sources of deposits from the upper strata of the planet's crust. The primary pollution of hydrocarbons is crude oil spills and combustion of fossil fuels. The deposits are composed mainly of non-aromatic hydrocarbons, and PAHs are still found in crude oil. Incomplete combustion of organic materials forms PAHs. Organic material pollution include the burning of houses, garbage, trees, coal, gasoline, oil and the smoking of cigarettes. High-temperature decomposition of organic material in the industries, traffic and agriculture cause a release of PAHs in the environment. Discharge of these hydrocarbons into the atmosphere is also caused by the recycling of sewage sludge, continuing wastewater irrigation and fertilizer use. (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

1.4.2.2 *Persistent Organic Pollutants: Polychlorinated and Polybrominated pollutants.*

There are around 209 possible polychlorinated biphenyls (PCB) congeners. PCBs are liquids with high viscosity and low volatility, they are unreactive and stable and were used much in everyday life such as in hydraulic fluids, plasticizers in paints, heat transformers, additives to lubricants, vacuum pump fluids and coolants. PCBs are banned or regulated in most countries today, since the 1970s by several governments, but it still persists today in the environment (Kukharchyk *et al.*, 2007). They have low solubility in water (hydrophobic) though they are highly soluble in low polarity oils (lipophilic) and organic solvents (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). PCBs congeners have a number attached to the name where the first two digits reveal the number of carbons in the ring, and the last two numbers indicate the proportion of chlorine in the product, such as Aroclor 1254, showing that the compound contains 12 carbons in the ring, and 54% of chlorine by weight (US EPA, 2017). PCBs are toxic due to their bioaccumulation in the environment and food chain, not because they are toxic to touch. They present abundant affinity to lipid membranes of cells; thus, PCBs are stored in fatty tissues (Ashraf, 2017). They are hazardous to humans due to their mutagenic effects. They are classified as persistent organic pollutants (Kukharchyk *et al.*, 2007). PCBs bioaccumulate in human's tissues, breast milk and blood. These can end up in humans from the ingestion of fish, meat and dairy products. They have been associated with several chronic effects such as bronchitis, immune system damage and hormonal interferences which lead to cancer, low birth-weight in children, behavioural disorders and also hearing loss at high exposure (Jing, Fusi and Kjellerup, 2018).

Dioxin is one of the most popular compounds from the polychlorinated dibenzodioxins (PCDDs) group. It is 2,3,7,8-tetrachlorodibenzodioxin. It is an extremely toxic compound to mammals. There are around 75 possible PCDDs congeners. They are made up of two benzene rings linked by two oxygen bridges and have a flat molecule. They are hydrophobic, lipophilic but have limited solubility in most organic solvents. The congeners are manufactured as by-products during the synthesis of other products. They are also produced when PCBs are combusted and when chlorophenols interact during their disposal in municipal waste (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Commercial herbicides, like 2,4-D, contain dioxins which have caused complications to the environment. In the 1960s, it was released onto the Vietnamese jungles by the U.S. Air Force, as an agent called Agent Orange, to remove the foliage in the forest to aid the U.S. Troops pass through the jungle. A lot of Vietnamese and U.S. soldiers died due to the dispersal of Agent Orange (History.com, 2011).

Polychlorinated dibenzofurans (PCDFs) are similar to PCDDs, in that they are not synthesised on purpose but are produced as by-products. Polybrominated biphenyls (PBBs) are similar to PCBs in structure, and some are used as fire retardants (Chovancová, Kočan and Jursa, 2005).

1.4.2.3 *Pesticides*

Pesticides have been used widely around the globe, especially to increase the crop yield though it has been used for other purposes such as to keep infrastructures free from pests. There are different types of molecules, both organic and inorganic. The class pesticides can be divided into different groups, which includes insecticides, molluscicides, fungicides, herbicides, rodenticides, nematicides, and plant growth promoters. Classification of these pesticides depends on their mode of action, chemical structure, their target and the mode of uptake into the organism (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

1.4.2.3.1 Organochlorine Insecticides

This class of pesticides has been used against a variety of pests, diseases and insects in the food production. Around two million tonnes of organochlorine insecticide is used by Europe and the USA every year, which amounts to 69% of the total use. At the same time, the rest of the world accounts for the remainder 31% (Fang *et al.*, 2017). As a class, they are stable solids with low vapour pressure, resist oxidation, low solubility in water and high lipophilicity, making them less likely to degrade and more likely to bioaccumulate. They can be extremely tenacious in their original shape or as stable metabolites; they have extended-range migration properties and are highly toxic (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). They have been found in seashells, whales, wolves and breast milk thus contaminating both the hydrosphere and lithosphere (Fang *et al.*, 2017). The three main categories of organochlorine insecticides are DDT and its related compounds, hexachlorocyclohexanes (HCHs) such as lindane, and chlorinated cyclodiene insecticides such as Aldrin. DDT and its relatives, together with cyclodiene insecticides, have been banned from being used, with some exceptions. (Miglioranza *et al.*, 2002; C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

1.4.2.3.2 Organophosphorus Insecticides

This category of insecticides was developed at the time of the Second World War. They were developed for two reasons, one being as an insecticide, and one as a nerve gas to be used in chemical warfare. It acts by inhibiting the enzyme acetylcholinesterase, thus acting as a neurotoxin (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Organophosphorus insecticides are mostly lipophilic, water-soluble, slightly volatile, and are in liquid form, though there is a small amount that are present in solid form. They are less stable and readily broken down by chemical and biochemical agents compared to the organochlorine family (Dar, Kaushik and Villareal Chiu, 2020).

200,000 deaths per year, and around three million poisonings have been reported with the use of organophosphorus insecticides. Inhibiting the enzyme causes a triphasic effect in man. Upon exposure, it first causes an accumulation of acetylcholine at the nicotinic, muscarinic and central nervous system synapses which would need immediate treatment. Symptoms would appear between two to four days after being exposed. There would be accumulation at the neuromuscular junction, which will cause pre- and postsynaptic dysfunction, causing respiratory failure causing the person affected to need ventilator care. The third phase is seen after 21 days of exposure, where delayed polyneuropathy is caused due to phosphorylation of esterase, causing the peripheral muscles to become weak with an inconsistent sensory component (‘Organophosporous Insecticide Poisoning’, 1999).

1.4.2.3.3 Carbamate Insecticides

This class of insecticides is similar to the organophosphorus class. They inhibit the acetylcholinesterase enzyme causing overstimulation of the nervous system and are also readily degradable by chemical and biochemical agents. This class is mostly present in the solid form, rather than in the liquid form, and they vary in their water-solubility properties. These have been developed later on from the other previous insecticides and are derivatives of carbamic acid (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Carbaryl (1-naphthyl N-methylcarbamate) is used often now to prevent infestations in over 120 crops and house plants, and kills over 160 types of insects. It is a broad-spectrum insecticide which has low mammalian toxicity and has a short lifetime in the environment (Tiwari, Kharwar and Tiwari, 2019).

1.4.2.3.4 Pyrethroid Insecticides

These synthetic pyrethroid insecticides were produced on the natural pyrethrin, from extracts of the flower species *Chrysanthemum*. The pyrethroid insecticides are neurotoxins which act similar to DDTs. They have very low water solubility, low polarity and are found in the solid form. The synthetic form is more stable than the natural pyrethrin though they are biodegradable, have short half-lives, and can bind to soil particles. Pyrethroids were created to control insects affecting both agriculture and household items, and also eliminate human lice. They are highly selective as they have a higher insect nerve sensitivity when compared to mammals which have weaker skin absorption and a higher efficient hepatic metabolism. When a large amount of pyrethroids is ingested, severe and fatal effects are caused. These are toxic to fish and non-target invertebrates, and have an effect on animals at sub-lethal levels (Beasley and Temple, no date; C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

1.4.2.3.5 Neonicotinoids

This insecticide is also neurotoxic and is structurally comparable to the natural compound nicotine. Neonicotinoids are less polar than the natural compound and show tendencies of being more toxic to insects compared to vertebrates. They interact with the nicotinic receptors in animals which are situated in the cholinergic synapses. It is used in crops which have an aphid infestation or as prevention from the infestation (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). It is the most used insecticide where the crops are treated with neonicotinoid seed dressings, which are taken up by the plants on watering, though only five percent of the dissolved amount is taken up by the plants, while the rest is dispersed into the environment. In Germany and Italy, it has been implicated in mass poisonings of honeybees (Wood and Goulson, 2017). It is found in the soil and pollen, which have caused severe effects on the honeybees' navigation, which is altered, in addition to their survival. It has also affected the bumblebee colony development and queen production (Buszewski *et al.*, 2019).

1.4.2.3.6 Plant Growth Regulators – Phenoxy Herbicides

Phenoxy herbicides are one of the most critical groups of herbicides. They are synthetic analogues of the auxin plant growth hormone. They act in the same way as indoleacetic acid which is a natural plant growth regulator. They are highly water-soluble when formulated as alkali salts while they are lipophilic when they are formulated as esters. They are used to control dicot weeds and are thus selectively toxic (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Phenoxy herbicides are swiftly biodegradable and do not persist in the soil and living organisms. They are toxic due to unwanted phytotoxicity because of their volatility, and sometimes they have been contaminated with 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD), known as Agent Orange (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012; Jayakody, Harris and Coggon, 2015).

1.4.2.3.7 Anticoagulant Rodenticides

Warfarin has been used for an extended period to kill off rodents. It has low water solubility, is lipophilic, and acts by antagonising the vitamin K (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Recently, resistance was being seen, so a variety of second-generation anticoagulant rodenticides were produced (Watt *et al.*, 2005). These were more toxic to rodents and also became more toxic to their predators and scavengers, such as birds and other mammals (Brown and Waddell, 2014). They vary from warfarin in that they have a polycyclic hydrocarbon as a side chain, making them long-acting and potent (Watt *et al.*, 2005).

1.4.2.3.8 Emerging Organic Pollutants

Emerging pollutants can be described as chemicals which are not monitored and can either be synthetic or natural and which have appeared recently in the environment. These are usually known to cause health effects to humans or pollution to the environment. Emerging organic pollutants include pharmaceuticals, including hormones such as ethinylestradiol, endocrine disruptors, in addition to cosmetics and detergents; micropollutants, such as bacteria and viruses (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Detergents have polar and nonpolar properties. They tend to enter the hydrosphere from sewage plants, though they are sometimes used to remove oil spills and in some pesticide formulations. They can lead to the formation of alkylphenols which causes endocrine disruption triggering various adverse effects (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012; De Coster and Van Larebeke, 2012). Chlorophenols are acidic, water-soluble, and chemically reactive. An example of chlorophenols is pentachlorophenol, which is used to preserve wood, used as an insecticide, herbicide and a molluscicide (Proudfoot, 2003; C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Ethinylestradiol has been found in surface water and has been noted in fish. These findings are of concern as it was documented that male fish have become feminised, thus become infertile reducing the amount of fish in the area drastically (Hannah *et al.*, 2009; C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

Pharmaceuticals include veterinary drugs, agricultural practices, human drugs, cosmetic and personal hygiene products. They are known as Pharmaceuticals and Personal Care Products (PPCPs) which end up in sewage outflows and soils (Barceló and Petrovic, 2007; C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). The drug diclofenac was found to cause a decrease in the number of vultures in India as they fed on decomposing cattle which were treated with the drug and ended up getting poisoned by it (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

Since bacteria can adapt rapidly genetically through chromosomal mutations, they become resistant to antibiotics and other drugs in the soil due to excess human use of these drugs and excess use in livestock (Furuya and Lowy, 2006; Rodriguez-Eugenio, McLaughlin and Pennock, 2018). Examples of bacteria found in agricultural soils are Pseudomonas spp., Thiobacillus ferrooxidans, Rhizobiurn and Bradyrhizobiurn spp.(Van Elsas and Heijnen, 1990).

Microbes can also become resistant to antibiotics through the horizontal exchange of the foreign antibiotic-resistant genes, among related or unrelated bacteria. Foreign antibiotic resistant genes can come through (i) bacteria that were introduced through agricultural practices; (ii) bacteria that are naturally present in the soil; and (iii) animal droppings on the soil. This horizontal genetic exchange occurs through transformation, transduction and also through conjugation. These resistant bacteria have killed many humans and have been predicted to kill more than cancer (Furuya and Lowy, 2006; Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

1.4.3 Organometallic Compounds

Several metals, when bound to organic ligands, are greatly enhanced. This binding alters their lipophilicity, thus changing their properties with regards to the distribution and behaviour of the metal in the environment, together with its behaviour in organisms. Tin is a metal ion that is used in linings of food products which is safe, but tin, bound to an organic ligand, is toxic and is found in pesticide formulations. Natural synthesis of metal ions into organometallic compounds are mercury and arsenic in the soil, which are both methylated naturally (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Toxic forms of organic species of mercury are methylmercury, ethylmercury, phenylmercury and dimethylmercury. If mercury is dumped into rivers and seas, the bacteria found in the sediments change it to methylmercury which can then move along the food chain, even causing human deaths as was seen in Japan in the 1950s (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Rice paddy fields is another place where methylmercury is produced as flooding occurs when the rice is growing. Methylmercury is more easily absorbed by the rice than the mercury ions (Haydee and Dalma, 2017; Liu *et al.*, 2019).

1.4.4 Radionuclides

Background radiation can be naturally produced from the cosmic ray particles in our atmosphere and through the natural decay of radioactive isotopes (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Anthropogenic sources of radionuclides come from (i) nuclear weapons and the dust they leave behind; (ii) nuclear facilities; (iii) coal ore mining; (iv) coal transportation; (v) coal fire powered plants; (vi) disposing of coal ash in sludge lagoons; (vii) radioactive ore mining; (viii) mineral fertilizers; (ix) nuclear waste management and removal; and (x) nuclear accidents (Certini, Scalenghe and Woods, 2013; Ćujić *et al.*, 2015). Radionuclides produced both naturally, and through anthropogenic sources are 232 thorium, 238 uranium, 235 uranium, 40 potassium, 134 caesium, 137 caesium, 239 plutonium, 90 strontium (Ćujić *et al.*, 2015; Nieder *et al.*, 2018)(C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012; Certini, Scalenghe and Woods, 2013; Ćujić *et al.*, 2015; Nieder *et al.*, 2018; Rodriguez-Eugenio, McLaughlin and Pennock, 2018). A few accidents have occurred over time where some have caused minimum damage while others have a lot of deaths and environment pollution to account for (Table 1).

Table 1: Nuclear accidents around the world (Battist and Peterson, 1980; McLaughlin, Jones and Maher, 2012; Union of Concerned Scientists, 2013).

Reactor and Place	**Date of nuclear accidents**
Fukushima Daiichi, Japan	March 2011
Chernobyl, Ukraine	April 1986
Three Mile Island, Pennsylvania USA	March 1978
Enrico Fermi Unit, Michigan USA	October 1966
SL-1, Idaho USA	January 1961
Sodium Reactor Experiment, California USA	July 1959
Windscale, Cumbria UK	October 1957

The worst accident was the Chernobyl accident which released 131 iodine. This killed approximately 50 people, and has affected many people till today (WHO, UNDP and IAEA, 2005; WHO, 2016).

Properties of radioactive isotopes which determine if they are hazardous to the organism, are the half-life; the nature of the radioactive decay and the intensity based on the mass and energy produced by the particles, and the biochemistry of the radioactive element (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Most agricultural areas near nuclear accidents have been abandoned for several years, as it was impossible to remove all the topsoil due to the amount of radioactive waste, and to diminish the number of radioactive elements entering into the food chain (Yang *et al.*, 2017).

1.4.5 Gaseous Pollutants

Ozone, at the ozone layer, is significant as it absorbs ultraviolet light from penetrating. Though ozone produced in photochemical snogs is a pollutant, it irritates the animal's respiratory epithelia and also affects growth in plants. It is one of the main reasons for the forest die-back in Germany, and also effects Tobacco plants which are very sensitive to it (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Nitrogen oxides are produced from sulphur-based fossil fuel combustion. Nitrogen oxide reacts with radicles in the atmosphere or with ozone, and produces nitrogen dioxide. Nitrogen dioxide reacts with volatile organic compounds through sunlight, as a catalyst, causing more ozone. Carbon dioxide is not toxic unless in confined areas. Carbon monoxide is produced through partial fossil fuel combustion and sulphur based combustion, and can cause death (El Morabet, 2018). Sulphur dioxide in the air dissolves with rainwater causing acid rain which is damaging to plants, soils, waters and buildings (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

1.4.6 Pathogenic Microorganisms

A variety of organisms live in the soil with more than 10,000 species per square metre; thus many organisms have acquired a chemical defence to survive and eradicate their competitor (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). Most of them are harmless to humans, but some of them can cause soil-borne disease. These pathogens can be opportunistic, meaning that they infect a weak host, or obligate, where they have to infect a host to survive and multiply. Some soil-borne infectious diseases caused by these pathogens are Lyme disease, hookworm, tetanus and anthrax (Jeffery and Putten, 2011; Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Animal faeces may leave pathogens on the soil which can then be transmitted to humans (Rodriguez-Eugenio, McLaughlin and Pennock, 2018). Such bacteria found in soil due to animal faeces and use of wastewater are *Escherichia coli, Salmonella* spp*, Mycobacterium tuberculosis, Bacillus anthracis, Streptococcus* spp., among others (Mawdsley *et al.*, 1995; Balkhair, 2016). Crops grown from soils which are irrigated with untreated wastewater, or untreated domestic waste, can transmit these pathogens, especially in crops that are usually eaten raw such as lettuce. Thus, these pathogenic microorganisms have been classified as food contaminants (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

1.4.7 Nanoparticles

Nanoparticles are particles with a size of less than 100 x 10^{-6} mm (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). The nanoparticles that are of concern are the ones that are produced through anthropogenic sources. Examples of these nanoparticles are paint, cosmetics, spray, pesticide formulation and surface coatings amongst others (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012; Simonin and Richaume, 2015). Nanoparticles concentration have seen to be higher in soil than in the waters or atmosphere. These particles can enter the soil through sewage sludge, landfills, accidental spills and atmospheric deposition (Simonin and Richaume, 2015). Soil treated with sewage sludge had an increase in titanium dioxide and silver. Nanoparticles may be made of compounds such as titanium oxide, silver, cerium oxide, aluminium oxide, carbon or zinc oxide (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Magnetite nanoparticles have a variety of uses such as pigments, magnetic coatings, catalysts and nanotherapies, and are used to remove contaminants. Cerium oxide nanoparticles are used to improve emission-quality, by acting as a catalyst in diesel fuels.

Cerium oxide is also found in agricultural and pharmaceutical products. Nanoparticles of tin oxide are used as catalysts, in optoelectronic devices and also in electrochemical energy storage. Nanoparticles have been seen to interact with a variety of microbial communities which inhabit the soil (Vittori Antisari *et al.*, 2013).

1.5 Heavy Metals

1.5.1 Properties of Heavy Metals and Metalloids

Heavy metals are classified as non-biodegradable as they cannot be broken down. Metal ions in organisms are usually detoxified through a process where the active element is hidden within a protein, or they are deposited in an insoluble form in the intracellular granules where they are excreted with the faeces or stored long term. They are classified as dangerous when entering the body as they bioaccumulate in the body. Bioaccumulation proceeds to cause complications, both physiological and biological (Gautam *et al.*, 2016). On the other hand, some heavy metals are required for life for a variety of physiological and biological functions and are thus called essential elements (Duffus, 2002). However, if found in large quantities, they can then be toxic. These heavy metals have been widely used in our everyday life such as in medicine and agriculture and other sectors, to the effect that these elements have been spread all over our spheres (Wang, 2009; Tchounwou *et al.*, 2012).

Toxicological properties are observed in metalloids since they form covalent bonds which lead to two important outcomes. Elements can combine covalently with organic groups to form lipophilic ions and compounds, such as tributyltin oxide and arsenic methylated forms. These are all toxic, and they can bind to non-metallic elements found in cellular macromolecules, generating a toxic effect such as the binding of mercury and lead to sulfhydryl groups of the protein. Having lipophilic properties means that distribution of the metalloids within the biosphere can have varied toxic effects compared to the action of simple ions (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). There are four pathways where a heavy metal can enter the human body; ingestion of food contaminated with them, inhalation of the metal from the atmosphere, drinking of contaminated waters and lastly through the skin in cases of agriculture, manufacturing , industrial and pharmaceutical processes (Masindi and Muedi, 2018).

Essential elements are classified into three groups; (i) major elements; (ii) macrominerals; and (iii) trace elements. The major elements significantly vary as they are the building blocks of nearly all living matter and are made up of hydrogen, nitrogen, carbon and oxygen. Macrominerals are integral elements and are needed to maintain the ionic balance of amino acids, structural compounds and nucleic acids. These macro minerals are sodium, phosphorous, magnesium, sulphur, chlorine, calcium and potassium. There are 13 trace elements which are made up of mostly heavy metals; arsenic, silicon, chromium, vanadium, iron, manganese, nickel, cobalt, zinc, copper, molybdenum, selenium and iodine (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012; Tchounwou *et al.*, 2012). Essential elements are crucial for the preservation of skeletal structure development, colloidal system upkeep and acid-base equilibrium regulation (Villanueva and Bustamante, 2006). They are significant as constituents of key enzymes, hormones and proteins such as zinc which is a constituent for several enzymes, selenium is indispensable for the glutathione peroxidase enzyme while iron is needed for haemoglobin (Villanueva and Bustamante, 2006; C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012; Tchounwou *et al.*, 2012). On the other hand, nonessential metals do not play a vital role in the body, though these can still cause toxicity as they can alter the levels of the essential elements (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

Mitochondria, lysosomes, cell membranes, nuclei and enzymes are examples of cell organelles that have been affected by heavy metals. It has been known that metal ions interact with nuclear proteins and DNA causing a catastrophic process where DNA is damaged hence leading to cell cycle modulation which leads to apoptosis or worse carcinogenesis (Tchounwou *et al.*, 2012).

1.5.2 Entry, Transportation and Effects of Heavy Metals into the Ecosystem

As previously noted, heavy metals can enter the spheres through natural ways such as volcanic activity and the erosion of rocks. The anthropogenic activity is one of the main concerns of heavy metals entering our system. Not all pollutions can be avoided as some may be caused accidentally such as shipwrecks, mining, fires and oils spills. Nevertheless, most pollutions are intended release of heavy metals into the spheres, such as waste disposal from sewage or industrial effluents, and applications of biocides such as instances of vector controls. Transportation of these metals depends on factors such as surface water movement and direction, temperature, speed of wind and circulation of air masses. Other factors include polarity, vapour pressure, partition coefficient and molecular stability (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

1.5.3 Soil Contamination

Contamination of soil with heavy metals can be both deliberate or not. Instances of deliberate pollution include animal manure, pesticides, wastewater irrigation, fertilizers, leaded paint, sewage sludge, mine tailing, petroleum distillates spillage, waste dumping and coal combustion residues (Alloway and Jackson, 1991; Aronsson and Perttu, 2001; Muchuweti *et al.*, 2006; C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012; Gupta, Khan and Santra, 2012; Masindi and Muedi, 2018). One of the main problems in agricultural land for the pollutants is watering with untreated wastewater and sewage (Alloway and Jackson, 1991; Muchuweti *et al.*, 2006). Flooding of waters can unintentionally bring heavy metals onto agricultural lands as it brings in sewage-contaminated water and any spills that occurred from the vehicle transporting any toxic chemicals. They remain in the soil for a very long time since they are not biodegradable and thus cannot undergo degradation whether chemical or microbial (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

Bioavailability of heavy metals together with metalloids are affected according to the soil's sorptive capacity. Metal uptake by plants and soil biota can only be done in ionic form. Metals have an affinity and adsorbed to the surface of clay minerals, humus, iron and manganese hydrous oxides and calcium carbonate salts. Some metals have an affinity for forming complex compounds with organic molecules. The sorption process is usually pH-dependent, where it is highest in less acidic soils and are desorped and released when the soil is acidic (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

The heavy metals entering the food chain are a cause of great concern. Biodegradability of other pollutants, such as organic pollutants, is also affected, making the heavy metals even less degradable. A negative effect is caused as pollution would increase twofold (Masindi and Muedi, 2018). Risks are caused through these metals present in the soils as they will be taken up by plants and continue in the food chain (Muchuweti *et al.*, 2006; Gupta, Khan and Santra, 2012). They also alter the soil properties including, colour, pH, porosity and the natural chemistry of the soil. Concluding that all of these factors will impact the quality of the soil, and water will be contaminated (Masindi and Muedi, 2018).

1.5.4 The Fate of the Heavy Metals in Soil

Localisation of high quantities of heavy metals increases toxicity of the metal. Some areas around the world have built their industrial chimneys at a higher altitude so that the heavy metals being emitted are dispersed further and do not fall at one particular spot, but are dispersed over a larger area. The high altitude sometimes also has a negative effect, since emissions rise higher due to the taller chimneys, and thus makes it more inclined for acid rain. The earth is perceived as one compartment, which is made up of several other compartments such as individual cells or organisms. Possible toxins on any being may then be further compartmentalized into insoluble deposits, which continues to prevent any interactions in the cytoplasm with essential biochemical reactions (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

Metals are nonbiodegradable and persevere in the environment for a prolonged period since they cannot be degraded. Heavy metals found in sediment and soil after a while will eventually be eluted to further compartments. Reactions can occur with other elements in the soil which can result in more toxic products. Such an example is the transformation from inorganic mercury to the poisonous methyl mercury due to bacteria present in the soil (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

Where an anthropogenic activity has produced heavy metal pollution, vegetation can sparsely grow, and only metal-tolerant strains of plants manage to grow in the area. In zones where soils are prone to the exposure of metals, capping is introduced. The procedure introduces an impermeable layer placed on top of the contaminated soil, where new soil is then placed on top of it. Capping will let vegetation grow without absorbing any heavy metals and besides, does not let any water seep any heavy metals into the groundwater (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

Most common heavy metals still being used are copper, arsenic, chromium and lead, which may still be present in certain pesticides. Sewage sludge is also used by many farmers to mix with the soil on their land, but these may contain heavy metals, especially if these come from industries. Some of the most popular heavy metals present at high concentrations after sampling soils are usually copper, zinc, cadmium, lead and chromium (Carrondo et al., no date; Jackson and Alloway, 1991; Aronsson and Perttu, 2001; Muchuweti et al., 2006; Gupta, Khan and Santra, 2012). Smelting is one of the industries that emit several heavy metals into the atmosphere which eventually settle on the soils. Apart from vegetation problems, even the amount of organisms are decreased drastically, such as woodlice and earthworms, which are very important to aerate the soil and decompose vegetation (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012; Chibuike and Obiora, 2014).

Another occasion where lead was released into the atmosphere was through the use of lead-contaminated gasoline, which in previous years released lead into the atmosphere. Lead shotgun pellets, which are still used mainly in hunting season, also releases lead into the ground, and lead fishing weights which releases lead into the waters. Some activities or uses, have been banned in certain areas around the world. Shotgun pellets, unfortunately, are sometimes carried along the food chain when the birds are eaten by other predators and have also transported lead to other areas. If clay content in the soil is high, pH is more acidic and organic matter are high, then metal tends to bind much more to the soil. Less elemental elements are found in the soil when it is more acidic as the elements tend to become more soluble and thus leach further down in the ground where the roots do not reach thus resulting in nutrient deficiency to the plant (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012).

1.5.5 Uptake of Metals by Plants and Entry into the Food Chain

Absorption of heavy metals by the plant depends upon soil properties such as temperature, pH, moisture, organic matter and nutrient availability. Heavy metal absorption depends on the species of the plant and also the metal itself and its properties (Onakpa, Njan and Kalu, 2018). If the metals are not readily translocated by the plant, even though it is highly toxic to the plant, it is not toxic to humans or animals, and does not enter the food chain. Chaney had stated this and called it the "Soil-Plant Barrier" (Chaney, 2015). Chaney divided the metals into four categories. The first group are not taken up by plants, and thus are of low risk to food chain contamination. Examples of metals from this group are silver, tin, chromium, titanium, yttrium and zirconium. The second group contains mercury and lead and are metals that are strongly sorbed onto soil surfaces and roots but are not translocated readily to edible parts of the plant. The only way of entering the food chain is if grazing animals mistakenly ingest the contaminated soil. Group three are taken up quickly by the plant, but at the level of being a risk to humans, these metals are phytotoxic. This group consists of boron, manganese, copper, molybdenum, nickel and zinc. The last group are high-risk food chain contaminants, are not phytotoxic, and are thus toxic to both animals and humans. These include cadmium, arsenic, cobalt, selenium, molybdenum and thallium. Apart from being toxic to humans and animals, these heavy metals can decrease the crop productivity; they alter various parameters in the soil such as the composition, amount, and activity of the microbial community thus altering the nutrient cycle and consequently decreasing the nutrient availability (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Apart from heavy metals being taken up by plants and entering the food chain, heavy metals can also enter the food chain when it enters rivers and seas. Heavy metals can exist in diverse states in surface waters; in solution or in suspension form. They can be transported over an extensive distance by water. Particulate materials can descend to the bottom of the water. Liquid droplets can either descend to the sediment or rise to the surface. Distance travelled in rivers depends on the currants, stability and physical state of the pollutant. When transported into the sea and oceans, wind and currents transport the pollutant further. Difference of density of the sea water plays another factor in the transportation to a higher concentration of salt or due to a fall in temperature. The persistent pollutants such as heavy metals can then enter the food chain through marine life such as fish which can then affect predators such as bigger fish, birds and mammals, including humans, which migrate and transport the pollutant to different ecosystems (C.H. Walker, R.M. Sibly, S.P. Hopkin, 2012). Insectivorous birds may take up heavy metals by preying on insect that were exposed to heavy metals, whilst herbivorous birds may eat plants that have taken up the heavy metal (Sparling and Lowe, 1996). These will also be part of a food chain and transport the heavy metal to different ecosystems.

1.6 Metal ions

Some metals will be discussed further to see how they are found in our environment through natural and anthropogenic sources, what they are used for, and what adverse effects they can cause if they are taken in large quantities.

1.6.1 Aluminium

Aluminium is ubiquitous and originates in the Earth's crust, primarily in the ore bauxite and also cryolite. It makes up a total of eight percent of the total amount of the Earth's core mass. Aluminium is lightweight compared to other metals, is durable and is resilient to oxidation. It is the 3rd most abundant element found on Earth after oxygen and silicon. Alloys are easily formed with different elements such as manganese, magnesium, silicon and zinc.

Its properties include having a low density, non-toxic, easily cast, high thermal conductivity, non-magnetic and non-sparking. It is the second most malleable metal and the sixth most ductile metal (WHO, 2000; Keith *et al.*, 2008).

Aluminium is found in many household items such as kitchen utensils, aluminium foils, mirrors, packaging such as cans, electrical transmission lines, telescope mirrors, fireworks and explosives, and cars. In addition, it is found in consumer products which include certain medications, cosmetics, antiperspirants and food additives. It is widely used in aerospace due to its properties (WHO, 2000; Keith *et al.*, 2008).

Aluminium is oxidized rapidly becoming a stable compound making it very hard to refine. Aluminium minerals also form part of some gemstones such as rubies, sapphires, emeralds and aquamarines. Aluminium oxide forms what is known as corundum which is a transparent gemstone. Both rubies and sapphires are a corundum. Their colours then come from cobalt producing the blue hue for sapphires and chromium which produces the red hue for rubies. Aluminium silicate with traces of iron, then forms the gemstone topaz, which has a yellow hue (Zrinzo, 2015).

Particular food and drinks contain a higher concentration of this metal than others. These include soft drinks, coffee and tea, processed cheese, sponge cakes and anticaking agents together with food colouring agents (Shaw and Tomljenovic, 2013). Aluminium can be taken up by the crops through contaminated soils (Marschner, 1991). Pharmaceuticals also contain aluminium such as antacid formulations which will be ingested, dermal skin contact through antiperspirants and cosmetic (Shaw and Tomljenovic, 2013).

Aluminium is found in the +3 oxidation state and can be found in many forms which include aluminium phosphates; aluminosilicates made up of tetrahedral and octahedral crystals, sesquioxides and crystalline or amorphous clays; and ionically bound organic compounds. Soil properties affect the metal and how it reacts in the soil. Soils having a neutral to slightly alkaline pH will make the aluminium have a lower solubility and make it biologically inactive. In alkaline soils, aluminium will have higher water solubility. Aluminium becomes more soluble as pH decreases; thus, this makes it to be absorbed more by organisms and thus being more toxic. The metal can react with other organic complexes and inorganic molecules, including humic acid, fulvic acid, fluoride, phosphate, sulphate, hydroxides and bicarbonates (Sparling and Lowe, 1996).

In acidic soils and waters, aluminium tends to be absorbed by the plants, which can cause several adverse effects and is readily leached into the surface. To reduce the bioavailability of aluminium, the addition of other elements to the soil causes competition for the binding sites. These elements are potassium, calcium and sodium (Sparling and Lowe, 1996). Sources for aluminium ending up in soils and waters are mining, disruption of soils and sediment, coal piles and waste, motor emissions and industrial emissions. Aluminium tends to be excreted rapidly and thus returns to waters and soils (Short, Black and Birge, 1990; Sparling and Lowe, 1996; Matsumoto, 2000).

Tea plantations are one of the plant species that are more prone to aluminium uptake than other plants (Bengtsson *et al.*, 1988; Rahman *et al.*, 2018). Aluminium in its soluble form, due to acidic soil is toxic and causes abnormalities to both the root and shoot of the plant (Hagvall, Persson and Karlsson, 2015). The roots are usually inhibited from elongation as cell division is inhibited due to the DNA being affected by the aluminium. The metal becomes localized, and the plants' mineral nutrient acquisition capacity is influenced, thus leading to drought stress causing a lesser crop production. When the shoots are affected, nutrient and water deficiencies occur; thus, leaf size and stomatal openings are reduced, causing a decrease in photosynthetic efficiency. The shoot will then be affected by chlorosis and foliar death, where many vital enzymes are altered, causing plant death (Bengtsson *et al.*, 1988; Rahman *et al.*, 2018).

To reduce aluminium toxicity and its adverse effects, phosphorous or calcium (liming) can be applied to the soil, which encourages root respiration, plant growth and chlorophyll content. However, both methods are expensive and are environmentally risky. Other methods are the addition of gypsum, magnesium, sulphur and silicon, all of which alleviate the aluminium toxicity (Rahman et al., 2018).

Aluminium toxicity affects many organisms, including insects and crustaceans, by affecting the ion regulation and calcium uptake. Stoneflies and mayflies are aluminium sensitive and decrease in amount when there is aluminium in the waters, which affects the food chain since these are food for fish and water birds. Dragonflies have their oxygen transport affected, and thus respiration rates are altered. Aluminium in waters can cause asphyxiation in fish as it damages the gills (Exley, Chappell and Birchall, 1991; Sparling and Lowe, 1996).

Toxicity of this metal also causes a lot of adverse effects in humans. Such adverse effects are dementia, listlessness, trembling and central nervous damage, leukocytosis, dysfunction of kidney and liver, lung damage and also pulmonary fibrosis, hypoparathyroidism, and osteomalacia. In adults, aluminium toxicity can mimic neurological diseases such as Amyotrophic Lateral Sclerosis and Parkinsonism Dementia Complex (ALS-PDC) and another neurological disease such as Alzheimer’s disease (Shaw and Tomljenovic, 2013; Zrinzo, 2015).

1.6.2 Vanadium

Vanadium is the 20th most abundant metal in the Earth's crust. It is silvery-white in colour and very soft and ductile (ATSDR, 2012d). It is found in around 65 different minerals such as vanadinite, patronite, camotite and roscoelite. It is furthermore found in rocks, in several iron ores and crude oils in the form of organic complexes. It is very reactive with hot acids such as hot sulphuric acid (Pedersen, 2017).

It has many uses such as in the production of springs, rust-resistant and high-speed steel tools (ATSDR, 2012d; Pedersen, 2017). Vanadyl sulphate and sodium metavanadate are both found in a few dietary supplements. These supplements are used to treat a variety of conditions such as oedema, diabetes, hypoglycaemia and hypercholesterolemia. More evidence is needed regarding the treatment of these diseases with the use of vanadium (MedicineNet, 2011; Pedersen, 2017). The compound vanadium oxide is used in ceramic glass as a green pigment. Furthermore, it is used in the production of super magnets (Pedersen, 2017).

This metal is found naturally in food which includes mushrooms, shellfish, parsley and black pepper, grains, beer and wine (ATSDR, 2012d). Natural sources of vanadium are volcanic eruptions and emissions, marine aerosols and mainland dust. Anthropogenic sources include oil refineries and power plants (WHO, 2000). Vanadium in the air then settles onto soils and surface waters. People who smoke are at risk of inhaling vanadium as the tobacco plants absorb it from the soil (ATSDR, 2012d).

At low levels, vanadium produces positive effects to plants such as increasing the plant height and root length, chlorophyll biosynthesis enhancement and thus biomass production elevation, seed germination increase, nitrogen absorption and utilization is amplified together with the uptake of essential elements. When vanadium is found at a more significant concentration, the plants may die. High concentrations disrupt energy metabolism and matter cycling, inhibiting some processes such as protein synthesis, ion transportation, key enzymes which aid in energy production of the plant, and other physiological activities which can lead to growth hindrance, root and shoot irregularities. All these may end up with the plant dying. All this depends on the type of plant, the soil pH, organic matter, and the other elements present in the soil which compete for its bioavailability. Chickpea is one of the plants that absorbs a high concentration of vanadium (Aihemaiti *et al.*, 2019).

Human adverse effects due to vanadium toxicity, include severe throat pain, nose bleeds and nose irritations, eye irritations, headaches and nausea, dizziness, rashes, central nervous system impairment, tremors, liver and kidney haemorrhage, cardiac diseases, gastrointestinal organs inflammation, paralyses, teeth and tongue blackening and behavioural changes (Browne, 1955; WHO, 2000; ATSDR, 2012d).

1.6.3 Chromium

Chromium is the 22nd most abundant element, on the Earth's crust. It is a hard metal with a shiny steel-grey colour and is relatively active and reacts with most acids. On exposure to air, it forms a layer of chromium (III) oxide, which makes the metal less corrosive. The ore that chromium is extracted from is called chromite (Barnhart, 1997).

Chromium is used in a variety of items such as the production of alloys, in industries of leather tanning, metal ceramics and plating, in the manufacturing of synthetic rubies, in dye paints, and chromium salts are used as a dye to make the glass green (Barnhart, 1997; ATSDR, 2012b). It can be found from cement and cement dust, asbestos lining erosion, catalytic converter erosion which forms particles that are transported with dust, antifreeze agents, anti-algae agents, wood preservatives, photoengraving and tattooing (ATSDR, 2012d).

The chromium metal is found in many foods such as fruits and vegetables, shellfish, meat, yeasts and grains. There are two different oxidations states of chromium. These are chromium (III) which is found both naturally and through anthropogenic activity and chromium (VI) which is only found due to anthropogenic activity. Chromium (III) is produced mostly in the textile, leather and steel manufacturing while the chromium (VI) is produced in the textile, leather and chemical manufacturing together with electroplating manufacturing. During all these processes, chromium is released into the air, and the industrial waste will leach the chromium into the soil and waters (ATSDR, 2012b). Chromium (III) is an essential element in the body, and if it is found at low concentrations it can cause metabolic disturbances, diabetes, and cardiac complications (Ware, 2015).

On the other hand, too much chromium, especially chromium (VI), can be harmful to humans (Martin Sabine and Griswold Wendy, 2009). It can give rise to a variety of cytotoxic and genotoxic reaction, which can affect the immune system of the person. Most chromium enters a person through oral intake and inhalation and to a lesser degree much through dermal contact (ATSDR, 2012b).

Taking oral chromium (VI) can cause a variety of adverse effects which can eventually lead to death. Some of the side effects caused depend on the amount taken, and are ulceration in the gastrointestinal tract, nausea, vomiting, gingivitis, diarrhoea, fever, vertigo, toxic nephritis and hepatic and kidney damage. The adverse effects can lead to coma and also death if toxicity is high. The fatality dose of chromium is usually between 1-3g. Inhaling the hexavalent form can cause bronchitis, pneumonia, sinusitis, mucous membrane irritation, and lung cancer (Martin Sabine and Griswold Wendy, 2009; ATSDR, 2012b). It was thought that carcinoma from chromium is usually from the hexavalent chromium through inhalation, causing lung cancer (WHO, 2000; Dayan and Paine, 2001; Soltan, 2015), however it has been noted that carcinoma in the gastrointestinal tract and the central nervous system, can also occur with chromium. It can cause eczema and allergic contact dermatitis, which can lead to chrome holes usually in the hands, fingers, forearms, and nose. These can also lead to secondary infections. Intake of chromium usually occurs with chromium (III) and not (VI) though too much of the third oxidative state of chromium will still present adverse effects (ATSDR, 2012b).

Hexavalent chromium at physiological pH is present in the oxyanion form with a minus two charge making chromium taken up by the cells through the anionic transport system. Chromium accumulates in the cell at more substantial amounts than customarily found at extracellular levels. Intracellular reductants found in the cell, such as ascorbic acid, convert hexavalent chromium to trivalent chromium. An increase in intracellular reductants will increase the uptake of chromium (VI) and thus, toxicity is magnified. The trivalent chromium formed reacts with cellular macromolecules. It can adduct with DNA usually with the phosphate backbone of the DNA strand, preferably two adjacent guanine bases together with the intracellular reducer forming a ternary complex (Costa and Klein, 2006).

Plants generally do not tend to absorb chromium at a great extent, though if the soil is acidic chromium will be absorbed to a more considerable extent. Three phases occur in plants when chromium is taken up. Translocation and partitioning, reactive oxygen species production causing damage to the plant and then differential defensive response. All this leads the plants to have less energy, thus germination process, root, stem and leave growth will be affected resulting in a decrease in total dry matter production and yield of the plant or crop (Rai *et al.*, 2004; Shanker *et al.*, 2005).

1.6.4 Manganese

This metal is quite common on Earth and is one of the essential trace elements in humans. It is the 5th most abundant metal in the crust. The highest prevailing minerals of the metal found are manganese dioxide known as pyrolusite and manganese carbonate known as rhodochrosite. Manganese is a silvery metal which is hard and brittle. It is a versatile element and exists in six oxidation states (Kaye and Laby, 1986; Dobson, Erikson and Aschner, 2004; Haynes, 2011).

Since the metal is brittle, it is used mostly in alloys and not kept in its pure state. Alloys containing manganese make up drinking cans, to improve corrosion resistance. Manganese (IV) oxide is used as a rubber additive, a catalyst and removes the green colour of glass due to iron impurities. Manganese (II) oxide is used during quantitative analysis and is a powerful oxidizing agent. Other items containing manganese are fertilizers; thus, soil can have an upsurge in these elements, fireworks and cosmetics also contain the metal. Smoking tobacco may also cause a person to take up manganese more than a non-smoking person. Pesticides have manganese present in the form of manganese sulphate. A combination of manganese, antimony, copper and aluminium causes an extremely magnetic alloy to form (Kaye and Laby, 1986; Dobson, Erikson and Aschner, 2004; Haynes, 2011). It can be found daily in our food, in items such as grains and rice, teas, herbs, parsley, spinach, bran, soya beans, nuts, green beans, oysters and olive oil (Marcus, 2013).

Manganese is found in the atmosphere due to the burning of fossil fuels and industrial processes of the steel industry. It is found as small dust particles which then land on soils or surface waters. Generally, manganese is found in the solid form in soils and tiny particles in the surface water (Van Wendel De Joode et al., 2016).

Since it is an essential metal in the body, low amounts can have a negative effect and causes adverse effects such as the interference with the growth process, bone formation and reproduction. With a low concentration of manganese, bones will tend to grow spongier and will thus be easily broken (ATSDR, 2012c). Manganese is also needed for the absorption of vitamin B1, so a low amount will also cause vitamin B1 deficiency which will cause more adverse effects. On the contrary, a high intake of manganese may cause hypotension. Poisoning with this metal is known as manganism, where the adverse effects caused are dependent on the age of the poisoned person, the form of the metal, health of the person and also route of the exposure (ATSDR, 2012c). Symptoms that appear in high toxic effects of manganese are complications in the nervous systems, which are dullness, lethargy, behavioural changes and weakness (Iregren, 1990). Manganism mimics Parkinson's disease since the metal accumulates at the basal ganglia, which is the organ affected by Parkinson's. The symptoms seen are tremors, difficulty in controlling movements, akathisia, dystonia, slurred speech, anxiety and lack of facial expression (Iregren, 1990; Roels *et al.*, 1992; Mergler *et al.*, 1994; United States Environmental Protection Agency, 2004). When a person inhales the fumes of manganese, these can cause a diverse type of symptoms which affect the reproductive system causing sperm damage and loss of sex drive, and pneumonia (WHO, 2000; Dobson, Erikson and Aschner, 2004).

1.6.5 Cobalt

Cobalt is a silvery-blue lustrous metal which has magnetic properties. It is the 32nd most abundant metal on the Earth. It is found in ores such as cobaltite which is a sulphide mineral made of sulphur, cobalt and arsenic; erythrite, known as red cobalt, is made up of arsenic and cobalt; and skutterudite, a cobalt arsenide compound. Cobalt is a trace element and is needed in small amounts. It forms part of the active site of the Vitamin B12 molecule. Its properties include being magnetised and thus producing magnets, especially if alloyed with nickel and aluminium. It is used in jet turbines and gas turbine generators. It is sometimes used in electroplating. The salts produce a bright blue colour and has been used in colours in paint, glass, pottery, porcelain and enamels. Some countries use the radioactive 60 cobalt to irradiate food thus preserving it, and it is also used to treat cancer (Kaye and Laby, 1986; Haynes, 2011). The anthropogenic source of cobalt is through poultry and pig manure as it is sometimes given as a feed additive, coal-fired power stations, incinerators, sewage sludge, vehicle exhaust and mining and phosphate fertilizers (WHO, 2006; Cobalt Institute, 2017).

Adverse effects of cobalt usually result in skin and respiratory issues. Acute effects are congestion, oedema, ventilator function reduction and lung haemorrhage, when inhaled. Chronic inhalation can cause wheezing, asthma, respiratory irritation, lung function reduction, pneumonia and fibrosis. Cardiac effects, liver and kidney congestion, conjunctiva, cardiomyopathy, nausea and vomiting, diarrhoea, allergic dermatitis and liver disorders were reported when inhalation or ingestion of cobalt occurs (Lauwerys and Lison, 1994; ATSDR, 2004b; Leyssens *et al.*, 2017).

1.6.6 Nickel

Nickel is found as minerals such as nickel oxide, or in the form of nickel/iron sulphides an example of which is pentlandite, and other minerals like garnierite, in the Earth's core. It was proved that most of the nickel present on Earth have come from meteorites. It has a silvery appearance and is the 24th most abundant element in the Earth's crust. It is absorbed from the surroundings by coal and oil. Different levels of nickel can be found depending on the soil type, such as clay soils, which will have a higher level of nickel (Kaye and Laby, 1986;

Haynes, 2011). Foods rich in nickel are whole wheat and grains, millet, oat and rye, cocoa, chocolate, tea, baking powder, legumes, red kidney beans, soy products and soybeans, chickpeas, nuts, peas and lentils (ATSDR, 2017).

Nickel is used in many everyday things such as jewellery, stainless steel alloy, coins, plating, welding, armour plating, batteries, rocket engines and boat propeller shafts. Since nickel resists corrosion, it is thus used to plate other metals, which would corrode on their own, thus avoiding corrosion. The nichrome alloy is used in toasters and other appliances which need heat since it will remain non-corrosive at high temperatures (Kaye and Laby, 1986; Haynes, 2011). Nickel allergy is a prevalent metal allergy that causes an allergic reaction to the skin (Sharma, 2013). The metal is present in the environment due to the burning of fossil fuel, trash incinerators and power plants, burning of coals and smelting industrial waste. Particles are distributed into the air, which then settles onto the ground as dust particles or through being washed down with raindrops. The nickel will then adhere to the soil particles and is generally immobile except if the soil is acidic where in this circumstance will exude into the groundwater (ATSDR, 2017). If nickel seeps into rivers or seas due to the release of industrial wastes, this can be very lethal to the aquatic life (United States Environmental Protection Agency, 1998).

Humans can take up nickel in different ways through food, crops containing a high level of nickel through contaminated soils and chocolate. Tobacco leaves have nickel present, and thus smokers can take up a higher concentration than a non-smoker. Consumption of nickel can cause a variety of adverse effects such as lung embolism, respiratory failure, asthma, dizziness when inhaling gas exposure, allergic reactions like when wearing nickel-containing jewellery, and increased possibilities of acquiring cancer (Sharma, 2013; ATSDR, 2017). Soluble nickel compounds like nickel sulphide and nickel oxide are all carcinogenic. All employees working in the nickel industry and are exposed to inhaling the metal are at significant risk of developing lung and nasal cancer (WHO, 2000; Denkhaus and Salnikow, 2002; ATSDR, 2017).

Nickel is essential for plant growth and is an essential micronutrient. Nickel is phytotoxic at an elevated concentration in soils. The activity of antioxidant enzymes is altered due to nickel where plants exhibit growth inhibition, chlorosis generation, necrosis and also wilting. The metabolic reaction in plants is induced strongly with nickel, where the reactive oxygen species is generated and continues to initiate oxidative stress. Plant growth is affected by inhibition of cell division in roots, and also photosynthesis and respiration are also negatively affected when nickel is elevated in the soil (Bhalerao, Sharma and Poojari, 2015).

1.6.7 Copper

Copper is the 26th most abundant element in the Earth's crust which has a reddish-golden colour and is sometimes found in its natural state. It is mostly found in minerals mainly chalcopyrite and the peacock ore called bornite, both of which contain copper, iron and sulphide. Examples of copper alloys are bronze and brass. Copper is an essential element and also is essential for some crustaceans. Forest fires, oceanic spray and putrefying foliage, is how copper is found in the atmosphere apart from being found naturally in the Earth's crust. It is used in everyday objects such as copper wires since copper is a good conductor of electricity and heat, coins, plating, fertilizer, and preservation of wood, preservation of fabric, and in creams to help as a barrier cream. Copper sulphate is used as a fungicidal on mildew and as an algicide in water purification. Copper compounds are also used in chemical tests such as Fehling's solution for sugar detection (Kaye and Laby, 1986; ATSDR, 2004a; Haynes, 2011).

Copper is released into the air through fuel combustion which then descends onto the soil after raining where it dissolves in the droplets. Dumping of copper-containing waste on river banks causes sludge thus leaching copper into the waters (ATSDR, 2004a). Soils containing high levels of copper will affect crops as these will not grow, effecting farm animals who graze on plants, especially sheep. Animals grazing on plants which have been grown in copper-rich soil, which is also low in molybdenum, will acquire excess copper. Sheep are given foot baths using copper sulphate, and sometimes livestock is given excess copper supplements (Dalefield, 2017).

Houses still containing copper pipes in their houses affects the drinking water as copper is leached slowly, and people who drink from the tap are at a higher risk of having a higher concentration of copper in their bodies. People working in copper industries or live near factories which process this metal are also are a risk of having a higher level of copper in their bodies compared to other people (ATSDR, 2004a; Haynes, 2011).

Adverse effects of high concentrations of copper in a person due to over-exposure include flu-like symptoms. Symptoms usually subside after around two days though higher exposure will cause diarrhoea, vomiting, irritation of the eyes, dizziness and irritation caused in the mouth cavity. An acute dose of copper salts causes acute gastroenteritis as the copper irritates the tissues and causes necrosis. If copper is taken in excess, then the liver is affected, causing hepatocellular degeneration and also necrosis. The liver is the organ that excretes excess copper from the body; thus, copper becomes cytotoxic to erythrocytes which leads to haemolysis. Intentional copper swallowing will cause hepatic and kidney disease. Copper poisoning can cause Wilson's disease, where the metal accumulates in the brain, liver and other organs instead of being excreted by bile, causing the person to have a lack of appetite, fatigue, jaundice, Kayser-Fleisher rings (where there will be a golden-brown eye discolouration observed), speech impairment, swallowing difficulties and uncontrolled movement. Brain damage may be caused by copper poisoning together with demyelination hepatic cirrhosis. Death has also been noted after copper poisoning (ATSDR, 2004a).

All this occurs due to copper influencing the functioning of vital organs such as the nervous system, the immune system and the endocrine system since copper is an essential element in the body needed by these three systems. The metal regulates the synthesis of neurotransmitters; thus, poisoning can express psychiatric symptoms and is a cofactor in the neurotransmitter dopamine conversion to norepinephrine. More copper will cause more norepinephrine conversion, which will cause adverse effects such as insomnia, anxiety, agitation and restlessness (Tsafrir, 2017).

Copper is necessary for plants at low levels, but in high amounts, it is phytotoxic at physiological, morphological and molecular levels. The metal interferes with several metabolic processes which are vital for the development and the growth of the plant. Some species are more prone to toxicity, and some are more tolerant of copper. Copper toxicity affects mostly root growth than shoot growth. Due to the negative effect on plant growth, the yield of the crops will also decrease (Adrees *et al.*, 2015).

1.6.8 Zinc

It is the 25th most abundant element found on the Earth's crust. It is a silvery white metal which gives a blue tinge to the metal. There are a variety of zinc ores present, though two of the most common ores are made up of zin sulphide which is an ore known as zinc blende, and another order made up of zinc silicate which is known as calamine. The heavy metal zinc tarnishes in air (Kaye and Laby, 1986; Haynes, 2011). The metal is an essential element and catalyses over 100 enzymes for human metabolism. Zinc assists in protein folding and in the gene expression regulation (Salgueiro *et al.*, 2000). A variety of food have more zinc levels than others such as lamb, beef, cheese, herring and sunflower seeds. The metal is used in galvanisation of other metals to prevent rusting. Metals galvanised by zinc are iron and steel which is used in lamp posts and car bodies, amongst others. Die-castings are produced using zinc. Die-castings are important to many industries, including automobile and electrical industries. Paints, cosmetics and soaps, deodorants, anti-dandruff shampoo, weapons, electrical equipment, batteries, plastics, ink, pharmaceuticals, textiles and rubber are manufactured with one if its components being zinc oxide. X-ray screens, luminous paint, fluorescent lights are made from zinc sulphide (Kaye and Laby, 1986; Haynes, 2011). Zinc is mixed with other metals to form alloys such as brass and bronze and is used to form the united states penny (ATSDR, 2005).

Anthropogenic sources of zinc are mining, smelting, tailings, coal and bottom fly ash, sewage sludge, fertilizers, waste combustion and steel manufacturing. When taken in excess, zinc can be carcinogenic. It is said to produce ‘zinc chills’ if freshly made zinc (II) oxide is inhaled. If high doses of zinc are ingested, the adverse effects caused are nausea and vomiting and stomach cramps. Chronic intake of excess zinc is anaemia, decrease in high-density lipoprotein (HDL) cholesterol, pancreatic complications (ATSDR, 2005), nausea and vomiting, fatigue, epigastric pain, copper deficiency, anaemia, impaired immune function, neutropenia (Fosmire, 1990).

1.6.9 Molybdenum

This metal is found naturally in the oceans and the crust and is the 54th most abundant element on the Earth’s crust. It has a shiny silvery appearance. The principal ore found is made up of molybdenum disulphide, which is called molybdenite. It has the highest melting point out of all the trace metals. Molybdenum’s properties help it to be an excellent alloying agent and it benefits steel by making it harder and increases the strength of the steel. Some of its uses are electrodes, in nuclear energy operation, as a catalyst in the refinement of petroleum. At the right dose, it is essential for the survival of plants (Kaye and Laby, 1986; Jones, 1994; Haynes, 2011). Foods which contain higher amounts of the metal are grains, nuts and legumes (Ratini, 2018).

Molybdenum converts to a higher solubility in soil that is alkaline and is absorbed, by legumes such as lentils, beans and peas. Molybdenum is an essential element for both plants and animals. A variety of enzyme that contains molybdenum, is used by plants and animals. Nitrogen-fixing bacteria have an enzyme called nitrogenase which contains molybdenum and is used to make nitrogen available to plants from the air. Legumes are a type of plants that have these bacteria present at their root nodules (Kaye and Laby, 1986; Haynes, 2011).

When people inhale molybdenum fumes, it may cause decreased appetite, fatigue, anorexia, headaches, listlessness, weakness, chest pain, arthralgia and myalgia, gout and hypochromic microcytic anaemia. Anaemia is caused due to molybdenum being a co-factor which is required for transferases to bind to iron which augments the production of xanthine oxidase. An increased amount of molybdenum decreases the amount of copper in the body, causing copper deficiency toxic side effects. Chronic molybdenum intake has been noted to cause testicular atrophy (Momcilović, 1999). Animals grazing on molybdenum contaminated grass or hay sometimes perished due to a deficiency in copper (Neunhäuserer, Berreck and Insam, 2001).

1.6.10 Arsenic

Arsenic can be found on the Earth’s crust in three allotropic forms in small quantities. It is the 55th most abundant element on the Earth and is a bright silvery-grey brittle semi-metal. A minor quantity can be found in its natural form. The most prevalent mineral found of arsenic is called arsenopyrite, an iron arsenic sulphide with an opaque silvery-white colour. Other arsenic minerals found are realgar, which is an arsenic sulphide also known as ‘ruby of arsenic’ and has a red to orange colour; enargite, which is a copper arsenic sulphosalt mineral with a metallic colour; and orpiment, which is an arsenic sulphide mineral with a lemon-yellow to a brownish yellow colour. This metal can be found in both types of compounds, both organic and inorganic forms (Kaye and Laby, 1986; WHO, 2000; Haynes, 2011).

Arsenic is released naturally in the air through two primary means. Volcanic activity releases arsenic at around 3000 tons per year while the most abundant sources are the microorganisms which approximately release around 20,000 tons of arsenic per year as methylarsine. Anthropogenic source for arsenic pollution is the largest source which releases around 80,000 tons of the metal into the atmosphere through the burning of fossil fuels. Areas which are neighbouring power plants which use arsenic-rich coals, cause atmospheric arsenic concentrations to surpass $1\mu^3$ (WHO, 2000).

Uses of arsenic are the preservation of wood, manufacturing of certain types of glass, preparations of insecticides, doping agent in semiconductors such as gallium arsenide which is used to change electric current into laser light. It is used in pyrotechnics and in bronzing too. Release of arsenic into the atmosphere is caused during the processes of production of copper, zinc and lead, and in agricultural use in insecticides. The metal cannot be destroyed and thus accumulates (Kaye and Laby, 1986; Haynes, 2011). It is spread by being carried with the wind and thus reaching further areas which then settles on soils and surface water which can then affect plants, animals and humans. It is one of the highest toxic elements found on Earth. Plants take up the metal quickly, which can then enter the food chain. When present in water, fish that take up an amount of inorganic arsenic become toxic to their predators which include birds and humans. Genetic alterations in fish have been noted when freshwater organisms ate arsenic-contaminated plants (ATSDR, 2007a).

People are usually exposed to the metal if they work in industries producing the metals copper, zinc and lead. Houses made out of wood have been usually covered with arsenic as wood preservation which makes the habitants have an increased risk of arsenic exposure. Arsenic is now banned in insecticides, though people who live in areas, previously exposed to the insecticide, are still at risk of exposure. Adverse effects of inorganic arsenic exposure are gastrointestinal irritation, lung irritation, a reduction in the production of red blood cells and white blood cells, and skin alterations. It has been thought that exposure has also caused cancer in people. High exposure can lead to miscarriages and infertility, cardiac problems, brain damage and damage to deoxyribonucleic acid (DNA). Organic arsenic produces a different portfolio of adverse effects such as stomach upsets and nerve damage. The organic compound does not affect the DNA and does not cause cancer. Organic arsenic is found in large amounts in some foods such as prawns (Martin Sabine and Griswold Wendy, 2009).

Both forms of inorganic arsenic (arsenate and arsenite), are taken up by the plant’s roots. Arsenate is then converted to arsenite in the plant where arsenite is more toxic than arsenate. They both interrupt the plant’s metabolism but through various metabolic pathways. Arsenate is translocated by phosphate transport proteins across cellular membranes, since it is a chemical analogue of phosphate, and thus disrupts some phosphate-dependent aspects of metabolism. This disruption leads to an imbalance in the phosphate supply. Enzymes which comprises compactly spaced cysteine residues, or dithiol co-factors, are bound to and possibly inactivated by the dithiol reactive compound arsenite.

Arsenic is reduced, detoxified and then quarantined, it mimics phosphate, binds to the sulfhydryl groups and leads to the oxidative stress in the plant (Finnegan and Chen, 2012).

1.6.11 Silver

Silver is the 65th most abundant element in the Earth's crust and is usually found in excessive mineral areas. It has a silvery appearance and is a soft, shiny metal. Sulphur compounds in the air slowly tarnish the appearance of silver, developing a black silver sulphide. It is found in its natural form and can be found in ores such as argentite which is a cubic silver sulphide at high temperatures, which then forms acanthite which is a monoclinic silver sulphide at average temperatures. Silver is also found in the ore called chlorargyrite which is made of silver chloride and is also known as cerargyrite and horn silver when it is weathered by desert air. It is usually produced as a by-product when other metals are refined (Kaye and Laby, 1986; Haynes, 2011).

Silver has many uses today in items such as jewellery; photography, which uses silver bromide and silver iodide; mirrors, since it has excellent reflector properties of visible light, tableware, dentistry and in life-long batteries. Since it has excellent conductive properties of electricity and heat, it has been used in the electricity industry. It is used in some medical devices such as dressings and sprays due to its antibacterial properties which aids to kill lower organisms. It has been used in deodorants to help with unpleasant odours and is found in gloves which are suitable for touchscreens. At a concentration of up to 2g of soluble silver salts, such as silver nitrate, are proved to be lethal. Corneal injury can be caused if liquid silver comes into contact with the eyes. Dermal contact with silver can also cause skin irritation which can also continue to cause allergic dermatitis and a condition known as argyria which can make the skin turn a purple-grey colour. Inhalation of the metal causes adverse effects such as dizziness and headaches, breathing problems and respiratory inflammation. Higher concentrations if inhalation of silver will cause confusion and staggering, drowsiness, unconsciousness, coma and also death has been reported at very high doses. Ingestion of the metal will cause gastrointestinal effects such as nausea and vomiting, diarrhoea, stomach discomfort and narcosis, and at higher levels will cause cardiac abnormalities and brain damage (Martin Sabine and Griswold Wendy, 2009).

In agriculture, silver nanoparticles are used as plant growth stimulators, agents used to enhance the ripening of fruit, and it is found in fungicides to inhibit fungal disease. Release of silver nanoparticles in the environment have the ability to permeate plant rhizospheres and thus are easily found in the food chain causing alarm to animals grazing the plants and humans eating these contaminated plants. Silver is known to be the second most toxic metal after mercury, in the aquatic sector. The nanoparticles leach non-degradable silver ions into the waters, which are bioaccumulative and very toxic to the organisms (Yan and Chen, 2019). Silver nanoparticles and silver ions have a substantial effect on root growth compared to shoot growth. Chlorophyll content decrease, and thus leaf chlorosis is induced. Oxidative stress results due to a decrease in photosynthetic pigment content and an increase in malondialdehyde content. Chloroplasts, nucleus ultrastructure and mitochondria are all damaged and are the main organelles affected by silver toxicity (Fayez, El-Deeb and Mostafa, 2017).

1.6.12 Cadmium

Cadmium is a toxic element classified as the 64th most abundant element on the Earth's crust. The metal has a silvery colour with a bluish tint. It is usually found in combination with zinc. Greenockite is a rare and only mineral ore made up of a large quantity of cadmium and is made up of cadmium sulphide with a honey-yellow to reddish-brown colour. It is produced usually as a result of zinc manufacturing (Kaye and Laby, 1986; Haynes, 2011). Natural sources of cadmium in the environment are through volcanic activity, and forest fires which generates cadmium into the atmosphere, rocks containing cadmium can release cadmium into the waters through erosion. A few of the anthropogenic sources of cadmium pollution, are through the use of fertilizers made from phosphate rock, and pesticides containing cadmium. It is a very water-soluble element (ATSDR, 2012a). Cadmium use has been reduced due to it being toxic, but it still has some uses such as in nickel-cadmium batteries, in pigmentation for glassware, in corrosion-resistant plating, in nuclear reactors and as a stabilizer in the production of plastic (Kaye and Laby, 1986; WHO, 2000; Haynes, 2011; ATSDR, 2012a).

Use of artificial fertilizers has increased the levels of this metal, which has exposed the soil to a higher level of cadmium which also leach it into the waters where plants may take up the metal. Absorption of cadmium by plants depends on the soil’s pH. An acidic soil increases the plants' absorbency. Microorganisms found in the soil together with other organisms such as earthworms can also absorb cadmium which will be present in the soil. On the contrary, cadmium in the aquatic ecosystem will tend to accumulate in organisms such as fish, shrimps and mussels (ATSDR, 2012a).

Cadmium rich foods are shellfish, mussels and shrimps, dried seaweed, liver and mushrooms. Tobacco contains a high amount of cadmium, causing smokers to take up a higher concentration of cadmium than non-smokers. Employees working in metal refineries through inhalation are at risk of taking up cadmium which can be lethal. When exposure occurs, cadmium primarily affects the kidneys, as the metal forms complexes which are transported to the kidneys, which then causes nephrotoxicity. Adverse effects caused by cadmium accumulation in the body are reproductive system failure causing infertility and nephrotoxicity, which causes alterations in the calcium metabolism and thus, bone fractures can occur. Other effects are psychological disorders, gastrointestinal disorders, central nervous system problems, immune system deficiencies, DNA impairment, and development of cancer. Itai-Itai disease is also caused by cadmium toxicity which was initially seen in Japanese who were found to have a high level of cadmium because of their diet, which generated symptoms of osteoporosis and renal dysfunction. It has been reported that cadmium is genotoxic and ecotoxic in animals by many researchers. Cadmium is classified as a toxic element, a carcinogenic, and a teratogenic element (IARC and WHO, 1993; ATSDR, 2012a).

Plants that are growing in cadmium contaminated soils show symptoms of stunting and chlorosis. Cadmium in the soil stops iron being taken up by the plant (Benavides, Gallego and Tomaro, 2005). The metal has also been seen to interfere with phosphorous, causing a deficiency in the plants and interferes with manganese transportation. It interferes with many other elements in the uptake, transportation and use of the elements (Das, Samantaray and Rout, 1997; Benavides, Gallego and Tomaro, 2005).

1.6.13 Selenium

Selenium is found in two forms, either a silvery metal or as a red powder. It is the 67th most abundant element in the Earth's crust and is found in a few rare minerals. It is usually obtained from anode muds that is produced from copper electrolytic refining. The anode muds are smelted with sodium bicarbonate, which discharges selenium. They can be roasted with sulphuric acid or with sodium bicarbonate which releases the element (Kaye and Laby, 1986; Haynes, 2011). Selenium is found in the atmosphere as the methyl derivative. Natural sources of selenium in the environment are through weathering of rock containing the element releasing it into the soil, or the particles are adsorbed onto dust particles, making them pollute the atmosphere. Anthropogenic activities cause selenium release through coal and oil combustion. Applications of fertilizer synthesised from phosphate rocks, causes an increase in selenium found in the soil. Waste disposal can also cause a deposit of the element (Kaye and Laby, 1986; ATSDR, 2003; Haynes, 2011).

Selenium has superior photoconductive and photovoltaic properties and thus is used extensively in electronics. Selenium is highly used as a colourant to glass. Some compounds give it a red pigment colour while others can decolourise the glassware. Architectural glass can use selenium to reduce the transmission of sunlight, giving the glass a bronze tint. Pigments from selenium are thus used for glassware, ceramics, paint and plastics. Selenium selenite is included in animal feeds, it is added to supplements which provide vitamins and minerals. The anti-dandruff shampoos also contain selenium compounds. 150 tons of selenium manufacturing originates from old photocopiers and industrial waste, out of the 1500 tons of selenium produced per year (Kaye and Laby, 1986; ATSDR, 2003; Haynes, 2011).

As a natural element, it does not pose much risk to humans and other organisms as it is immobile. However, when selenium reacts with oxygen, the compound becomes mobile and thus increasing its toxicity. Apart from the oxygen factor having to be taken into account regarding selenium in the soil, pH also plays a role in selenium's mobility, making it leach into the water table and water surfaces. Selenium released into the atmosphere will be in the form of selenium dioxide. When this comes into contact with moisture such as rain droplets, it forms selenious acid, which is very caustic when it comes in contact with the skin and eyes. Selenious oxide is usually broken down into water and selenium, which are safer to organisms (ATSDR, 2003).

Some selenium-rich foods are found, and these include grains and cereals, meat and Brazilian nuts. These average amounts are entirely safe for humans and beneficial since it is an essential element in the body. However, when it exceeds the concentration needed through the intake of contaminated crops with selenium, adverse effects can later be noted. Fertilizers increase selenium in soil, and waters also may contain selenium if waste containing selenium is dumped nearby. Employees working in manufacturing industries such as copper refining are at a higher risk of selenium exposure through inhalation (Yang *et al.*, 1983; ATSDR, 2003).

Inhalation adverse effects of selenium are dizziness, mucous membrane irritations and fatigue. A significant exposure to selenium may cause symptoms which include bronchitis, deformed and loss of nails, brittle and loss of hair, rashes (Yang *et al.*, 1983), severe pain, headaches and fever, skin lesions, hepatomegaly, tooth decay, conjunctivitis, swelling of the skin, gastrointestinal effects such as vomiting, abdominal pain and diarrhoea, garlic breath, pneumonia, nervous system disorders, reproductive failure and also congenital disabilities have been reported. It is also classified as a carcinogen (ATSDR, 2003).

Excess selenium in soils induces oxidative stress to the plant and protein structure and function distortion. Toxicity to plants is caused in two ways. One mechanism is where the selenoproteins are malformed, and the other mechanism induces oxidative stress (Gupta and Gupta, 2017).

1.6.14 Mercury

Mercury is a silvery liquid at room temperature but is rarely found in its natural form. It can be found as droplets in the mercury sulphide ore called cinnabar and is the 66th most abundant element in the Earth’s crust (Kaye and Laby, 1986; Haynes, 2011). Volcanic active and forest fires are two of the natural sources of finding mercury in the environment. It is usually found as mercury salts, or as the organic compound, which is derived from the breakdown of minerals. The mineral breakdown usually occurs through the erosion of rocks and soil which are exposed to water or wind. Anthropogenic activity release mercury into the environment through the burning of fossil fuels which releases it into the atmosphere, together with mining and smelting, fertilizers containing mercury release it into the soils and waters, and also waste disposal adds mercury to our environment (ATSDR, 1999).

Mercury is converted to methylmercury in surface waters by microorganisms which is more toxic since it is easily absorbed by organisms including fish. Methylmercury thus enters the food chain as a consequence and results in the accumulation of mercury throughout the food chain since it is not degraded. Plants do not tend to have mercury unless specifically sprayed with mercury-containing products (ATSDR, 1999). Mushrooms are one of the plants that have the aptitude of absorbing mercury from the soils (Li *et al.*, 2017).

Mercury was used in our everyday lives in the thermometer and barometers as it has a high degree of thermal expansion and high density, respectively. Household thermometers containing mercury have mostly been replaced with alcohol or digital thermometers due to it being poisonous if broken and swallowed (Kaye and Laby, 1986; Haynes, 2011). Mercury can cause lung irritation if inhaled, eye irritation, rashes, and gastrointestinal adverse effects such as vomiting and diarrhoea. It has industrial use such as in the manufacturing of chlorine, where it is used as a liquid electrode (ATSDR, 1999), and it is used for its amalgamating properties with gold. It is thus used in the recovery of gold by retrieving it from the ore. It is was used as tooth fillings in dentistry and compact fluorescent lightbulbs (Kaye and Laby, 1986; Haynes, 2011). Calomel, which is mercury (I) chloride compound, was used in photochemistry and calomel electrodes. Vermillion, which is mercuric sulphide, is a bright red paint pigment. Corrosive sublimate, which is the compound mercury (II) chloride, was used in insecticides and rat poison. All these uses have nearly all been phased out due to its toxicity (Kaye and Laby, 1986; ATSDR, 1999; Haynes, 2011). Mercury is still being used today as a catalyst in chemical industries and rectifiers and electrical switches (Kaye and Laby, 1986; Haynes, 2011).

Thimerosal is an organic compound of mercury which was used in vaccines as a preservative. Thiomerosal in vaccines will break down into ethylmercury, which, unlike methylmercury, is not toxic. Thimerosal use in vaccines has been reduced since the single-use vaccine have been invented instead of multi-dose formulations (Centres for Disease Control and Prevention, 2013).

Adverse effects of mercury toxicity can be quite severe. It is genotoxic and damages the DNA and the chromosomes, which cause mongolism, also known as Down’s syndrome. It has adverse effects on the reproductive system, which can lead to miscarriages, congenital disabilities and also sperm damage in men. Its effects also cause neurological disorders when a high concentration which causes a disease known as Minamata disease or Chisso-Minamata disease (Li *et al.*, 2017). Its adverse effects include learning disabilities, speech defects, memory loss, tremors and muscle incoordination, deafness, vision complications, and personality changes, insanity, paralysis, and when severe also coma and death. It is teratogenic and thus affects the foetus if the woman is pregnant and has high levels of mercury in her body (ATSDR, 1999; Martin Sabine and Griswold Wendy, 2009).

Mercury pollution is mostly caused by power plants which use coal-fired boilers. Mercury is released into the neighbouring area as particulate form and as gaseous form. These are deposited onto plant’s foliage where the plants absorb the mercury. Plants also take up mercury from the roots, but mercury on leave foliage has been proved to be absorbed from ambient air and not from the soils. Mercury plant absorption makes crops grown near power plants, have a higher amount of mercury in them since the atmosphere will be filled with mercury particulates (Tomiyasu *et al.*, 2005; Li *et al.*, 2017).

1.6.15 Lead

Lead in its natural form is seen as a dull silvery-grey metal which is a very soft metal that can easily be worked into sheets. It is found as the 37th most abundant metal on the Earth's crust. It is found as a mineral ore known as galena which is made up of lead sulphide or in combination with other metals such as zinc, silver and copper (Kaye and Laby, 1986; Haynes, 2011). It is mined in substantial quantities of around six million tons per year though some is being recycled as it was estimated that the supply would finish shortly (ATSDR, 2007b).

Sources of lead in the environment are mostly due to anthropogenic activity. Some activities are burning of gasoline and car engines which use it as an anti-knocking additive in petrol. These are a great source of lead pollution through the release of lead chloride, lead oxides and lead bromines which are released from the car's exhaust pipes and thus released into the atmosphere (Kaye and Laby, 1986; ATSDR, 2007b; Haynes, 2011). Lead particle matters that are large will immediately fall to the ground while smaller particles will be carried along further away before settling down or washed down with moisture and rain (ATSDR, 2007b). Leaded petrol is not used any more due to the lead causing a variety of health adverse effects, and most cars have switched over to unleaded petrol (ATSDR, 2007b; Mayo Clinic, 2016).

Lead was widely used before in pottery lead glazes, hair dyes and insecticides, though these have been replaced and banned due to their detrimental effects especially to children. Lead is still widely used today in all aspects of our everyday lives (ATSDR, 2007b). It is used in car lead-acid batteries, sheeting in computer screens which help shield the radiation, ammunition, projectiles, cable sheathing, lead crystal glass, diving weight belts, in sports equipment and is used to store corrosive liquids. Sometimes lead is still used in architecture for roofing due to it being a corrosive-resistant metal and also in stained glass windows

(ATSDR, 2007b; WHO, 2018). Foods that have a higher content of lead are fruit and vegetables, grains, seafood, red meat, wine and soft drinks. Cigarette smoke may also contain an amount of lead. Some houses still have lead piping making lead present in their tap waters (ATSDR, 2007b).

Adverse effects caused by lead being present at a higher concentration in the body are hypertension, miscarriages, premature and low births, stillbirths, renal damage, brain complications, abdominal pain, pica, peripheral nerve damage, sperm damage and thus a decrease in male fertility, encephalopathic signs, disruption of haemoglobin synthesis and thus iron deficiency, cognitive impairment, brain development and central nervous system development in children are altered. Pregnant women who have lead stored in their bones due to excess uptake will have lead slowly released in the bloodstream, which will then affect the foetus. Children are more affected to lead poisoning, and some adverse effects seen are reduced intelligence, a decline in educational achievement, a reduction in the attention span and an increase in anti-social behaviour. In waters, lead can upset the phytoplankton, which will have a global effect since oxygen levels in the water can be decreased with a reduction in phytoplankton (ATSDR, 2007b). It has also been noted that soil organisms are also affected by a high amount of lead present (Zeng *et al.*, 2006).

1.7 Carcinogens

Some elements are classified depending on their carcinogenicity in humans, from group 1 being the most carcinogenic and group 4 being least or not a carcinogenic element according to the International Agency of Research on Cancer (IARC) (WHO, 2000, 2020; Brunning, 2015).

Elements in Group 1 are carcinogenic due to the sufficient evidence collected. This group contains the heavy metals arsenic, and its inorganic compounds; cadmium and its compounds; chromium VI compounds; and nickel compounds (WHO, 2000, 2020; Brunning, 2015).

Group 2A is a probable carcinogenic group, which has limited evidence that the heavy metal causes cancer. Some studies show that it is carcinogenic in animals. This group contains the inorganic lead compounds (WHO, 2000, 2020; Brunning, 2015).

Group 2B contains elements and compounds, which might be carcinogenic. There is limited evidence that elements in this group are carcinogenic to humans and animals. This group contains the compounds vanadium pentoxide, methylmercury, molybdenum trioxide, metallic nickel, nickel alloys, and the element lead (WHO, 2000, 2020; Brunning, 2015).

In Group 3, the carcinogenicity is not classifiable. There is insufficient evidence of these elements being carcinogens in both humans and animals. The elements in this group contain chromium (III) compounds and chromium metallic compounds, copper, selenium and its compounds, mercury and its inorganic compounds, and arsenic organic compounds which are not metabolized by the human species (WHO, 2000, 2020; Brunning, 2015).

The last group is Group 4, which are elements that are probably not carcinogens. There is no evidence to suggest that they cause cancer in either humans or animals. Elements in this group contain manganese, zinc and silver (WHO, 2000, 2020; Brunning, 2015).

1.8 Aim and Objectives

The aim of the study was to evaluate whether heavy metals found in soil i) are present in high amounts; ii) are present differently across Malta and Gozo; iii) if there are soil limits regulating heavy metals.

The objective of the study was (i) to develop and validate a method for the analysis of heavy metals in soil using an X-Ray Fluorescent (XRF) Spectrometer; (ii) to take samples from around Malta and Gozo and analyse the quantities of the heavy metals present in agricultural soil; (iii) to observe differences in heavy metal content between localities and districts; and (iv) to research established limits for heavy metals concentration in soil used for food and to compare the thresholds found with the quantities investigated.

Chapter 2: Materials and Methods

2.1 Pilot study

A pilot study was conducted to familiarise with how the XRF spectrometer operates, how the analysis is performed, and how to follow the respective protocols that were present in the laboratory. During the pilot study, five samples of soil were collected from the Government Farm Malta in Għammieri and analysed using the XRF spectrometer.

The global positioning system (GPS) coordinates which indicate from where the samples were collected, were recorded and documented (Table 2), together with a photo using Google Earth, to mark the different areas of sampling (Figure 5). The samples were labelled alphabetically from A-E.

Table 2: GPS Coordinates of Għammieri Samples

Sample	**GPS Coordinates**
Sample A	35°52'17''N 14°28'40''E
Sample B	35°52'22''N 14°28'45''E
Sample C	35°52'19''N 14°28'41''E
Sample D	35°52'21''N 14°28''42''E
Sample E	35°52'20''N 14°28''43''E

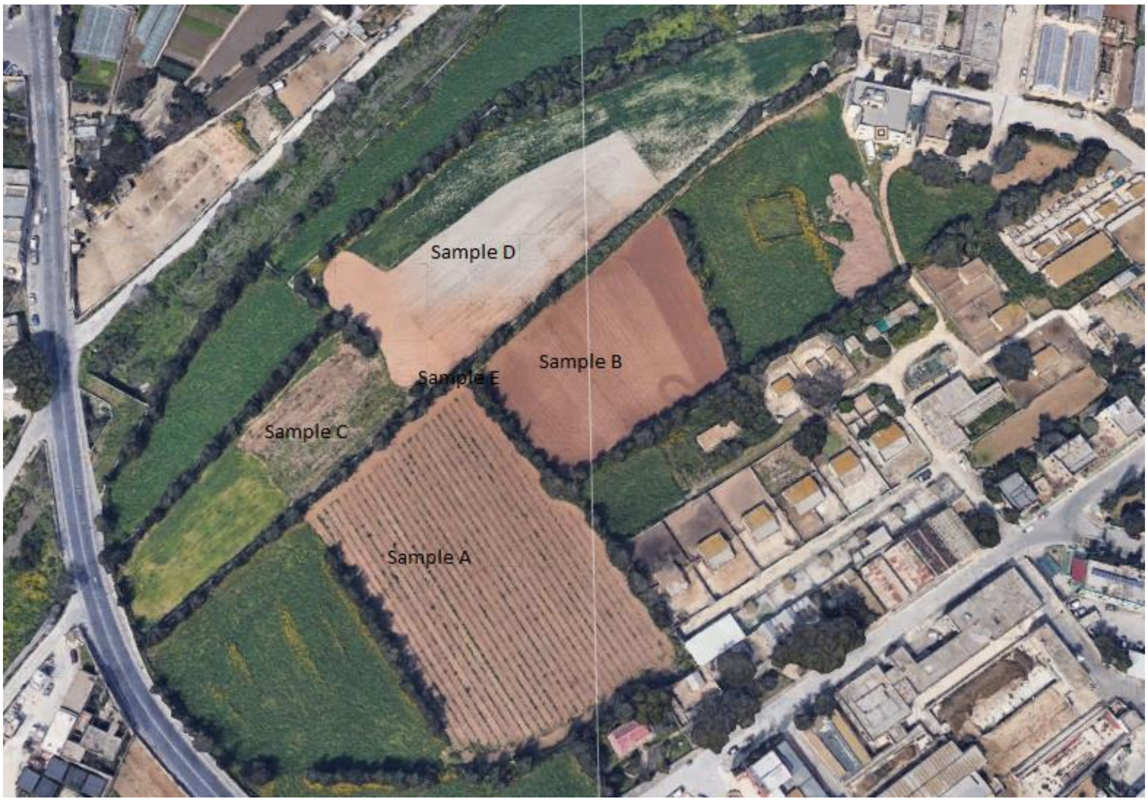


Figure 5: Għammieri fields and Sample Locations

The S2 Ranger Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer was used for the analysis of the collected soil samples, employing the sample cup method. Analyses were conducted at the laboratory of the Department of Chemistry, at the University of Malta. The test was repeated three times for each sample, to determine if there were any statistically significant differences between the results obtained, to show and ensure that the spectrometer provided reliable results.

Statistical analysis was conducted using the software package using the IBM® SPSS® Statistics 26. Three statistical analyses tests were used, namely the Shapiro-Wilk test, One-Way ANOVA and the Kruskal-Wallis test, to determine if the elemental score distribution between the five samples are significant or not. The Shapiro-Wilk test was used to determine whether an element score distribution was normal or skewed. The null hypothesis specifies that the score distribution is normal and is not rejected if the ρ-value exceeds the 0.05 level of significance. The alternative hypothesis specifies that the score distribution is skewed (not normal) and is not rejected if the ρ-value is less than the 0.05 criteria.

If the score distribution is skewed, then the One-Way ANOVA test and the Kruskal-Wallis test would be used to compare the mean element scores between the five samples. The One-Way ANOVA is a parametric test and is used when the element score distribution is normal, while the Kruskal-Wallis test is a non-parametric test and is used when the score distribution is skewed. For both tests, the null hypothesis specifies that the mean element scores differ marginally between the samples and is rejected if the ρ-value exceeds the 0.05 level of significance. The alternative hypothesis specifies that the element scores vary significantly between the samples and is not rejected if the ρ-value is less than the 0.05 criteria.

In the initial phase of testing, apart from going through the protocol on how to use the XRF, the method needed to be validated to ensure that the results provided were accurate. The five samples that were collected in the pilot study were divided into two identical batches consisting of five samples. Batch one was tested the XRF, while the second was tested by an accredited lab situated in Germany. The samples of batch two were tested using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The laboratory was accredited according to DIN EN ISO/IEC 17025:2005 notification under the DAkkS German Accreditation System for Testing. The laboratory was (D-PL-14081-01-00) accredited. The method used for the ICP-MS by the accredited lab was DIN EN 13657: 2003-01 using aqua regia digestion.

Two statistical tests were used to determine if the XRF results correlate with the result of the ICP-MS. The Spearman correlation coefficient was used to measure the strength of the relationship between the two continuous variables (XRF and ICP-MS) and ranges from -1 to 1. A correlation coefficient close to 1 indicates a strong positive relationship; a correlation coefficient close to -1 indicates a strong negative relationship and a correlation coefficient close to 0 indicates no relationship.

The Binomial test was used to compare mean XRF score with the accredited ICP-MS value. The null hypothesis specifies that the mean XRF score is comparable to the ICP-MS value and is not rejected if the ρ-value exceeds the 0.05 level of significance. The alternative hypothesis specifies that the mean XRF differs significantly from the ICP-MS specification and is not rejected if the ρ-value is less than the 0.05 criteria.

2.2 Sample Collection

The analysed soil samples were collected from Malta and Gozo. Agricultural soil samples were taken from each locality, were possible, in at least two different areas, to ensure representation. Localities were selected through stratified sampling and samples were collected between February 2019 and August 2019. Verbal permission was obtained from each owner and anonymity was ensured. Localities that were not sampled were Floriana, Marsa, Paola, Senglea, Valletta, Vittoriosa, Birkirkara, Gżira, Ħamrun, Msida, Santa Venera, Ta' Xbiex, Tal-Pieta, Tas-Sliema, Ħal-Balzan, Mtarfa, Għarb, Munxar, Nadur, Qala, San Lawrenz and Comino. These localities were not tested as either no agricultural soil was present, or permission for testing was not granted.

Soil samples were collected from the four corners of the agricultural land, up till where crops were grown, together with a fifth one from the centre (Figure 6). Top vegetation was removed before digging, and holes were dug up to 12 inches deep and the uprooted soil was mixed properly before collecting, to obtain a homogenous sample. Samples were placed in sterile containers. The hand trowel was made of plastic and cleaned after every use to avoid contaminating the samples. If any activity surrounding the field was noted, such as landfills, this was taken into account and written on the container's label. A total of 101 samples were collected.

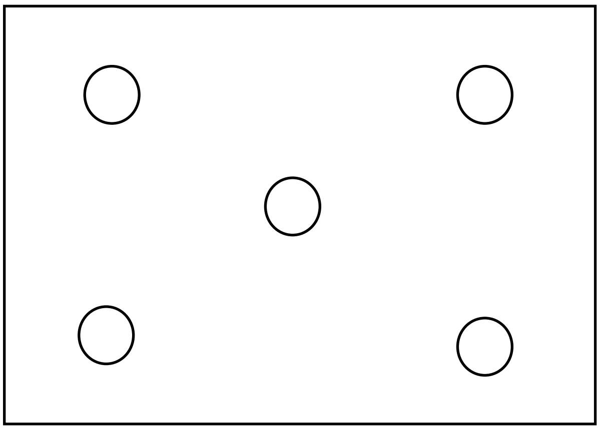


Figure 6: Map of sampling method

Malta and Gozo were divided according to the Nomenclature of Territorial Units for Statistics (NUTS) classification to ensure representation (NSO, 2017). The islands were divided into six districts: Southern Harbour, Northern Harbour, South-Eastern, Western, Northern and Gozo and Comino, using the Local Administrative Unit 1 (LAU1) (Figure 7) (NSO, 2017).

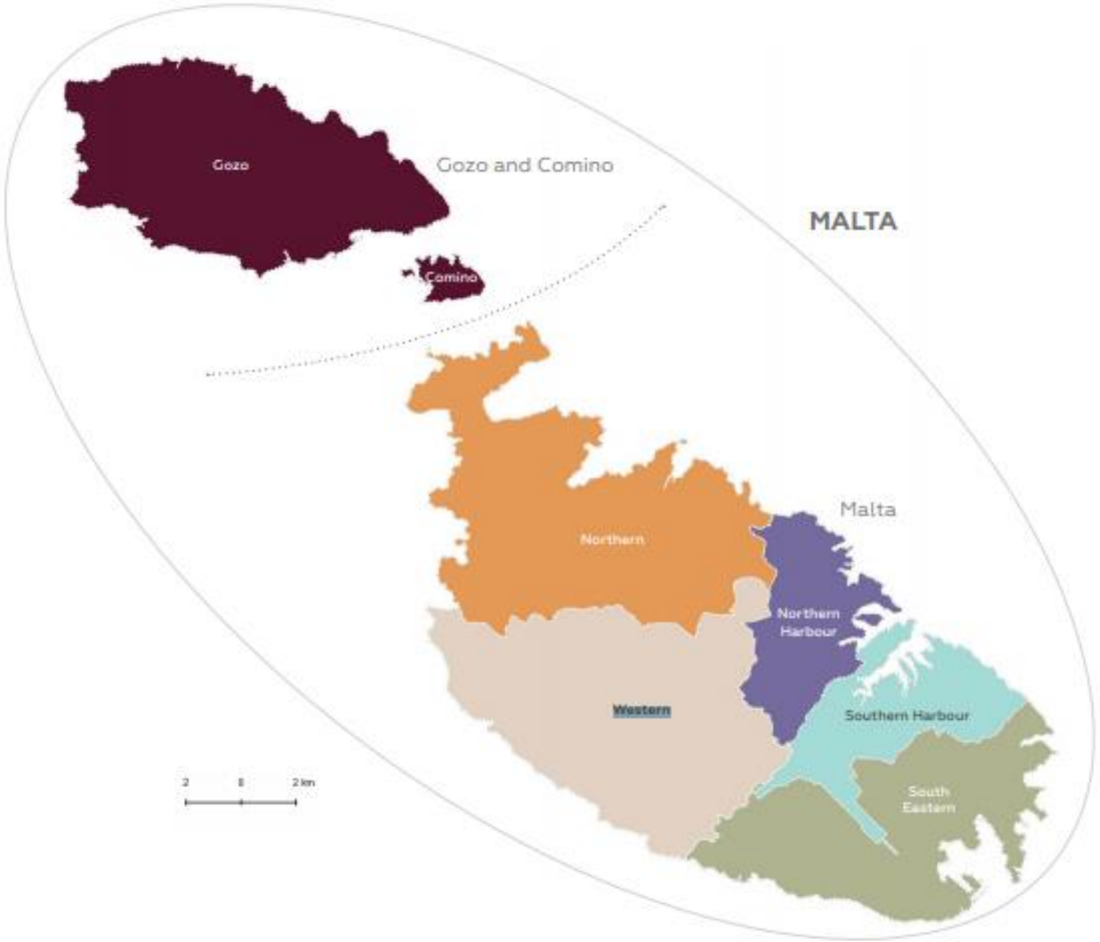


Figure 7: Graphical Image of Malta, Gozo and Comino using NUTS Classification according to the LAU1 (NSO, 2017)*.*

2.3 Reference control using organic farms

A reference was needed to see if there are any differences between the heavy metal levels observed in the fields, as opposed to organic farms that are regularly tested.

Permission was sought to collect soil samples from two organic farms, which are located in Mġarr and Manikata. The estates possess an Organic Farming Council Regulation (EC) No 834/2007 according to the EU Agriculture. The Binomial test was performed to compare the results from the 101 samples collected, to each of the controls. Four possible outcomes could result from these comparisons.

In both Binomial tests, the null hypothesis is not rejected meaning that the sample mean of the 101 observations vary marginally from the control one value, and the control two value.

In both Binomial tests, the alternative hypothesis is not rejected meaning that the sample mean of the 101 observations vary significantly from the control one value, and the control two value.

The null hypothesis is not rejected in the first Binomial test, and the alternative hypothesis is not rejected in the second Binomial test meaning that the sample mean of the 101 observations vary marginally from the control one value, but vary significantly from the control two value.

The alternative hypothesis is not rejected in the first Binomial test, and the null hypothesis is not rejected in the second Binomial test meaning that the sample mean of the 101 observations vary significantly from the control one value, but vary marginally from the control two value.

2.4 Sample Preparation and Analysis

Each sample was sieved using a 45 µm mesh, to remove any plant matter or stones which could alter the results. The collected sieved samples were placed in a watch glass and heated in an oven at 110°C for over 24 hours. Heating was performed to reduce moisture from the soil sample to avoid interference with the XRF analyses and since moisture could alter the soil matrix for which the spectrometer would have been calibrated. During this process, diligence was maintained so that sample cross-contamination or external contamination would not occur. The resulting soil was then sieved again following the heating process, to make it more homogenous and finer and then stored in containers containing desiccators, until further use (Agrafioti, Kalderis and Diamadopoulos, 2014).

2.5 XRF instrumentation and sample cup preparation

The X-ray Fluorescence (XRF) spectrometry element analysis is established on the basis where the individual atoms are excited by an external energy source, which releases X-ray photons having energy or wavelength that is specific to each element. Elements can be identified and quantitated by calculating the number of photons from the energy released. XRF can be used to analyse solids and liquids and can analyse both major and trace elements. The atom's inner electronic shells release distinctive radiation, thus identifying the element under certain conditions. The X-ray photons coming from the emitted quanta of radiation, has specific energies, thus permitting the identification of the atom's source. The chemical bonding is not taken into consideration as only the inner electron shells are involved during the emission of the X-rays. The advantage of the XRF is that samples can be analysed without destruction of the sample to be prepared. The sample has to be homogenous, and the powder has to be refined to have better results. If the particle size is more than 50 µm, errors of 50% can occur thus particle size is an essential factor when testing the sample. All this was brought about due to the inconsistency of the X-ray penetration extent with energy (Jenkins, 1988; Jenkins, Ron; Gould, R. W.; Gedcke, 1995).

Analyses were carried out using the sampling cup method to quantify the heavy metals in the sample. This procedure consisted of assembling the plastic cup with a 3.6 µm SpectroMembrane® Mylar® Thin-film. The film is checked to see if it is taut for accurate readings. Soil was gently poured into the cup, tapped and pressed gently to make it more compact and that no air pockets are present. The lid was secured onto the cup and labelled accordingly. The film was checked for any breakage before placing onto a ring and loaded into the XRF.

Quantification was obtained by using the automatic Bruker S2 Ranger XFlash® technology 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 under a helium atmosphere and a current of 2 mA, and having a silicon drift detector. The elements detected in the soil samples were expressed as oxides. They were calculated using calcium carbonate as a matrix while using the instrument's software, Spectra EDX Launcher, to read the data. The fitting parameter R/R_0 has to be below 30 for the results to be more accurate. (Agrafioti, Kalderis and Diamadopoulos, 2014)

Before placing samples in the XRF, the instrument was calibrated every time a new batch was going to be analysed. A copper disc calibration was analysed first followed by a quality check. These processes were done to ensure that the XRF was working accurately. Each batch consisted of approximately fourteen samples, taking an average of 12 minutes for each sample to be analysed. The data given was semi-quantitative, and the concentrations of the elements were then established by using a fitting method which is supplied by Bruker. When reading the values, for each scan, the fitting parameter R/R_0 was less than 30, as the lower the fitting parameter was, the better the fit.

The Shapiro-Wilk test was used to determine whether an element score distribution between the six districts is normal or skewed. The null hypothesis specifies that the score distribution is normal and is not rejected if the ρ-value exceeds the 0.05 level of significance. The alternative hypothesis specifies that the score distribution is skewed (not normal) and is not rejected if the ρ-value is less than the 0.05 criteria. If the score distribution is skewed, then the One-Way ANOVA test and the Kruskal-Wallis test would be used.

If the score distribution is skewed, than the One-Way ANOVA test and the Kruskal-Wallis test would be used to compare the mean element scores between the six districts using the IBM® SPSS® Statistics 26. The former is a parametric test and is used when the element score distribution is normal, while the latter is a non-parametric test and is used when the score distribution is skewed. For both tests, the null hypothesis specifies that the mean element scores vary marginally between the districts and is not rejected if the ρ-value exceeds the 0.05 level of significance. The alternative hypothesis specifies that the mean element scores vary significantly between the districts and is not rejected if the ρ-value is below the 0.05 criteria.

Chapter 3: Results

3.1 Pilot Study

The pilot study was conducted to observe how the XRF operates and how the samples were to be prepared and the protocol to follow. The pilot study was prepared to assess if the spectrometer results were acceptable.

3.1.1 Repetitive sampling to test consistency

Each sample was repeated three times to see that the results were consistent. The Shapiro-Wilk test was first used to see if the results were skewed or not. Some of the Shapiro-Wilk ρ-values exceeded the 0.05 level of significance, indicating that the element score distribution is normal. In contrast, other ρ-values were less than the 0.05 criteria indicating that the element score distribution was skewed and did not satisfy the normality assumption (Appendix 1). For this reason, both non-parametric and parametric tests were used to analyse the data. The One-Way ANOVA and the Kruskal-Wallis test were used to compare the mean element scores between the repetitive samples. The former is a parametric test and is used when the elements score distribution is normal while the latter is a non-parametric test and is used when the score distribution is scored. For both these, the null hypothesis specifies that the mean element scores differ marginally between the samples and is not rejected if the ρ-value exceeds the level of significance. The alternate hypothesis specifies that the mean element scores vary significantly between the samples and is not rejected if the ρ-values are less than the criteria.

Repetitive sampling was done to see if there were any difference when the sample was re-run using the same technique. Using the One-Way ANOVA and the Kruskal-Wallis test, it showed that overall, the most of the samples had a level of significance which was more than 0.05; thus, there was only a marginal difference between the same sample testing. A few samples though had a less than 0.05 level of significance showing that the sample results, marginally varied when repeated. It was noted that chromium peaks were always present in the graphs, though when the R/R0 was calculated by the programme to get a good fit, chromium was occasionally not listed in the data as one of the metals being present, even though when the graph was read, it was seen as being present. Other elements that were seen when reading the graph, but occasionally were marked as 0, were nickel and vanadium.

3.1.2 Comparison of XRF and ICP-MS values

The five samples from Għammieri were tested using two different analysis methods, the accredited ICP-MS and the XRF at the University of Malta. The ρ-value was calculated to see if there was any statistical significance in the results provided. Appendix 3 illustrates the ICP-MS results from the accredited lab. An average of each of the mean XRF results, were then compared with the results from the accredited lab which had used the ICP-MS (Table 3).

Table 3: XRF mean value compared to ICP-MS values in ppm

	Sample	Arsenic	Lead	Cadmium	Chromium	Copper	Nickel	Mercury	Thallium	Zinc
XRF	A	7.57	131.51	24.01	0.00	96.93	11.26	0.00	0.00	177.55
ICP-MS	A	7.30	98.00	0.50	52.00	70.00	33.00	0.39	<0.20	157.00
XRF	B	12.62	95.00	37.48	0.00	97.46	18.86	0.00	0.00	180.77
ICP-MS	B	7.60	74.00	0.40	54.00	70.00	35.00	0.26	<0.20	167.00
XRF	C	6.56	76.12	37.48	0.00	101.99	4.45	0.00	0.00	104.44
ICP-MS	C	7.20	76.00	0.40	41.00	73.00	32.00	0.16	<0.20	150.00
XRF	D	0.00	153.48	3.81	0.00	59.65	0.00	0.00	0.00	131.76
ICP-MS	D	4.90	136.00	0.30	35.00	59.00	23.00	0.76	<0.20	148.00
XRF	E	14.64	101.50	43.33	0.00	101.72	22.53	0.00	0.00	189.87
ICP-MS	**E**	**25.53**	**75.00**	**0.50**	**59.00**	**68.00**	**39.00**	**0.28**	**<0.20**	**176.00**

Two statistical tests were used to compare the results between the equipment. The binomial test was used to calculate the ρ-value and its level of significance, while the Spearman correlation coefficient measured the strength of the relationship. When using the

Binomial test, all the ρ-values exceeded the 0.05 level of significance, indicating that the mean XRF score is comparable to the ICP-MS value, thus the XRF results are positively related to the ICP-MS (Table 4). When using the Spearman correlation coefficient, except for thallium, mercury and chromium, all the other elements showed that the XRF readings were positively related to the ICP-MS readings (Figure 8-11).

Table 4: Binomial test ρ-values for XRF vs ICP-MS scores

Element	Sample	XRF Mean	XRF St. Dev	ICP-MS	P-value
Arsenic	A	7.5730	13.117	7.3	1.000
	B	12.623	11.343	7.6	1.000
	C	6.563	11.368	7.2	1.000
	D	0.000	0.000	4.9	0.250
	E	14.6433	13.234	7.1	1.000
Lead	A	131.510	19.078	98	0.250
	B	94.997	17.024	74	0.250
	C	76.123	16.735	76	1.000
	D	153.480	1.421	136	0.250
	E	101.497	19.848	75	0.250
Cadmium	A	24.010	21.049	0.5	0.250
	B	37.480	23.511	0.4	0.250
	C	37.480	24.854	0.4	0.250
	D	3.803	0.508	0.3	0.250
	E	43.337	15.626	0.5	0.250
Chromium	A	0.000	0.000	52	0.250
	B	0.000	0.000	54	0.250
	C	0.000	0.000	41	0.250
	D	0.000	0.000	35	0.250
	E	0.000	0.000	59	0.250
Copper	A	96.930	16.781	70	0.250
	B	97.460	16.834	70	0.250
	C	101.967	17.726	73	0.250
	D	59.647	12.837	59	1.000
	E	101.723	26.926	68	0.250
Nickel	A	11.263	19.510	33	1.000
	B	18.860	20.144	35	1.000
	C	4.453	7.713	32	0.250
	D	0.000	0.000	23	0.250
	E	22.523	22.019	39	1.000
Mercury	A	0.000	0.000	0.39	0.250
	B	0.000	0.000	0.26	0.250
	C	0.000	0.000	0.16	0.250
	D	0.000	0.000	0.76	0.250
	E	0.000	0.000	0.28	0.250
Thallium	A	0.000	0.000	0.2	0.250
	B	0.000	0.000	0.2	0.250
	C	0.000	0.000	0.2	0.250
	D	0.000	0.000	0.2	0.250
	E	0.000	0.000	0.2	0.250
Zinc	A	177.550	3.504	157	0.250
	B	180.763	8.949	167	0.250
	C	104.443	7.003	150	0.250
	D	131.757	4.475	148	0.250
	E	189.87	8.359	176	0.250

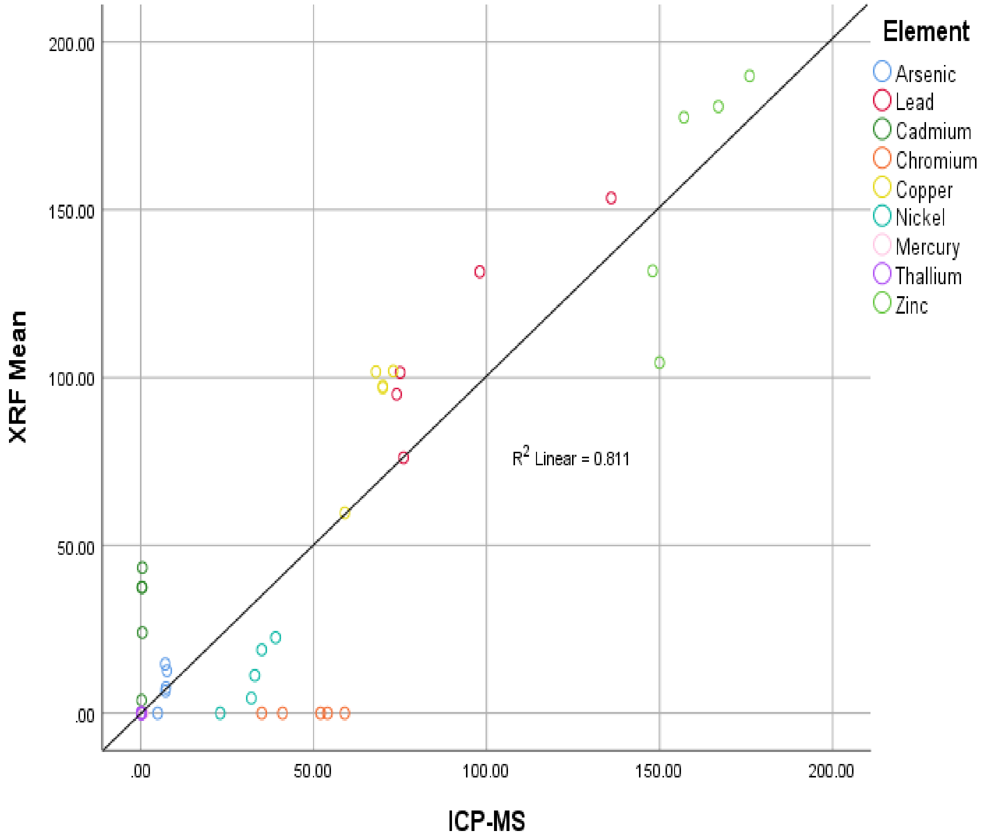


Figure 8: Positive correlation co-efficient of all the elements between XRF and ICP-MS measurements in mg/kg

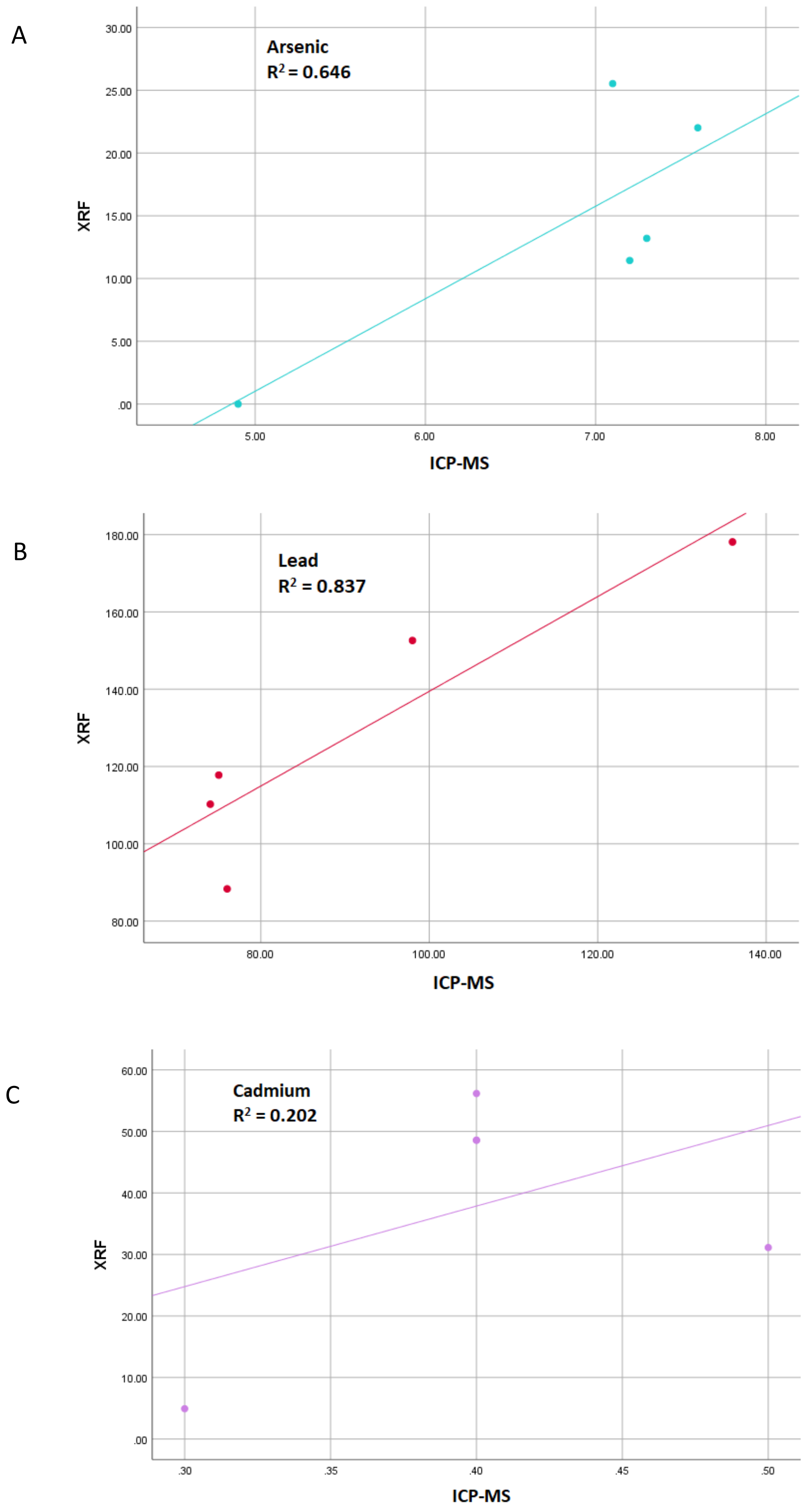


Figure 9: Positive linear correlation co-efficient between equipment measured in mg/kg for A) arsenic; B) lead; C) cadmium

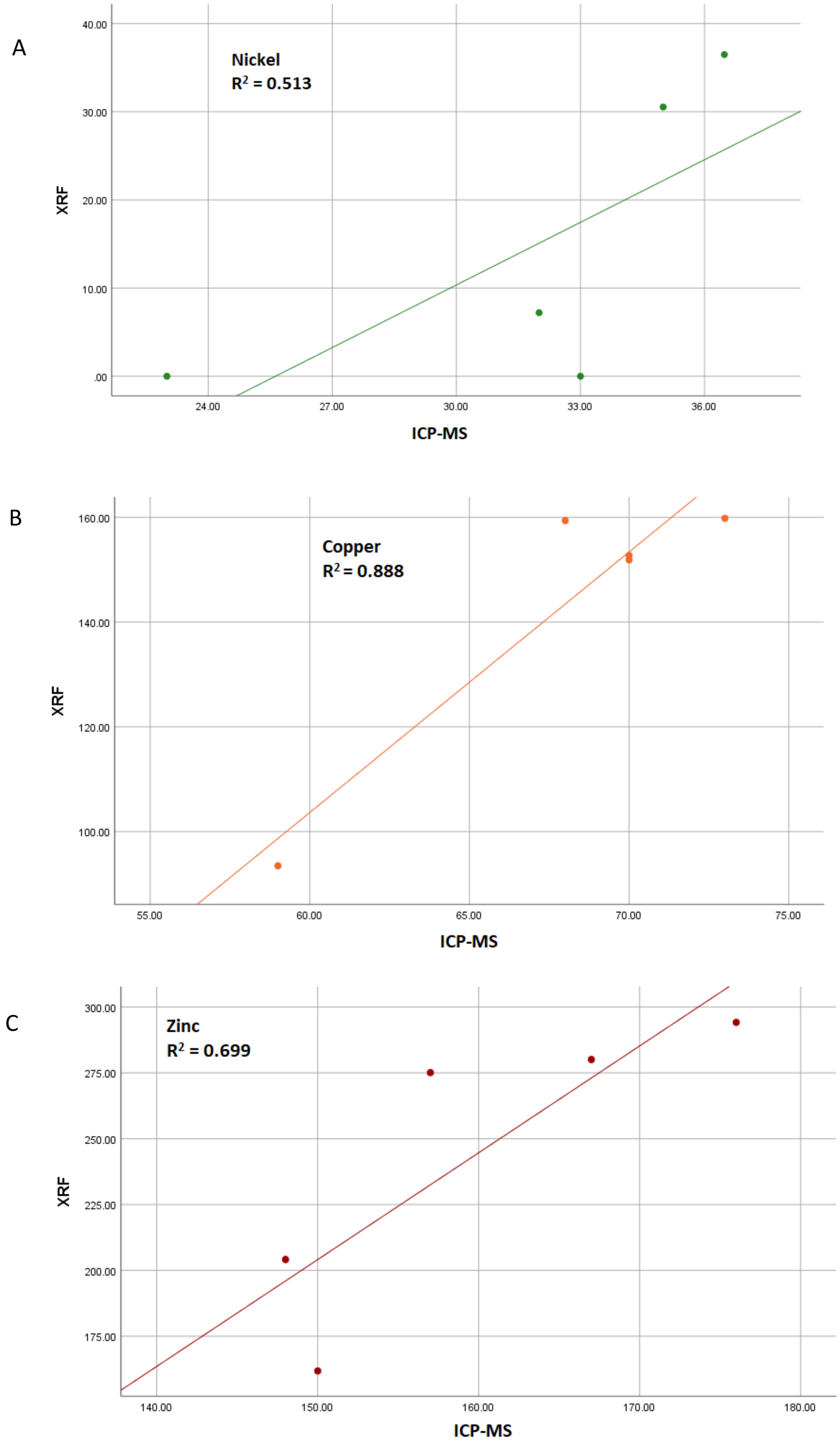


Figure 10: Positive linear correlation co-efficient between equipment measured in mg/kg for A) nickel; B) copper; C) zinc

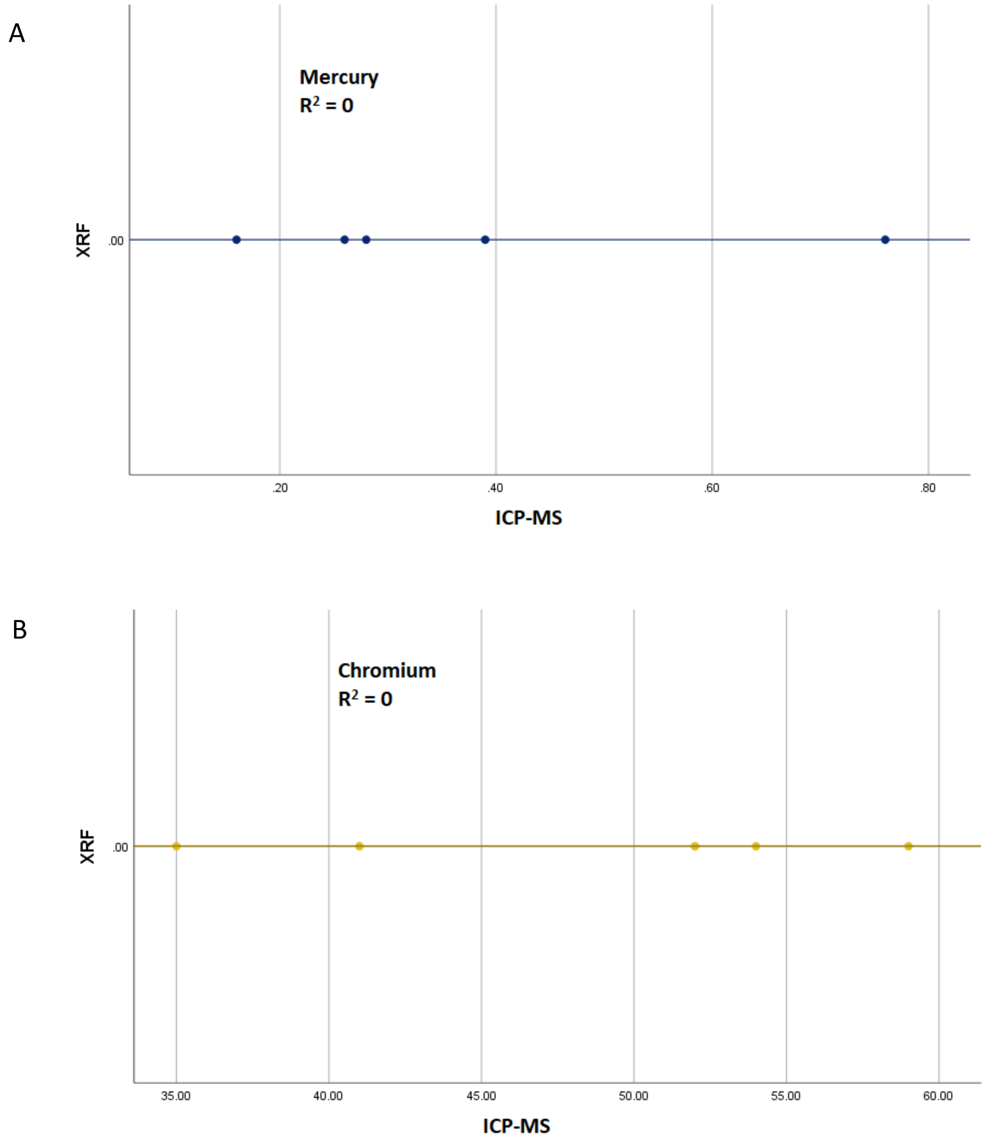


Figure 11: Zero linear correlation co-efficient for A) mercury; B) chromium

3.2 Results obtained from XRF spectrometer

Results of the heavy metals from the 101 samples collected were then analysed. They were divided according to the districts using the LAU1, and then compared between themselves (Figure 12).

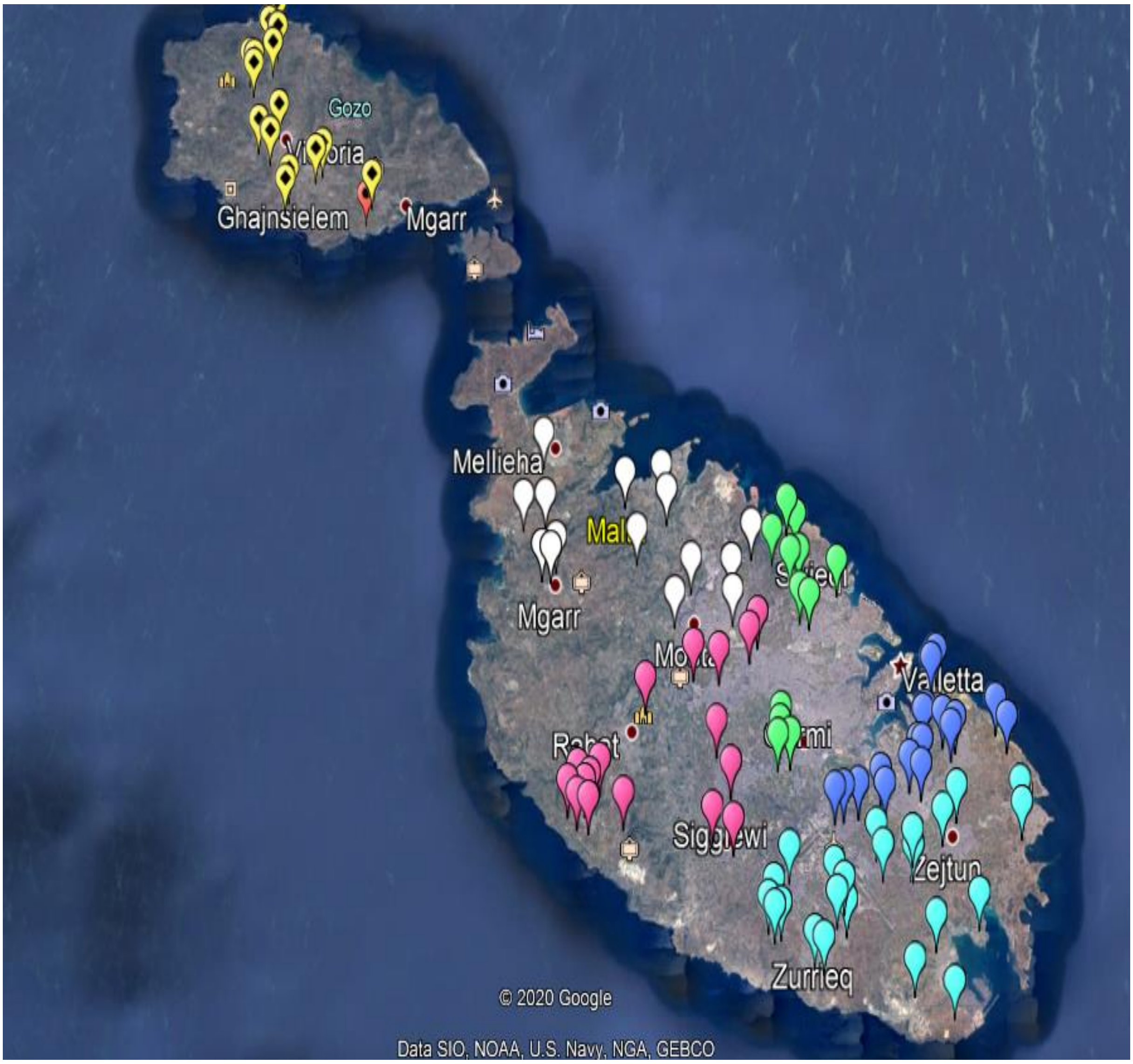


Figure 12: Google Earth Pro Map illustrating the areas of the 101 samples

Southern Harbour:

One sample from the Ħal-Luqa locality was situated close to the airport, and one sample from Xgħajra was collected from an area close to a cement plant (Table 5).

Table 5: Southern Harbour Samples

District	Locality	Number of Samples
Southern Harbour	Cospicua	2
	Fgura	2
	Ħal Luqa	3
	Ħaż-Żabbar	3
	Kalkara	2
	Santa Luċija	2
	Ħal Tarxien	2
	Xgħajra	2

Northern Harbour:

A sample from San Ġwann was collected from the area known as 'Tal-Ballal'. Another sample from the Swieqi area was collected from the locality of Madliena (Table 6).

Table 6: Northern Harbour Samples

District	Locality	Number of Samples
Northern Harbour	Ħal-Qormi	4
	Pembroke	2
	San Ġwann	2
	St Julians	1
	Swieqi	3

South-Eastern:

In Birżebbuġia, samples were taken from areas close to Delimara and the Freeport. In Marsaskala, a sample was taken from near the WasteServ. In Qrendi, two out of the four samples collected were taken from fields close to where the fireworks were ignited (Table 7).

Table 7: South-Eastern Samples

District	Locality	Number of Samples
South-Eastern	Birżebbuġia	3
	Gudja	2
	Ħal-Għaxaq	2
	Ħal-Kirkop	2
	Ħal-Safi	2
	Marsaskala	2
	Marsaxlokk	1
	Mqabba	1
	Qrendi	4
	Żejtun	2
	Żurrieq	2

Western:

From the Western District, 18 samples were collected in total (Table 8).

Table 8: Western Samples

District	Locality	Number of Samples
Western	Ħad-Dingli	8
	Ħal Lija	1
	Ħ'Attard	2
	Ħaż-Żebbuġ	2
	Iklin	1
	Mdina	1
	Rabat	1
	Siġġiewi	2

Northern:

Another sample was collected that was exposed to fireworks in the locality of Ħal-Għargħur. Mosta included a sample from Bidnija, and St Paul's Bay included samples from Burmarrad and Wardija (Table 9).

Table 9: Northern Samples

District	Locality	Number of Samples
Northern	Ħal-Għargħur	1
	Mellieħa	3
	Mġarr	3
	Mosta	3
	Naxxar	2
	St Paul's Bay	3

Gozo and Comino

A total of 15 samples were collected from Gozo (Table 10).

Table 10: Gozo and Comino Samples

District	Locality	Number of Samples
Gozo and Comino	Fontana	1
	Għajnsielem	1
	Għasri	3
	Ta' Kerċem	1
	Ta' Sannat	2
	Victoria	1
	Xewkija	2
	Żebbuġ	4

When using the Shapiro-Wilk test, all the ρ-values were less than the 0.05 level of significance indicating that the elements score distribution were skewed and did not satisfy the normality assumption, thus the null hypothesis of normal distribution has been rejected. For this reason, the parametric and non-parametric test was used to analyse the data (Appendix 4).

The One-Way ANOVA and the Kruskal-Wallis test were used to compare the mean element scores between the repetitive samples. The former is a parametric test and is used when the elements score distribution is normal while the latter is a non-parametric test and is used when the score distribution is scored. For both these, the null hypothesis specifies that the mean element scores differ marginally between the samples and thus the alternative hypothesis is rejected if the ρ-value exceeds the level of significance. The alternate hypothesis specifies that the mean element scores vary significantly between the samples and thus the null hypothesis is rejected if the ρ-values are less than the 0.05 level of significance.

The results show that only some of the element scores differ between the districts since most of the element ρ-value were less than the 95% confidence interval. These elements include copper, yttrium, lead, strontium and nickel and niobium, which are both borderline (Appendix 5).

For better comparison, the elements were divided into four groups; micronutrients, macronutrient, noble gases and heavy metals. The group heavy metals include transition metals, basic metals, metalloids, lanthanides and actinides. Cluster Bar graphs using the IBM® SPSS® Statistics 26 were used to compare the same group elements according to the district (Figure 13).

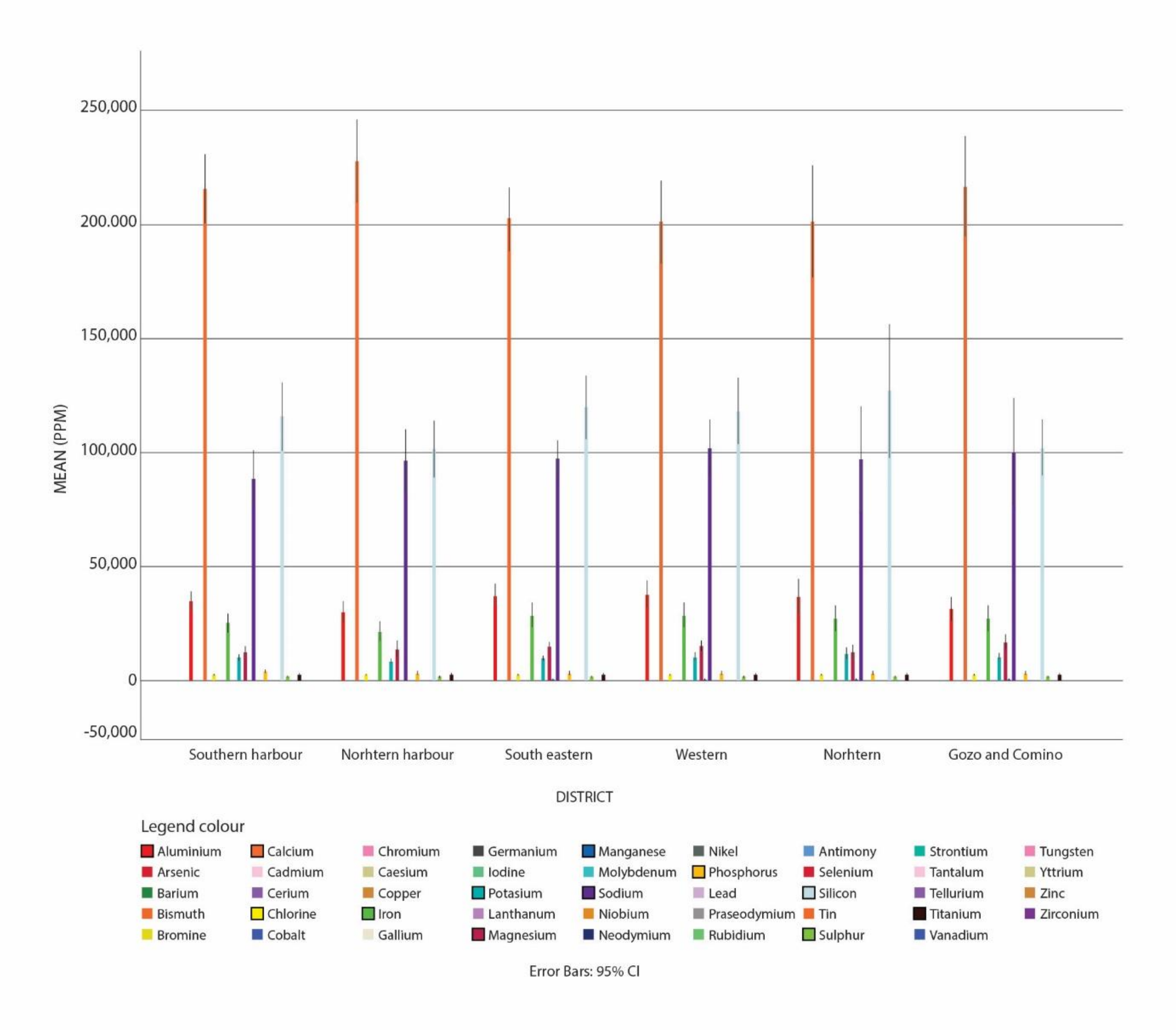


Figure 13: Mean element concentrations in ppm in each district

3.2.1 Macronutrients Group

Macronutrients include calcium, magnesium, phosphorous, potassium and sulphur. Other macronutrients which are not included in the results are hydrogen, oxygen and carbon since these could not be detected by the XRF. According to the One-Way ANOVA, calcium had the highest mean value and is the highest macronutrient found in the soil samples.

Table 11: Mean Values for Macronutrients

Element	Mean value ppm (mg/kg)
Calcium	210615.00
Magnesium	14441.89
Potassium	10338.61
Phosphorous	3719.98
Sulphur	2021.93

According to the Kruskal-Wallis test, all the elements had a ρ-value of more than 0.05, showing that there was not a statistical significance between the districts, regarding the elemental quantity. Clustered bar graphs were plotted to have an idea of the amount of each element present in the group. Two bar graphs were plotted, one with all the macronutrients involved (Figure 14) and one without calcium to compare the rest of the elements in the group (Figure 15).

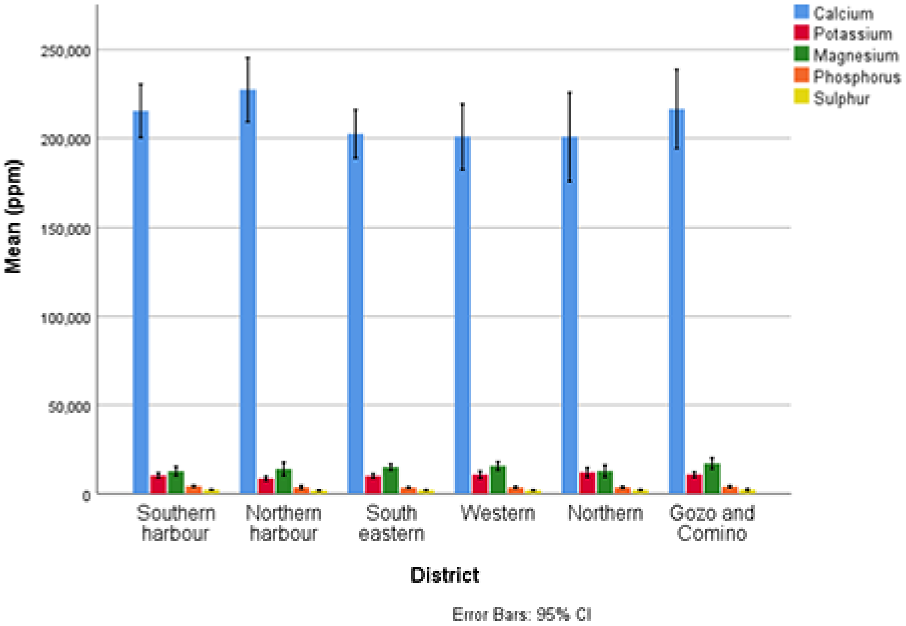


Figure 14: Macronutrient's concentrations in each district

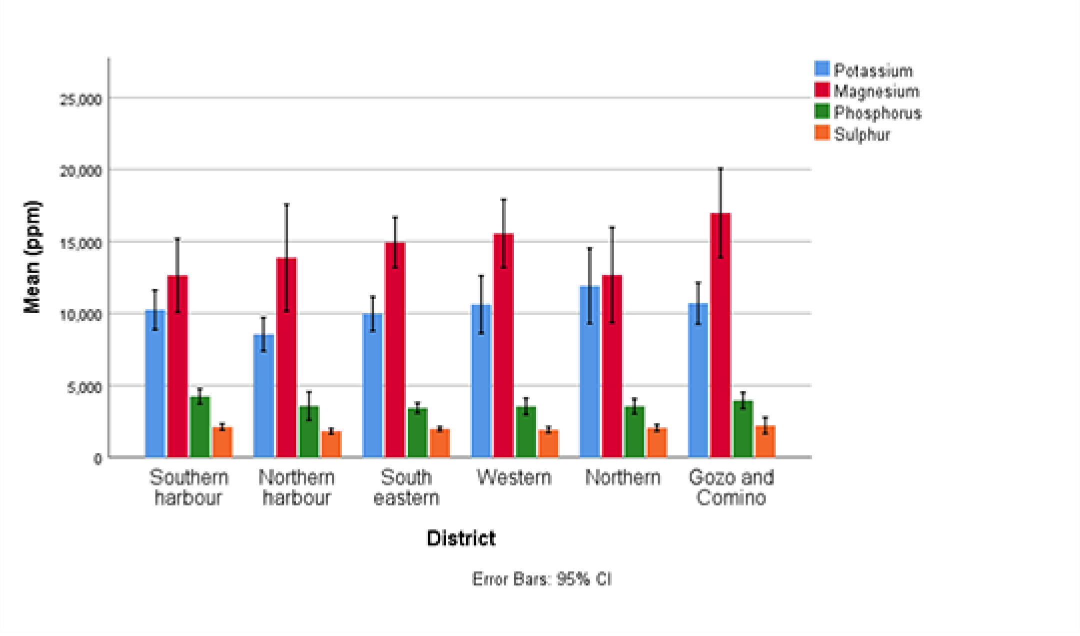


Figure 15: Macronutrient's concentrations excluding calcium in each district

Calcium resulted as having a higher concentration when compared to the rest of the elements in the group. Magnesium and potassium have higher concentrations when compared to phosphorous and sulphur in the soil samples.

The highest concentration of magnesium was present in the district of Gozo and Comino at 16981.61 mg/kg and the lowest concentration was observed in the Southern Harbour at 12637.04 mg/kg. Phosphorous was found with similar concentrations throughout the districts, with concentration of 3719.98 mg/kg. The highest concentration of potassium was observed in the Northern District with a concentration of 11914.9 mg/kg and the lowest concentration was observed in the Northern Harbour with a concentration of 8557.46 mg/kg. The other macronutrient sulphur is found with an average concentration of 2021.93 mg/kg in Malta and Gozo. Gozo and Comino had the highest concentration of sulphur with an average of 2218.77 mg/kg.

3.2.2 Micronutrients Group

Micronutrients include chlorine, cobalt, copper, iron, manganese, molybdenum, sodium and zinc. When it comes to the micronutrients, they are essential, though they need to be present in small amounts unlike the macronutrients. After the One-Way ANOVA was completed for these elements, it emerged that the micronutrients were found to have iron as the highest element present and molybdenum was found as the lowest element present (Table 12.)

Table 12: Mean Value of Micronutrients

Element	Mean Value in ppm (mg/kg)
Iron	26648.37
Chlorine	2739.41
Manganese	473.51
Zinc	174.09
Copper	62.82
Molybdenum	8.85

Using the Kruskal-Wallis test, iron, chlorine, manganese, zinc and molybdenum showed to have ρ-values which exceed the 0.05 level of significance which were 0.356, 0.263, 0.118, 0.187 and 0.134 respectively. Consequently, the elements across the districts vary marginally. Iron was found to have an average concentration of 26648.37 mg/kg where it was present at a higher concentration in the South-Eastern District of 28810.43 mg/kg, and the lower concentration in the Northern Harbour of 21769.76 mg/kg. Chlorine had an average concentration of 2739.41 mg/kg across the districts. Zinc was found at an average concentration of 174.09 mg/kg across the islands, where the highest concentration was found in the Southern Harbour at 251.33 mg/kg and the least concentration was found in the Gozo and Comino district at nearly half the amount at 128.12 mg/kg.

A clustered bar graph was plotted, displaying the amounts of each element, compared between each district and between each element. The first graph plotted, showed iron to be at a considerable contrast in concentration compared to the rest of the macronutrients (Figure 16). The second graph was plotted to remove iron from the graph, so that the rest of the micronutrients can be compared (Figure 17).

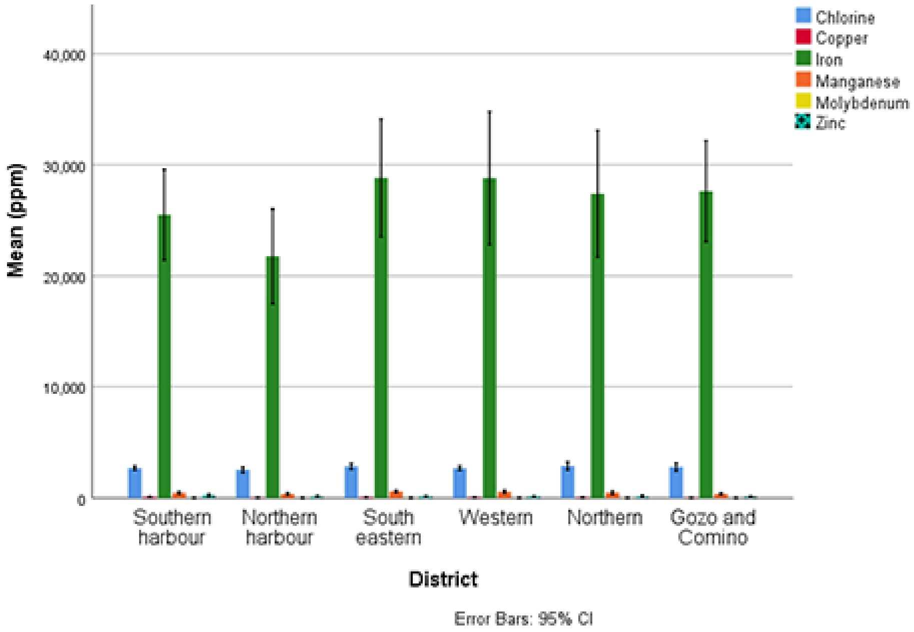


Figure 16: Micronutrient's concentrations in each district

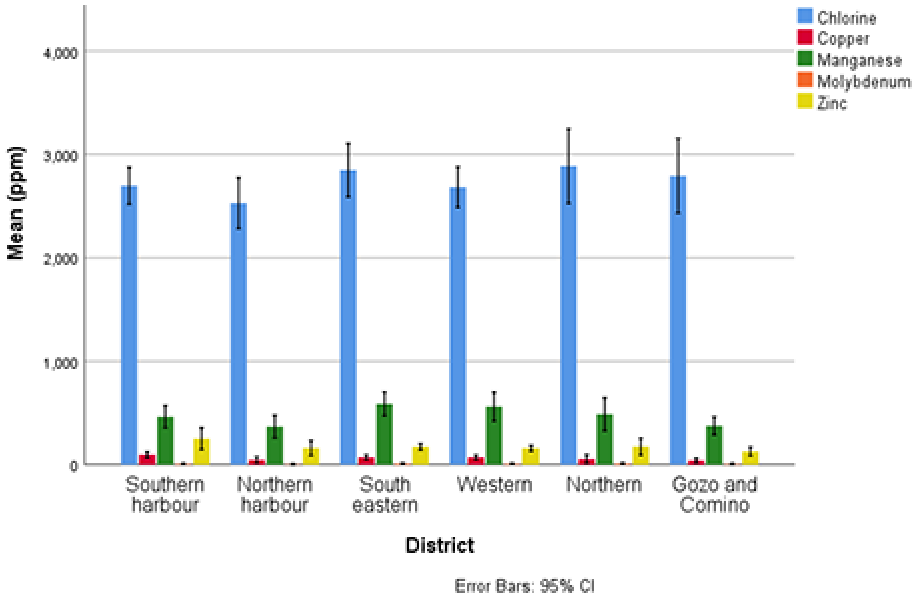


Figure 17: Micronutrient's concentrations excluding iron in each district

The heavy metals of this group were seen globally through the Datawrapper® programme, which provided an image through the shading of colour, where the highest concentration of the elements was seen both by the locality and the district.

3.2.2.1 *Manganese*

As seen through the One-Way ANOVA, the map depicting manganese concentrations by districts, shows that the highest concentration globally found across the islands, was in the South-Eastern District. In contrast, the lowest concentration found were in the South Eastern District (Figure 18).

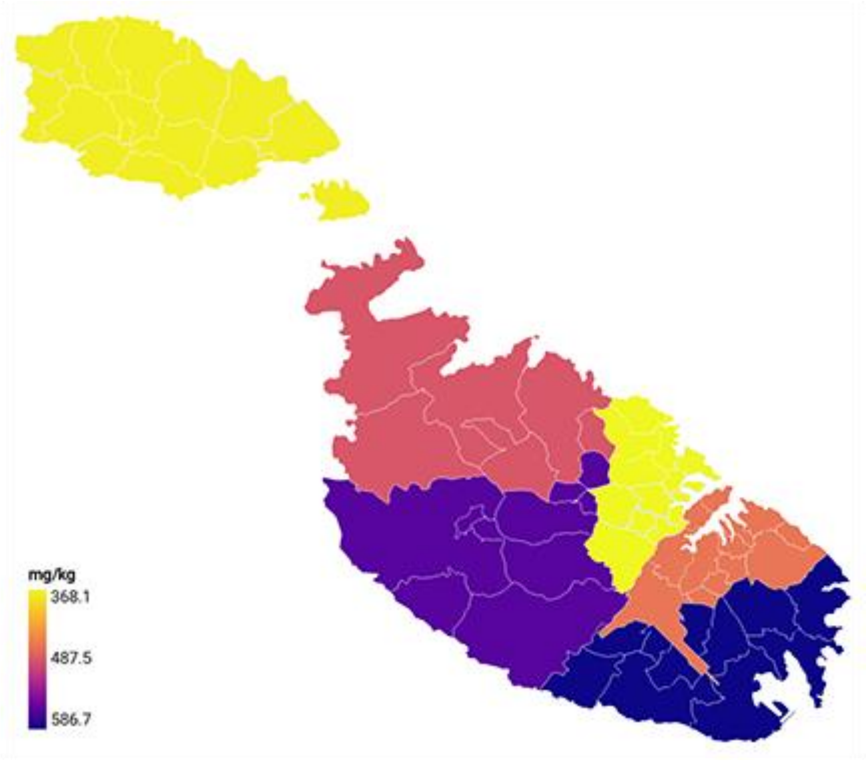


Figure 18: Manganese concentrations by district

Using the samples collected from all around Malta and Gozo, another map was created depicting the levels in each locality. The results illustrated that the least concentration of manganese were found in Mosta, Mqabba, Kerċem and Birżebbuġia. The locality having the highest concentration of manganese can be seen in Qrendi and Marsaxlokk (Figure 19).

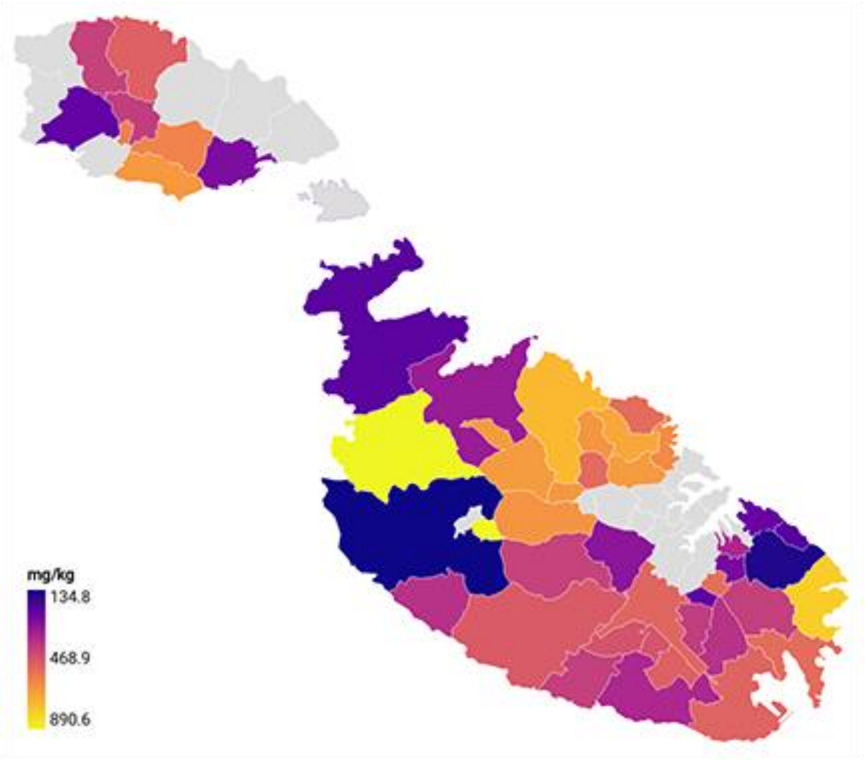


Figure 19: Manganese concentrations by locality sampled

3.2.2.2 *Copper*

A map illustrating the results from the One-Way ANOVA was drawn to display the results of copper concentration by district. South Harbour had the highest concentration of copper, while the Gozo and Comino District had the lowest concentration of copper (Figure 20). Another map showing manganese concentration according to the localities, illustrates that St. Julian's, Għargħur, Cospicua, Żabbar, Rabat (Malta), Qrendi and Għajnsielem in Gozo had the highest concentration of copper. Swieqi, Mqabba, Pembroke, Mosta, Birżebbuġia, Rabat in Gozo and Għasri had the lowest concentration of copper present in their soils (Figure 21).

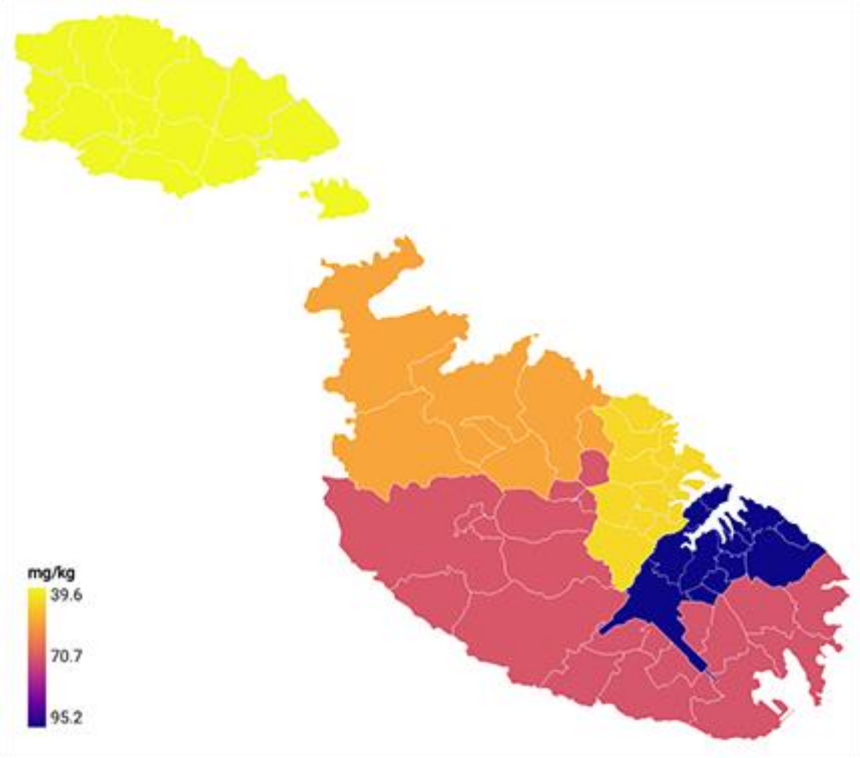


Figure 20: Copper concentrations by district

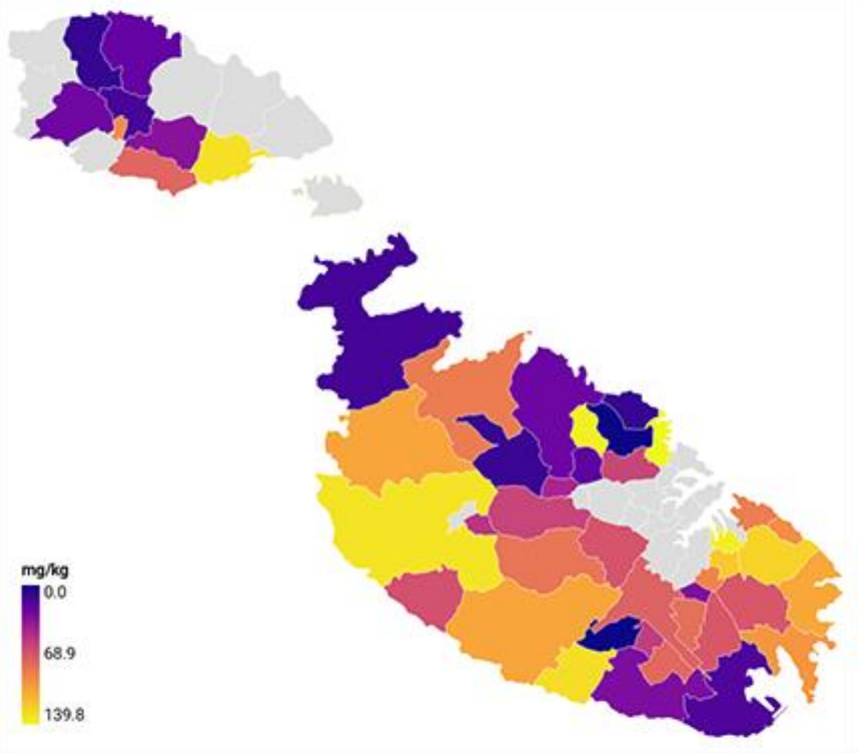


Figure 21: Copper concentrations by localities sampled

3.2.2.3 *Molybdenum*

Molybdenum average concentration was mapped according to the district, which revealed that it was present with an average concentration of 8.85 mg/kg around the islands. The Northern District had the highest concentration of molybdenum with an average of 12.09 mg/kg and the lowest concentration was found in the Northern Harbour 5.55 mg/kg (Figure 22).

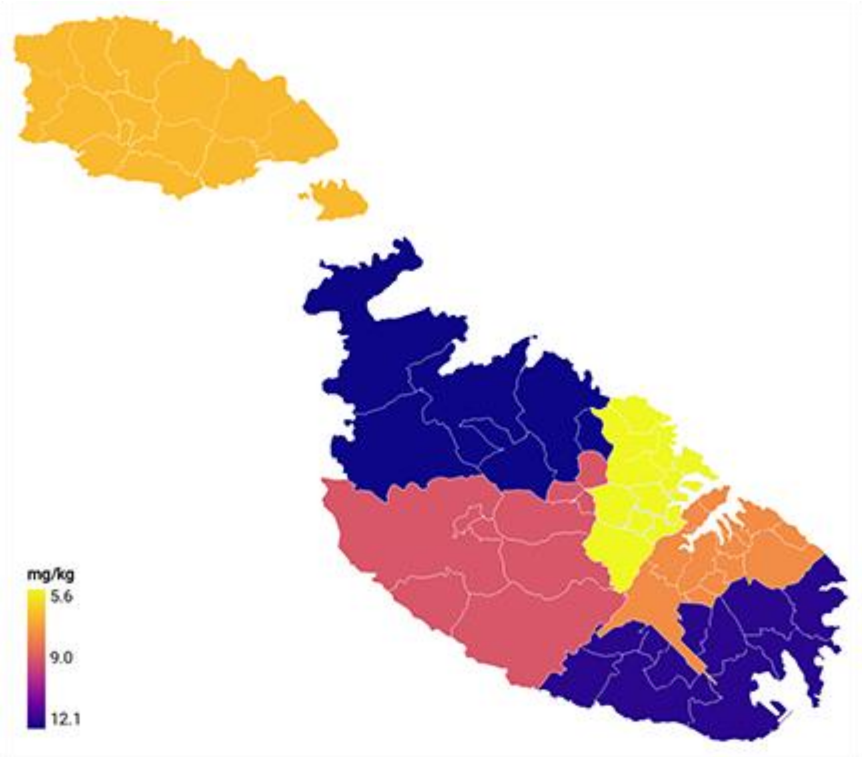


Figure 22: Molybdenum concentrations by district

When molybdenum was mapped by locality, it resulted that the highest concentration was found in Għajnsielem in Gozo, followed by Qrendi, Għargħur and Marsaxlokk. The localities with the last molybdenum concentrations present were in Mqabba, Mdina and Fontana soil (Figure 23).

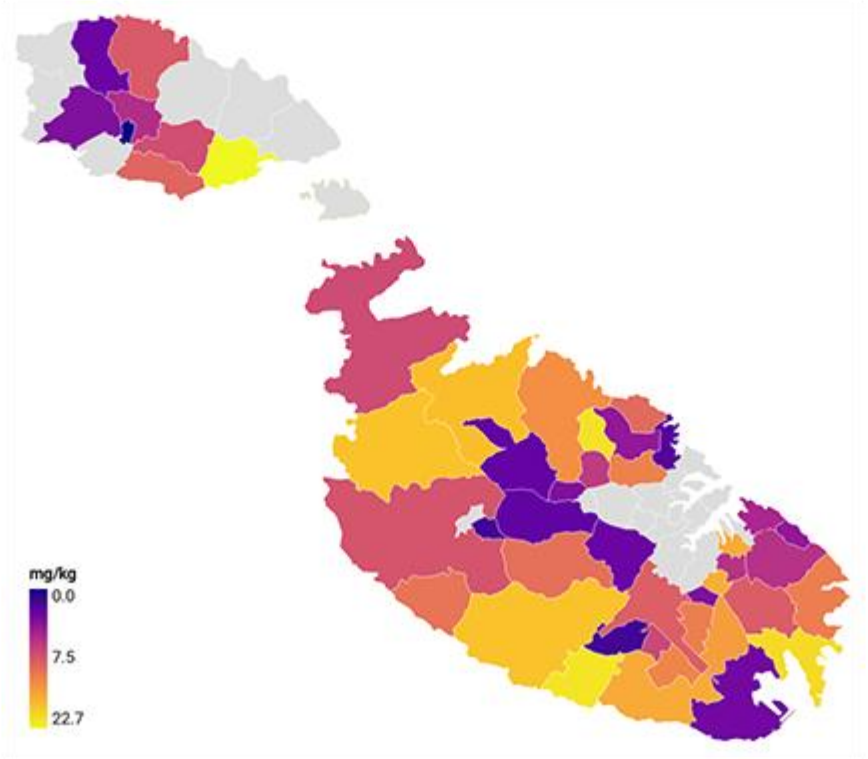


Figure 23: Molybdenum concentrations by localities sampled

3.2.2.4 *Zinc*

Zinc was found at an average of 174.09 mg/kg around the islands of Malta and Gozo. The highest concentration of zinc was noted in the Southern Harbour at 251.33 mg/kg (Figure 24). The localities with the highest zinc concentration were Żabbar followed by Mġarr, Bormla and Għajnsielem (Figure 25).

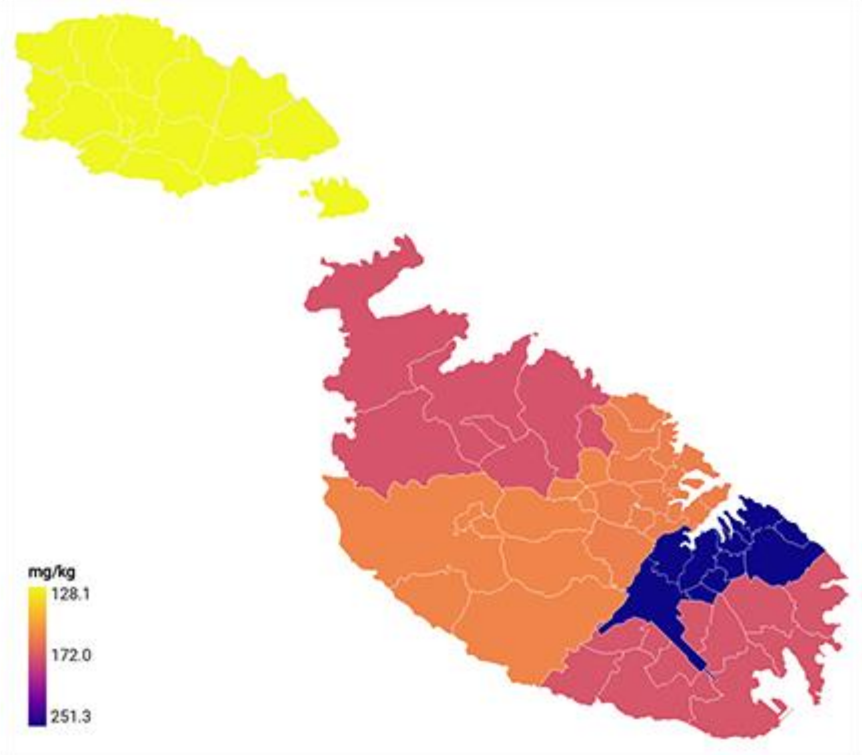


Figure 24: Zinc concentrations by districts

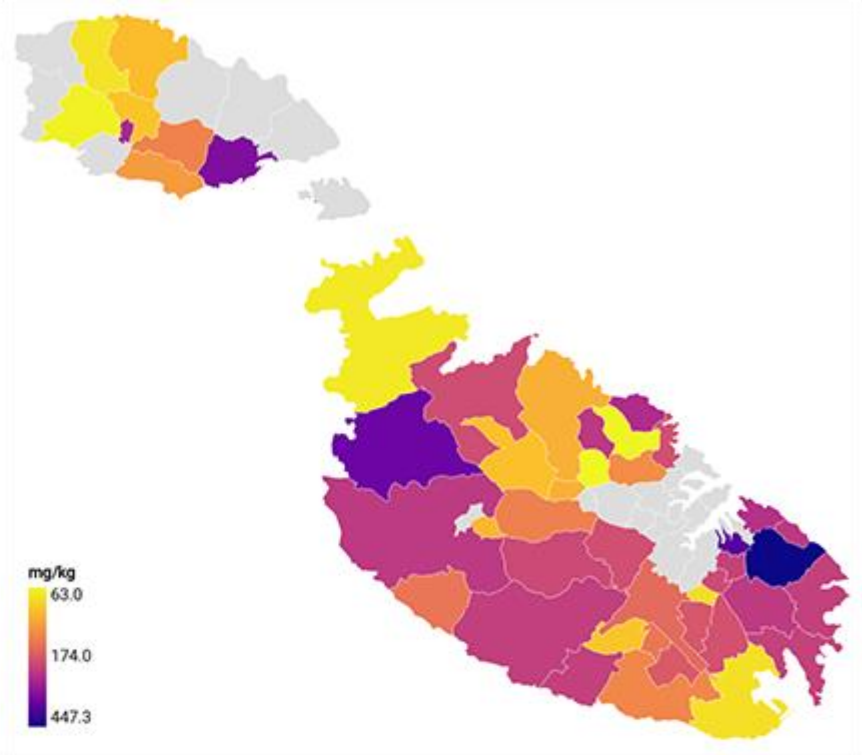


Figure 25: Zinc concentrations by locality

3.2.3 Halogens Group

Halogens consist of bromine and iodine. Although chlorine is classified as a halogen, for this purpose, it was grouped with the micronutrients group. Iodine and bromine were seen to have similar concentrations between the district and themselves (Figure 24).

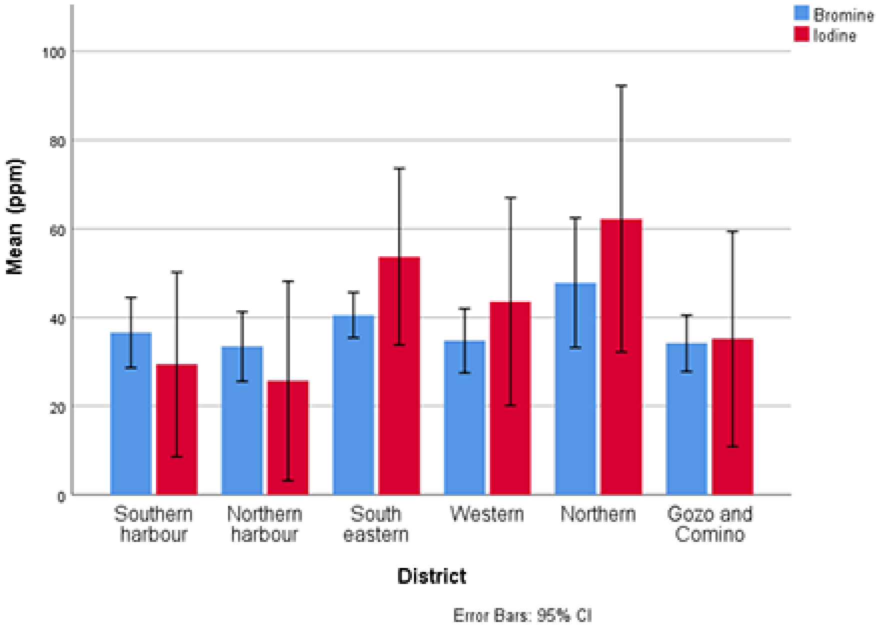


Figure 26: Halogens concentrations in each district

3.2.4 Heavy Metals Group

Heavy metals that have appeared in the results, excluding manganese, copper, zinc and molybdenum which were grouped in the micronutrients, include (i) aluminium; (ii) arsenic; (iii) barium; (iv) bismuth; (v) cadmium; (vi) cerium; (vii) chromium; (viii) caesium; (ix) gallium; (x) germanium; (xi) lanthanum; (xii) niobium; (xiii) neodymium; (xiv) nickel; (xv) lead; (xvi) rubidium; (xvii) antinomy; (xviii) selenium; (xix) tin; (xx) strontium; (xxi) tellurium; (xxii) titanium; (xxiii) vanadium; (xxiv) tungsten; (xxv) yttrium; and (xxvi) zirconium.

They were further subdivided by their blocks according to the periodic table. The D-Block includes transition metals; P-Block comprises metalloids and metals; S group contains alkaline metal and alkaline earth; and F group includes the lanthanides and actinides.

3.2.4.1 *D-block Elements*

These elements are grouped as the d-block elements as they have a valence electron in the d orbital. Transition metals are generally categorised by the incomplete d subshells in their cations or free elements. This block has similarities horizontally and vertically, unlike the rest of the blocks (Averill and Eldredge, 2011b). Elements in this block include arsenic, cadmium, chromium, niobium, nickel, lead, tantalum, titanium, vanadium, tungsten, yttrium, nickel and zirconium.

Using the results from the One-Way ANOVA, the mean values show that titanium was present with the highest concentration, while tungsten and tantalum were present in minimal concentration (Table 13). The Kruskal-Wallis proved that lead and yttrium had ρ-values of less than the 0.05 level of significance, showing that these elements score vary significantly and thus shows that their concentration differ significantly between the districts, thus the null hypothesis has been rejected.

Table 13: Mean element value of D-block elements

Element	Mean value ppm (mg/kg)
Titanium	2755.16
Zirconium	297.93
Lead	125.58
Vanadium	32.75
Yttrium	32.98
Cadmium	23.51
Chromium	22.29
Nickel	19.36
Niobium	13.10
Cobalt	6.69
Arsenic	5.37
Tungsten	0.38
Tantalum	0.00

Titanium was found to have a large concentration when compared to the rest of the elements (Figure 27). Another graph was plotted removing titanium, to observe the other elements (Figure 28). Furthermore, zirconium and lead were removed from the data to illustrate another bar chart the other elements (Figure 29).

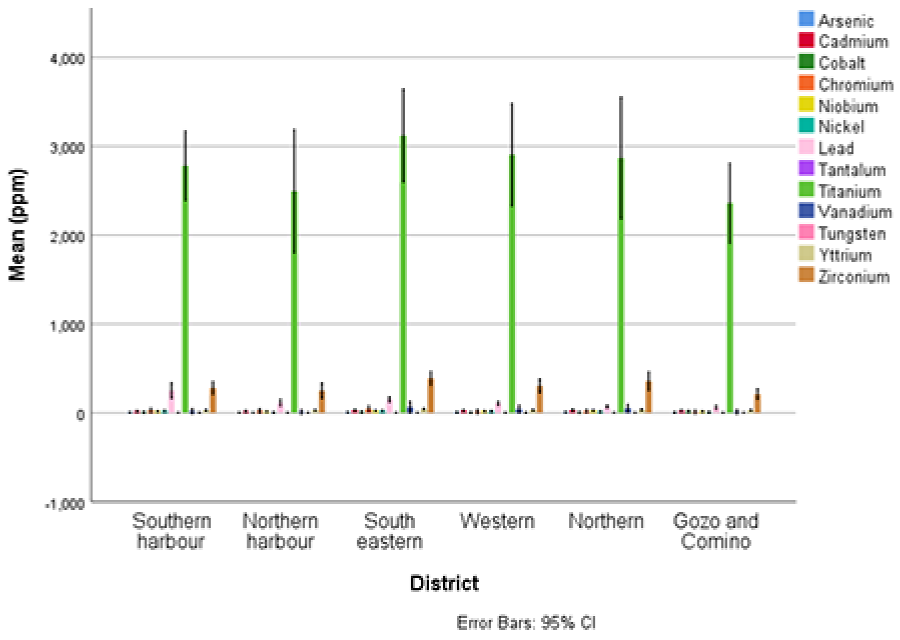


Figure 27: D-block concentrations in each district

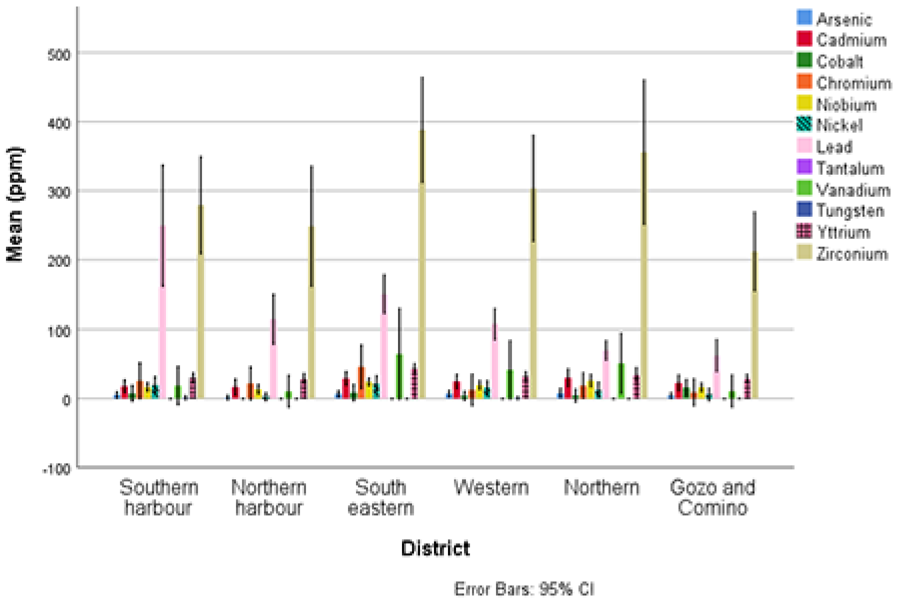


Figure 28: D-block concentrations in each district excluding titanium

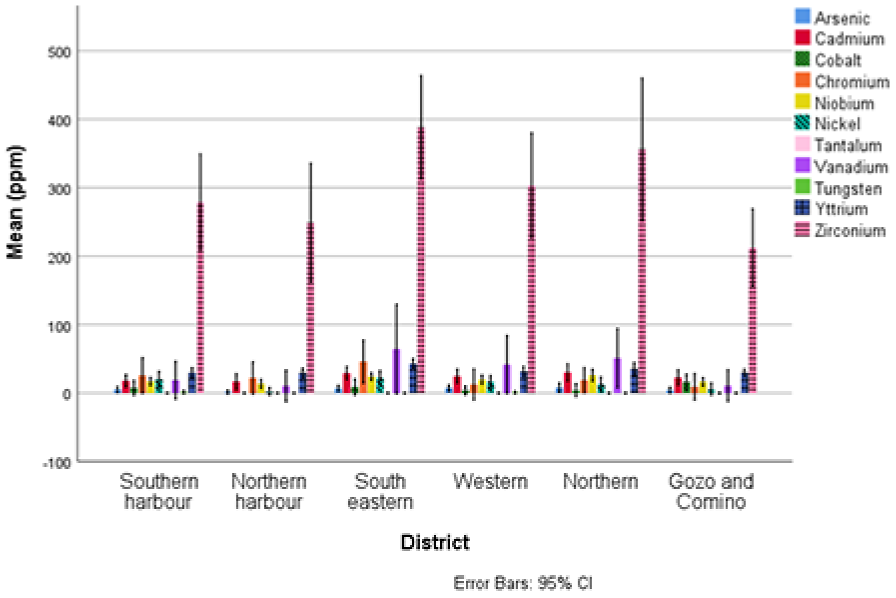


Figure 29: D-block concentrations in each district excluding titanium, zirconium and lead

The Datawrapper® was used to illustrate the distribution of lead, vanadium, chromium, cadmium, nickel, cobalt and arsenic.

3.2.4.1.1 Lead

Lead was seen at significant concentrations in the South-Eastern District and was seen with low concentrations in Gozo and Comino. The ρ-value of lead was 0.00, thus indicating that the score element distribution between the districts was significant (Figure 30). When mapping the concentrations of lead found according to the locality, it was seen that a very high concentration was found in Żabbar, followed by Kalkara and Fgura (Figure 31).

Figure 30: Lead concentrations by district

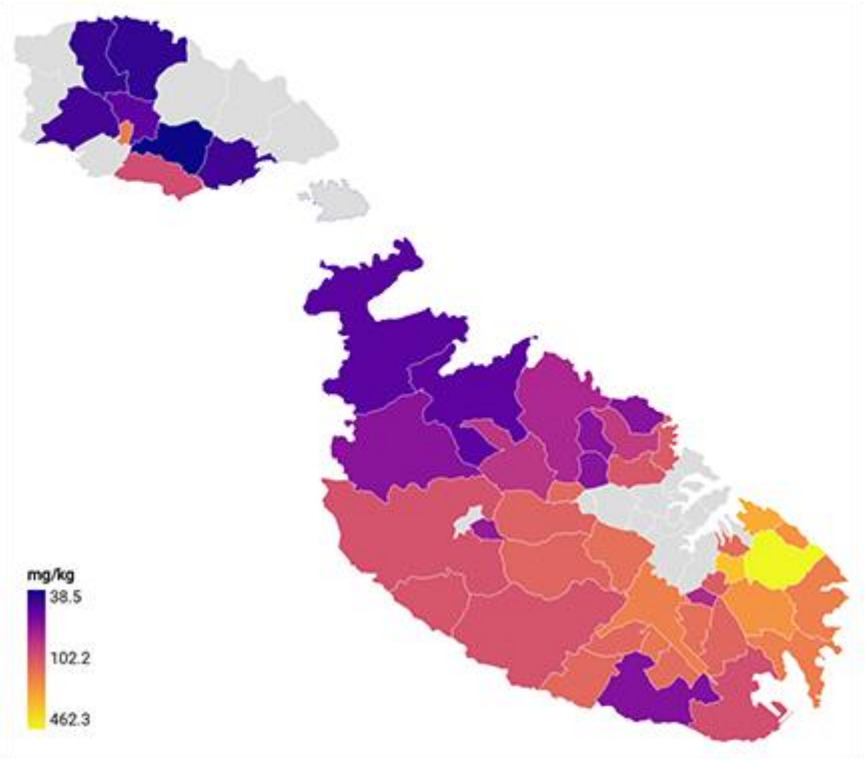


Figure 31: Lead concentrations by localities sampled

3.2.4.1.2 Vanadium

Vanadium did not have a statistical significance between the districts, since it had a ρ-value of 0.336, which exceeds the 0.05 level of significance. It was noted that the South-Eastern District had the highest concentration of vanadium with a mean value of 64.25 mg/kg, and the lowest concentration was seen in the Northern Harbour with a 10.41 mg/kg (Figure 32). When comparing concentration by locality, Qrendi, Marsaxlokk and Għajnsielem were the three localities that had the highest concentrations (Figure 33).

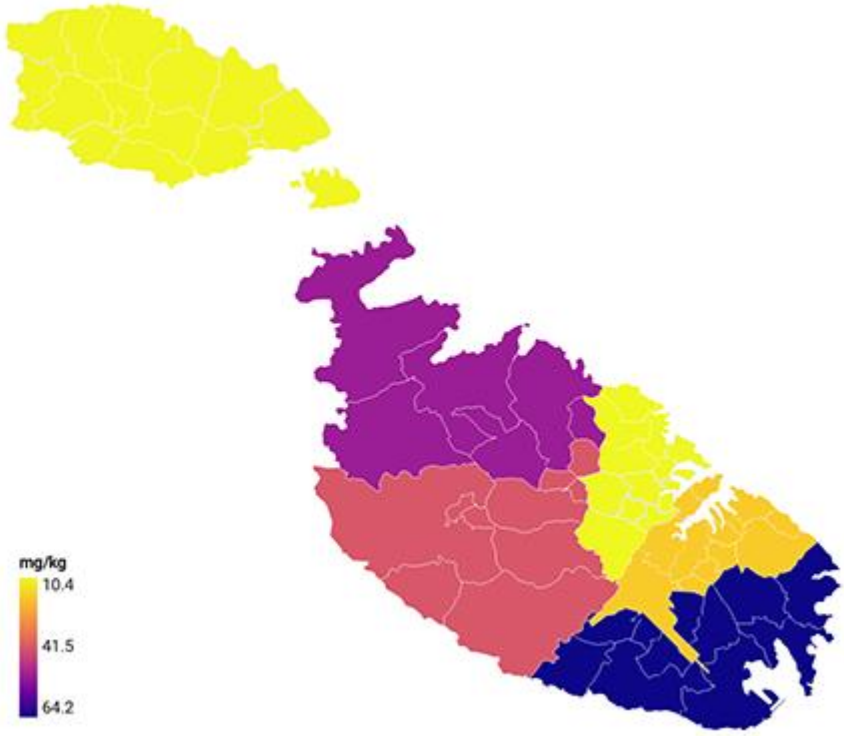


Figure 32: Vanadium concentrations by district

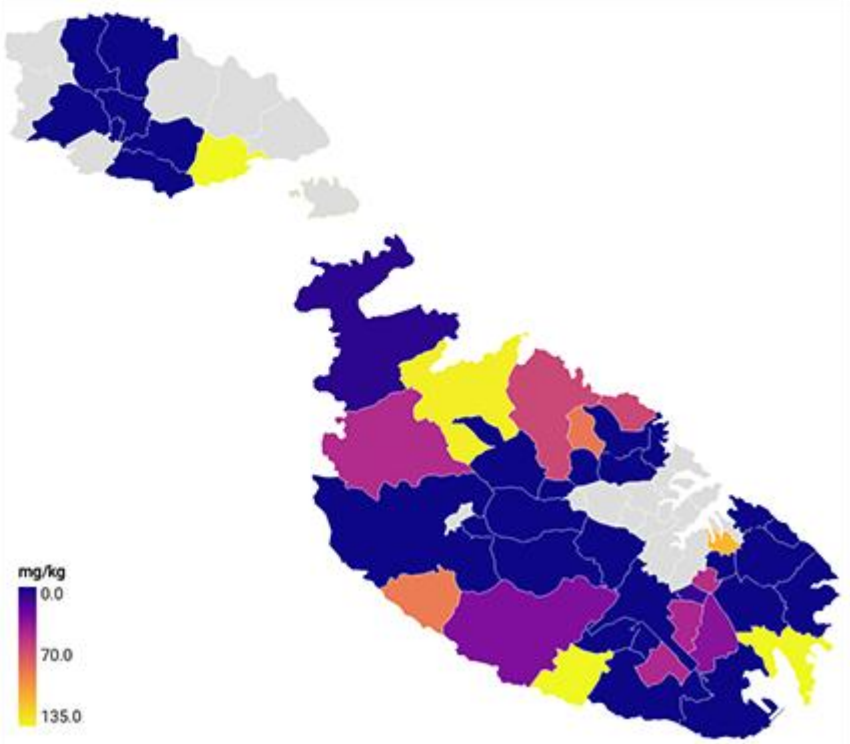


Figure 33: Vanadium concentrations by localities sampled

3.2.4.1.3 Chromium

The heavy metal chromium resulted to have a ρ-value of 0.450, making it exceed the 0.05 level of significance, and thus the element score between the districts was not statistically significant. It had an overall average concentration of 22.29 mg/kg. It was found at a slightly higher concentration in the South-Eastern Harbour at 45.93 mg/kg and a slightly lower concentration in the district of Gozo and Comino at 8.99 mg/kg (Figure 34) when comparing with the other districts. When observing the concentration according to the locality, the most considerable amount found was in Fontana in Gozo, followed by Żejtun, Għaxaq and Marsaxlokk (Figure 35).

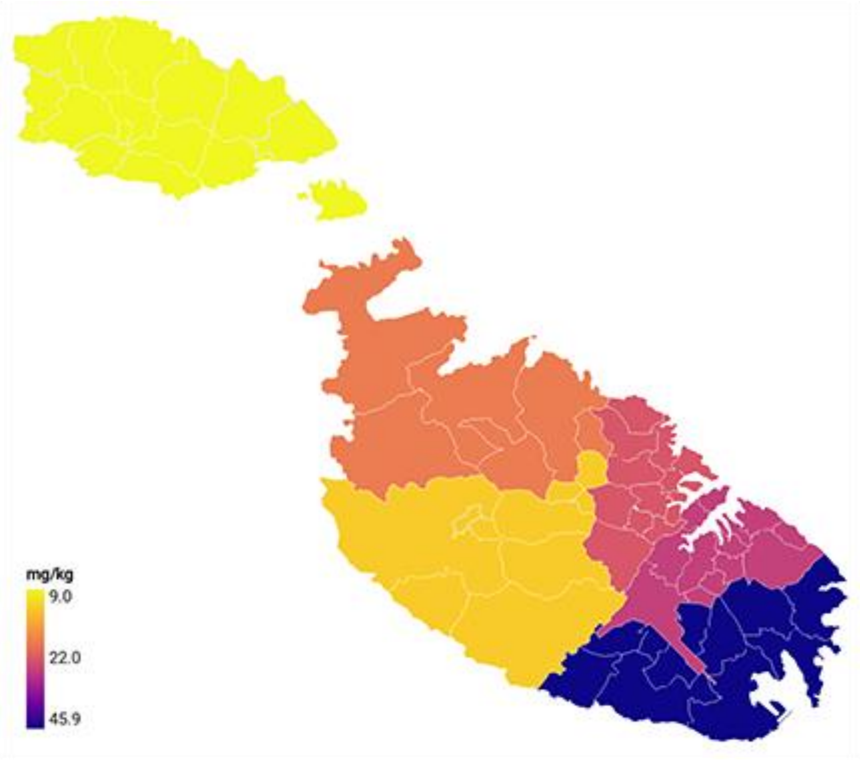


Figure 34: Chromium concentrations by district

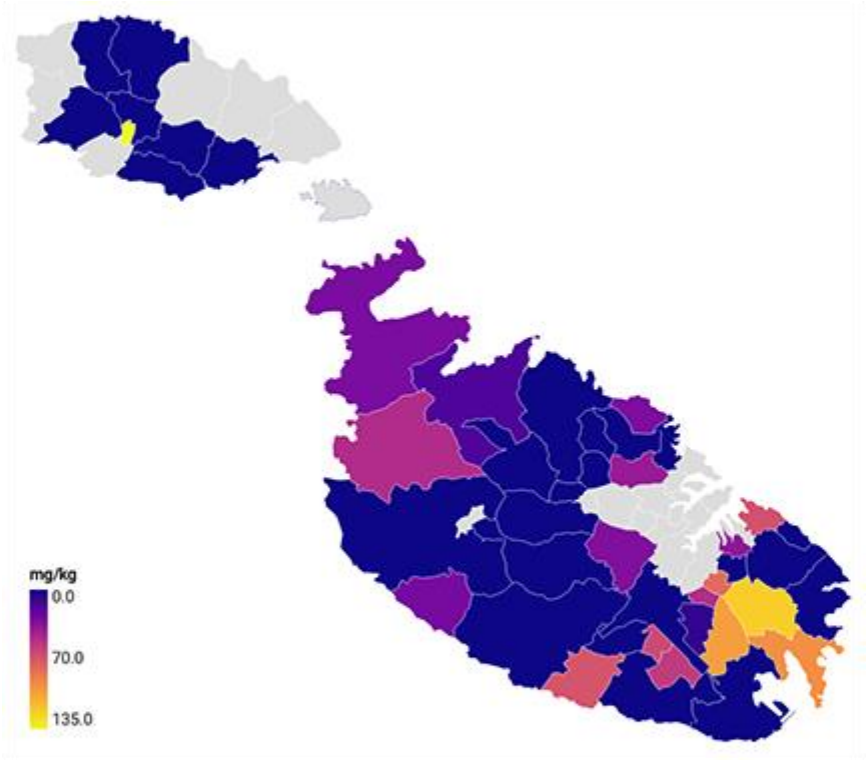


Figure 35: Chromium concentrations by localities sampled

3.2.4.1.4 Cadmium

Cadmium was present with an average concentration of 23.51 mg/kg across the Maltese islands. The metal showed a ρ-value of 0.560; thus, exceeding the 0.05 level of significance, meaning the element scores vary marginally between the districts. It was found to be present with the highest concentration in the Northern District at 30.10 mg/kg and lowest in the Northern Harbour at 16.69 mg/kg (Figure 36). When comparing localities, it was seen that cadmium was found mostly in Għajnsielem in Gozo, followed by Mġarr, Għargħur, Qrendi and Siġġiewi (Figure 37).

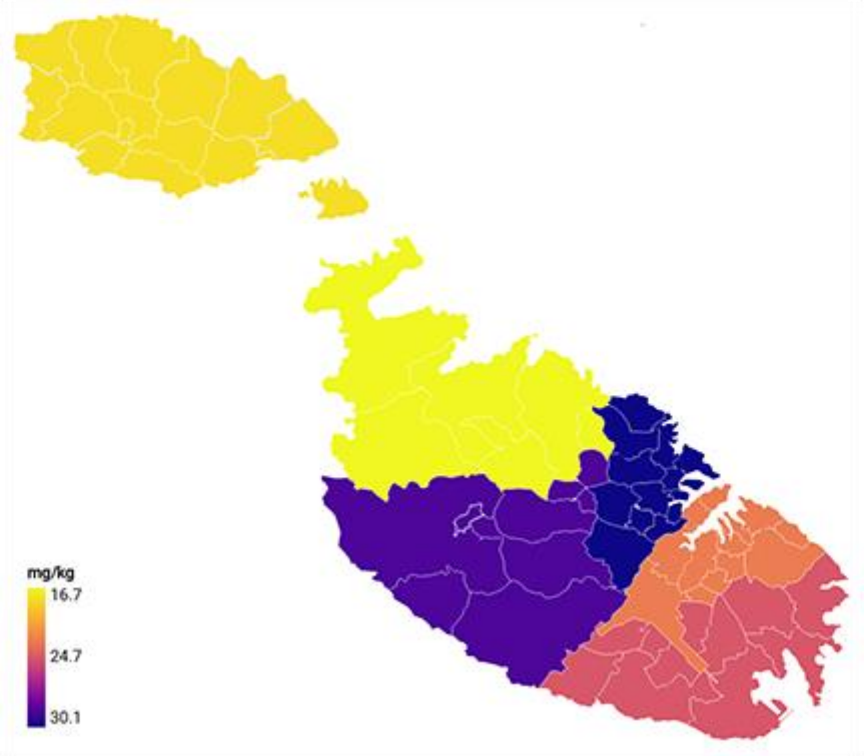


Figure 36: Cadmium concentrations by district

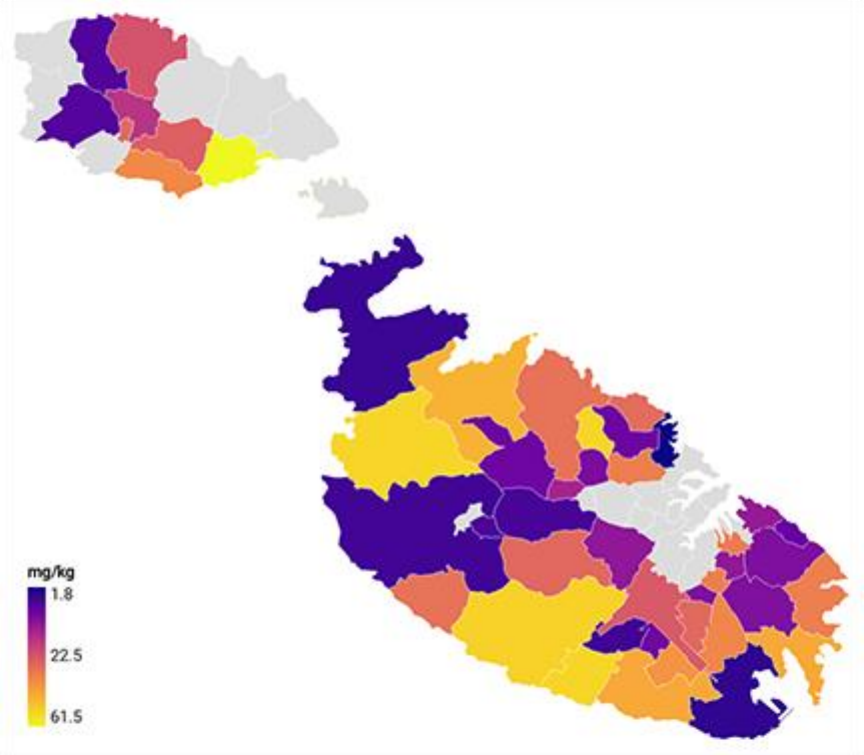


Figure 37: Cadmium concentrations by localities sampled

3.2.4.1.5 Nickel

This heavy metal had a borderline ρ-value of 0.060. It had a mean concentration of 13.10 mg/kg where it was found in the South-Eastern District with the highest concentration with a value of 21.90 mg/kg, and was present with the least concentration in the Northern Harbour District with a value of 2.49 mg/kg (Figure 38). When interpreting the concentrations found in the localities, Nickel was present at its highest in Għajnsielem, followed by Qrendi, Marsaxlokk and Bormla (Figure 39).

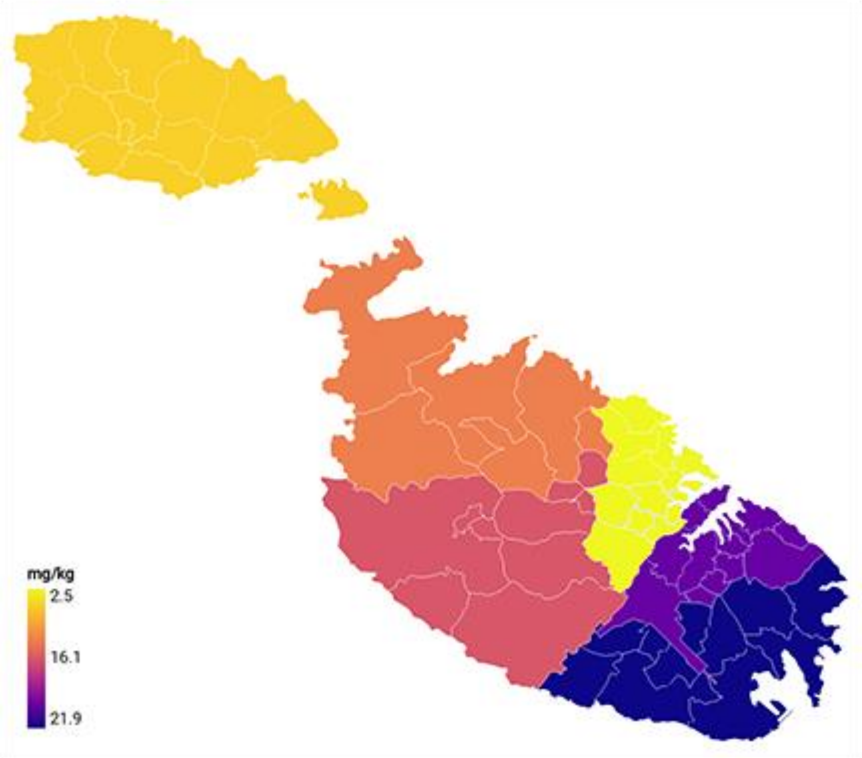


Figure 38: Nickel concentrations by district

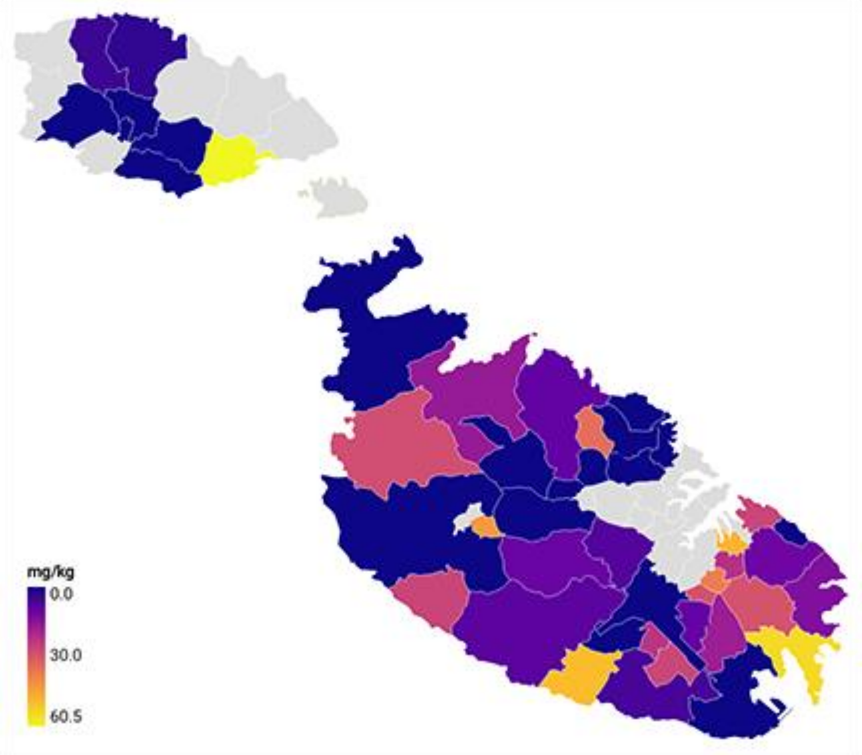


Figure 39: Nickel concentrations by localities sampled

3.2.4.1.6 Cobalt

With a ρ-value of 0.437, cobalt exceeded the 0.05 level of significance stating that the element score between the districts vary marginally. (Figure 41).

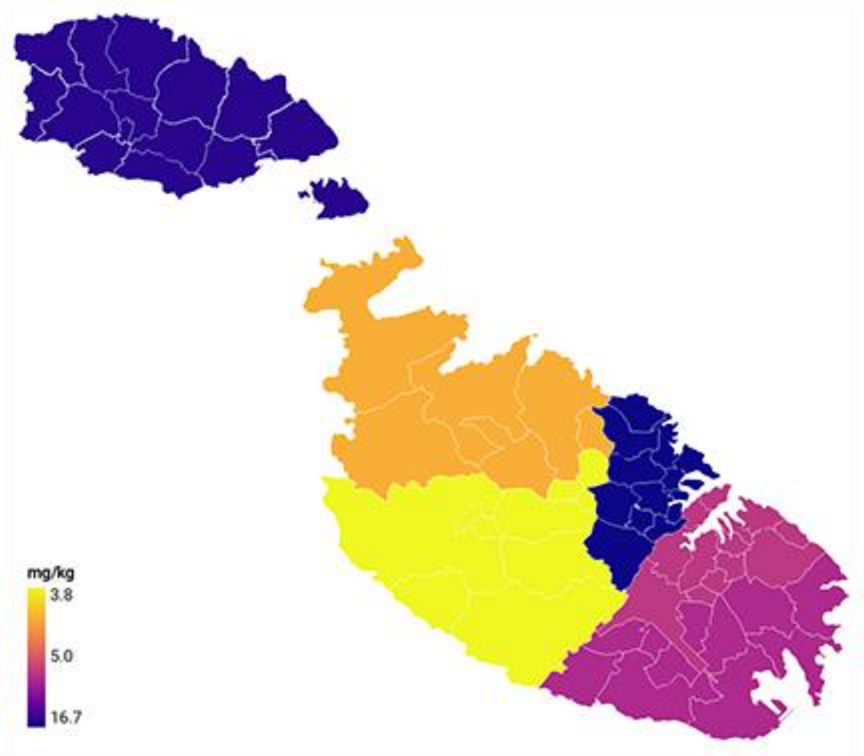


Figure 40: Cobalt concentrations by district

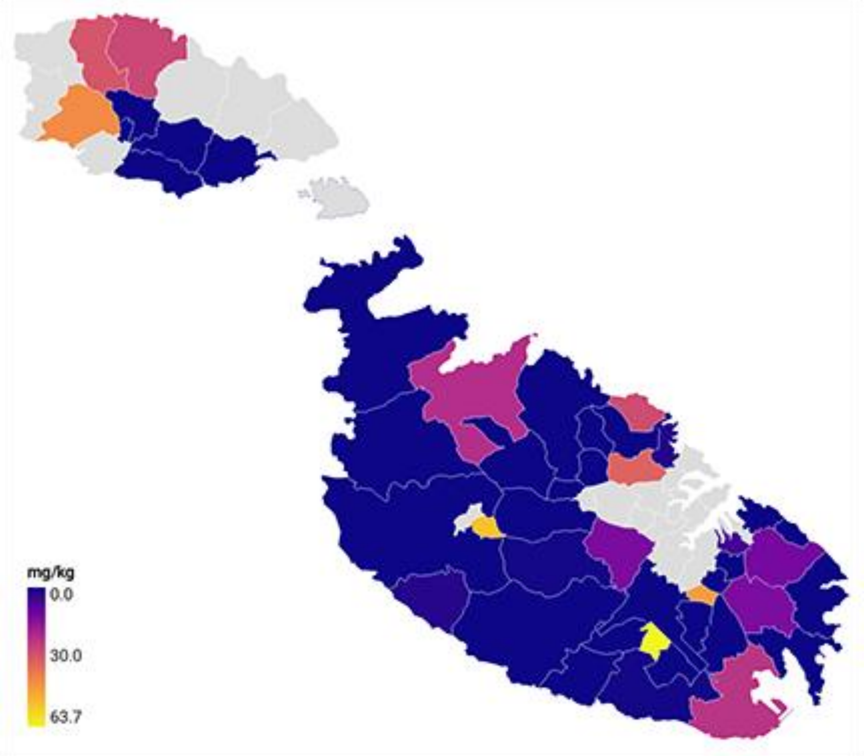


Figure 41: Cobalt concentrations by localities sampled

3.2.4.1.7 Arsenic

Arsenic has a ρ-value of 0.245, indicating that there was no significant difference between the districts since the ρ-value was more than 0.05. It has a mean concentration across the districts of 5.37 mg/kg. The Northern District had the highest concentration at 7.93 mg/kg, and the lowest concentration was found in the Northern Harbour at 1.33 mg/kg (Figure 42). When observing the result, it was seen that the highest concentration were present in Qrendi, Marsaxlokk, Għargħur and Għajnsielem (Figure 43).

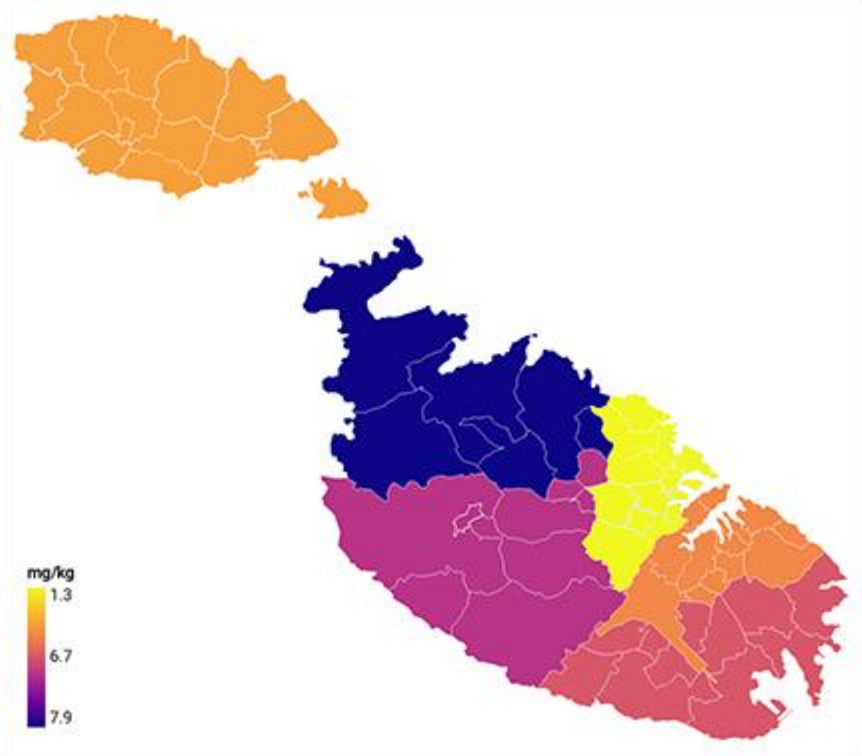


Figure 42: Arsenic concentrations by district

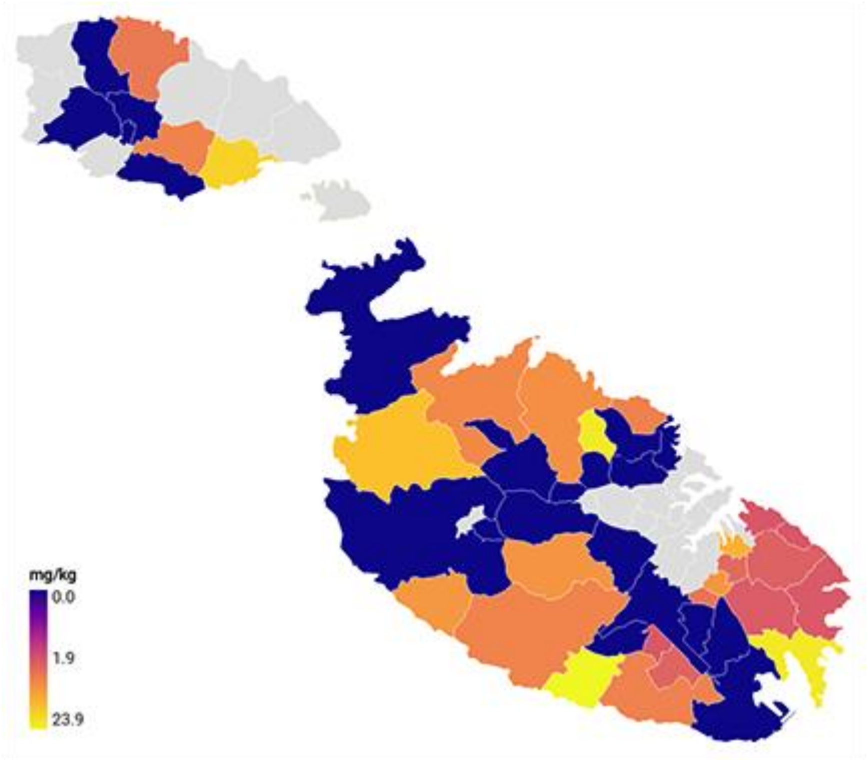


Figure 43: Arsenic concentrations by localities sampled

3.2.4.2 *P-block elements*

The p-block elements consist of silicon, aluminium, bismuth, gallium, germanium, antimony, selenium, tin and tellurium. The p-block elements are described so as the last electron moves into one of the three p-orbitals of their corresponding shells (Averill and Eldredge, 2011c) (Table 14).

Table 14: Mean element value of P-block elements

Element	Mean value ppm (mg/kg)
Silicon	114070.40
Aluminium	54998.05
Tin	130.07
Antinomy	45.54
Tellurium	44.16
Bismuth	28.97
Selenium	12.31
Gallium	12.01
Germanium	2.36

All the elements in the p-group had ρ-values that exceeded the 0.05 level of significance; therefore, all the elements were shown to vary marginally. When comparing the p-block elements, silicon and aluminium had a very high value compared with the rest of the elements (Figure 44) thus another bar graph was illustrated excluding aluminium and silicon from the graphs (Figure 45).

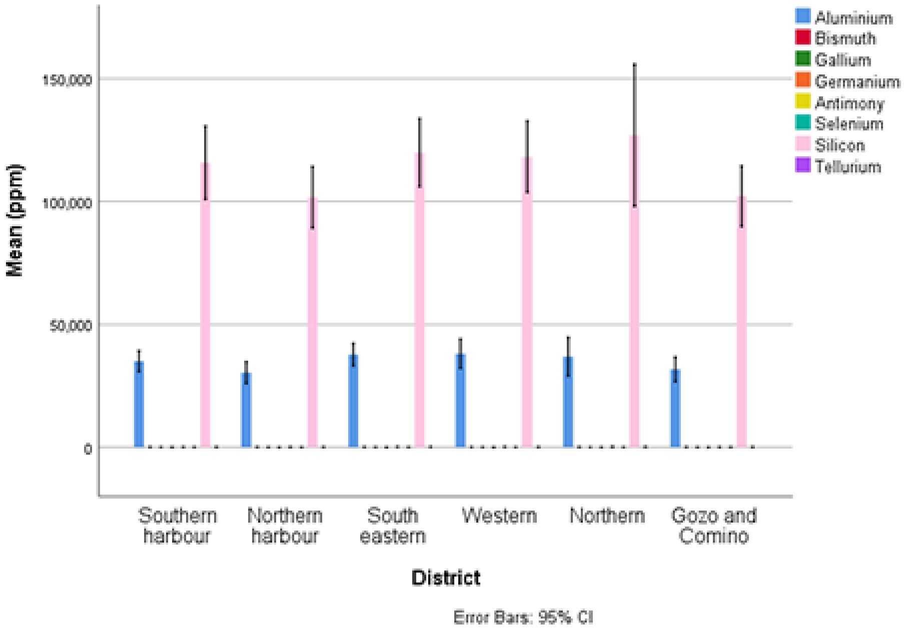


Figure 44: P-block element concentrations in each district

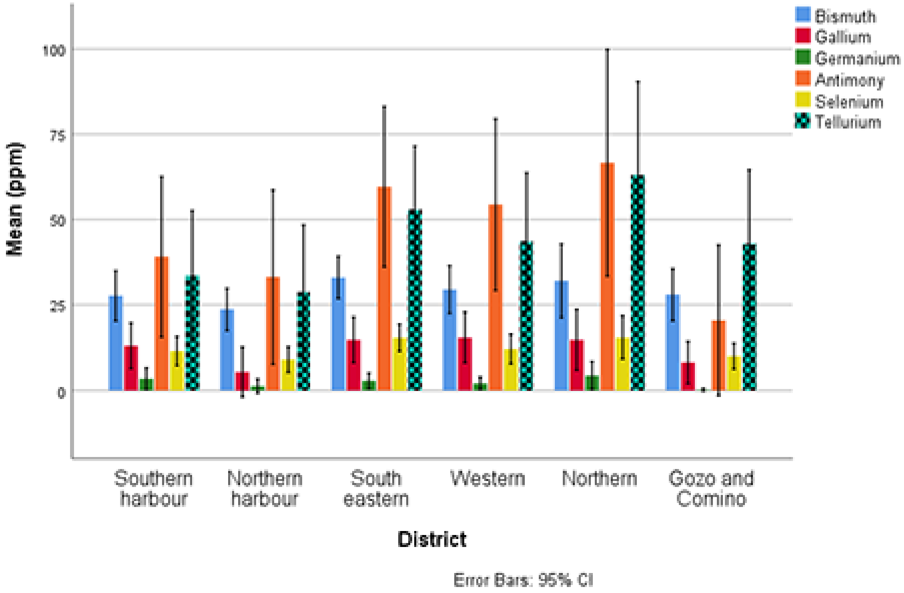


Figure 45: P-block concentrations in each district excluding aluminium and silicon

After both silicon and aluminium were removed from the graph, the metals were found to be as follows in descending order; tin, antimony, tellurium, bismuth, selenium, and gallium. The element with the least concentration in the group was germanium. Aluminium was illustrated further using the Datawrapper®.

3.2.4.2.1 Aluminium

The Western District has the highest concentration of aluminium at 38106.00 mg/kg, while the lowest concentration of aluminium was found in the Northern Harbour at 30414.23 mg/kg (Figure 46). Kerċem had the lowest amount of aluminium from all the samples with a value of 14713.00 ppm, while Marsaxlokk had the highest values of 54512.75 ppm (Figure 47).

Figure 46: Aluminium concentrations by district

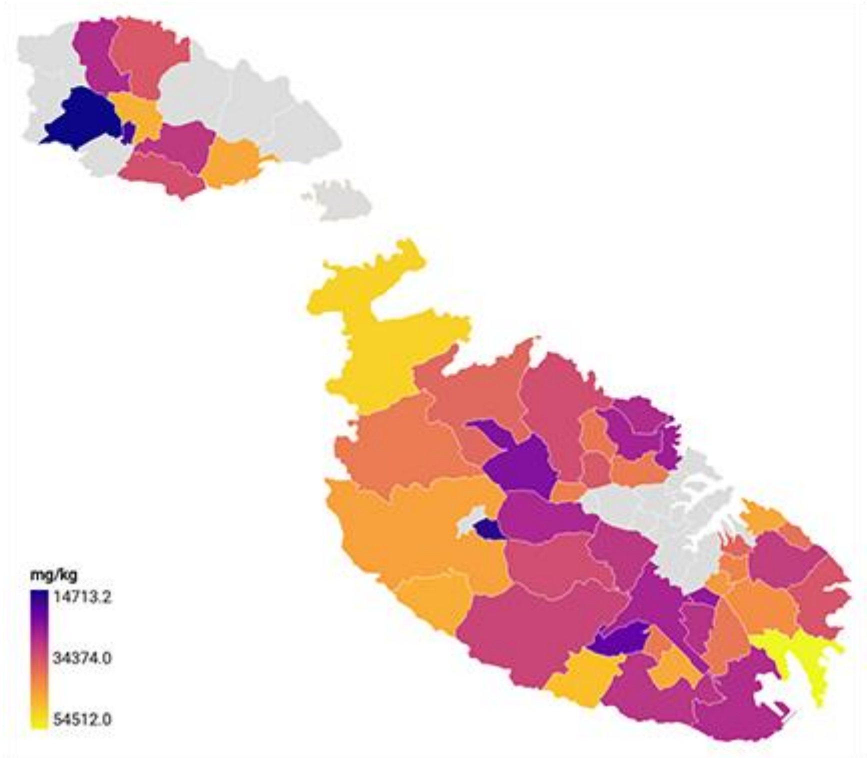


Figure 47: Aluminium concentrations by localities sampled

3.2.4.2.2 Selenium

High concentration of 15.51 mg/kg was seen in both the Northern District and South-Eastern district when compared to the other districts. The Northern Harbour had the lowest concentration of Selenium at 9.13 mg/kg (Figure 48). It had an average of 12.31 mg/kg across Malta and Gozo. Localities having high concentrations were Qrendi, Siġġiewi, Għargħur, Mġarr, Marsaxlokk, Żurrieq and St. Paul’s Bay (Figure 49).

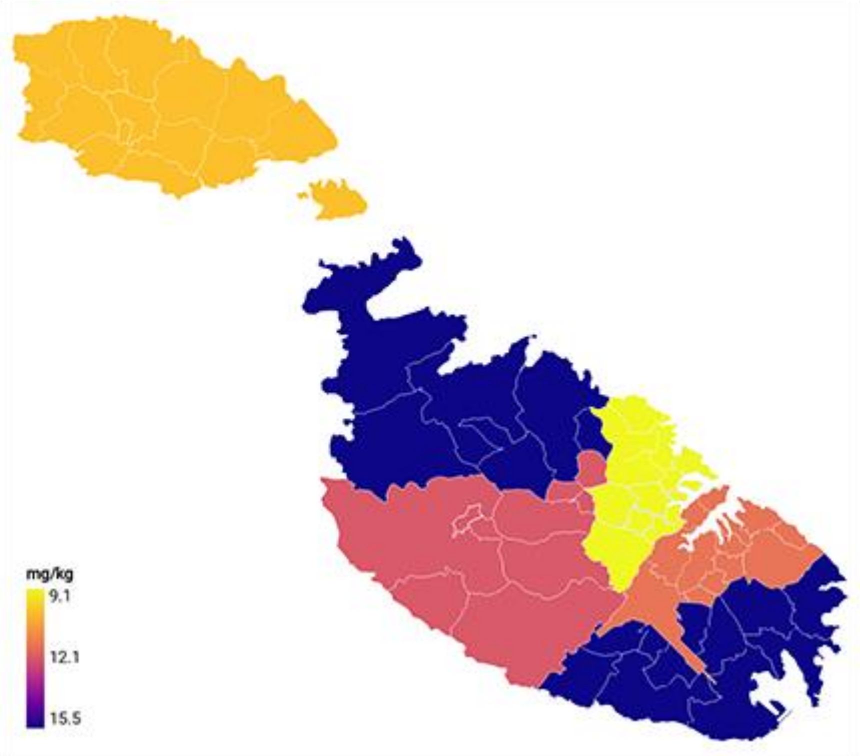


Figure 48: Selenium concentrations by district

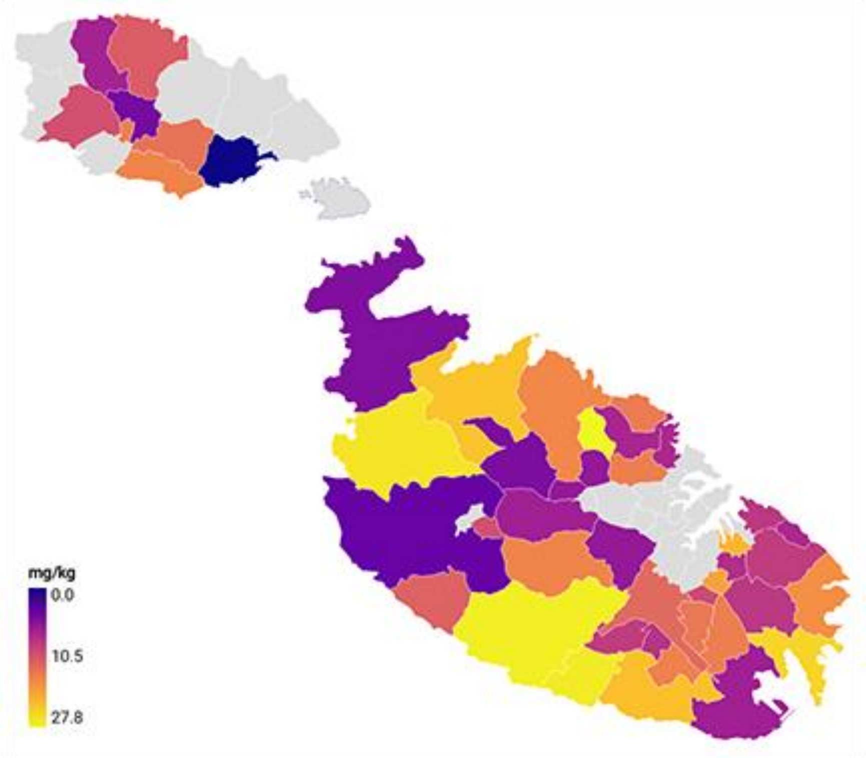


Figure 49: Selenium concentrations by locality

3.2.4.3 *S-block elements*

The s-block elements are made up of group 1 and 2 in the periodic table. s-block elements have atoms having their last valence electron, which is present in the s-orbital (Averill and Eldredge, 2011a).

The mean values of the elements of this group from the One-Way ANOVA show that sodium is the highest element found in the group, followed by strontium, barium, rubidium and caesium (Table 15).

Table 15: Mean element values of S-block elements

Element	Mean value ppm (mg/kg)
Sodium	96984.42
Strontium	315.32
Barium	185.43
Rubidium	76.39
Caesium	4.30

The bar graph (Figure 50) showed that sodium had a considerable difference in concentrations compared with the rest of the elements in the group. It was then removed from the data to draw a bar graph without it (Figure 51). Strontium also proved to have a high concentration compared to the rest of the elements in the group, while caesium had the lowest concentration. The Kruskal-Wallis test showed that strontium had a ρ-value of 0.008, which was less than the 0.05 level of significance. Thus the concentrations of the element was proved to have a statistical difference between the districts.

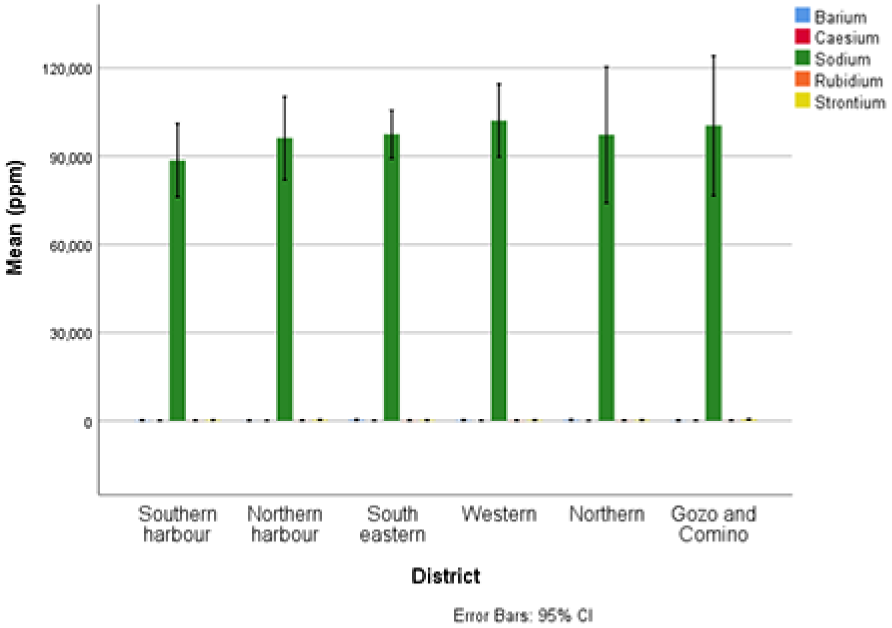


Figure 50: S-block concentrations in each district

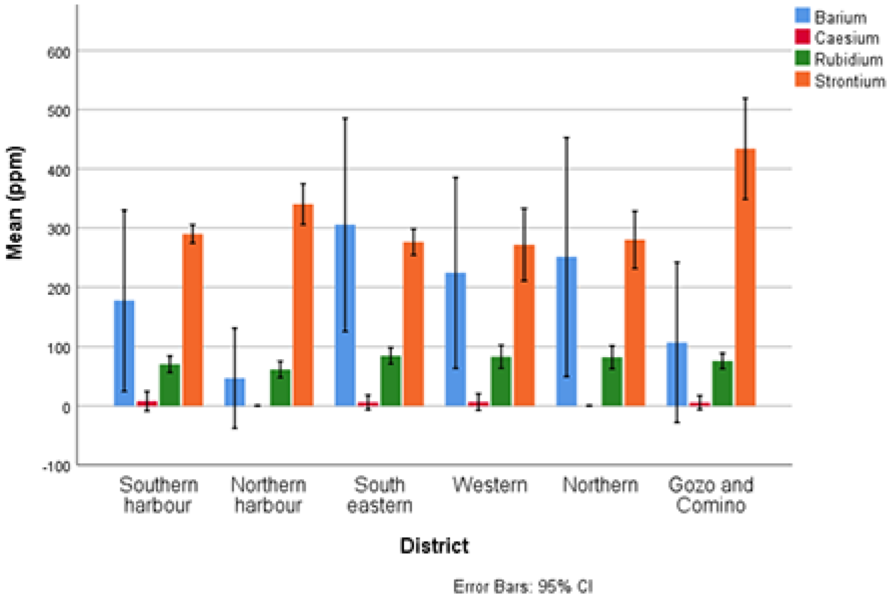


Figure 51: S-block concentrations in each district excluding sodium

3.2.4.4 *F-Block elements*

Elements in the f-block have atoms with valence electrons in the f-orbital. These are the inner transition elements from the d-block and are subdivided into two subgroups. If the last electron moves into the 4f orbital, the elements are placed under the group lanthanides. If the last electron moves into the 5f orbital, they are placed into the group actinides (Carroll, 2017). The group includes cerium, lanthanum, neodymium and praseodymium (Table 16).

Table 16: Mean element value for F-block elements

Element	**Mean value ppm (mg/kg)**
Lanthanum	29.71
Neodymium	5.24
Cerium	0.74
Praseodymium	0.00

The One-Way ANOVA showed that Lanthanum was found at a higher concentration than the rest of the elements in this group. All have a ρ-value which exceeded the 0.05 level of significance showing they did not vary marginally between the districts. The results showed that the elements in the group were not present in the district of Gozo and Comino. In the Northern, Western and Northern Harbour District, only lanthanum was seen, although the Western district had a lesser amount when compared to the other 2 districts. Neodymium was seen in both South-Eastern and Southern Harbour District, while cerium was only observed in the Southern Harbour. Praseodymium was not seen in any of the districts (Figure 52).

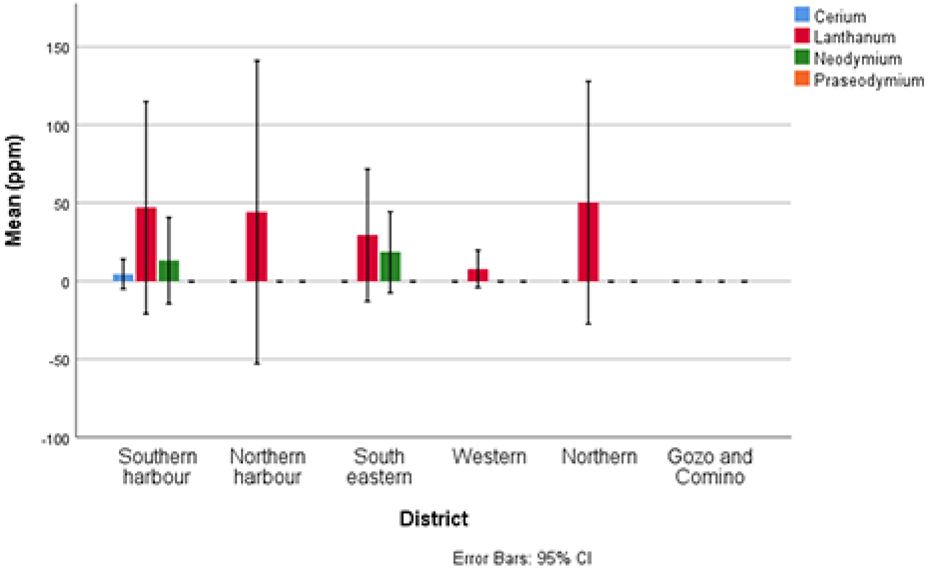


Figure 52: F-block concentrations in each district

3.2.5 Localities and districts most affected by the heavy metals

Donut charts using the Datawrapper® were drawn for each heavy metal illustrating were the element was present at highest concentrations in the localities. Nearly all metals were seen to be present, mostly in Marsaxlokk and Qrendi. Other common localities between them are Għajnsielem, Għargħur and Żabbar (Figure 53). Another chart was created to illustrate the percentage of the element found in the districts (Figure 54).

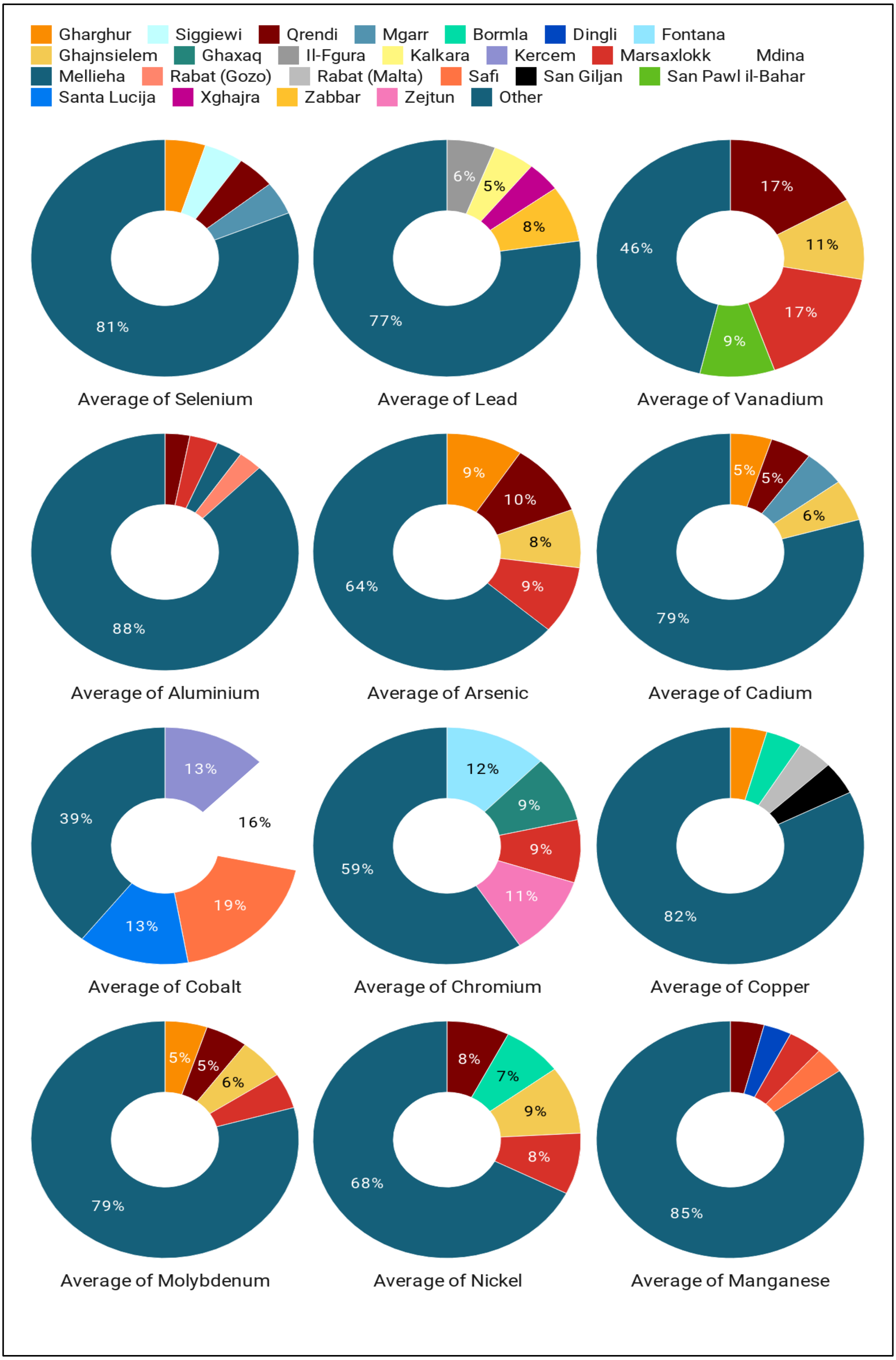


Figure 53: Elements according to percentage concentration by locality

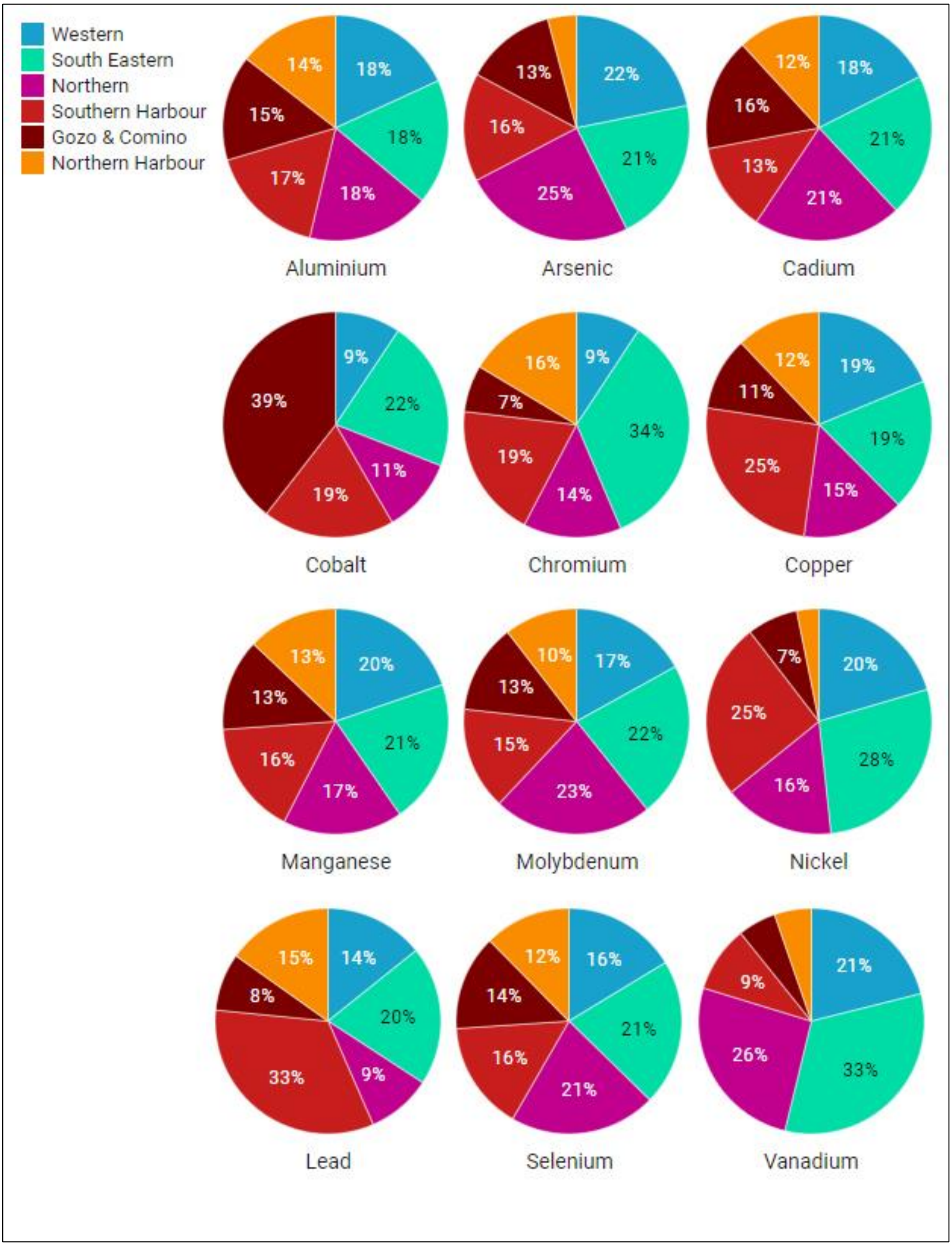


Figure 54: Percentage concentration of heavy metals by district

Another chart was illustrated using pie charts to depict the percentage difference between the districts and the highest metal in each district. Aluminium was seen to have the highest concentration in all of them (Figure 55). Another chart was created, removing aluminium from the data. Manganese was then shown to have second highest concentration of the heavy metals in all district, followed by lead, copper and vanadium (Figure 56).

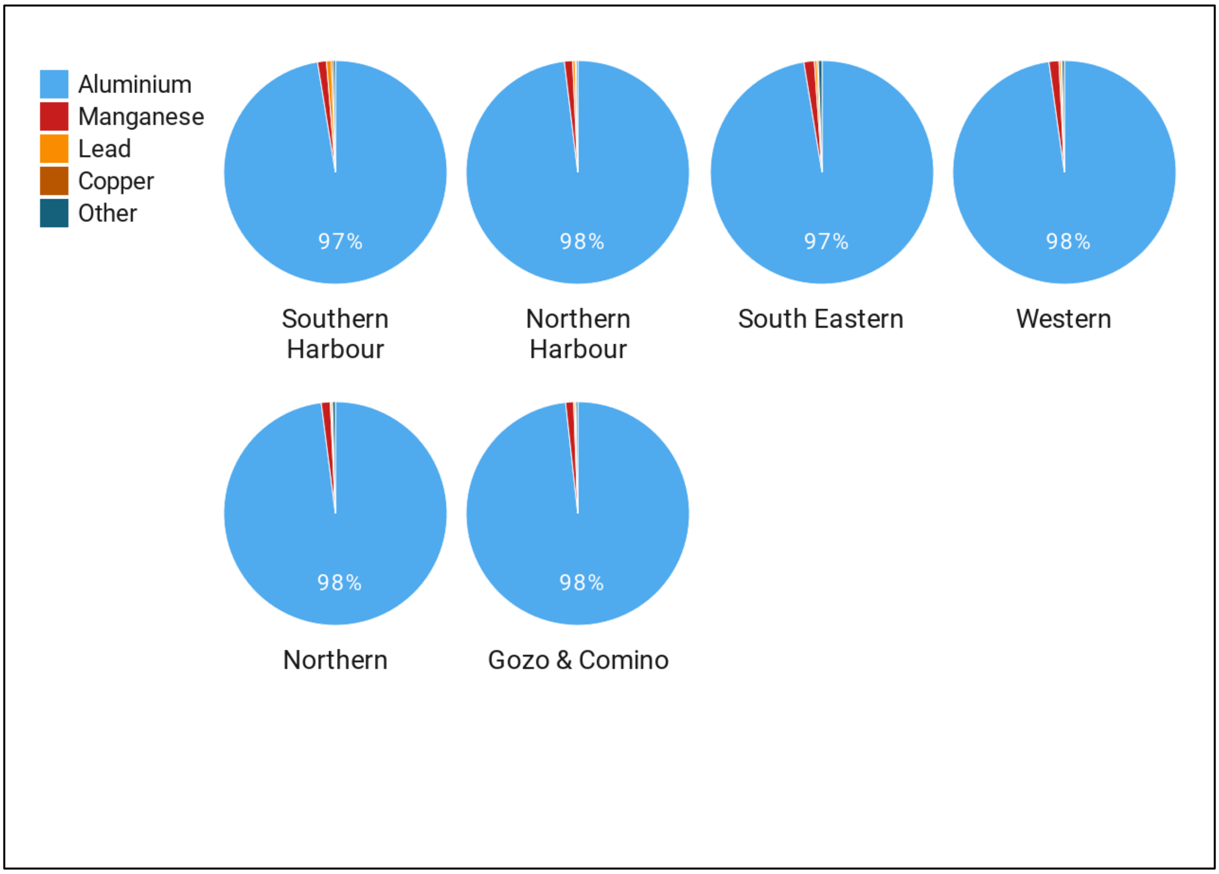


Figure 55: Percentage of heavy metals found in each district

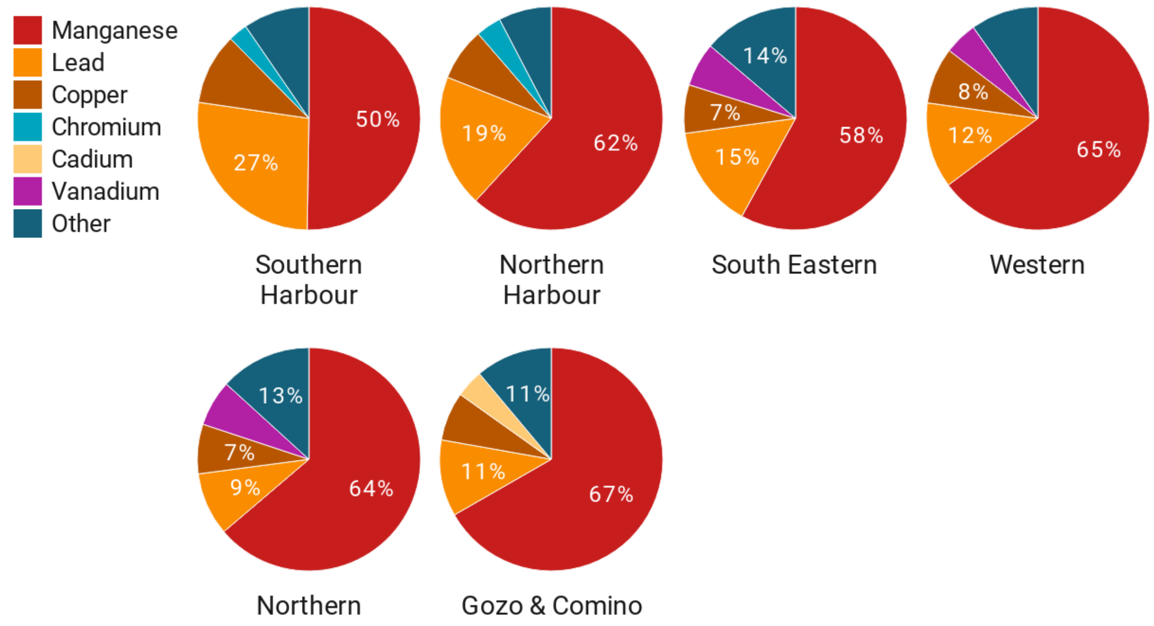


Figure 56: Percentage of heavy metals found in each district excluding aluminium

3.3 Control sample results

The results of the 101 samples taken were compared to the two control samples, consequently seeing if there were any differences in concentrations between an uncontaminated soil and the rest of the soil samples which were exposed to fertilizers, pesticides and other contaminants. The Binomial test was used to compare the mean district scores with the control values. Nearly all ρ-values, with both controls, were less than the 0.05 level of significance, meaning that the district score, differs significantly from the control value (Table 17 and Table 18).

Table 17: Binomial analysis between mean district value and Control 1.

Element	Number of Samples	Districts Mean	Districts St. Dev	Standard	ρ-value
Aluminium	101	35447.17	10740.71	20217.35	0
Arsenic	101	5.63	8.959	1.2	0.005
Barium	101	200	328.538	55	0.005
Bismuth	101	29.41	14.578	7.005492	0
Bromine	101	38.07	16.365	30.02	0.163
Cadmium	101	24.01	20.523	16	0.111
Cerium	101	0.79	7.938	0	0
Chlorine	101	2751.29	522.099	2500	0.003
Cobalt	101	6.98	19.877	5.62	0
Chromium	101	23.98	51.071	0	0
Caesium	101	4.72	23.806	0	0
Copper	101	65.17	63.605	65.31	0.691
Iron	101	26994.54	10158.57	20238	0
Gallium	101	12.57	14.16	4.664441	0.32
Germanium	101	2.45	5.05	0	0
Iodine	101	42.73	46.066	19.5	0.232
Potassium	101	10368.57	3294.815	16852	0
Lanthanum	101	29.11	105.111	0	0
Magnesium	101	14477.14	5221.708	13990.53	0
Manganese	101	487.89	248.112	389.21	0.017
Molybdenum	101	9.16	7.661	1.093126	0
Sodium	101	96946.41	29358.69	82346.46	0
Niobium	101	19.84	12.822	5.997763	0
Neodymium	101	6.51	37.041	0	0
Nickel	101	14.4	20.73	0	0.111
Phosphorus	101	3712.55	1074.65	2679.619	0
Lead	101	131.01	105.713	78.9072	0.017
Praseodymium	101	0	0	0	0
Rubidium	101	77.51	31.142	74.06721	0.32
Antimony	101	47.1	51.059	36.2709	0.001
Selenium	101	12.63	8.832	11.385	0.009
Silicon	101	115067.4	33100.65	92361.57	0
Tin	101	131.4	28.788	127.5445	0.32
Sulphur	101	2025.02	516.395	1926.405	0.163
Strontium	101	309.42	105.595	213.0887	0
Tantalum	101	0	0	0	0
Tellurium	101	44.95	41.347	24.00099	0.073
Titanium	101	2797.16	1074.09	2016.27	0
Vanadium	101	35.75	91.9	0	0
Tungsten	101	0.4	2.709	0	0
Yttrium	101	33.78	14.781	9.260294	0
Zinc	101	176.21	125.296	116.4127	0.046
Zirconium	101	306.16	162.415	254.18	0.551

Table 18: Binomial analysis between mean district value and Control 2

Element	Number of Samples	Districts Mean	Districts St. Dev	Standard	ρ-value
Aluminium	101	35447.17	10740.71	23014.35	0
Arsenic	101	5.63	8.959	0.8	0.005
Barium	101	200	328.538	50	0.005
Bismuth	101	29.41	14.578	10	0
Bromine	101	38.07	16.365	32	0.32
Cadmium	101	24.01	20.523	10	0.003
Cerium	101	0.79	7.938	0	0
Chlorine	101	2751.29	522.099	2770	0.551
Cobalt	101	6.98	19.877	5	0
Chromium	101	23.98	51.071	0	0
Caesium	101	4.72	23.806	0	0
Copper	101	65.17	53.605	48.73046	0.32
Iron	101	26994.54	10158.57	23000	0.005
Gallium	101	12.57	14.16	5.01	0.32
Germanium	101	2.45	5.05	0	0
Iodine	101	42.73	46.066	15.31	1
Potassium	101	10368.57	3294.815	12038	0
Lanthanum	101	29.11	105.111	0	0
Magnesium	101	14477.14	5221.708	12013	0
Manganese	101	487.89	248.112	352.64	0
Molybdenum	101	9.16	7.661	1.53	0
Sodium	101	96946.41	29358.69	95824.68	1
Niobium	101	19.84	12.8222	5.62	0
Neodymium	101	6.51	37.041	0	0
Nickel	101	14.4	20.73	0	0.111
Phosphorus	101	3712.55	1074.649	2549.68	0
Lead	101	131.01	105.713	76.1224	0.005
Praseodymium	101	0	0	0	0
Rubidium	101	77.51	31.142	75.0348	0.232
Antimony	101	47.1	51.059	30.246	0.551
Selenium	101	12.63	8.832	10.24	0.046
Silicon	101	115067.4	33100.65	98057.39	0
Tin	101	131.4	28.788	125.876	0.691
Sulphur	101	2025.02	516.395	2000.325	0.842
Strontium	101	309.42	105.595	146.287	0
Tantalum	101	0	0	0	0
Tellurium	101	44.95	41.347	0	0
Titanium	101	2797.16	1074.09	1958.6	0
Vanadium	101	35.75	91.9	0	0
Tungsten	101	0.4	2.709	0	0
Yttrium	101	33.78	14.781	15.021	0
Zinc	101	176.21	125.296	113.2794	0.028
Zirconium	101	306.16	162.415	201.65	0

Chapter 4: Discussion

4.1 Comparison in the pilot study

When comparing the results obtained during the pilot study, it can be observed that the values between the XRF and the ICP-MS vary. When reading the binomial test, which was used to evaluate the level of significance, all results showed that the ρ-value exceeded the 0.05 level of significance. Thus, the mean XRF score, is comparable to the ICP-MS value.

The ρ-values obtained were all 1.00 or 0.25, attributing to the fact that for the XRF, only three readings of each sample where taken. When comparing the results using the Spearman correlation coefficient, nearly all comparisons proved to have a correlation coefficient of close to 1, indicating that there was a positive relationship between the results of the ICP-MS and the XRF. The difference lies in how each instrument works and how they exhibit their results.

ICP-MS is a very reliable instrument; it is a multipurpose technique that can accomplish limits of detections many orders of a degree lower than the XRF instrument. It has excellent accuracy but has the disadvantage that the sample has to be in a liquid form requiring acid digestion and long sample preparation time when compared to the XRF spectrometer. ICP-MS cost more to use, including consumables. XRF spectrometer is easier to use and a rapid technique when comparing it to the other analysis method. It can also read both solid forms and liquid forms (Al Maliki *et al.*, 2017).

The ICP-MS is a quantitative instrument and has been growing in popularity over various other instrumentation. It has detection limits which can go below the single part per trillion of any element, and it can achieve isotopic analysis. The concentration of each element present in the sample is determined by relating the counts measured of a specific isotope with an external calibration curve which was previously created for that particular element (Pröfrock and Prange, 2012; Bulska and Wagner, 2016).

On the contrary, the XRF results are semi-quantitative. Semi-quantitative data ascertain the relative element concentrations between the samples, but it will not give absolute concentration amounts. These results are calculated by calculating the area under the peak of interest, thus showing why the results of both instruments are not identical or similar, for the elements tested (Bruker, 2020).

4.2 XRF peaks

When reading the XRF spectra, some difficulties may arise when reading them, which can cause false positive or false negatives, like the chromium and nickel in the results given. XRF spectra can have peak overlaps which appear due to the presence of individual and multiple elements in the sample together with limited detector resolution. Peaks seen in the XRF spectrum can be caused by several sources apart from the metal itself. Artefact peaks arise due to the X-ray tube source. When the X-ray source photons interact with the samples, some characteristic features are generated in the XRF spectrum, which may include Rayleigh peaks, Compton peaks and Bremsstrahlung. Artefact peaks may also be caused by electrons which have a high kinetic energy of around 10-50 kV, and which strike the atoms in the X-ray tube source-target which will then transfer energy and cause a peak (Brouwer, 2010; Chemistry LibreTexts, 2019).

Rayleigh Peaks are caused by the elastic scattering from the sample. The elastic scattering cause peaks on the spectra due to the target anode present in the X-ray tube, which is made of palladium. During this process, energy is not lost; thus, the peaks show up at energies which are less than the distinctive X-ray tube target energies. Rayleigh peaks are usually seen when the samples are dense, and these are observed as weak peaks due to the amplification of the absorption of palladium’s photons by the sample (Chemistry LibreTexts, 2019).

Compton Peaks are caused by the inelastic scattering from the sample. Once again, these peaks occur in the spectrum from the palladium element found in the X-ray tube. During this process, energy is slightly lost; thus, the peaks show up at energies which are slightly less than the distinctive X-ray tube target energies. Compton peaks are usually seen when the samples have a low density, and these are observed as fairly intense peaks. Bremsstrahlung is a backscatter or continuum from a cellulose which is present in all XRF spectra, where a backscattering of X-rays caused by the sample to the detector causes vast peaks. It can be seen mostly in less dense samples which tend to scatter more palladium photons back to the detector. The maximum peak energy limited by kV, which is applied to the X-ray tube, causes a peak of maximum intensity of around two-thirds of the applied keV. Other artefact peaks may be caused by the detection process where the X-ray fluorescence photons interact from the sample with the detector which can generate a variety of artefact peaks in the spectrum. These artefact peaks are either sum peaks or escape peaks. Sum peaks are caused by two photons which arrive at the detector at the same time. Sum peaks are mostly seen when there are high concentrations of an element in the sample. Sum peaks can be kept on the low side by keeping count rate lows. Escape peaks are caused, by the absorption of part of the energy of a photon, by silicon atoms present in the detector. Escape peaks are mostly seen in spectra which have high concentrations of an element which are lower Z elements. Escape peaks can also be reduced by keeping the count rates low. Some other artefact peaks may occur from the sampling cup packaging together with the Mylar film if any contaminants are present on the XRF window (Brouwer, 2010; Chemistry LibreTexts, 2019).

4.3 Heavy Metals Found in each District and Locality

When seeing the results obtained for each heavy metal and seeing where it was found at its highest concentration, it can be concluded from where the heavy metal might have originated. Gozo and Comino District, and the Northern Harbour, where the districts having the least heavy metal contamination. The districts that had the most pollution of heavy metals present in their soils, were the South-Eastern District and the Southern Harbour. This stands to reason since most of the polluting industries are based in these districts.

4.3.1 Aluminium

No limits regarding threshold for aluminium in soil was found. Aluminium was found nearly in similar amounts all over the Maltese islands. Equal concentrations of aluminium were observed in the South-Eastern District, Northern District and Western District. Aluminium is usually present in soils at high concentrations between 10,000 mg/kg and 300,000 mg/kg, since it is the most abundant metal in the Earth's crust. The average of the metal present across Malta and Gozo was 34998.05 mg/kg the highest amount observed was in Marsaxlokk with an average concentration of 54513 mg/kg. Aluminium is identified as a contaminant of potential concern, but this is only true for those soils that have a pH of less than 5.5 since it is the only pH where aluminium is present in its soluble form (U.S. Environmental Protection Agency, 2003; ATSDR, 2008).

4.3.2 Manganese

WHO states that the maximum permissible limit of the heavy metal in medicinal plants is 200 mg/kg (WHO, 2005; Shah *et al.*, 2013). In the United States, the average concentration of manganese in the soil is between 40-900 mg/kg (ATSDR, 2012c). Though no thresholds are found to state the maximum limit of manganese in soil. The average concentration of manganese around the islands was 473.51 mg/kg. It was observed to be present at a higher concentration in the South-Eastern District and Western District at 586.67 mg/kg and 560.75 mg/kg respectively, when compared to the rest of the districts. Manganese was present more in these districts probably due to the Delimara power station, smelting of steel (Rotatori *et al.*, 2003; ERA, 2018) and fertilizers. Qrendi situated in the Western District, had an average concentration of 887.25 mg/kg, and one particular sample in the locality had a concentration of 1061 mg/kg. This was where the soil collected from was from land that was situated close to the area where fireworks had been ignited the week before, and remnants of the fireworks where still present in the surrounding areas. In Siġġiewi, steel industries are present which also might be why more manganese was present in the Western District.

4.3.3 Lead

Finland is one of the countries which have soil limits for heavy metals. Finland states that soil is declared contaminated if one or more of their listed elements is more than the lower guideline value. The natural concentration of lead in the soil is 5 mg/kg, and the threshold value is 60 mg/kg. The lower guideline level is stated to be 200 mg/kg, and if the limit is exceeded health risks are predicted. If the amount is more than the higher guideline level which is stated to be 750 mg/kg, then it predicted to be of ecological risk (Ministry of the Environment Finland, 2007). The Dutch limit for lead in soil is stated to be 85 mg/kg, which is very low compared to the Finland guideline (Ogundele, Adio and Oludele, 2015).

Lead is an element that has brought about much concern about its pollution. It was observed to have a global average of 125.58 mg/kg. It was present at a very high concentration of 249.51 mg/kg in the Southern Harbour. The increase in lead in that area could be due to vehicle emissions, primarily since it used to be added as an anti-knock vehicle agent (ATSDR, 2019); the shipyard (Papaioannou, 2004; OECD, 2010; Marine Strategy Framework Directive, 2016) since ships are sandblasted and scraped; use of sewage sludge ; fuel combustion (Marine Strategy Framework Directive, 2016; Huang *et al.*, 2017; ERA, 2018) when there was the Marsa power station still working, oil and fuel terminals (Marine Strategy Framework Directive, 2016), together with the thermal treatment facility (National Research Council (US) Committee on Health Effects of Waste Incineration, 2000; ERA, 2018) found in Marsa. All this causes lead particles to spread, and since lead cannot be destroyed, then it will remain in the soil for long periods and keeps on accumulating.

With regards to localities, it was seen at higher concentrations when compared to the other localities, in Żabbar, Fgura and Kalkara. Żabbar had an average concentration of 462.33 mg/kg, Fgura was found to have an average concentration of 352.00 mg/kg, and Kalkara had an average concentration of 301.00 mg/kg. One of the samples of Żabbar had an alarming concentration of 829.00 mg/kg. Compared to previous studies done in 2006, where Paola's topsoil was found to have a lead concentration in its topsoil of 451 mg/kg, Żabbar was seen to have a very high amount (State of the Environment Indicators, 2006). In various countries, lead thresholds for residential land is stated with different thresholds according to the country, as seen in the report by the FAO (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Lead concentrations in the district and in the localities with high concentrations all exceed the Dutch and Finland thresholds. The concentrations even exceed the lower level guideline making lead toxic in these areas.

4.3.4 Copper

The Dutch permissible limit for copper in the soil is 36 mg/kg (Ogundele, Adio and Oludele, 2015). The Finland law states that the natural concentration of copper is 22 mg/kg, and the threshold value is 100 mg/kg. The lower guideline value, which can be of ecological risk is 150 mg/kg (Ministry of the Environment Finland, 2007). Quite a lot of localities had more than the lower guideline value of the Finland soil contamination law, and only a few localities had less than the 36 mg/kg as stated in the Dutch permissible limit law (Ogundele, Adio and Oludele, 2015). The FAO states a variety of copper limits for residential land depending on the country (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

The highest concentration of copper was noted in the Southern Harbour area, with an average concentration of 95.15 mg/kg. Increase in copper concentrations observed in the Southern Harbour District could be due to the shipyard's activity (Papaioannou, 2004; OECD, 2010; Marine Strategy Framework Directive, 2016) and the previous power station (Marine Strategy Framework Directive, 2016; Huang *et al.*, 2017). Other methods of copper pollution could be due to the use of fungicidal in plants which is sometimes added in excess in the agricultural land due to pig and cow manure (Xiong *et al.*, 2010; Jiang, Dong and Zhao, 2011), and the use of sewage sledge (Marine Strategy Framework Directive, 2016; US EPA, 2019a). It was found at higher concentration in the localities of Qrendi and Għargħur soil samples at 128.75 mg/kg and 137 mg/kg respectively, due to the fireworks activities since copper is one of the elements used to project the blue colour. Bormla at 136 mg/kg, Fgura at 120.50 mg/kg and Żabbar at 124.67 mg/kg, have high concentrations since they are situated in the Southern Harbour. St. Julians had the highest concentration of 140 mg/kg, though the source of pollution was not discovered.

Most values exceed the Dutch threshold and the copper concentrations found in the localities with the highest concentrations exceed Finland's threshold value.

4.3.5 Vanadium

According to Finland's permissible limits, the natural occurrence of vanadium is 38 mg/kg, the threshold value is 100 mg/kg, and the lower and higher guideline values are 150 mg/kg and 250 mg/kg respectively (Ministry of the Environment Finland, 2007). Vanadium had an average concentration of 32.75 mg/kg. The South-Eastern District had the highest concentration of vanadium present when compared to the rest of the districts with an average of 64.25 mg/kg. Fly ash from power stations is one of the reasons for vanadium to be present in the soil after settling or washed from the atmosphere (ATSDR, 2012d).

Qrendi and Marsaxlokk had very high concentrations of vanadium of 244.75mg/kg and 244 mg/kg respectively, where in one of the Qrendi samples, vanadium was present at a concentration of 683 mg/kg. When seeing localities and individual samples. Qrendi might have resulted in a high concentration of vanadium due to the fireworks since both aluminium and vanadium elements can be found in titanium powders which are used for fireworks (ATSDR, 2012d; Ogundele, Adio and Oludele, 2015).. When seeing the concentrations by districts, vanadium concentrations are within range, though when comparing the individual samples, the Qrendi and Marsaxlokk samples were in excess and over the thresholds.

4.3.6 Cadmium

According to the Finland law, the natural concentration of cadmium is 0.03 mg/kg, and the threshold value is 1 mg/kg. The law also states that the lower guideline limit and the upper guideline limits are 10 mg/kg and 20 mg/kg, respectively (Ministry of the Environment

Finland, 2007). The permissible limit by the Dutch standard is 0.8 mg/kg (Ogundele, Adio and Oludele, 2015). Cadmium had an average concentration of 23.51 mg/kg around Malta and Gozo. The district with the highest cadmium present was in the Northern district at 30.10 mg/kg. This might be due to the Magħtab landfill, which in the past, batteries were part of the waste delivered and no capping was present. Batteries contain cadmium and could have leached out of the landfill (Panero *et al.*, 1995). It was also found at high concentrations in the South-Eastern District at 28.95 mg/kg which might have been caused by the Delimara power station (Rotatori *et al.*, 2003; Marine Strategy Framework Directive, 2016; Huang *et al.*, 2017) or the use of sewage sludge (Marine Strategy Framework Directive, 2016; US EPA, 2019a). It was found in Għajnsielem and Ta' Sannat in Gozo as the localities that contained cadmium at high concentrations which might come from phosphate fertilizers (Cupit *et al.*, 2002) or from the cement plant located in the locality which is a source of cadmium pollution (ERA, 2018; US EPA, 2019b) or from the sewage plant situated in Għajnsielem, Ras il-Ħobż (Lindqvist-Östblom and Eklund, 1999) .

Cadmium is found at very high concentrations when compared to the Dutch standard and Finland standard which exceed the upper level guideline (Ministry of the Environment Finland, 2007; Ogundele, Adio and Oludele, 2015).

4.3.7 Chromium

According to the Dutch standard, the limit of permissible chromium is 100 mg/kg (Ogundele, Adio and Oludele, 2015). The Finland standard states that the natural concentration of chromium is 31 mg/kg, and the threshold value should be 100 mg/kg. When seeing the lower guideline value, this is stated as 200 mg/kg and the higher guideline value is stated to be 300 mg/kg to be of ecological risk (Ministry of the Environment Finland, 2007). The average concentration of chromium is 22.29 mg/kg and was found to be highest in the South-Eastern District with an average concentration of 45.93 mg/kg. Chromium might be released into the atmosphere through the Delimara power stations (Rotatori *et al.*, 2003; Marine Strategy Framework Directive, 2016) and oil and fuel terminals (Marine Strategy Framework Directive, 2016). Chromium in this research was not detected to see which oxidation was present, whether it was chromium (III) or chromium (VI). The oxidation makes all the difference when it comes to chromium toxicity. Chromium might be released into the atmosphere through the Delimara power stations (Rotatori *et al.*, 2003; Marine Strategy Framework Directive, 2016).

Some localities had an amount of more than 100 mg/kg of chromium and thus were more than the permissible limit compared to both Finland and the Dutch thresholds.

4.3.8 Arsenic

The Finland standard states that the natural concentration of arsenic is 1 mg/kg and the threshold concentration is 5 mg/kg. Lower and higher guideline values are 50 mg/kg and 100 mg/kg which will cause risk to the ecology (Ministry of the Environment Finland, 2007). One of the toxic elements is arsenic which was found in the Northern district at higher concentrations when compared to the other districts at 7.93 mg/kg. The high amount of arsenic in the Northern District after talking to the farmers could be as poultry and pig manure was used in their soils which might have contained arsenic.

With regards to localities, arsenic was found mostly in Qrendi, with an average concentration of 23.75 mg/kg, Għargħur, with an average concentration of 22 mg/kg, and Marsaxlokk, with an average concentration of 22mg/kg. In the past arsenic was used in fireworks to give more colour. Since it is toxic, it has been reduced or not used at all, though it was seen at high amounts in both places were soil samples were taken just after the fireworks were displayed, thus fireworks might be the cause of the increase of arsenic in these samples. Sewage sludge also may contain arsenic in it (US EPA, 2019a) and if farmers used it untreated, this could be the cause for an increase in the metal presence. In the locality of Marsaxlokk, the amount of arsenic observed could be due to the release from the power station since arsenic is detected in electricity generation plants (Rotatori *et al.*, 2003; ERA, 2018) or through the wear of tyres and breaks (ERA, 2018). It was used as a rat poison in previous times and still might linger in the soil since it is not biodegradable (Brown and Waddell, 2014). Arsenic in Qrendi was found to be at 23.75 mg/kg which is alarmingly high for an element so toxic when compared to the threshold value stated by Finland

4.3.9 Cobalt

The threshold value from the Finland standard is 20 mg/kg. The lower and upper guideline values are stated as 100 mg/kg and 250 mg/kg (Ministry of the Environment Finland, 2007). Cobalt can be seen at 15.83 mg/kg in the district of Gozo and Comino, which has the highest average concentration of the metal present. Cobalt can be present in fertilizers, sewage sludge and animal feed (Cobalt Institute, 2017; US EPA, 2019a). Kirkop was one of the localities with the highest average concentration of cobalt at 63.50 mg/kg. This increase in cobalt in this area could be due to airport traffic which releases cobalt into the air (ATSDR, 2004b).

As an average concentration and district, cobalt is observed to be below the threshold stated by Finland. When looking at some individual localities such as Ħal-Safi, the concentration exceeds the threshold stated.

4.3.10 Nickel

The Dutch standard states that the permissible limit for nickel should be 35 mg/kg (Ogundele, Adio and Oludele, 2015). According to the Finland standard, the threshold concentration of nickel should be 50 mg/kg and the lower and higher guideline values are 100 mg/kg and 150 mg/kg respectively (Ministry of the Environment Finland, 2007). An average concentration of 13.10 mg/kg of nickel was observed around Malta and Gozo. The heavy metal nickel was found to be present at a high concentration in the South-Eastern District and the South Harbour. It was present at 21.90 mg/kg and 19.95 mg/kg respectively. These districts might have showed a higher concentration due to the shipyards (Papaioannou, 2004; OECD, 2010), the Delimara power station (Rotatori *et al.*, 2003; ERA, 2018), waste incineration (ERA, 2018), oil and fuel terminals (Marine Strategy Framework Directive, 2016) and the combustion of fuel in ships (ERA, 2018).The localities which had the highest concentration of this element was Għajnsielem, with an average of 61 mg/kg probably due to the sewer plant , and Marsaxlokk had an average of 55 mg/kg probably due to the Delimara power station (Marine Strategy Framework Directive, 2016). Qrendi had one of its samples show a concentration of 63 mg/kg, which might have been caused by the ignition of fireworks (Helmenstine, 2020), and Bormla had one sample showing an amount of 79 mg/kg of nickel, probably due to shipyards (Papaioannou, 2004; OECD, 2010).

On seeing the values of the soil samples collected, on average, the amount of nickel present is less than both the Dutch and the Finland standard. Some agricultural lands have more than the permissible limit.

4.3.11 Molybdenum

No threshold limits were found on this metal. It was found with an average of 8.85 mg/kg around Malta and Gozo. It was found at higher concentration in the Northern District with an average of 12.09 mg/kg. This could be due to the wastewater treatment plant and the landfill situated in this district (ATSDR, 2004b). When observing localities, the highest concentration was found in Għajnsielem with an average concentration of 23.00 mg/kg which could be due to the sewage plant there (ATSDR, 2004b). It was followed by Qrendi and Għargħur with average concentrations of 21.00 mg/kg for the both of them. This could be due to the fireworks as molybdenum can be carbonised to suppress smoke in the fireworks (Stanford Advanced Materials, 2017). It was found with an average concentration of 20.00 mg/kg in Marsaxlokk showing that the pollution may have been caused by the Delimara power station (ATSDR, 2004b).

4.3.12 Selenium

No threshold limits for selenium present in soil, were found. It was present with an average concentration of 12.31 mg/kg and although it was found at similar concentrations all over the islands, it had a slightly higher in the South-Eastern District with an average of 15.50 mg/kg probably due to the Delimara power station, since selenium is one of the pollutants caused by energy generation industries (Staicu *et al.*, 2017). On seeing localities, the sample in Għargħur showed selenium to be present at 28 mg/kg.

4.3.13 Zinc

The natural concentration and threshold value of zinc, according to the Finland legislation, are 31 mg/kg and 200mg/kg. The lower guideline value is stated as 250 mg/kg and the upper guideline value is stated as 400 mg/kg (Ministry of the Environment Finland, 2007). The maximum limit by the Dutch standard is 50mg/kg (Ogundele, Adio and Oludele, 2015)(Ogundele <i>et al.</i>, 2017). The average concentration across the islands was at 174.09 mg/kg. It was found with a very high concentration in the Southern Harbour at 251.33 mg/kg when compared to the other districts. This high concentration may be due to the shipyard activities (Papaioannou, 2004; Marine Strategy Framework Directive, 2016), sewage sludge, oil and fuel terminals, and the old Marsa power station (Marine Strategy Framework Directive, 2016).

The localities with the most zinc present in their soil were in the locality of Żabbar which was found with a concentration of 447.20 mg/kg. Following Żabbar, zinc was found at high concentrations in Bormla at 376.80 mg/kg, Mġarr at 350.80 mg/kg and Għajnsielem at 326.20 mg/kg. Żabbar and Bormla may had high concentrations due to the shipyard, old Marsa power station and oil and fuel terminals. Mġarr may had high concentrations due to the addition of poultry and pig manure (Jiang, Dong and Zhao, 2011), since this was confirmed by the farmer. Ghajnsielem's zinc increase may be due to the sewage plant or the cement plant (ERA, 2018; US EPA, 2019b).

4.4 Controls

In both Binomial tests, H1 was not rejected since the sample mean of the 101 observations vary significantly from the control one values and control two values. The heavy metals in both controls were significantly lower than the rest of the samples. Copper in control one is not significantly different as the ρ-value exceed the 0.05 level of significance since the element was confirmed to be used by the farmer as a fungicide, increasing the amount of copper in the soil. Concentration of chlorine in control two, was observed to be higher than control one values, and this may have been brought about by strong winds which carries sea droplet onto the soil due to the close proximity of the agricultural land to the sea.

4.5 Limitations and Recommendations for Future Work

When preparing the soil, the sampling cup technique was used for this research study. One of the disadvantages is that the soil had to be fine, no air pockets, moisture or organic matter had to be present. If any of these were present the R/R_0 would increase, the fit would not be good, and thus results will be even less accurate. For better analytical results, another sampling technique could have been used, which is the pressed pellet technique. Pellets have a higher signal to noise ratio than when testing the loose powder form. The lightest elements in the sample are detected, and the lighter elements are also detected without being underestimated. Unlike loose powder, where lighter elements might go undetected. When arranging the loose soil in the sample cup, pockets of air can also affect the reading and thus from one sample to the next, the reading may vary depending on how homogenous the sample was and how compact it was prepared. The advantage of loose powder is an effortless preparation. Pressed pellets, on the contrary, need more preparation. The process of pressed pellets involves the sample being ground to very fine particle size. This fine particle soil sample is then mixed with a binder in a grinder or mixing vessel. The mixture achieved is then poured into a pressing die where the mixture is pressed at a pressure between 15T and 35T. Contamination is one of the aspects that needs to be seen when preparing it. Some details should be done with care when using the pressed pellet, such as the particle size, binder choice, ratio of dilution, amount of pressure used to form the pellet and the thickness of the pellet, to get high-quality results (Coler, 2017).

Another limitation for these results is that each sample was only tested three times to get a global picture of the result. For better correlation values, more readings could have been done, where each sample could have been repeated at least 15 times to get a more accurate analysis.

When comparing the ICP-MS and the XRF, it could be seen that elements present in low amounts, such as mercury which is a very toxic heavy metal, was not seen in the XRF results. Some elements such as chromium and nickel were present in the sample but were not calculated by the XRF programme. This was due to the R/R_0 fitting which sometimes eliminated these elements, even though the peak was present. XRF oxidation states of elements was another issue while using the XRF as the oxidation state could not be identified, changing the scenario for some heavy metals where one oxidation state can be toxic and other not. Case in point is chromium, which can be present as chromium (III) or chromium (VI) which have very different properties and toxicity properties. Chromium (VI) is very toxic, while chromium (III) is not.

An important parameter which can be taken into account to get a better picture of toxicity is the soil's pH. The difference in soil pH, as previously explained, can cause the element to be absorbed or not absorbed by the plant. Thus, pH will decide if the heavy metal will be toxic to the plant and thus toxic to the rest of the food chain. In most heavy metals, the more acidic the soil is, the more the heavy metal will be absorbed, and thus the more toxic the element becomes. Other parameters include the oxidation state, the organic matter, and redox reactions. The type of plant grown in the soil and plant pattern can also be another factor which causes a difference in the absorbance of the heavy metal. Dicotyledons tend to absorb heavy metals more than monocotyledons.

Another area that could be looked into are soil from glasshouses. The soil in these glasshouses are not contaminated by air pollutants, since no dissolved contaminants can reach the soil. The soil in the glasshouses could have shown that plants grown in the enclosed area would contain fewer contaminants than plants grown outside.

4.5.1 Practices to Target High Levels of Heavy Metal Concentrations

A lot of technologies or treatments are present to try and remove the heavy metals from the contaminated soils. Some techniques can be done on-site, while other techniques need the soil to be removed and treated off-site.

Remediation techniques can be divided into three types; (i) physical, (ii) chemical, (iii) biological. Physical remediation techniques include methods such as thermal, solidification, vapour extraction, washing and treating, air sparging, particle sorting, and electromediation. Chemical remediation methods include oxidation, hydrolysis, reduction, solubilisation, pH manipulation and dechlorination. The third type of method is uses the biological techniques which include landfarming, microbial activity, bioreactor, composting, bioleaching, phytostabilisation, plant activity, phytoextraction and photodegradation (Rodriguez-Eugenio, McLaughlin and Pennock, 2018).

Some of the methods might be too expensive or time-consuming. Massive volumetric sludge is generated when using the chemical technologies and these also increase the costs. Thermal methods, apart from being expensive to perform, can also damage essential soil components. Traditionally, onsite management of heavy metal contaminated soil remediation occurred, or excavation of the contaminated soil which was disposed to a landfill. Though this has proven to being just a transportation of the contaminated soil, to a different location instead of reducing or eliminating the contamination, this method increases the chance to contaminate other areas next to the landfills. An alternative method that is used is soil washing. This method can be used instead of the excavation method, and involves washing the soil to remove the metals. However, it is costly, and the residue produced is highly abundant in the metals that were eliminated, and would thus need further treatment. From all these methods, it can be observed that soil remediation using physio-chemical technologies tends to eradicate all the biological activities, and thus reduces the medium for the plant growth (Wuana and Okieimen, 2011). Phytoremediation and intercrop are newer techniques which are widely being used.

4.5.2 Phytoremediation

Phytoremediation has become a more popular method since it is less expensive and environmentally friendly. Plants are planted in soils that are contaminated with heavy metals to aid in the removal. Apart from removing heavy metals from soils, phytoremediation has also been used to remove heavy metals from sediment and waters. These type of plants are known as hyperaccumulator plants (Hao *et al.*, 2012).

Plant root systems are selective in their uptake and thus prove to be an advantage in phytoremediation. This also includes translocation of the contaminant, bioaccumulation and the degradation of the entire plant to remove the heavy metal. Inorganic compounds removal involved in this process usually takes place through phytostabilisation and phytoextraction. Phytoextraction involves the heavy metal being translocated from the roots into the shoots. In contrast, phytostabilisation involves certain plant species which absorb and accumulate the heavy metals in certain parts of the plants and thus stop the movement of the element from going back into the soil. The removal of organic compounds is usually achieved through phytodegradation, rhizodegradation and rhizofiltration. Rhizodegradation needs microbial activity to degrade the contaminants in the rhizosphere, which is improved by the plant roots. Rhizofiltration consists of the precipitation or the adsorption of the contaminants into the roots that are in the solution surrounding the root by wetting the land (Tangahu *et al.*, 2011).

Certain factors which influence the uptake of the metal is the plant species; the properties of the medium include, the pH of the soil, the organic matter present and the phosphorous amount present together with other factors; the root zone; vegetative uptake which is affected by the temperature since it affects the root length; and the chelating agent added which influences the bioavailability of the heavy metals. Some examples of a chelating agent used are ethylenediaminetetraacetic acid EDTA (Chen, Li and Shen, 2004; Tangahu *et al.*, 2011; Wuana and Okieimen, 2011).

The Chinese Brake plant known as *Pteris vittata* L. absorbs around 0.7 mg/g or more of arsenic in the dry weight in the whole plant. The black poplar, known as *Populus nigra* absorbs around 0.2 mg/g arsenic per dry weight in its roots. Lead is absorbed by the plant *Brassica carinata* A. Braun also known as Abyssinian cabbage or Abyssinian mustard, which absorbs lead at more than 50 mg/g of dry plant weight. Tomato plants, *Solanum lycopersicum,* absorb cadmium in its shoots and lead in its roots. The tomato itself is also a part of the plant that absorbs excess cadmium. *Thlaspi caerulescens* is a hyperaccumulator for zinc and cadmium. It can take up to 10,000 mg/kg of zinc and cadmium is taken up by the shoots with an amount of 100 mg/kg of dry plant weight. The plants do not show signs of toxicity when taking up the heavy metals (An *et al.*, 2011a).

4.5.3 Intercropping

Intercropping involves the simultaneous growth of two plants or more. Intercropping helps twofold to improve the plant biomass, and in aiding with the accumulation of heavy metals. Phytoremediation can be further improved by intercropping with another plant species to help increase heavy metal absorption. This combination of methods will help to be more environmentally friendly, unlike the use of chelators (Li *et al.*, 2009; Cui *et al.*, 2018). For a successful intercropping system to happen, the appropriate component species or population needs to be selected. Apart from decreasing the heavy metals, intercropping helps in increasing income for the farmers (Wan and Lei, 2018).

Due to the intercropping method, some benefits that are acquired include stability and diversity brought to the fields, fertilizer application reduction and crops used together to share resources. Lastly, there can be a reduction of weeds, insects or disease acquirement (Lowry and Smith, 2018). Three types of intercropping exist, (i) mixed intercropping - when the different crops are harvested together; (ii) row intercropping - the method used when the different crops are grown in alternative rows; and (iii) relay cropping – when the reproductive stage of the first crop is waited for until the second crop can be sown (Lithourgidis *et al.*, 2011).

Examples of intercropping plants used and the heavy metal affected by the method are, maize and chickpea plants. Maize absorbs a decent amount of cadmium from the soil, but when it is intercropped with chickpea, the amount is increased (Li *et al.*, 2009). Another example is tomato intercropped with the Japan clover herb. Iron concentration increases in the tomato root when it is harvested with the Japan clover herb. Also with this intercropping, cadmium was found at higher quantities in is shoots, roots and fruit. Japan clover herb had high values of cadmium when intercropped with both the tomato plant and the maize plant (An *et al.*, 2011b).

4.5.4 Organic Farming

There are several organic farms registered in Malta, were no artificial pesticides and synthetic fertilizers are used to control their plants. Increased use of pesticides and fertilizer has reduced the biodiversity around the lands in Malta since it is not only toxic to the pests, but also to the other insects and reptiles. Such as the *Coccinellidae* which is known as the ladybird, *Lumbricus* spp. known as the earthworm, *Apis mellifera ruttneri* which is the Maltese honey bee.

On the contrary, organic farming uses the biodiversity to their advantage. Many insects and reptiles have habitats in the area which roam the lands and remove any unwanted pests themselves. Unlike other farmers who make use of chemicals to remove the pests. Since habitats and food is increased, wild fauna and flora increase in the area, including pest predators and pollinators. According to the organic farmers that were talked to during the research, examples of natural pest predators are spiders which emerge during the night removing quite a lot of pest insects from the crops. Chameleons are insectivores and help in the removal of insects such as whiteflies and red spiders, which can destroy the crops. Butterflies and honey bees are found in higher quantities which help in pollination. Ladybirds are found in large quantities which are known to kill aphids which remove the sap from the plant (FAO, 2020).

Apart from organic farms benefiting the microbial activity and also the biodiversity in Malta, it also uses no chemicals and is thus pollution-free. Since figures show that the heavy metals were low in the organic farms, it can be deduced that the crops grown in these farms will not cause any toxic effects to animals or humans since less amount were found in the soil, for them to be absorbed.

4.6 Conclusion

Heavy metal pollution has been given a lot of attention since heavy metals is a source of toxicity. They are not biodegradable and remain in the soil indefinitely. The bioaccumulation of heavy metals in soil can be the cause of detriment to plants, animals and humans as the metals can be absorbed by the plants, and end up in the food chain, which may produce adverse effects including death.

This study has shown how heavy metal pollution in Maltese soils, may have been brought about. Sources of heavy metal pollution, have been noted to be more abundant in areas where there is industrialisation which has been observed as heavy metals was observed in the South-Eastern and South Harbour Districts. Lead, arsenic, cadmium and zinc were some of the heavy metals which were found to surpass thresholds according to the Finland and Dutch legislation. Methods to address excess heavy metals in soils can be applied to reduce the metals such as remediation and intercropping. The study revealed that organic farming is a way of growing crops without the use of pesticides and artificial fertilizers, which has shown that soils in organic farms, have a less concentration of each of the heavy metals discussed.

Chapter 5: Bibliography

Adrees, M. *et al.* (2015) ‘The effect of excess copper on growth and physiology of important food crops: a review’, *Environmental Science and Pollution Research*. Springer Verlag, 22(11), pp. 8148–8162. doi: 10.1007/s11356-015-4496-5.

Agrafioti, E., Kalderis, D. and Diamadopoulos, E. (2014) ‘Arsenic and chromium removal from water using biochars derived from rice husk, organic solid wastes and sewage sludge’, *Journal of Environmental Management*. Academic Press, 133, pp. 309–314. doi: 10.1016/j.jenvman.2013.12.007.

Aihemaiti, A. *et al.* (2019) ‘Review of plant-vanadium physiological interactions, bioaccumulation, and bioremediation of vanadium-contaminated sites’, *Science of the Total Environment*. Elsevier B.V., p. 135637. doi: 10.1016/j.scitotenv.2019.135637.

Aktar, W., Sengupta, D. and Chowdhury, A. (2009) ‘Impact of pesticides use in agriculture: Their benefits and hazards’, *Interdisciplinary Toxicology*, 2(1), pp. 1–12. doi: 10.2478/v10102-009-0001-7.

Albanese, S. *et al.* (2007) ‘Geochemical background and baseline values of toxic elements in stream sediments of Campania region (Italy)’, *Journal of Geochemical Exploration*, 93(1), pp. 21–34. doi: 10.1016/j.gexplo.2006.07.006.

Alloway, B. J. and Jackson, A. P. (1991) ‘The behaviour of heavy metals in sewage sludge-amended soils’, *Science of the Total Environment, The*, 100(C), pp. 151–176. doi: 10.1016/0048-9697(91)90377-Q.

An, L. *et al.* (2011a) ‘Heavy metal absorption status of five plant species in monoculture and intercropping’, *Plant and Soil*, 345(1), pp. 237–245. doi: 10.1007/s11104-011-0775-1.

An, L. *et al.* (2011b) ‘Heavy metal absorption status of five plant species in monoculture and intercropping’, *Plant and Soil*, 345(1), pp. 237–245. doi: 10.1007/s11104-011-0775-1.

Aronsson, P. and Perttu, K. (2001) ‘Willow vegetation filters for wastewater treatment and soil remediation combined with biomass production’, *Forestry Chronicle*. Canadian Institute of Forestry, 77(2), pp. 293–299. doi: 10.5558/tfc77293-2.

Ashraf, M. A. (2017) ‘Persistent organic pollutants (POPs): a global issue, a global challenge’, *Environmental Science and Pollution Research*. Springer Verlag, pp. 4223–4227. doi: 10.1007/s11356-015-5225-9.

ATSDR (1999) *Toxicological Profile for Mercury*. Available at: https://www.atsdr.cdc.gov/toxprofiles/tp46.pdf (Accessed: 29 June 2018).

ATSDR (2003) *Toxicological Profile for Selenium*. Available at: https://www.atsdr.cdc.gov/ToxProfiles/tp92.pdf (Accessed: 29 June 2018).

ATSDR (2004a) *Toxicological Profile for Copper*. Available at: https://www.atsdr.cdc.gov/toxprofiles/tp132.pdf (Accessed: 29 June 2018).

ATSDR (2004b) *Toxicological Profile of Cobalt*. Available at: https://www.atsdr.cdc.gov/ToxProfiles/tp33-c1-b.pdf.

ATSDR (2005) *Toxicological Profile for Zinc*. Available at: https://www.atsdr.cdc.gov/ToxProfiles/tp60.pdf.

ATSDR (2007a) *Toxicological Profile for Arsenic*. Available at: https://www.atsdr.cdc.gov/toxprofiles/tp2.pdf (Accessed: 29 June 2018).

ATSDR (2007b) *Toxicological Profile for Lead*. Available at: https://www.atsdr.cdc.gov/toxprofiles/tp13.pdf (Accessed: 29 June 2018).

ATSDR (2008) *Toxicological Profile for Aluminium*. Available at:

https://www.atsdr.cdc.gov/toxprofiles/tp22.pdf.

ATSDR (2012a) *Toxicological Profile for Cadmium*. Georgia. Available at: https://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=48&tid=15 (Accessed: 29 June 2018).

ATSDR (2012b) *Toxicological Profile for Chromium*. Available at: https://www.atsdr.cdc.gov/csem/chromium/docs/chromium.pdf (Accessed: 29 June 2018).

ATSDR (2012c) *Toxicological Profile for Manganese*.

ATSDR (2012d) *Toxicological Profile for Vanadium*. Available at: https://www.atsdr.cdc.gov/toxprofiles/tp58.pdf (Accessed: 25 June 2018).

ATSDR (2017) *Toxicological Profile for Nickel*. Available at: https://www.atsdr.cdc.gov/ToxProfiles/tp15-c1-b.pdf (Accessed: 29 June 2018).

ATSDR (2019) *Toxicological Profile for Lead*.

Averill, B. A. and Eldredge, P. (2011a) 'Periodic Trends and the s-Block Elements', in *General Chemistry: Principles, Patterns, and Applications*. Saylor Foundation.

Averill, B. A. and Eldredge, P. (2011b) 'The d-Block Elements', in *General Chemistry: Principles, Patterns, and Applications*. Saylor Foundation. Available at: https://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0m/s27-the-d-block-elements.html (Accessed: 5 March 2020).

Averill, B. A. and Eldredge, P. (2011c) 'The p-Block Elements', in *General Chemistry: Principles, Patterns, and Applications*. Saylor Foundation.

Axiak, P. V. (2004) *Assessing the marine environmental quality of the coastal waters exposed to the Maghtab Solid Waste Disposal Site FINAL REPORT ENVIRONMENT PROTECTION DIRECTORATE Malta Environment and Planning Authority*.

Baderna, D. *et al.* (2011) 'A combined approach to investigate the toxicity of an industrial landfill's leachate: Chemical analyses, risk assessment and in vitro assays', *Environmental Research*, 111(4), pp. 603–613. doi: 10.1016/j.envres.2011.01.015.

Baishya, K. (2015) 'Impact of Agrochemicals Application on Soil Quality Degradation - A Review', *International Journal of Science Technology and Management*, 4(1).

Balkhair, K. S. (2016) 'Microbial contamination of vegetable crop and soil profile in arid regions under controlled application of domestic wastewater', *Saudi Journal of Biological Sciences*, 23(1), pp. 83–92. doi: Balkhair, K. S. (2016). Microbial contamination of vegetable crop and soil profile in arid regions under controlled application of domestic wastewater. Saudi Journal of Biological Sciences, 23(1), S83–S92. doi:10.1016/j.sjbs.2015.10.029.

Barceló, D. and Petrovic, M. (2007) 'Pharmaceuticals and personal care products (PPCPs) in the environment', *Analytical and Bioanalytical Chemistry*, pp. 1141–1142. doi: 10.1007/s00216-006-1012-2.

Barnes, J. (2009) *Assessment of Air Quality in the Vicinity of Delimara Power Station, Malta Baseline*.

Barnhart, J. (1997) 'Occurrences, Uses, and Properties of Chromium', *Regulatory Toxicology and Pharmacology*. Academic Press Inc., 26(1 I), pp. S3–S7. doi: 10.1006/rtph.1997.1132.

Basile, B. P., Middleditch, B. S. and Oró, J. (1984) 'Polycyclic aromatic hydrocarbons in the Murchison meteorite', *Organic Geochemistry*, 5(4), pp. 211–216. doi: 10.1016/0146-6380(84)90008-1.

Battist, L. and Peterson, H. T. (1980) 'Radiological Consequences of the Three Mile Island Accident', in *Radiation Protection*. Oxford: Pergamon Press, pp. 677–684.

Bayat, J. *et al.* (2016) 'Fingerprinting aliphatic hydrocarbon pollutants over agricultural lands surrounding Tehran oil refinery', *Environmental Monitoring and Assessment*. Springer International Publishing, 188(11). doi: 10.1007/s10661-016-5614-7.

Beasley, M. and Temple, W. (no date) 'Pyrethroid toxicity and its management', *Best Practice Journal - Hazardous Substances Series*.

Benavides, M. P., Gallego, S. M. and Tomaro, M. L. (2005) 'Cadmium toxicity in plants', *Brazilian Journal of Plant Physiology*. Sociedade Brasileira de Fisiologia Vegetal, pp. 21–34. doi: 10.1590/S1677-04202005000100003.

Bengtsson, B. *et al.* (1988) 'Influence of aluminium on phosphate and calcium uptake in beech (Fagus sylvatica) grown in nutrient solution and soil solution', *Physiologia Plantarum*, 74(2), pp. 299–305. doi: 10.1111/j.1399-3054.1988.tb00635.x.

Bhalerao, S. A., Sharma, A. S. and Poojari, A. C. (2015) 'Toxicity of Nickel in Plants', *Interrnational Journal of Pure and Applied Bioscience*, 3(2), pp. 345–355.

Birch, G. F. and Scollen, A. (2003) 'Heavy metals in road dust, gully pots and parkland soils in a highly urbanised sub-catchment of Port Jackson, Australia', *Australian Journal of Soil Research*, 41(7), pp. 1329–1342. doi: 10.1071/SR02147.

Blaser, P. *et al.* (2000) 'Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils', *Science of the Total Environment*, 249(1–3), pp. 257–280. doi: 10.1016/S0048-9697(99)00522-7.

Bogden, J. D. and Louria, D. B. (1975) 'Soil contamination from lead in paint chips', *Bulletin of Environmental Contamination and Toxicology*. Springer-Verlag, 14(3), pp. 289–294. doi: 10.1007/BF01685637.

Bolívar, J. P., García-Tenorio, R. and García-León, M. (1995) 'Enhancement of natural radioactivity in soils and salt-marshes surrounding a non-nuclear industrial complex', *Science of the Total Environment*, 173–174(C), pp. 125–136. doi: 10.1016/0048-9697(95)04735-2.

Brady, N. C. (1990) *The Nature and Properties of Soils*, *Macmillan Publishing Company*. Available at: https://www.nrcs.usda.gov/wps/portal/nrcs/detail/nj/home/?cid=nrcs141p2_018993 (Accessed: 1 March 2020).

Brouwer, P. (2010) 'Theory of XRF. Getting acquainted with the principles', *PANalytical*.

Brown, A. J. and Waddell, L. S. (2014) 'Rodenticides', in *Small Animal Critical Care Medicine, Second Edition*. Elsevier Health Sciences, pp. 591–596. doi: 10.1016/B978-1-4557-0306-7.00111-2.

Browne, R. C. (1955) 'Vanadium poisoning from gas turbines.', *British journal of industrial medicine*. BMJ Publishing Group, 12(1), pp. 57–9. Available at: http://www.ncbi.nlm.nih.gov/pubmed/14351648 (Accessed: 29 June 2018).

Bruker (2020) *XRF Data Differences: Quantitative, Semi-Quantitative, and Qualitative Data*. Available at: https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/handheld-xrf/xrf-data-primer-quantitative-semi-quantitative-qualitative.html (Accessed: 8 March 2020).

Brunning, A. (2015) *A Rough Guide to the IARC's Carcinogen Classifications | Compound Interest*, *Compound Interest*. Available at: https://www.compoundchem.com/2015/10/26/carcinogens/ (Accessed: 19 January 2019).

Bulska, E. and Wagner, B. (2016) 'Quantitative aspects of inductively coupled plasma mass spectrometry', *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*. Royal Society of London, p. 20150369. doi: 10.1098/rsta.2015.0369.

Bundschuh, J. *et al.* (2012) 'One century of arsenic exposure in Latin America: A review of history and occurrence from 14 countries', *Science of the Total Environment*, pp. 2–35. doi: 10.1016/j.scitotenv.2011.06.024.

Buszewski, B. *et al.* (2019) 'A holistic study of neonicotinoids neuroactive insecticides—properties, applications, occurrence, and analysis', *Environmental Science and Pollution Research*. Springer, pp. 34723–34740. doi: 10.1007/s11356-019-06114-w.

C.H. Walker, R.M. Sibly, S.P. Hopkin, D. B. P. (2012) *Principles Of Ecotoxicology*. 4th Editio. Edited by T. and F. Group. CRC Press.

Carabott, S. and Macdonald, V. (2018) 'Major fire at Magħtab waste facility casts dark cloud over Malta', *The Times of Malta*. Available at: https://timesofmalta.com/articles/view/major-fire-in-maghtab.688003 (Accessed: 20 February 2020).

Carlon, C. (2007) *Derivation Methods of Soil Screening Values in Europe. A review and Evaluation of National Procedures Towards Harmonisation*. Luxomberg.

Carroll, M. (2017) *F-Block Elements on the Periodic Table: Properties & Overview*. Available at: https://study.com/academy/lesson/f-block-elements-on-the-periodic-table-properties-lesson-quiz.html (Accessed: 5 March 2020).

Carrondo, M. J. T. *et al.* (no date) *Analysis Of Heavy Metals In Sewage Sludge, Sewages And Final Effluent*.

CCID (2015) *Special Policay Study on Soil Pollution Management*. Available at: https://www.iisd.org/sites/default/files/publications/CCICED/prevention/2015/policy-study-on-soil-pollution-management.pdf.

Centres for Disease Control and Prevention (2013) *Understanding Thimerosal, Mercury, and Vaccine Safety*. Available at: http://www.cdc.gov/vaccines/conversations (Accessed: 29 June 2018).

Certini, G., Scalenghe, R. and Woods, W. I. (2013) 'The impact of warfare on the soil environment', *Earth-Science Reviews*, pp. 1–15. doi: 10.1016/j.earscirev.2013.08.009.

Chaney, R. L. (2015) 'Trace Metal Movement: Soil-Plant Systems and Bioavailability of Biosolids-Applied Metals', in *Sewage Sludge: Land Utilization and the Environment*. Madison, WI, USA: American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, pp. 27–31. doi: 10.2134/1994.sewagesludge.c5.

Charlton, A. *et al.* (2016) 'Long-term impact of sewage sludge application on soil microbial biomass: An evaluation using meta-analysis', *Environmental Pollution*. Elsevier Ltd, 219, pp. 1021–1035. doi: 10.1016/j.envpol.2016.07.050.

Chemistry LibreTexts (2019) *Interpretation of XRF Spectra*. Available at: https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Analytical_Sciences_Digital_Library/JASDL/Courseware/Introduction_to_XRF-_An_Analytical_Perspective/2._Interpretation_of_XRF_Spectra (Accessed: 15 March 2020).

Chen, Y., Li, X. and Shen, Z. (2004) 'Leaching and uptake of heavy metals by ten different species of plants during an EDTA-assisted phytoextraction process', *Chemosphere*, 57(3), pp. 187–196. doi: 10.1016/j.chemosphere.2004.05.044.

Chibuike, G. U. and Obiora, S. C. (2014) 'Heavy metal polluted soils: Effect on plants and bioremediation methods', *Applied and Environmental Soil Science*. Hindawi Publishing Corporation. doi: 10.1155/2014/752708.

Chovancová, J., Kočan, A. and Jursa, S. (2005) 'PCDDs, PCDFs and dioxin-like PCBs in food of animal origin (Slovakia)', *Chemosphere*, 61(9), pp. 1305–1311. doi: 10.1016/j.chemosphere.2005.03.057.

Cobalt Institute (2017) *Cobalt in soils*. Available at: https://www.cobaltinstitute.org/cobalt-in-soil.html (Accessed: 16 March 2020).

Coler, D. (2017) *6 Things to Consider when Making Pressed Pellets for XRF Analysis*. Available at: https://www.armi.com/blog/6-things-to-consider-when-making-pressed-pellets-for-xrf-analysis (Accessed: 14 March 2020).

Conneely, V. (2019) *The Number Of Vehicles Registered In Malta Continues To Rise*. Available at: https://www.maltachamber.org.mt/en/the-number-of-vehicles-registered-in-malta-continues-to-rise (Accessed: 25 March 2020).

Costa, M. and Klein, C. B. (2006) 'Toxicity and carcinogenicity of chromium compounds in humans', *Critical Reviews in Toxicology*, pp. 155–163. doi: 10.1080/10408440500534032.

De Coster, S. and Van Larebeke, N. (2012) 'Endocrine-disrupting chemicals: Associated disorders and mechanisms of action', *Journal of Environmental and Public Health*. Hindawi Publishing Corporation, pp. 1–52. doi: 10.1155/2012/713696.

Cui, T. *et al.* (2018) 'Intercropping of Gramineous Pasture Ryegrass (LoliumperenneL.) and Leguminous Forage Alfalfa (Medicago sativaL.) Increases the Resistance of Plants to Heavy Metals', *Journal of Chemistry*, p. 11.

Ćujić, M. *et al.* (2015) 'Radionuclides in the soil around the largest coal-fired power plant in Serbia: radiological hazard, relationship with soil characteristics and spatial distribution', *Environmental Science and Pollution Research*. Springer Verlag, 22(13), pp. 10317–10330. doi: 10.1007/s11356-014-3888-2.

Cupit, M. *et al.* (2002) 'Assessment and management of risks arising from exposure to cadmium in fertilisers - II', *Science of the Total Environment*. Elsevier, 291(1–3), pp. 189–206. doi: 10.1016/S0048-9697(01)01099-3.

Dalefield, R. (2017) 'Metals', in *Veterinary Toxicology for Australia and New Zealand*. Elsevier, pp. 233–253. doi: 10.1016/B978-0-12-420227-6.00013-X.

Dar, M. A., Kaushik, G. and Villareal Chiu, J. F. (2020) 'Pollution status and biodegradation of organophosphate pesticides in the environment', in *Abatement of Environmental Pollutants*. Elsevier, pp. 25–66. doi: 10.1016/b978-0-12-818095-2.00002-3.

Das, P., Samantaray, S. and Rout, G. R. (1997) 'Studies on cadmium toxicity in plants: A review', *Environmental Pollution*, pp. 29–36. doi: 10.1016/S0269-7491(97)00110-3.

Dayan, A. D. and Paine, A. J. (2001) 'Mechanisms of chromium toxicity, carcinogenicity and allergenicity: Review of the literature from 1985 to 2000', *Human & Experimental Toxicology*. Sage PublicationsSage CA: Thousand Oaks, CA, 20(9), pp. 439–451. doi: 10.1191/096032701682693062.

Denkhaus, E. and Salnikow, K. (2002) 'Nickel essentiality, toxicity, and carcinogenicity.', *Critical reviews in oncology/hematology*. Elsevier, 42(1), pp. 35–56. doi: 10.1016/S1040-8428(01)00214-1.

Department of Environment and Conservation (2010) *Assessment Levels for Soil, Sediment and Water*. Available at: https://www.der.wa.gov.au/images/documents/your-environment/contaminated-sites/guidelines/2009641_-_assessment_levels_for_soil_sediment_and_water_-_web.pdf.

Dobson, A. W., Erikson, K. M. and Aschner, M. (2004) 'Manganese Neurotoxicity', *Annals of the New York Academy of Sciences*. Wiley/Blackwell (10.1111), 1012(1), pp. 115–128. doi: 10.1196/annals.1306.009.

Dœlsch, E., Saint Macary, H. and Van de Kerchove, V. (2006) 'Sources of very high heavy metal content in soils of volcanic island (La Réunion)', *Journal of Geochemical Exploration*, 88(1-3 SPEC. ISS.), pp. 194–197. doi: 10.1016/j.gexplo.2005.08.037.

Duffus, J. H. (2002) '"Heavy metals" a meaningless term?', *Pure and Applied Chemistry*. International Union of Pure and Applied Chemistry, 74(5), pp. 793–807. doi: 10.1351/pac200274050793.

Van Elsas, J. D. and Heijnen, C. E. (1990) 'Methods for the introduction of bacteria into soil: A review. Biology and Fertility of Soils.', *Biol Fertil Soils*, 10(2), pp. 127–135. doi: 10.1007/bf00336248.

Environment & Resources Authority (2016a) *Soils defined*. Available at: https://era.org.mt/en/Pages/Soils-defined.aspx (Accessed: 29 February 2020).

Environment & Resources Authority (2016b) *Sources and Health Effects of Air Pollution*. Available at: https://era.org.mt/en/Pages/Sources-and-Health-Effects-of-air-pollution.aspx (Accessed: 29 February 2020).

Environmental Protection UK (no date) *Aviation Pollution*. Available at: https://www.environmental-protection.org.uk/policy-areas/air-quality/air-pollution-and-transport/aviation-pollution/ (Accessed: 13 April 2020).

Environmental Software and Services (2011) *Environmenal Impact Assessment Case Study: Delimara Thermal Power Station, Malta*. Available at: https://www.ess.co.at/AIRWARE/MALTA/delimara.html (Accessed: 29 February 2020).

ERA (2018) *State of the Environment Report*.

European Commission (2001) *Disposal and Recycling Routes for Sewage Sludge. Part 2 - Regulatory Report*.

European Commission (2010) *Shutting down old landfills for good-Projects - Regional Policy -*. Available at: https://ec.europa.eu/regional_policy/en/projects/major/malta/shutting-down-old-landfills-for-good (Accessed: 24 February 2020).

European Commission (2019) *2019 report on the economic and social situation of Gozo (Malta)*. Brussels. Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:52019DC0463&rid=8 (Accessed: 5 March 2020).

Exley, C., Chappell, J. S. and Birchall, J. D. (1991) 'A mechanism for acute aluminium toxicity in fish', *Journal of Theoretical Biology*, 151(3), pp. 417–428. doi: 10.1016/S0022-5193(05)80389-3.

Fang, Y. *et al.* (2017) 'Organochlorine pesticides in soil, air, and vegetation at and around a contaminated site in southwestern China: Concentration, transmission, and risk evaluation', *Chemosphere*. Elsevier Ltd, 178, pp. 340–349. doi: 10.1016/j.chemosphere.2017.02.151.

FAO (2020) *Organic Agriculture: What are the environmental benefits of organic agriculture?* Available at: http://www.fao.org/organicag/oa-faq/oa-faq6/en/ (Accessed: 20 March 2020).

Fayez, K. A., El-Deeb, B. A. and Mostafa, N. Y. (2017) 'Toxicity of biosynthetic silver nanoparticles on the growth, cell ultrastructure and physiological activities of barley plant', *Acta Physiologiae Plantarum*. Polish Academy of Sciences, 39(7), p. 155. doi: 10.1007/s11738-017-2452-3.

Fertile Soil (Preservation) Act (1973). Available at: http://www.justiceservices.gov.mt/DownloadDocument.aspx?app=lom&itemid=8736&l=1.

Fesenko, S. V. *et al.* (2007) 'An extended critical review of twenty years of countermeasures used in agriculture after the Chernobyl accident', *Science of the Total Environment*, pp. 1–24. doi: 10.1016/j.scitotenv.2007.05.011.

Fiałkiewicz-Kozieł, B. *et al.* (2016) 'Anthropogenic- and natural sources of dust in peatland during the Anthropocene', *Scientific Reports*. Nature Publishing Group, 6. doi: 10.1038/srep38731.

Finnegan, P. M. and Chen, W. (2012) 'Arsenic toxicity: The effects on plant metabolism', *Frontiers in Physiology*, 3 JUN. doi: 10.3389/fphys.2012.00182.

Fosmire, G. J. (1990) ‘Zinc Toxicity’, *The American Journal of Clinical Nutrition*, 51(2), pp. 225–227. doi: 10.1093/ajcn/51.2.225.

Fritt-Rasmussen, J. *et al.* (2012) ‘Hydrocarbon and toxic metal contamination from tank installations in a northwest greenlandic village’, *Water, Air, and Soil Pollution*, 223(7), pp. 4407–4416. doi: 10.1007/s11270-012-1204-7.

Furuya, E. Y. and Lowy, F. D. (2006) ‘Antimicrobial-resistant bacteria in the community setting’, *Nature Reviews Microbiology*, pp. 36–45. doi: 10.1038/nrmicro1325.

García-Pérez, J. *et al.* (2007) ‘Description of industrial pollution in Spain’, *BMC Public Health*, 7. doi: 10.1186/1471-2458-7-40.

Garfì, M., Tondelli, S. and Bonoli, A. (2009) ‘Multi-criteria decision analysis for waste management in Saharawi refugee camps’, *Waste Management*, 29(10), pp. 2729–2739. doi: 10.1016/j.wasman.2009.05.019.

Gautam, P. K. *et al.* (2016) *Heavy metals in the environment: Fate, transport, toxicity and remediation technologies Thermodynamic profiling of pollutants View project Materials for Solid oxide fuel cells View project Heavy Metals In The Environment: Fate, Transport, Toxicity And Rem*. Available at: https://www.researchgate.net/publication/314465070 (Accessed: 1 November 2019).

Geissen, V. *et al.* (2015) ‘Emerging pollutants in the environment: A challenge for water resource management’, *International Soil and Water Conservation Research*. International Research and Training Center on Erosion and Sedimentation and China Water and Power Press, 3(1), pp. 57–65. doi: 10.1016/j.iswcr.2015.03.002.

Grech, H. (2017) *Last Heavy Fuel Oil turbine switched off, Delimara running entirely on natural gas*, *The Malta Independent*. Available at: https://www.independent.com.mt/articles/2017-04-24/local-news/Last-Heavy-Fuel-Oil-turbine-switched-off-Delimara-running-entirely-on-natural-gas-6736173456 (Accessed: 14 March 2020).

Gupta, M. and Gupta, S. (2017) ‘An overview of selenium uptake, metabolism, and toxicity in plants’, *Frontiers in Plant Science*. Frontiers Research Foundation, 7. doi: 10.3389/fpls.2016.02074.

Gupta, N., Khan, D. K. and Santra, S. C. (2012) ‘Heavy metal accumulation in vegetables grown in a long-term wastewater-irrigated agricultural land of tropical India’, *Environmental Monitoring and Assessment*, 184(11), pp. 6673–6682. doi: 10.1007/s10661-011-2450-7.

Hagvall, K., Persson, P. and Karlsson, T. (2015) ‘Speciation of aluminum in soils and stream waters: The importance of organic matter’, *Chemical Geology*. Elsevier, 417, pp. 32–43. doi: 10.1016/j.chemgeo.2015.09.012.

Hahladakis, J. N. *et al.* (2018) ‘An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling’, *Journal of Hazardous Materials*. Elsevier B.V., pp. 179–199. doi: 10.1016/j.jhazmat.2017.10.014.

Halling-Sørensen, B. *et al.* (1998) ‘Occurrence, fate and effects of pharmaceutical substances in the environment- A review’, *Chemosphere*. Elsevier Ltd, 36(2), pp. 357–393. doi: 10.1016/S0045-6535(97)00354-8.

Hannah, R. *et al.* (2009) ‘Exposure assessment of 17α-ethinylestradiol in surface waters of the United States and Europe’, *Environmental Toxicology and Chemistry*, 28(12), pp. 2725–2732. doi: 10.1897/08-622.1.

Hao, H. *et al.* (2012) ‘The intercropping influence on heavy metal uptake for hyperaccumulators’, in *Proceedings - 2012 International Conference on Biomedical Engineering and Biotechnology, iCBEB 2012*. IEEE, pp. 1826–1828. doi: 10.1109/iCBEB.2012.427.

Hatfield, J. L., Sauer, T. J. and Cruse, R. M. (2017) 'Soil: The Forgotten Piece of the Water, Food, Energy Nexus', in *Advances in Agronomy*. Academic Press Inc., pp. 1–46. doi: 10.1016/bs.agron.2017.02.001.

Haydee, K. M. and Dalma, K. E. (2017) 'Concerning Organometallic Compounds in Environment: Occurrence, Fate, and Impact', in *Recent Progress in Organometallic Chemistry*. InTech. doi: 10.5772/67755.

Haynes, W. M. (2011) *CRC Handbook of Chemistry and Physics*. 92nd edn. Edited by W. M. Haynes. Florida: CRC Press.

He, Z. L., Yang, X. E. and Stoffella, P. J. (2005) 'Trace elements in agroecosystems and impacts on the environment', *Journal of Trace Elements in Medicine and Biology*. Elsevier GmbH, pp. 125–140. doi: 10.1016/j.jtemb.2005.02.010.

Helmenstine, A. M. (2020) *Chemical Elements in Fireworks*, *ThoughtCo*. Available at: https://www.thoughtco.com/elements-in-fireworks-607342 (Accessed: 15 March 2020).

Herawati, N. *et al.* (2000) 'Cadmium, copper, and zinc levels in rice and soil of Japan, Indonesia, and China by soil type', *Bulletin of Environmental Contamination and Toxicology*, 64(1), pp. 33–39. doi: 10.1007/s001289910006.

History.com (2011) *Agent Orange*, *A&E Television Networks*. Available at: https://www.history.com/topics/vietnam-war/agent-orange-1 (Accessed: 29 March 2020).

Ho, S. F., Sam, C. T. and Bin Embi, G. (1998) 'Lead exposure in the lead-acid storage battery manufacturing and PVC compounding industries', *Occupational Medicine*, 48(6), pp. 369–373. doi: 10.1093/occmed/48.6.369.

Horckmans, L. *et al.* (2005) 'Local background concentrations of trace elements in soils: A case study in the Grand Duchy of Luxembourg', *Catena*, 59(3), pp. 279–304. doi: 10.1016/j.catena.2004.09.004.

Huang, X. *et al.* (2017) 'Heavy metal pollution and ecological assessment around the Jinsha coal-fired power plant (China)', *International Journal of Environmental Research and Public Health*. MDPI AG, 14(12), p. 1589. doi: 10.3390/ijerph14121589.

IARC and WHO (1993) *Beryllium, cadmium, mercury, and exposures in the glass manufacturing industry.* IARC. Available at: http://publications.iarc.fr/Book-And-Report-Series/Iarc-Monographs-On-The-Evaluation-Of-Carcinogenic-Risks-To-Humans/Beryllium-Cadmium-Mercury-And-Exposures-In-The-Glass-Manufacturing-Industry-1993 (Accessed: 29 June 2018).

Idriss, H. *et al.* (2016) 'Environmental-Impact Assessment of Natural Radioactivity Around a Traditional Mining Area in Al-Ibedia, Sudan', *Archives of Environmental Contamination and Toxicology*. Springer New York LLC, 70(4), pp. 783–792. doi: 10.1007/s00244-016-0271-y.

Industrial Emissions (Integrated Pollution Prevention and Control) Regulations (2013).

Iregren, A. (1990) 'Psychological test performance in foundry workers exposed to low levels of manganese', *Neurotoxicology and Teratology*. Pergamon, 12(6), pp. 673–675. doi: 10.1016/0892-0362(90)90085-Q.

Israel Ministry of Environmental Protection (2015) *The Impact of Air Pollution from Energy Production on Public Health*. Available at: http://www.sviva.gov.il/English/env_topics/Health-and-Environment/Health-Impact-of-Environmental-Nuisances/Pages/The-Impact-of-Energy-Production-on-Public-Health.aspx (Accessed: 15 March 2020).

Itai, T. *et al.* (2014) 'Variation and distribution of metals and metalloids in soil/ash mixtures from Agbogbloshie e-waste recycling site in Accra, Ghana', *Science of the Total Environment*. Elsevier, 470–471, pp. 707–716. doi: 10.1016/j.scitotenv.2013.10.037.

Jackson, A. P. and Alloway, B. J. (1991) ‘The transfer of cadmium from sewage-sludge amended soils into the edible components of food crops’, *Water, Air, and Soil Pollution*. Kluwer Academic Publishers, 57–58(1), pp. 873–881. doi: 10.1007/BF00282950.

Jayakody, N., Harris, E. C. and Coggon, D. (2015) ‘Phenoxy herbicides, soft-tissue sarcoma and non-Hodgkin lymphoma: A systematic review of evidence from cohort and case-control studies’, *British Medical Bulletin*. Oxford University Press, 114(1), pp. 75–94. doi: 10.1093/bmb/ldv008.

Jeffery, S. and Putten, W. H. van der (2011) *Soil Borne Diseases of Humans*. Publications Office of the European Union. doi: 10.2788/37199.

Jenkins, Ron; Gould, R. W.; Gedcke, D. (1995) *Quantitative X-Ray Spectrometry*. Second. Marcel Dekker.

Jenkins, R. (1988) *X-Ray Fluorescence Spectrometry*. John Wiley and Sons Ltd.

Jennings, A. A. (2013) ‘Analysis of worldwide regulatory guidance values for the most commonly regulated elemental surface soil contamination’, *Journal of Environmental Management*, 118, pp. 72–95. doi: 10.1016/j.jenvman.2012.12.032.

Jiang, X., Dong, R. and Zhao, R. (2011) ‘Meat products and soil pollution caused by livestock and poultry feed additive in Liaoning, China’, *Journal of Environmental Sciences*, 23(SUPPL.). doi: 10.1016/S1001-0742(11)61095-4.

Jing, R., Fusi, S. and Kjellerup, B. V. (2018) ‘Remediation of Polychlorinated Biphenyls (PCBs) in contaminated soils and sediment: State of knowledge and perspectives’, *Frontiers in Environmental Science*. Frontiers Media S.A. doi: 10.3389/fenvs.2018.00079.

Jones, C. E. (1994) ‘Molybdenum in the environment and implications to mine decommissioning in British Columbia’, in *18th Annual Columbia Mine Reclamation SYmposium in Vernon*. doi: 10.14288/1.0042249.

Ju, X. T. *et al.* (2007) ‘Changes in the soil environment from excessive application of fertilizers and manures to two contrasting intensive cropping systems on the North China Plain’, *Environmental Pollution*, 145(2), pp. 497–506. doi: 10.1016/j.envpol.2006.04.017.

Kalmykova, Y. *et al.* (2013) ‘Partitioning of polycyclic aromatic hydrocarbons, alkylphenols, bisphenol A and phthalates in landfill leachates and stormwater’, *Water Research*, 47(3), pp. 1317–1328. doi: 10.1016/j.watres.2012.11.054.

Kanter, D. R. (2018) ‘Nitrogen pollution: a key building block for addressing climate change’, *Climatic Change*. Springer Netherlands, 147(1–2), pp. 11–21. doi: 10.1007/s10584-017-2126-6.

Karnchanawong, S. and Limpiteeprakan, P. (2009) ‘Evaluation of heavy metal leaching from spent household batteries disposed in municipal solid waste’, *Waste Management*, 29(2), pp. 550–558. doi: 10.1016/j.wasman.2008.03.018.

Kassa, J. (2002) ‘Review of oximes in the antidotal treatment of poisoning by organophosphorus nerve agents’, *Journal of Toxicology - Clinical Toxicology*, pp. 803–816. doi: 10.1081/CLT-120015840.

Kaye, G. W. C. and Laby, T. H. (1986) *Tables of Physical and Chemical Constants*. 15th edn. United States: John Wiley and Sons Ltd.

Keith, S. *et al.* (2008) *Toxicological Profile for Aluminium*. Available at: https://www.atsdr.cdc.gov/toxprofiles/tp22.pdf (Accessed: 30 June 2018).

Kim, H. S. *et al.* (2017) ‘Influence of Road Proximity on the Concentrations of Heavy Metals in Korean Urban Agricultural Soils and Crops’, *Archives of Environmental Contamination and Toxicology*. Springer New York LLC, 72(2), pp. 260–268. doi: 10.1007/s00244-016-0344-y.

Kobayashi, A. (2009) 'Geographies of peace and armed conflict: Introduction', *Annals of the Association of American Geographers*, pp. 819–826. doi: 10.1080/00045600903279358.

Kovacic, P. and Somanathan, R. (2014) 'Nitroaromatic compounds: Environmental toxicity, carcinogenicity, mutagenicity, therapy and mechanism', *Journal of Applied Toxicology*. John Wiley and Sons Ltd, 34(8), pp. 810–824. doi: 10.1002/jat.2980.

Kukharchyk, T. I. *et al.* (2007) 'Polychlorinated biphenyls in soils of Belarus: Sources, contamination levels, and problems of study', *Eurasian Soil Science*, 40(5), pp. 485–492. doi: 10.1134/S1064229307050031.

Kumar, V., Kothiyal, N. C. and Saruchi (2016) 'Analysis of Polycyclic Aromatic Hydrocarbon, Toxic Equivalency Factor and Related Carcinogenic Potencies in Roadside Soil within a Developing City of Northern India', *Polycyclic Aromatic Compounds*. Taylor and Francis Inc., 36(4), pp. 506–526. doi: 10.1080/10406638.2015.1026999.

Labunska, I. *et al.* (2008) 'Chemical Contamination at E-Waste Recycling and Disposal Sites in Accra and Korforidua, Ghana', *Greenpeace Research Laboratories*.

Lauwerys, R. and Lison, D. (1994) 'Health risks associated with cobalt exposure - an overview', *Science of the Total Environment, The*, 150(1–3), pp. 1–6. doi: 10.1016/0048-9697(94)90125-2.

Leyssens, L. *et al.* (2017) 'Cobalt toxicity in humans—A review of the potential sources and systemic health effects', *Toxicology*. Elsevier Ireland Ltd, pp. 43–56. doi: 10.1016/j.tox.2017.05.015.

Li, N. Y. *et al.* (2009) 'Cadmium uptake from soil by maize with intercrops', *Water, Air, and Soil Pollution*, 199(1–4), pp. 45–56. doi: 10.1007/s11270-008-9858-x.

Li, R. *et al.* (2017) 'Mercury pollution in vegetables, grains and soils from areas surrounding coal-fired power plants', *Scientific Reports*. Nature Publishing Group, 7(1), p. 46545. doi: 10.1038/srep46545.

Li, W. C. (2014) 'Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil', *Environmental Pollution*, pp. 193–201. doi: 10.1016/j.envpol.2014.01.015.

Van Liedekerke, M. *et al.* (2014) *Progress in the management of Contaminated Sites in Europe*. doi: 10.2788/4658.

Lindqvist-Östblom, A. and Eklund, M. (1999) 'Cadmium in sewage sludge in a Swedish region: sources and reduction opportunities', *Environmental Engineering and Policy*. Springer Science and Business Media LLC, 2(3), pp. 145–154. doi: 10.1007/s100220000026.

Lithner, D., Larsson, A. and Dave, G. (2011) 'Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition', *Science of the Total Environment*, 409(18), pp. 3309–3324. doi: 10.1016/j.scitotenv.2011.04.038.

Lithourgidis, A. S. . *et al.* (2011) 'Annual Intercrops: An Alternative Pathway for Sustainable Agriculture', *Australian Journal of Crop Science*, 5(4), pp. 396–410.

Liu, J. *et al.* (2019) 'Methylmercury production in a paddy soil and its uptake by rice plants as affected by different geochemical mercury pools', *Environment International*. Elsevier Ltd, 129, pp. 461–469. doi: 10.1016/j.envint.2019.04.068.

Lowry, C. J. and Smith, R. G. (2018) 'Weed Control Through Crop Plant Manipulations', in *Non-Chemical Weed Control*. Elsevier, pp. 73–96. doi: 10.1016/b978-0-12-809881-3.00005-x.

Lu, Y. *et al.* (2015) 'Impacts of soil and water pollution on food safety and health risks in China', *Environment International*. Elsevier Ltd, 77, pp. 5–15. doi: 10.1016/j.envint.2014.12.010.

Ma, J. and Zhou, Y. (2011) 'Soil pollution by polycyclic aromatic hydrocarbons: A comparison of two Chinese cities', *Journal of Environmental Sciences*, 23(9), pp. 1518–1523. doi: 10.1016/S1001-

0742(10)60592-X.

MacEwan, R., Dahlhaus, P. and Fawcett, J. (2012) ‘Hydropedology, Geomorphology, and Groundwater Processes in Land Degradation: Case Studies in South West Victoria, Australia’, in *Hydropedology*. Elsevier, pp. 449–481. doi: 10.1016/B978-0-12-386941-8.00014-9.

Mackay, A. K. *et al.* (2013) ‘Identification of environmental lead sources and pathways in a mining and smelting town: Mount Isa, Australia’, *Environmental Pollution*. Elsevier Ltd, 180, pp. 304–311. doi: 10.1016/j.envpol.2013.05.007.

Mahmood, I. *et al.* (2016) ‘Effects of pesticides on environment’, in *Plant, Soil and Microbes: Volume 1: Implications in Crop Science*. Cham: Springer International Publishing, pp. 253–269. doi: 10.1007/978-3-319-27455-3_13.

Al Maliki, A. *et al.* (2017) ‘Comparison between inductively coupled plasma and X-ray fluorescence performance for Pb analysis in environmental soil samples’, *Environmental Earth Sciences*. Springer Verlag, 76(12), p. 433. doi: 10.1007/s12665-017-6753-z.

MALSIS (2004) *A Soil Information for the Maltese Islands*. Available at: https://msdi.data.gov.mt/geonetwork/srv/eng/catalog.search#/metadata/fe6d0480-746c-43e1-b765-7015354bba00 (Accessed: 8 March 2020).

Malta Environment & Planning Authority state of the environment report (2005).

Mansouri, A. *et al.* (2017) ‘The Environmental Issues of DDT Pollution and Bioremediation: a Multidisciplinary Review’, *Applied Biochemistry and Biotechnology*. Humana Press Inc., pp. 309–339. doi: 10.1007/s12010-016-2214-5.

Manyi-Loh, C. E. *et al.* (2016) ‘An overview of the control of bacterial pathogens in cattle manure’, *International Journal of Environmental Research and Public Health*. MDPI AG. doi: 10.3390/ijerph13090843.

Marcus, J. B. (2013) ‘Vitamin and Mineral Basics: The ABCs of Healthy Foods and Beverages, Including Phytonutrients and Functional Foods’, in *Culinary Nutrition*. Elsevier, pp. 279–331. doi: 10.1016/b978-0-12-391882-6.00007-8.

Marine Strategy Framework Directive (2016) *Contamination by Hazardous Substances*. Available at: https://era.org.mt/en/Documents/MSFD-InitialAssessment-Contamination.pdf.

Marschner, H. (1991) ‘Mechanisms of adaptation of plants to acid soils’, *Plant and Soil*. Kluwer Academic Publishers, 134(1), pp. 1–20. doi: 10.1007/BF00010712.

Martin, I. (2019) ‘Wied Fulija rubbish dump to become national park’, *The Times of Malta*. Available at: https://timesofmalta.com/articles/view/wied-fulija-to-become-wooded-park.727051.

Martin Sabine and Griswold Wendy (2009) ‘Human Health Effects of Heavy Metals’, *Environemtal Science and Technology Briefs for Citizens*, (15). Available at: http://www.engg.ksu.edu/CHSR/outreach/resources/docs/15_HumanHealthEffectsofHeavyMetals2013.pdf (Accessed: 29 June 2018).

Marttinen, S. K., Kettunen, R. H. and Rintala, J. A. (2003) ‘Occurrence and removal of organic pollutants in sewages and landfill leachates’, *Science of the Total Environment*. Elsevier, 301(1–3), pp. 1–12. doi: 10.1016/S0048-9697(02)00302-9.

Masindi, V. and Muedi, K. L. (2018) ‘Environmental Contamination by Heavy Metals’, in *Heavy Metals*. InTech. doi: 10.5772/intechopen.76082.

Matsumoto, H. (2000) ‘Cell biology of aluminum toxicity tolerance in higher plants’, *International Review of Cytology*. Academic Press Inc., pp. 1–46. doi: 10.1016/s0074-7696(00)00001-2.

Mawdsley, J. L. *et al.* (1995) 'Pathogens in livestock waste, their potential for movement through soil and environmnetal pollution', *Applied Soil Ecology*, 2(1), pp. 1–15. doi: Mawdsley, J. L., Bardgett, R. D., Merry, R. J., Pain, B. F., & Theodorou, M. K. (1995). Pathogens in livestock waste, their potential for movement through soil and environmental pollution. Applied Soil Ecology, 2(1), 1–15. doi:10.1016/0929-1393(94)00039-a.

Mayo Clinic (2016) *Lead poisoning*. Available at: https://www.mayoclinic.org/diseases-conditions/lead-poisoning/symptoms-causes/syc-20354717 (Accessed: 29 June 2018).

McLaughlin, P., Jones, B. and Maher, M. M. (2012) 'An update on radioactive release and exposures after the Fukushima Dai-ichi nuclear disaster', *British Journal of Radiology*, pp. 1222–1225. doi: 10.1259/bjr/27017231.

MedicineNet (2011) *Vanadium*. Available at: https://www.medicinenet.com/vanadium/supplements-vitamins.htm (Accessed: 30 June 2018).

Medvedeva, N. *et al.* (2008) 'The effect of mustard gas on the biological activity of soil', *Environmental Research*, 106(3), pp. 289–295. doi: 10.1016/j.envres.2007.04.003.

Megharaj, M. *et al.* (2000) 'Effects of long-term contamination of DDT on soil microflora with special reference to soil algae and algal transformation of DDT', *Environmental Pollution*, 109(1), pp. 35–42. doi: 10.1016/S0269-7491(99)00231-6.

MEPA (2009) *Black dust in Malta- A background to this issue and an account of investigations carried out to date*.

Mergler, D. *et al.* (1994) 'Nervous System Dysfunction among Workers with Long-Term Exposure to Manganese', *Environmental Research*. Academic Press, 64(2), pp. 151–180. doi: 10.1006/ENRS.1994.1013.

Mielke, H. W. and Reagan, P. L. (1998) 'Soil is an important pathway of human lead exposure.', *Environmental Health Perspectives*, 106(suppl 1), pp. 217–229. doi: 10.1289/ehp.98106s1217.

Miglioranza, K. S. B. *et al.* (2002) 'Agricultural soil as a potential source of input of organochlorine pesticides into a nearby pond', *Environmental Science and Pollution Research*, 9(4), pp. 250–256. doi: 10.1007/BF02987499.

Mileusnić, M. *et al.* (2014) 'Assessment of agricultural soil contamination by potentially toxic metals dispersed from improperly disposed tailings, Kombat mine, Namibia', *Journal of Geochemical Exploration*. Elsevier B.V., 144(PC), pp. 409–420. doi: 10.1016/j.gexplo.2014.01.009.

Ministry of the Environment Finland (2007) *Government Decree on the Assessment of Soil Contamination and Remediation Needs 214/2007*.

Momcilović, B. (1999) 'A case report of acute human molybdenum toxicity from a dietary molybdenum supplement--a new member of the "Lucor metallicum" family.', *Arhiv za higijenu rada i toksikologiju*, 50(3), pp. 289–97. Available at: http://www.ncbi.nlm.nih.gov/pubmed/10649845 (Accessed: 29 June 2018).

El Morabet, R. (2018) 'Effects of Outdoor Air Pollution on Human Health', in *Reference Module in Earth Systems and Environmental Sciences*. Elsevier. doi: 10.1016/b978-0-12-409548-9.11012-7.

Muchuweti, M. *et al.* (2006) 'Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: Implications for human health', *Agriculture, Ecosystems and Environment*, 112(1), pp. 41–48. doi: 10.1016/j.agee.2005.04.028.

Muscat, C. (2019) 'As country was engulfed in toxic cloud, Ministry spent €700,000 on advertising', *The Shift News*. Available at: https://theshiftnews.com/2019/02/27/as-country-engulfed-in-toxic-waste-cloud-ministry-spent-e700000-on-advertising/ (Accessed: 20 February 2020).

National Research Council (1977) *Arsenic: Medical and Biological Effects of Environmental Pollution*. Washington, DC: The National Academics Press.

National Research Council (US) Committee on Health Effects of Waste Incineration (2000) *Waste Incineration and Public Health*. Washington DC: National Academic Press.

Ndiokwere, C. L. (1984) 'A study of heavy metal pollution from motor vehicle emissions and its effect on roadside soil, vegetation and crops in Nigeria', *Environmental Pollution. Series B, Chemical and Physical*, 7(1), pp. 35–42. doi: 10.1016/0143-148X(84)90035-1.

Neunhäuserer, C., Berreck, M. and Insam, H. (2001) 'Remediation of soils contaminated with molybdenum using soil amendments and phytoremediation', *Water, Air, and Soil Pollution*, 128(1–2), pp. 85–96. doi: 10.1023/A:1010306220173.

Nicholls, P. H. (1988) 'Factors influencing entry of pesticides into soil water', *Pesticide Science*, 22(2), pp. 123–137. doi: 10.1002/ps.2780220204.

Nieder, R. *et al.* (2018) 'Health Risks Associated with Radionuclides in Soil Materials', in *Soil Components and Human Health*. Dordrecht: Springer Netherlands, pp. 451–501. doi: 10.1007/978-94-024-1222-2_9.

NSO (2017) *Regional Statistics Malta*.

NSO (2019) *Regional Statistics Malta*. Malta: National Statistics Office.

OECD (2010) *Environmental and Climate Change Issues in the Shipbuilding Industry*. Available at: https://www.oecd.org/sti/ind/46370308.pdf.

Ogundele, D. T. ., Adio, A. A. . and Oludele, O. E. (2015) 'Heavy Metal Concentrations in Plants and Soil along Heavy Traffic Roads in North Central Nigeria', *Journal of Environmental & Analytical Toxicology*. OMICS Publishing Group, 05(06), pp. 1–5. doi: 10.4172/2161-0525.1000334.

Ogundele, L. T. *et al.* (2017) 'Heavy metals in industrially emitted particulate matter in Ile-Ife, Nigeria', *Environmental Research*. Academic Press Inc., 156, pp. 320–325. doi: 10.1016/j.envres.2017.03.051.

Ogunkunle, C. O. and Fatoba, P. O. (2014) 'Contamination and spatial distribution of heavy metals in topsoil surrounding a mega cement factory', *Atmospheric Pollution Research*. Dokuz Eylul Universitesi, 5(2), pp. 270–282. doi: 10.5094/APR.2014.033.

Onakpa, M. M., Njan, A. A. and Kalu, O. C. (2018) 'A review of heavy metal contamination of food crops in Nigeria', *Annals of Global Health*. Levy Library Press, pp. 488–494. doi: 10.29024/aogh.2314.

'Organophosporous Insecticide Poisoning' (1999) *Electronic Journal of the International Federation of Clinical Chemistry and Laboratory*, 11(2).

Pace, C. (2014) *A study of chlorates in Malta's environment*.

Panero, S. *et al.* (1995) 'Impact of household batteries in landfills', *Journal of Power Sources*, 57(1–2), pp. 9–12. doi: 10.1016/0378-7753(95)02230-9.

Papaioannou, D. (2004) 'Environmental implications, related to the shipbuilding and ship repairing activitiy in Greece', *Journal of Maritime and Transportation Sciences*.

Paye, H. de S., Mello, J. W. V. de and Melo, S. B. de (2012) 'Métodos de análise multivariada no estabelecimento de valores de referência de qualidade para elementos-traço em solos', *Revista Brasileira de Ciência do Solo*, 36(3), pp. 1031–1042. doi: 10.1590/S0100-06832012000300033.

Pedersen, T. (2017) *Facts About Vanadium*, *Live Science*. Available at: https://www.livescience.com/29155-vanadium.html (Accessed: 25 June 2018).

Peña-Rodríguez, S. *et al.* (2012) 'Mercury content in volcanic soils across Europe and its relationship with soil properties', *Journal of Soils and Sediments*, 12(4), pp. 542–555. doi: 10.1007/s11368-011-0468-7.

Perkins, D. N. *et al.* (2014) 'E-waste: A global hazard', *Annals of Global Health*. Elsevier USA, pp. 286–295. doi: 10.1016/j.aogh.2014.10.001.

Popp, J., Pető, K. and Nagy, J. (2013) 'Pesticide productivity and food security. A review', *Agronomy for Sustainable Development*. Springer-Verlag France, pp. 243–255. doi: 10.1007/s13593-012-0105-x.

Pourang, N. and Noori, A. S. (2014) 'Heavy Metals Contamination in Soil, Surface Water and Groundwater of an Agricultural Area Adjacent to Tehran oil Refinery, Iran', *Int. J. Environ. Res*, 8(4), pp. 871–886.

Pröfrock, D. and Prange, A. (2012) 'Inductively coupled plasma-mass spectrometry (ICP-MS) for quantitative analysis in environmental and life sciences: A review of challenges, solutions, and trends', *Applied Spectroscopy*, pp. 843–868. doi: 10.1366/12-06681.

Proudfoot, A. T. (2003) 'Pentachlorophenol poisoning', *Toxicological Reviews*, pp. 3–11. doi: 10.2165/00139709-200322010-00002.

Rahman, M. A. *et al.* (2018) 'Importance of mineral nutrition for mitigating aluminum toxicity in plants on acidic soils: Current status and opportunities', *International Journal of Molecular Sciences*. MDPI AG. doi: 10.3390/ijms19103073.

Rai, V. *et al.* (2004) 'Effect of chromium accumulation on photosynthetic pigments, oxidative stress defense system, nitrate reduction, proline level and eugenol content of Ocimum tenuiflorum L.', *Plant Science*, 167(5), pp. 1159–1169. doi: 10.1016/j.plantsci.2004.06.016.

Ratini, M. (2018) *What are food sources of molybdenum?*, *WebMD*. Available at: https://www.webmd.com/food-recipes/qa/what-are-food-sources-of-molybdenum.

Reimann, C., Filzmoser, P. and Garrett, R. G. (2005) 'Background and threshold: Critical comparison of methods of determination', *Science of the Total Environment*. Elsevier, 346(1–3), pp. 1–16. doi: 10.1016/j.scitotenv.2004.11.023.

Rodriguez-Eugenio, N., McLaughlin, M. and Pennock, D. (2018) *Soil Pollution: A Hidden Reality*. Rome: Food and Agriculture Organization of the United Nations.

Roels, H. A. *et al.* (1992) 'Assessment of the permissible exposure level to manganese in workers exposed to manganese dioxide dust.', *British journal of industrial medicine*. BMJ Publishing Group Ltd, 49(1), pp. 25–34. doi: 10.1136/OEM.49.1.25.

Rotatori, M. *et al.* (2003) 'Characterisation and evaluation of the emissions from the combustion of orimulsion-400, coal and heavy fuel oil in a thermoelectric power plant', *Environmental Technology (United Kingdom)*, 24(8), pp. 1017–1023. doi: 10.1080/09593330309385640.

Sakshi, Singh, S. K. and Haritash, A. K. (2019) 'Polycyclic aromatic hydrocarbons: soil pollution and remediation', *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies, pp. 6489–6512. doi: 10.1007/s13762-019-02414-3.

Salgueiro, M. J. *et al.* (2000) 'Zinc as an essential micronutrient: A review', *Nutrition Research*, pp. 737–755. doi: 10.1016/S0271-5317(00)00163-9.

Salminen, R. and Gregorauskiene, V. (2000) 'Considerations regarding the definition of a geochemical baseline of elements in the surficial materials in areas differing in basic geology', *Applied Geochemistry*, 15(5), pp. 647–653. doi: 10.1016/S0883-2927(99)00077-3.

Sammut (2005) *State of the Environment Report for Malta 2005 – Background Report on Soil*.

Savci, S. (2012) ‘An Agricultural Pollutant: Chemical Fertilizer’, *International Journal of Environmental Science and Development*. EJournal Publishing, pp. 73–80. doi: 10.7763/ijesd.2012.v3.191.

Shah, A. *et al.* (2013) ‘Comparative Study of Heavy Metals in Soil and Selected Medicinal Plants’, *Journal of Chemistry*, p. 5. doi: 10.1155/2013/621265.

Shallari, S. (1998) ‘Heavy metals in soils and plants of serpentine and industrial sites of Albania’, *The Science of The Total Environment*. Elsevier B.V., 209(2–3), pp. 133–142. doi: 10.1016/S0048-9697(97)00312-4.

Shanker, A. K. *et al.* (2005) ‘Chromium toxicity in plants’, *Environment International*. Elsevier Ltd, pp. 739–753. doi: 10.1016/j.envint.2005.02.003.

Sharma, A. D. (2013) ‘Low Nickel Diet in Dermatology’, *Indian Journal of Dermatology*, 58(3), p. 240. doi: 10.4103/0019-5154.110846.

Shaw, C. A. and Tomljenovic, L. (2013) ‘Aluminum in the central nervous system (CNS): toxicity in humans and animals, vaccine adjuvants, and autoimmunity’, *Immunologic Research*, 56(2–3), pp. 304–316. doi: 10.1007/s12026-013-8403-1.

Short, T. M., Black, J. A. and Birge, W. J. (1990) ‘Effects of acid-mine drainage on the chemical and biological character of an alkaline headwater stream’, *Archives of Environmental Contamination and Toxicology*. Springer-Verlag, 19(2), pp. 241–248. doi: 10.1007/BF01056093.

Simonin, M. and Richaume, A. (2015) ‘Impact of engineered nanoparticles on the activity, abundance, and diversity of soil microbial communities: a review’, *Environmental Science and Pollution Research*. Springer Verlag, 22(18), pp. 13710–13723. doi: 10.1007/s11356-015-4171-x.

Smičiklas, I. and Šljivić-Ivanović, M. (2016) ‘Radioactive Contamination of the Soil: Assessments of Pollutants Mobility with Implication to Remediation Strategies’, in *Soil Contamination - Current Consequences and Further Solutions*. InTech. doi: 10.5772/64735.

Soltan, S. (2015) *The Biochemical and Physiological Effects of Chromium Bioaccumulation*. University of Malta.

Sparling, D. W. and Lowe, T. P. (1996) ‘Environmental hazards of aluminum to plants, invertebrates, fish, and wildlife.’, *Reviews of environmental contamination and toxicology*, pp. 1–127. doi: 10.1007/978-1-4612-2354-2_1.

Staicu, L. C. *et al.* (2017) ‘Industrial selenium pollution: Sources and biological treatment technologies’, in *Bioremediation of Selenium Contaminated Wastewater*. Cham: Springer International Publishing, pp. 75–101. doi: 10.1007/978-3-319-57831-6_4.

Stanford Advanced Materials (2017) *Application of Molybdenum in Chemical Industry*. Available at: https://www.samaterials.com/content/187-application-of-molybdenum-in-chemical-industry (Accessed: 5 April 2020).

State of the Environment Indicators (2006) *Lead Concentrations in Soil*.

Steinnes, E. *et al.* (1997) ‘Evidence of large scale heavy-metal contamination of natural surface soils in Norway from long-range atmospheric transport’, *Science of the Total Environment*, 205(2–3), pp. 255–266. doi: 10.1016/S0048-9697(97)00209-X.

Steinnes, E., Berg, T. and Uggerud, H. T. (2011) ‘Three decades of atmospheric metal deposition in Norway as evident from analysis of moss samples’, *Science of the Total Environment*, 412–413, pp. 351–358. doi: 10.1016/j.scitotenv.2011.09.086.

Sterba, J. H., Steinhauser, G. and Grass, F. (2013) ‘Illicit utilization of arsenic compounds in pyrotechnics? An analysis of the suspended particle emission during Vienna’s New Year fireworks’, in *Journal of Radioanalytical and Nuclear Chemistry*, pp. 237–243. doi: 10.1007/s10967-012-2001-x.

Stewart, W. M. *et al.* (2005) ‘The contribution of commercial fertilizer nutrients to food production’, *Agronomy Journal*, pp. 1–6. doi: 10.2134/agronj2005.0001.

Strzebońska, M., Jarosz-Krzemińska, E. and Adamiec, E. (2017) ‘Assessing Historical Mining and Smelting Effects on Heavy Metal Pollution of River Systems over Span of Two Decades’, *Water, Air, and Soil Pollution*. Springer International Publishing, 228(4). doi: 10.1007/s11270-017-3327-3.

Swartjes, F. A. (ed.) (2011) *Dealing with Contaminated Sites*, *Dealing with Contaminated Sites*. Springer Netherlands. doi: 10.1007/978-90-481-9757-6.

Swati *et al.* (2014) ‘Invitro toxicity evaluation of organic extract of landfill soil and its detoxification by indigenous pyrene-degrading Bacillus sp. ISTPY1’, *International Biodeterioration and Biodegradation*, 90, pp. 145–151. doi: 10.1016/j.ibiod.2014.03.001.

Szasz, F. M. (1995) ‘The Impact of World War II on the Land: Gruinard Island, Scotland, and Trinity SIte, New Mexico as Case Studies’, *Environmental History Review*, 19(4), pp. 15–30.

Tailings Info (2017) *What are tailings? - Their nature and production*. Available at: http://www.tailings.info/basics/tailings.htm (Accessed: 25 March 2020).

Tangahu, B. V. *et al.* (2011) ‘A Review on Heavy Metals (As, Pb, and Hg) Uptake by Plants through Phytoremediation’, *International Journal of Chemical Engineering*, p. 31.

Tarazona, J. V. (2014) ‘Pollution, Soil’, in *Encyclopedia of Toxicology: Third Edition*. Elsevier, pp. 1019–1023. doi: 10.1016/B978-0-12-386454-3.00531-5.

Tchounwou, P. B. *et al.* (2012) ‘Heavy Metal Toxicity and the Environment’, in *EXS*, pp. 133–164. doi: 10.1007/978-3-7643-8340-4_6.

The Committee for the Compilation of Materials on Damage Caused by the Atomic Bombs in Hiroshima and Nagasaki (1981) *Hiroshima and Nagasaki; The Physical, medical, and Social Effects of the Atomic Bombings*. Tokyp: Iwanami-Shoten.

The Council of the European Union (1996) ‘EUR-Lex - 31996L0061 - EN’, *Official Journal of the European Union L 257*. OPOCE, pp. 26–40. Available at: https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31996L0061:en:HTML (Accessed: 25 March 2020).

The Times of Malta (2009) ‘“Delimara health hazards”’. Available at: https://timesofmalta.com/articles/view/delimara-health-hazards.261650 (Accessed: 29 March 2020).

The Times of Malta (2011) ‘Scenic Wied il-Mielah free of sewage outflow at last’. Available at: https://timesofmalta.com/articles/view/scenic-wied-iil-mielah-free-of-sewage-outflow-at-last.373893.

The Times of Malta (2017) ‘Health warning issued as fierce fire rages at Sant’ Antnin waste recycling plant’, *The Times of Malta*. Available at: https://timesofmalta.com/articles/view/sant-antnin-plant-on-fire.648706 (Accessed: 20 February 2020).

The Times of Malta (2019) *Palumbo first in Europe for retrofitting ships to meet new pollution standards*. Available at: https://timesofmalta.com/articles/view/palumbo-first-in-europe-for-retrofitting-ships-to-meet-new-pollution.756898 (Accessed: 29 February 2020).

Tikilili, P. V. and Nkhalambayausi-Chirwa, E. M. (2011) ‘Characterization and biodegradation of polycyclic aromatic hydrocarbons in radioactive wastewater’, *Journal of Hazardous Materials*, 192(3), pp. 1589–1596. doi: 10.1016/j.jhazmat.2011.06.079.

Tiwari, B., Kharwar, S. and Tiwari, D. N. (2019) ‘Pesticides and Rice Agriculture’, in *Cyanobacteria*. Elsevier, pp. 303–325. doi: 10.1016/b978-0-12-814667-5.00015-5.

Tollefson, J. (2013) ‘Methane leaks erode green credentials of natural gas’, *Nature*, p. 12. doi: 10.1038/493012a.

Tomiyasu, T. *et al.* (2005) *Low Level Mercury Uptake by Plants from Natural Environments-Mercury Distribution in Solidago altissima L*, *Environmental Sciences*.

Trendel, J. M. *et al.* (1989) ‘Identification of des-A-triterpenoid hydrocarbons occurring in surface sediments’, *Tetrahedron*, 45(14), pp. 4457–4470. doi: 10.1016/S0040-4020(01)89081-5.

Tsafrir, J. (2017) *Copper Toxicity: A Common Cause of Psychiatric Symptoms*, *Pshychology Today*. Available at: https://www.psychologytoday.com/intl/blog/holistic-psychiatry/201709/copper-toxicity-common-cause-psychiatric-symptoms (Accessed: 7 July 2018).

U.S. Environmental Protection Agency (2003) *Ecological Soil Screening Level for Aluminium*.

Union of Concerned Scientists (2013) *A Brief History of Nuclear Accidents Worldwide*. Available at: https://www.ucsusa.org/resources/brief-history-nuclear-accidents-worldwide (Accessed: 11 February 2020).

United States Environmental Protection Agency (1998) *Ambient Water Quality Values for Protection of Aquatic Life for Nickel*. Available at: https://www.epa.gov/sites/production/files/2015-06/documents/ny_al_404_03121998.pdf (Accessed: 7 July 2018).

United States Environmental Protection Agency (2004) *Drinking Water Health Advisory for Manganese*. Available at: https://www.epa.gov/sites/production/files/2014-09/documents/support_cc1_magnese_dwreport_0.pdf (Accessed: 1 July 2018).

US EPA (2017) *Polychlorinated Biphenyls (PCBs)|Table of Aroclors*. Available at: https://www.epa.gov/pcbs/table-aroclors (Accessed: 25 March 2020).

US EPA (2019a) *Agriculture Nutrient Management and Fertilizer*. Available at: https://www.epa.gov/agriculture/agriculture-nutrient-management-and-fertilizer (Accessed: 16 March 2020).

US EPA (2019b) *Cement Manufacturing Enforcement Initiative*.

Varekamp, J. C. and Buseck, P. R. (1986) ‘Global mercury flux from volcanic and geothermal sources’, *Applied Geochemistry*, 1(1), pp. 65–73. doi: 10.1016/0883-2927(86)90038-7.

Vella, A. J. *et al.* (2015) ‘Perchlorate in dust fall and indoor dust in Malta: An effect of fireworks’, *Science of the Total Environment*. Elsevier, 521–522, pp. 46–51. doi: 10.1016/j.scitotenv.2015.03.071.

Venuti, A., Alfonsi, L. and Cavallo, A. (2016) ‘Anthropogenic pollutants on top soils along a section of the Salaria state road, central Italy’, *Annals of Geophysics*. Editrice Compositori s.r.l., 59(5). doi: 10.4401/ag-7021.

Villanueva, R. and Bustamante, P. (2006) ‘Composition in essential and non-essential elements of early stages of cephalopods and dietary effects on the elemental profiles of Octopus vulgaris paralarvae’, *Aquaculture, Elsevier*, 261(1), pp. 225–240. doi: 10.1016/j.aquaculture.2006.07.006ï.

Vittori Antisari, L. *et al.* (2013) ‘Toxicity of metal oxide (CeO2, Fe3O4, SnO2) engineered nanoparticles on soil microbial biomass and their distribution in soil’, *Soil Biology and Biochemistry*, 60, pp. 87–94. doi: 10.1016/j.soilbio.2013.01.016.

Wan, X. and Lei, M. (2018) ‘Intercropping efficiency of four arsenic hyperaccumulator Pteris vittata populations as intercrops with Morus alba’, *Environmental Science and Pollution Research*. Springer Verlag, 25(13), pp. 12600–12611. doi: 10.1007/s11356-018-1366-y.

Wang, J. *et al.* (2019) ‘Microplastics as contaminants in the soil environment: A mini-review’, *Science of the Total Environment*. Elsevier B.V., pp. 848–857. doi: 10.1016/j.scitotenv.2019.07.209.

Wang, L. K. (2009) *Heavy metals in the environment*. CRC Press.

Wang, Qi *et al.* (2008) 'Melting characteristics during the vitrification of MSWI fly ash with a pilot-scale diesel oil furnace', *Journal of Hazardous Materials*, 160(2–3), pp. 376–381. doi: 10.1016/j.jhazmat.2008.03.043.

Ware, M. (2015) *The benefits and risks of chromium*, *Medical News Today*. Available at: https://www.medicalnewstoday.com/articles/288177 (Accessed: 15 February 2020).

WasteServ Malta (2004) *Development of Rehabilitation Strategies Maghtab, Qortin and Wied Fulija Landfills*. Malta. Available at: https://msdec.gov.mt/en/Documents/Downloads/05a_mepafinal.pdf.

WasteServ Malta (2019) *Gozo Transfer Station and Materials Recovery Facility*. Available at: https://www.wasteservmalta.com/gozotransferstation (Accessed: 4 April 2020).

Water Services Corporation (2017) *Wastewater*. Available at: http://www.wsc.com.mt/about-us/wastewater/ (Accessed: 25 March 2020).

Watson, A. P. and Griffin, G. D. (1992) 'Toxicity of vesicant agents scheduled for destruction by the chemical stockpile disposal program', in *Environmental Health Perspectives*, pp. 259–280. doi: 10.1289/ehp.9298259.

Watt, B. E. *et al.* (2005) 'Anticoagulant rodenticides', *Toxicological Reviews*, pp. 259–269. doi: 10.2165/00139709-200524040-00005.

Wei, B. and Yang, L. (2010) 'A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China', *Microchemical Journal*, pp. 99–107. doi: 10.1016/j.microc.2009.09.014.

Weissenstein, K. and Sinkala, T. (2011) 'Soil pollution with heavy metals in mine environments, impact areas of mine dumps particularly of gold- and copper mining industries in Southern Africa', *Arid Ecosystems*. Pleiades Publishing, 1(1), pp. 53–58. doi: 10.1134/S2079096111010082.

Van Wendel De Joode, B. *et al.* (2016) 'Manganese concentrations in drinking water from villages near banana plantations with aerial mancozeb spraying in Costa Rica: Results from the Infants' Environmental Health Study (ISA)', *Environmental Pollution*. Elsevier Ltd, 215, pp. 247–257. doi: 10.1016/j.envpol.2016.04.015.

WHO (2000) *Air Quality Guidelines for Europe Second Edition*. Available at: http://wedocs.unep.org/bitstream/handle/20.500.11822/8681/Air_quality_guidelines.pdf?sequence=3&isAllowed=y. (Accessed: 29 June 2018).

WHO (2005) *Manganese and its Compounds: Environmental Aspects*.

WHO (2006) *Cobalt and Inorganic Cobalt Compounds*.

WHO (2016) '1986-2016: Chernobyl at 30 - An update', *WHO*. World Health Organization. Available at: https://www.who.int/ionizing_radiation/chernobyl/Chernobyl-update.pdf?ua=1&ua=1 (Accessed: 11 February 2020).

WHO (2018) *Lead poisoning and health*. Available at: http://www.who.int/en/news-room/fact-sheets/detail/lead-poisoning-and-health (Accessed: 29 June 2018).

WHO (2020) *Agents Classified by the IARC Monographs, Volume 1-125*, *International Agency for Research on Cancer*.

WHO, UNDP and IAEA (2005) 'Chernobyl - the true scale of the accident', *WHO*. Available at: https://www.who.int/mediacentre/news/releases/2005/pr38/en/.

Wijesekara, S. S. R. M. D. H. R. *et al.* (2014) 'Fate and transport of pollutants through a municipal solid waste landfill leachate in Sri Lanka', *Environmental Earth Sciences*. Springer Verlag, 72(5), pp. 1707–1719. doi: 10.1007/s12665-014-3075-2.

Wing, M. R. and Bada, J. L. (1991) 'The origin of the polycyclic aromatic hydrocarbons in meteorites', *Origins of Life and Evolution of the Biosphere*. Kluwer Academic Publishers, 21(5–6), pp. 375–383. doi: 10.1007/BF01808308.

Wood, T. J. and Goulson, D. (2017) 'The environmental risks of neonicotinoid pesticides: a review of the evidence post 2013', *Environmental Science and Pollution Research*. Springer Verlag, 24(21), pp. 17285–17325. doi: 10.1007/s11356-017-9240-x.

Wuana, R. A. and Okieimen, F. E. (2011) 'Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation', *ISRN Ecology*.

Xiong, X. *et al.* (2010) 'Copper content in animal manures and potential risk of soil copper pollution with animal manure use in agriculture', *Resources, Conservation and Recycling*, 54(11), pp. 985–990. doi: 10.1016/j.resconrec.2010.02.005.

Yan, A. and Chen, Z. (2019) 'Impacts of silver nanoparticles on plants: A focus on the phytotoxicity and underlying mechanism', *International Journal of Molecular Sciences*. MDPI AG, p. 1003. doi: 10.3390/ijms20051003.

Yang, B. *et al.* (2017) 'Effect of topsoil removal and selective countermeasures on radiocesium accumulation in rice plants in Fukushima paddy field', *Science of the Total Environment*. Elsevier B.V., 603–604, pp. 49–56. doi: 10.1016/j.scitotenv.2017.06.026.

Yang, G. Q. *et al.* (1983) 'Endemic selenium intoxication of humans in China', *The American Journal of Clinical Nutrition*, 37(5), pp. 872–881. doi: 10.1093/ajcn/37.5.872.

Yaron, B., Dror, I. and Berkowitz, B. (2012) *Soil-subsurface change: Chemical pollutant impacts*, *Soil-Subsurface Change: Chemical Pollutant Impacts*. Springer-Verlag Berlin Heidelberg. doi: 10.1007/978-3-642-24387-5.

Zahran, S. *et al.* (2013) 'Linking source and effect: Resuspended soil lead, air lead, and children's blood lead levels in Detroit, Michigan', *Environmental Science and Technology*, 47(6), pp. 2839–2845. doi: 10.1021/es303854c.

Zeng, L. S. *et al.* (2006) 'Effects of lead contamination on soil microbial activity and rice physiological indices in soil-Pb-rice (Oryza sativa L.) system', *Chemosphere*, 65(4), pp. 567–574. doi: 10.1016/j.chemosphere.2006.02.039.

Zhan, T. L. T. *et al.* (2014) 'Vertical migration of leachate pollutants in clayey soils beneath an uncontrolled landfill at Huainan, China: A field and theoretical investigation', *Science of the Total Environment*. Elsevier, 470–471, pp. 290–298. doi: 10.1016/j.scitotenv.2013.09.081.

Zhang, Hua *et al.* (2015) 'Identification of traffic-related metals and the effects of different environments on their enrichment in roadside soils along the Qinghai-Tibet highway', *Science of the Total Environment*. Elsevier B.V., 521–522, pp. 160–172. doi: 10.1016/j.scitotenv.2015.03.054.

Zhang, Haibo *et al.* (2015) 'Residues and potential ecological risks of veterinary antibiotics in manures and composts associated with protected vegetable farming', *Environmental Science and Pollution Research*. Springer Verlag, 22(8), pp. 5908–5918. doi: 10.1007/s11356-014-3731-9.

Zrinzo, R. (2015) *Biochemical and Physiological Effect of Aluminium Bioccumulation*. University of Malta.

Chapter 6: Appendices

Appendix 1: Shapiro Wilk test

	Statistics	**Shapiro-Wilk df**	**ρ-value**
Aluminium	0.838	15.000	0.012
Arsenic	0.713	15.000	0.000
Barium	0.719	15.000	0.000
Bismuth	0.895	15.000	0.080
Bromine	0.896	15.000	0.082
Calcium	0.916	15.000	0.168
Cadmium	0.828	15.000	0.008
Cerium	0.000	15.000	0.000
Chlorine	0.927	15.000	0.242
Cobalt	0.284	15.000	0.000
Chromium	0.000	15.000	0.000
Caesium	0.524	15.000	0.000
Copper	0.967	15.000	0.811
Iron	0.841	15.000	0.013
Gallium	0.827	15.000	0.008
Germanium	0.665	15.000	0.000
Iodine	0.819	15.000	0.007
Potassium	0.952	15.000	0.563
Lanthanum	0.284	15.000	0.000
Magnesium	0.838	15.000	0.012
Manganese	0.907	15.000	0.123
Molybdenum	0.899	15.000	0.091
Sodium	0.828	15.000	0.009
Niobium	0.909	15.000	0.132
Neodymium	0.000	15.000	0.000
Nickel	0.729	15.000	0.001
Phosphorus	0.965	15.000	0.779
Lead	0.919	15.000	0.188
Praseodymium	0.000	15.000	0.000
Rubidium	0.914	15.000	0.155
Antimony	0.816	15.000	0.006
Selenium	0.833	15.000	0.010
Silicon	0.868	15.000	0.031
Tin	0.839	15.000	0.012
Sulphur	0.890	15.000	0.068
Strontium	0.603	15.000	0.000
Tantalum	0.000	15.000	0.000
Tellurium	0.827	15.000	0.008
Titanium	0.787	15.000	0.002
Vanadium	0.604	15.000	0.000
Tungsten	0.000	15.000	0.000
Yttrium	0.911	15.000	0.139
Zinc	0.865	15.000	0.028
Zirconium	0.930	15.000	0.271

Appendix 2: One-Way ANOVA and Kruskal-Wallis test

		Sample Size	Mean	Std. Deviation	ρ-value
Aluminium	A	3.000	26921.183	319.017	0.012
	B	3.000	28844.125	1455.197	
	C	3.000	21734.533	2320.466	
	D	3.000	13337.100	521.251	
	E	3.000	28791.200	1894.242	
Arsenic	A	3.000	7.574	13.118	0.528
	B	3.000	12.623	11.344	
	C	3.000	6.564	11.369	
	D	3.000	0.000	0.000	
	E	3.000	14.643	13.234	
Barium	A	3.000	208.388	360.938	0.494
	B	3.000	440.361	402.439	
	C	3.000	221.226	383.174	
	D	3.000	0.000	0.000	
	E	3.000	392.593	387.905	
Bismuth	A	3.000	32.890	18.148	0.141
	B	3.000	37.674	16.805	
	C	3.000	33.787	16.278	
	D	3.000	14.950	2.740	
	E	3.000	43.056	17.509	
Bromine	A	3.000	36.000	13.856	0.083
	B	3.000	48.333	13.577	
	C	3.000	41.667	14.434	
	D	3.000	29.667	1.528	
	E	3.000	68.333	13.013	
Calcium	A	3.000	226707.887	2576.655	0.035
	B	3.000	226440.700	8670.197	
	C	3.000	243273.460	15970.970	
	D	3.000	271328.060	1746.960	
	E	3.000	208672.787	20104.354	
Cadmium	A	3.000	24.010	21.051	0.112
	B	3.000	37.478	23.510	
	C	3.000	37.478	24.850	
	D	3.000	3.806	0.507	
	E	3.000	43.334	15.623	
Cerium	A	3.000	0.000	0.000	1.000
	B	3.000	0.000	0.000	
	C	3.000	0.000	0.000	
	D	3.000	0.000	0.000	
	E	3.000	0.000	0.000	
Chlorine	A	3.000	2350.000	374.032	0.025
	B	3.000	2496.667	338.575	
	C	3.000	2376.667	304.357	
	D	3.000	1853.333	92.916	
	E	3.000	3290.000	470.319	
Cobalt	A	3.000	0.000	0.000	0.406
	B	3.000	0.000	0.000	
	C	3.000	3.932	6.811	
	D	3.000	0.000	0.000	
	E	3.000	0.000	0.000	

		Sample Size	Mean	Std. Deviation	ρ-value
Chromium	A	3.000	0.000	0.000	1.000
	B	3.000	0.000	0.000	
	C	3.000	0.000	0.000	
	D	3.000	0.000	0.000	
	E	3.000	0.000	0.000	
Caesium	A	3.000	0.000	0.000	0.190
	B	3.000	77.929	74.410	
	C	3.000	0.000	0.000	
	D	3.000	0.000	0.000	
	E	3.000	46.588	80.692	
Copper	A	3.000	96.928	16.782	0.133
	B	3.000	97.461	16.833	
	C	3.000	101.988	17.726	
	D	3.000	59.648	12.840	
	E	3.000	101.722	26.929	
Iron	A	3.000	23640.734	209.829	0.009
	B	3.000	25482.566	345.021	
	C	3.000	17089.406	213.679	
	D	3.000	11400.709	252.183	
	E	3.000	26764.855	672.084	
Gallium	A	3.000	13.391	12.690	0.190
	B	3.000	15.127	14.239	
	C	3.000	7.439	12.885	
	D	3.000	0.000	0.000	
	E	3.000	18.846	13.021	
Germanium	A	3.000	1.851	1.747	0.187
	B	3.000	7.405	7.292	
	C	3.000	0.000	0.000	
	D	3.000	0.000	0.000	
	E	3.000	3.240	3.947	
Iodine	A	3.000	41.000	57.297	0.918
	B	3.000	72.000	65.483	
	C	3.000	71.333	51.394	
	D	3.000	14.333	5.132	
	E	3.000	64.667	62.003	
Potassium	A	3.000	9491.382	1631.690	0.018
	B	3.000	11400.727	2129.999	
	C	3.000	7867.055	743.730	
	D	3.000	4983.667	481.081	
	E	3.000	11566.757	2786.057	
Lanthanum	A	3.000	0.000	0.000	0.406
	B	3.000	0.000	0.000	
	C	3.000	82.142	142.273	
	D	3.000	0.000	0.000	
	E	3.000	0.000	0.000	
Magnesium	A	3.000	14372.453	1055.464	0.305
	B	3.000	14493.061	1268.297	
	C	3.000	15658.939	4228.310	
	D	3.000	15819.749	857.788	
	E	3.000	18593.733	4342.028	

		Sample Size	Mean	Std. Deviation	ρ-value
Manganese	A	3.000	447.896	82.636	0.025
	B	3.000	527.149	71.755	
	C	3.000	343.602	88.622	
	D	3.000	143.017	16.652	
	E	3.000	546.252	62.752	
Molybdenum	A	3.000	12.664	8.081	0.186
	B	3.000	15.108	7.668	
	C	3.000	13.331	9.236	
	D	3.000	2.666	0.667	
	E	3.000	16.219	5.823	
Sodium	A	3.000	98667.380	3709.300	0.081
	B	3.000	90754.207	2384.746	
	C	3.000	117461.167	17825.235	
	D	3.000	115977.447	3659.508	
	E	3.000	117708.453	40186.176	
Niobium	A	3.000	21.437	11.536	0.125
	B	3.000	27.030	11.911	
	C	3.000	23.534	13.121	
	D	3.000	5.592	0.699	
	E	3.000	27.962	9.088	
Neodymium	A	3.000	0.000	0.000	1.000
	B	3.000	0.000	0.000	
	C	3.000	0.000	0.000	
	D	3.000	0.000	0.000	
	E	3.000	0.000	0.000	
Nickel	A	3.000	11.263	19.508	0.380
	B	3.000	18.859	20.142	
	C	3.000	4.453	7.713	
	D	3.000	0.000	0.000	
	E	3.000	22.526	22.021	
Phosphorus	A	3.000	4109.622	402.651	0.131
	B	3.000	4236.183	572.382	
	C	3.000	3069.487	309.284	
	D	3.000	3895.776	64.338	
	E	3.000	4067.434	631.408	
Lead	A	3.000	131.512	19.078	0.031
	B	3.000	94.998	17.025	
	C	3.000	76.122	16.736	
	D	3.000	153.482	1.418	
	E	3.000	101.496	19.852	
Praseodymium	A	3.000	0.000	0.000	1.000
	B	3.000	0.000	0.000	
	C	3.000	0.000	0.000	
	D	3.000	0.000	0.000	
	E	3.000	0.000	0.000	
Rubidium	A	3.000	69.800	10.072	0.022
	B	3.000	78.334	9.777	
	C	3.000	53.341	9.777	
	D	3.000	32.004	1.584	
	E	3.000	80.163	9.159	
Antimony	A	3.000	64.322	61.663	0.735
	B	3.000	97.179	61.535	
	C	3.000	91.332	53.111	
	D	3.000	31.743	5.081	
	E	3.000	48.172	83.436	

		Sample Size	Mean	Std. Deviation	ρ-value
Selenium	A	3.000	14.707	10.682	0.154
	B	3.000	18.977	11.570	
	C	3.000	17.553	9.818	
	D	3.000	5.693	0.712	
	E	3.000	20.400	10.706	
Silicon	A	3.000	100871.000	1471.273	0.026
	B	3.000	100658.640	7724.184	
	C	3.000	72457.232	13475.610	
	D	3.000	48481.788	2111.995	
	E	3.000	98959.760	12293.058	
Tin	A	3.000	129.442	31.451	0.168
	B	3.000	153.860	34.893	
	C	3.000	145.721	24.671	
	D	3.000	107.650	0.455	
	E	3.000	147.034	30.723	
Sulphur	A	3.000	1764.870	281.216	0.045
	B	3.000	2035.875	378.728	
	C	3.000	1788.900	96.148	
	D	3.000	1495.200	128.306	
	E	3.000	2690.025	488.911	
Strontium	A	3.000	341.900	4.808	0.014
	B	3.000	346.410	1.292	
	C	3.000	337.672	3.996	
	D	3.000	503.972	3.686	
	E	3.000	355.993	11.186	
Tantalum	A	3.000	0.000	0.000	1.000
	B	3.000	0.000	0.000	
	C	3.000	0.000	0.000	
	D	3.000	0.000	0.000	
	E	3.000	0.000	0.000	
Tellurium	A	3.000	53.567	51.739	0.925
	B	3.000	74.887	54.661	
	C	3.000	71.422	46.648	
	D	3.000	21.320	2.808	
	E	3.000	63.960	54.325	
Titanium	A	3.000	2697.030	27.465	0.038
	B	3.000	2802.913	30.166	
	C	3.000	2269.501	677.290	
	D	3.000	739.186	136.714	
	E	3.000	2978.720	213.082	
Vanadium	A	3.000	0.000	0.000	0.277
	B	3.000	22.594	37.210	
	C	3.000	24.461	42.367	
	D	3.000	0.000	0.000	
	E	3.000	38.838	46.764	
Tungsten	A	3.000	0.000	0.000	1.000
	B	3.000	0.000	0.000	
	C	3.000	0.000	0.000	
	D	3.000	0.000	0.000	
	E	3.000	0.000	0.000	

		Sample Size	Mean	Std. Deviation	ρ-value
Yttrium	A	3.000	43.309	11.759	0.080
	B	3.000	51.184	11.600	
	C	3.000	40.947	13.662	
	D	3.000	23.886	0.909	
	E	3.000	53.283	7.927	
Zinc	A	3.000	177.551	3.502	0.016
	B	3.000	180.765	8.946	
	C	3.000	104.442	7.004	
	D	3.000	131.758	4.473	
	E	3.000	189.870	8.362	
Zirconium	A	3.000	342.521	106.661	0.084
	B	3.000	397.058	109.130	
	C	3.000	325.494	119.052	
	D	3.000	84.150	8.770	
	E	3.000	417.047	110.321	

Appendix 3: ICP-MS Results

Eurofins Umwelt Ost GmbH - Löbstedter Strasse 78 - D-07749 - Jena

DNA Consultancy Services
Natural Remedies
69, Triq K. Galea
BKR1807 Birkirkara
MALTA

Title :	**Test report for order 11911607**
Test report number :	**AR-19-JE-011524-01**
Project name :	**soil samples**
Number of samples :	**5**
Sample type :	**soil**
Sample Taker:	**Client**
Sample reception date :	**2019-04-18**
Sample processing time :	**2019-04-18 - 2019-05-10**

The test results refer solely to the analysed test specimen. Unless the sampling was done by our laboratory or in our sub-order the responsibility for the correctness of the sampling is disclaimed. This test report is only valid with signature and may only be further published completely and unchanged. Extracts or changes require the authorisation of the EUROFINS UMWELT in each individual case.

Our General Terms & Conditions of Sale (GTCS) are applicable, as far as no specific agreements do exist. The GTCS are available on http://www.eurofins.de/umwelt/avb.aspx.

Accredited test laboratory according to DIN EN ISO/IEC 17025:2005 notification under the DAkkS German Accreditation System for Testing. The laboratory is according (D-PL-14081-01-00) accredited.

Astrid Sperrhacke	Digitally signed 5/10/2019
ASM / AQM	Astrid Sperrhacke
Phone +49 3641 4649 59	QMB/Prüfleitung

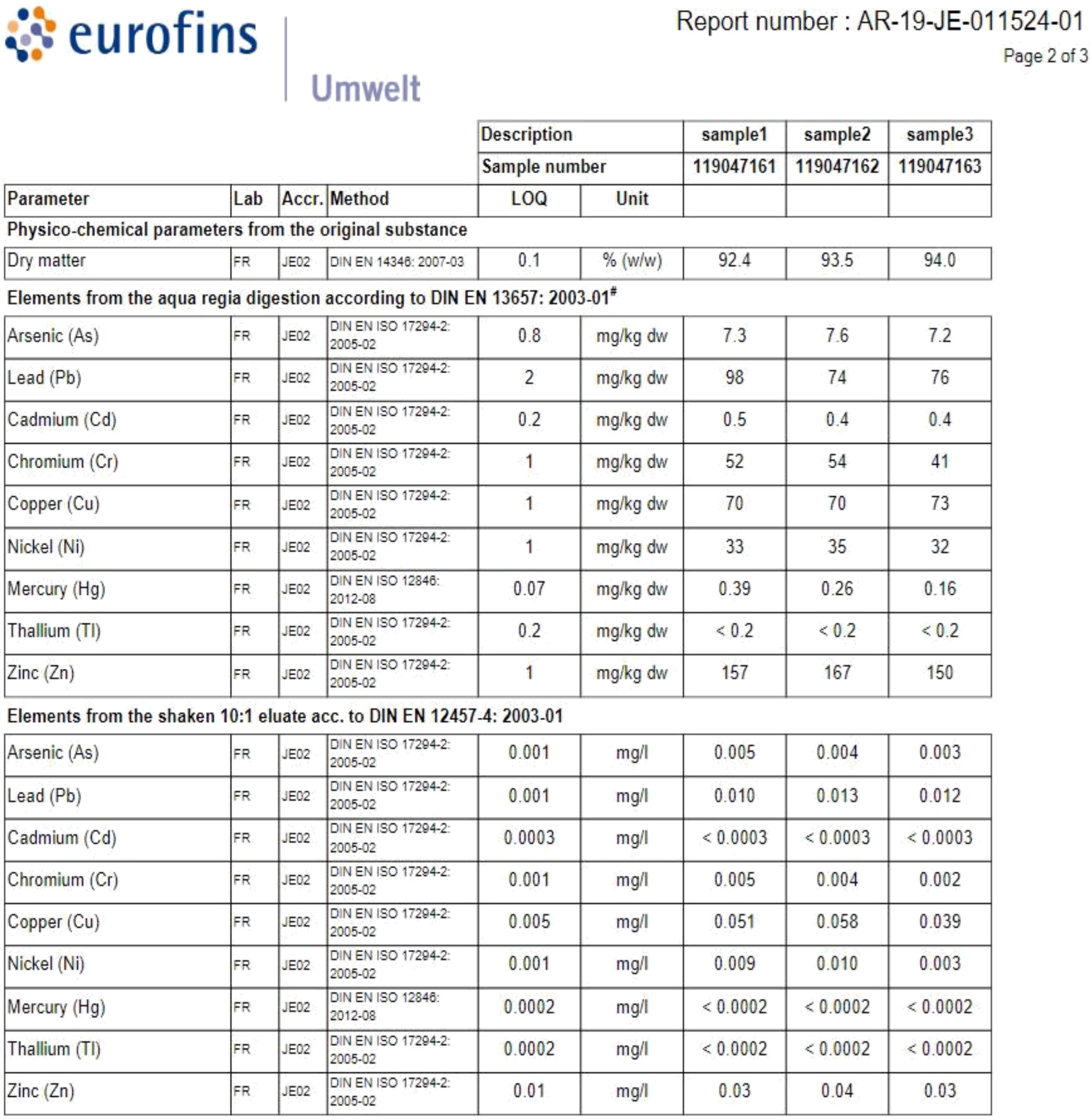
DAkkS
Deutsche
Akkreditierungsstelle
D-PL-14081-01-00

Eurofins Umwelt Ost GmbH
Löbstedter Strasse 78
D-07749 Jena

Phone +49 3641 4649 0
Fax +49 3641 4649 19
info_jena@eurofins.de
www.eurofins.de/umwelt

GF: Dr. Benno Schneider
Axel Ulbricht, Daniel Schreier
Amtsgericht Jena HRB 202596
USt.-ID.Nr. DE 151 28 1997

Bankverbindung: UniCredit Bank AG
BLZ 207 300 17
Kto 7000000550
IBAN DE07 2073 0017 7000 0005 50
BIC/SWIFT HYVEDEMME17



Parameter	Lab	Accr.	Method	LOQ	Unit	sample1	sample2	sample3
				Description		sample1	sample2	sample3
				Sample number		119047161	119047162	119047163
Physico-chemical parameters from the original substance								
Dry matter	FR	JE02	DIN EN 14346: 2007-03	0.1	% (w/w)	92.4	93.5	94.0
Elements from the aqua regia digestion according to DIN EN 13657: 2003-01#								
Arsenic (As)	FR	JE02	DIN EN ISO 17294-2: 2005-02	0.8	mg/kg dw	7.3	7.6	7.2
Lead (Pb)	FR	JE02	DIN EN ISO 17294-2: 2005-02	2	mg/kg dw	98	74	76
Cadmium (Cd)	FR	JE02	DIN EN ISO 17294-2: 2005-02	0.2	mg/kg dw	0.5	0.4	0.4
Chromium (Cr)	FR	JE02	DIN EN ISO 17294-2: 2005-02	1	mg/kg dw	52	54	41
Copper (Cu)	FR	JE02	DIN EN ISO 17294-2: 2005-02	1	mg/kg dw	70	70	73
Nickel (Ni)	FR	JE02	DIN EN ISO 17294-2: 2005-02	1	mg/kg dw	33	35	32
Mercury (Hg)	FR	JE02	DIN EN ISO 12846: 2012-08	0.07	mg/kg dw	0.39	0.26	0.16
Thallium (Tl)	FR	JE02	DIN EN ISO 17294-2: 2005-02	0.2	mg/kg dw	< 0.2	< 0.2	< 0.2
Zinc (Zn)	FR	JE02	DIN EN ISO 17294-2: 2005-02	1	mg/kg dw	157	167	150
Elements from the shaken 10:1 eluate acc. to DIN EN 12457-4: 2003-01								
Arsenic (As)	FR	JE02	DIN EN ISO 17294-2: 2005-02	0.001	mg/l	0.005	0.004	0.003
Lead (Pb)	FR	JE02	DIN EN ISO 17294-2: 2005-02	0.001	mg/l	0.010	0.013	0.012
Cadmium (Cd)	FR	JE02	DIN EN ISO 17294-2: 2005-02	0.0003	mg/l	< 0.0003	< 0.0003	< 0.0003
Chromium (Cr)	FR	JE02	DIN EN ISO 17294-2: 2005-02	0.001	mg/l	0.005	0.004	0.002
Copper (Cu)	FR	JE02	DIN EN ISO 17294-2: 2005-02	0.005	mg/l	0.051	0.058	0.039
Nickel (Ni)	FR	JE02	DIN EN ISO 17294-2: 2005-02	0.001	mg/l	0.009	0.010	0.003
Mercury (Hg)	FR	JE02	DIN EN ISO 12846: 2012-08	0.0002	mg/l	< 0.0002	< 0.0002	< 0.0002
Thallium (Tl)	FR	JE02	DIN EN ISO 17294-2: 2005-02	0.0002	mg/l	< 0.0002	< 0.0002	< 0.0002
Zinc (Zn)	FR	JE02	DIN EN ISO 17294-2: 2005-02	0.01	mg/l	0.03	0.04	0.03

Appendix 4: Shapiro-Wilk Test

	Statistic	**Shapiro-Wilk df**	**ρ-value**
Aluminium	0.961	101	0.005
Arsenic	0.671	101	0.000
Barium	0.660	101	0.000
Bismuth	0.907	101	0.000
Bromine	0.903	101	0.000
Calcium	0.978	101	0.096
Cadmium	0.825	101	0.000
Cerium	0.075	101	0.000
Chlorine	0.871	101	0.000
Cobalt	0.411	101	0.000
Chromium	0.545	101	0.000
Caesium	0.196	101	0.000
Copper	0.928	101	0.000
Iron	0.966	101	0.010
Gallium	0.833	101	0.000
Germanium	0.562	101	0.000
Iodine	0.802	101	0.000
Potassium	0.936	101	0.000
Lanthanum	0.303	101	0.000
Magnesium	0.829	101	0.000
Manganese	0.940	101	0.000
Molybdenum	0.863	101	0.000
Sodium	0.940	101	0.000
Niobium	0.875	101	0.000
Neodymium	0.171	101	0.000
Nickel	0.730	101	0.000
Phosphorus	0.964	101	0.007
Lead	0.708	101	0.000
Praseodymium	0.000	101	0.000
Rubidium	0.942	101	0.000
Antimony	0.797	101	0.000
Selenium	0.865	101	0.000
Silicon	0.917	101	0.000
Tin	0.922	101	0.000
Sulphur	0.760	101	0.000
Strontium	0.831	101	0.000
Tantalum	0.000	101	0.000
Tellurium	0.814	101	0.000
Titanium	0.957	101	0.003
Vanadium	0.447	101	0.000
Tungsten	0.134	101	0.000
Yttrium	0.922	101	0.000
Zinc	0.722	101	0.000
Zirconium	0.937	101	0.000

Appendix 5: One-Way ANOVA Test and Kruskal-Wallis Test (Districts)

		Sample Size	Mean	Std. Deviation	ρ-value
Aluminium	Southern harbour	18	35071.630	8559.020	0.268
	Northern harbour	12	30414.230	7095.803	
	South-Eastern	23	37756.230	10671.178	
	Western	18	38106.000	12018.356	
	Northern	15	36902.840	14210.091	
	Gozo and Comino	15	31737.360	9081.968	
Arsenic	Southern harbour	18	5.010	8.542	0.245
	Northern harbour	12	1.330	4.591	
	South-Eastern	23	6.720	9.847	
	Western	18	7.030	8.878	
	Northern	15	7.930	11.743	
	Gozo and Comino	15	4.190	7.314	
Barium	Southern harbour	18	177.390	306.910	0.312
	Northern harbour	12	46.800	133.231	
	South-Eastern	23	305.730	415.788	
	Western	18	224.460	323.458	
	Northern	15	251.260	364.011	
	Gozo and Comino	15	106.940	243.794	
Bismuth	Southern harbour	18	27.610	14.673	0.569
	Northern harbour	12	23.550	9.624	
	South-Eastern	23	32.950	14.278	
	Western	18	29.400	14.067	
	Northern	15	32.110	19.275	
	Gozo and Comino	15	28.170	13.708	
Bromine	Southern harbour	18	36.560	16.019	0.197
	Northern harbour	12	33.420	12.406	
	South-Eastern	23	40.520	11.920	
	Western	18	34.720	14.624	
	Northern	15	47.800	26.466	
	Gozo and Comino	15	34.130	11.538	
Calcium	Southern harbour	18	215397.000	30201.098	0.073
	Northern harbour	12	227375.900	28405.988	
	South-Eastern	23	202428.800	31510.428	
	Western	18	201035.700	36833.081	
	Northern	15	200924.400	44806.688	
	Gozo and Comino	15	216528.100	40285.145	
Cadmium	Southern harbour	18	17.910	17.952	0.560
	Northern harbour	12	16.690	17.912	
	South-Eastern	23	28.950	22.077	
	Western	18	24.690	20.197	
	Northern	15	30.100	22.876	
	Gozo and Comino	15	22.720	20.113	
Cerium	Southern harbour	18	4.430	18.804	0.437
	Northern harbour	12	0.000	0.000	
	South-Eastern	23	0.000	0.000	
	Western	18	0.000	0.000	
	Northern	15	0.000	0.000	
	Gozo and Comino	15	0.000	0.000	

		Sample Size	Mean	Std. Deviation	ρ-value
Chlorine	Southern harbour	18	2697.220	358.966	0.263
	Northern harbour	12	2529.170	386.181	
	South-Eastern	23	2847.390	594.92	
	Western	18	2683.330	392.593	
	Northern	15	2886.670	648.092	
	Gozo and Comino	15	2792.670	649.169	
Cobalt	Southern harbour	18	7.560	22.372	0.437
	Northern harbour	12	0.000	0.00	
	South-Eastern	23	8.650	27.134	
	Western	18	3.760	12.657	
	Northern	15	4.300	16.652	
	Gozo and Comino	15	15.830	20.823	
Chromium	Southern harbour	18	25.700	51.943	0.450
	Northern harbour	12	21.950	37.163	
	South-Eastern	23	45.930	72.310	
	Western	18	12.390	45.394	
	Northern	15	18.790	33.130	
	Gozo and Comino	15	8.990	34.802	
Caesium	Southern harbour	18	7.810	33.142	0.832
	Northern harbour	12	0.000	0.000	
	South-Eastern	23	5.860	28.083	
	Western	18	6.640	28.151	
	Northern	15	0.000	0.000	
	Gozo and Comino	15	5.480	21.215	
Copper	Southern harbour	18	95.150	56.719	0.042
	Northern harbour	12	45.600	47.032	
	South-Eastern	23	70.990	47.609	
	Western	18	70.650	41.594	
	Northern	15	54.910	71.596	
	Gozo and Comino	15	39.620	41.249	
Iron	Southern harbour	18	25509.770	8194.762	0.356
	Northern harbour	12	21769.760	6729.687	
	South-Eastern	23	28810.430	12239.424	
	Western	18	28797.090	12020.045	
	Northern	15	27385.020	10283.350	
	Gozo and Comino	15	27618.160	8184.606	
Gallium	Southern harbour	18	13.180	13.490	0.247
	Northern harbour	12	5.390	11.495	
	South-Eastern	23	14.780	15.247	
	Western	18	15.660	14.941	
	Northern	15	14.830	16.036	
	Gozo and Comino	15	8.230	11.107	
Germanium	Southern harbour	18	3.390	6.313	0.768
	Northern harbour	12	1.270	3.320	
	South-Eastern	23	2.810	5.226	
	Western	18	2.080	3.650	
	Northern	15	4.400	7.289	
	Gozo and Comino	15	0.230	0.896	
Iodine	Southern harbour	18	29.390	41.930	0.373
	Northern harbour	12	25.670	35.395	
	South-Eastern	23	53.700	46.061	
	Western	18	43.560	47.123	
	Northern	15	62.200	54.219	
	Gozo and Comino	15	35.130	43.858	

		Sample Size	Mean	Std. Deviation	ρ-value
Potassium	Southern harbour	18	10249.590	2751.518	0.164
	Northern harbour	12	8557.460	1827.554	
	South-Eastern	23	9975.520	2724.678	
	Western	18	10623.610	3994.561	
	Northern	15	11914.870	4704.408	
	Gozo and Comino	15	10710.600	2587.749	
Lanthanum	Southern harbour	18	46.940	136.658	0.991
	Northern harbour	12	44.060	152.611	
	South-Eastern	23	29.320	97.688	
	Western	18	7.720	23.772	
	Northern	15	50.190	140.304	
	Gozo and Comino	15	0.000	0.000	
Magnesium	Southern harbour	18	12637.040	5135.293	0.216
	Northern harbour	12	13869.920	5829.532	
	South-Eastern	23	14931.790	4023.22	
	Western	18	15555.080	4735.913	
	Northern	15	12675.90	5958.04	
	Gozo and Comino	15	16981.610	5582.731	
Manganese	Southern harbour	18	463.390	214.253	0.118
	Northern harbour	12	368.130	171.558	
	South-Eastern	23	586.670	264.078	
	Western	18	560.750	279.624	
	Northern	15	487.450	286.52	
	Gozo and Comino	15	374.680	156.732	
Molybdenum	Southern harbour	18	7.810	7.178	0.134
	Northern harbour	12	5.550	6.025	
	South-Eastern	23	11.850	7.739	
	Western	18	9.000	7.154	
	Northern	15	12.090	9.037	
	Gozo and Comino	15	6.800	7.046	
Sodium	Southern harbour	18	88648.150	24915.083	0.647
	Northern harbour	12	96138.870	22118.480	
	South-Eastern	23	97399.770	18815.25	
	Western	18	102088.200	24897.879	
	Northern	15	97233.120	41676.865	
	Gozo and Comino	15	100398.400	42850.892	
Niobium	Southern harbour	18	16.820	11.881	0.065
	Northern harbour	12	13.510	9.950	
	South-Eastern	23	24.070	12.428	
	Western	18	19.570	12.818	
	Northern	15	25.860	15.413	
	Gozo and Comino	15	16.310	10.841	
Neodymium	Southern harbour	18	13.050	55.370	0.217
	Northern harbour	12	0.000	0.000	
	South-Eastern	23	18.380	59.747	
	Western	18	0.000	0.000	
	Northern	15	0.000	0.000	
	Gozo and Comino	15	0.000	0.000	
Nickel	Southern harbour	18	19.950	23.176	0.060
	Northern harbour	12	2.490	8.620	
	South-Eastern	23	21.900	24.852	
	Western	18	16.070	18.676	
	Northern	15	12.470	19.328	
	Gozo and Comino	15	5.710	15.787	

		Sample Size	Mean	Std. Deviation	ρ-value
Phosphorus	Southern harbour	18	4247.580	1044.356	0.148
	Northern harbour	12	3574.280	1534.899	
	South-Eastern	23	3437.850	797.069	
	Western	18	3549.060	1133.783	
	Northern	15	3552.750	934.537	
	Gozo and Comino	15	3958.330	1003.054	
Lead	Southern harbour	18	249.510	175.818	0.000
	Northern harbour	12	114.260	56.064	
	South-Eastern	23	150.310	64.146	
	Western	18	107.320	43.958	
	Northern	15	69.810	25.163	
	Gozo and Comino	15	62.260	40.823	
Praseodymium	Southern harbour	18	0.000	0.000	1.000
	Northern harbour	12	0.000	0.000	
	South-Eastern	23	0.000	0.000	
	Western	18	0.000	0.000	
	Northern	15	0.000	0.000	
	Gozo and Comino	15	0.000	0.000	
Rubidium	Southern harbour	18	70.410	27.868	0.145
	Northern harbour	12	61.720	21.468	
	South-Eastern	23	84.720	31.453	
	Western	18	83.210	39.181	
	Northern	15	82.240	34.863	
	Gozo and Comino	15	76.020	23.578	
Antimony	Southern harbour	18	39.080	47.019	0.663
	Northern harbour	12	33.070	40.044	
	South-Eastern	23	59.710	54.285	
	Western	18	54.300	50.664	
	Northern	15	66.610	60.078	
	Gozo and Comino	15	20.490	39.687	
Selenium	Southern harbour	18	11.540	8.524	0.336
	Northern harbour	12	9.130	6.029	
	South-Eastern	23	15.500	9.070	
	Western	18	12.060	8.768	
	Northern	15	15.510	11.320	
	Gozo and Comino	15	10.110	6.921	
Silicon	Southern harbour	18	115700.800	29994.255	0.460
	Northern harbour	12	101614.300	19665.228	
	South-Eastern	23	119826.400	32131.894	
	Western	18	118199.600	29271.378	
	Northern	15	126948.800	52284.641	
	Gozo and Comino	15	102132.400	22299.761	
Tin	Southern harbour	18	131.540	27.589	0.259
	Northern harbour	12	117.760	22.199	
	South-Eastern	23	141.130	28.152	
	Western	18	131.670	28.562	
	Northern	15	136.160	36.163	
	Gozo and Comino	15	122.140	25.164	
Sulphur	Southern harbour	18	2122.870	416.356	0.382
	Northern harbour	12	1825.610	287.361	
	South-Eastern	23	1988.570	321.828	
	Western	18	1917.730	400.863	
	Northern	15	2058.040	396.061	
	Gozo and Comino	15	2218.770	1004.911	

		Sample Size	Mean	Std. Deviation	ρ-value
Strontium	Southern harbour	18	289.760	30.699	0.008
	Northern harbour	12	340.350	54.273	
	South-Eastern	23	276.210	50.524	
	Western	18	271.720	122.935	
	Northern	15	279.950	87.329	
	Gozo and Comino	15	433.900	153.972	
Tantalum	Southern harbour	18	0.000	0.000	1.000
	Northern harbour	12	0.000	0.000	
	South-Eastern	23	0.000	0.000	
	Western	18	0.000	0.000	
	Northern	15	0.000	0.000	
	Gozo and Comino	15	0.000	0.000	
Tellurium	Southern harbour	18	33.530	38.222	0.358
	Northern harbour	12	28.920	30.455	
	South-Eastern	23	52.730	43.039	
	Western	18	43.530	40.575	
	Northern	15	63.210	49.286	
	Gozo and Comino	15	43.010	38.958	
Titanium	Southern harbour	18	2780.600	782.126	0.503
	Northern harbour	12	2494.250	1090.385	
	South-Eastern	23	3121.260	1204.085	
	Western	18	2906.230	1157.672	
	Northern	15	2868.440	1235.728	
	Gozo and Comino	15	2360.200	808.672	
Vanadium	Southern harbour	18	18.640	55.276	0.336
	Northern harbour	12	10.410	36.061	
	South-Eastern	23	64.250	151.056	
	Western	18	41.450	84.732	
	Northern	15	51.010	77.864	
	Gozo and Comino	15	10.760	41.655	
Tungsten	Southern harbour	18	1.230	5.233	0.590
	Northern harbour	12	0.000	0.000	
	South-Eastern	23	0.000	0.000	
	Western	18	0.880	3.738	
	Northern	15	0.000	0.000	
	Gozo and Comino	15	0.160	0.614	
Yttrium	Southern harbour	18	29.840	14.140	0.033
	Northern harbour	12	28.940	10.777	
	South-Eastern	23	43.340	15.618	
	Western	18	31.450	14.038	
	Northern	15	34.750	17.239	
	Gozo and Comino	15	29.560	9.444	
Zinc	Southern harbour	18	251.330	210.663	0.187
	Northern harbour	12	160.350	113.805	
	South-Eastern	23	172.450	67.316	
	Western	18	158.810	55.181	
	Northern	15	173.480	145.836	
	Gozo and Comino	15	128.120	74.940	
Zirconium	Southern harbour	18	279.100	140.888	0.136
	Northern harbour	12	248.560	136.316	
	South-Eastern	23	388.250	174.769	
	Western	18	303.570	154.017	
	Northern	15	355.900	188.420	
	Gozo and Comino	15	212.180	102.137	

Appendix 6: Sample A

Sample A				
	1st try	2nd try	3rd try	Average
Aluminium	27256.375	26621.275	26885.900	26921.183
Arsenic	0.000	0.000	22.722	7.574
Barium	0.000	0.000	625.164	208.388
Bismuth	23.322	21.528	53.819	32.890
Bromine	28.000	28.000	52.000	36.000
Calcium	224837.580	229646.940	225639.140	226707.887
Cadmium	12.298	11.419	48.312	24.010
Cerium	0.000	0.000	0.000	0.000
Chlorine	2170.000	2100.000	2780.000	2350.000
Cobalt	0.000	0.000	0.000	0.000
Chromium	0.000	0.000	0.000	0.000
Caesium	0.000	0.000	0.000	0.000
Copper	79.886	97.461	113.438	96.928
Iron	23640.734	23430.905	23850.563	23640.734
Gallium	2.976	9.671	27.525	13.391
Germanium	2.083	3.471	0.000	1.851
Iodine	12.000	4.000	107.000	41.000
Potassium	8633.560	8467.530	11373.055	9491.382
Lanthanum	0.000	0.000	0.000	0.000
Magnesium	15437.824	13327.184	14352.352	14372.453
Manganese	392.651	408.140	542.896	447.896
Molybdenum	11.331	5.332	21.329	12.664
Sodium	102376.680	98667.380	94958.080	98667.380
Niobium	18.175	11.884	34.253	21.437
Neodymium	0.000	0.000	0.000	0.000
Nickel	0.000	0.000	33.789	11.263
Phosphorus	4538.768	3740.119	4049.978	4109.622
Lead	143.890	141.105	109.542	131.512
Praseodymium	0.000	0.000	0.000	0.000
Rubidium	64.923	63.094	81.382	69.800
Antimony	33.414	24.225	135.327	64.322
Selenium	8.539	8.539	27.042	14.707
Silicon	100021.560	100021.560	102569.880	100871.000
Tin	115.789	107.124	165.413	129.442
Sulphur	1565.955	1642.050	2086.605	1764.870
Strontium	345.846	336.545	343.310	341.900
Tantalum	0.000	0.000	0.000	0.000
Tellurium	31.181	16.790	112.730	53.567
Titanium	2673.056	2726.997	2691.037	2697.030
Vanadium	0.000	0.000	0.000	0.000
Tungsten	0.000	0.000	0.000	0.000
Yttrium	38.585	34.647	56.696	43.309
Zinc	173.534	179.158	179.962	177.551
Zirconium	293.167	269.476	464.921	342.521

Appendix 7: Sample B

Sample B				
	1st try	2nd try	3rd try	Average
Aluminium	28526.575	27573.925	30431.875	28844.125
Arsenic	21.964	0.000	15.905	12.623
Barium	789.068	0.000	532.016	440.361
Bismuth	51.128	18.837	43.056	37.674
Bromine	61.000	34.000	50.000	48.333
Calcium	224036.020	236059.420	219226.660	226440.700
Cadmium	57.096	11.419	43.920	37.478
Cerium	0.000	0.000	0.000	0.000
Chlorine	2740.000	2110.000	2640.000	2496.667
Cobalt	0.000	0.000	0.000	0.000
Chromium	0.000	0.000	0.000	0.000
Caesium	148.234	0.000	85.552	77.929
Copper	115.036	81.484	95.863	97.461
Iron	25319.366	25249.423	25878.910	25482.566
Gallium	28.269	0.000	17.110	15.127
Germanium	14.578	0.000	7.636	7.405
Iodine	128.000	0.000	88.000	72.000
Potassium	13199.385	9048.635	11954.160	11400.727
Lanthanum	0.000	0.000	0.000	0.000
Magnesium	14412.656	13266.880	15799.648	14493.061
Manganese	603.304	460.804	517.339	527.149
Molybdenum	22.662	7.332	15.330	15.108
Sodium	93474.360	89765.060	89023.200	90754.207
Niobium	38.447	14.680	27.962	27.030
Neodymium	0.000	0.000	0.000	0.000
Nickel	40.076	0.000	16.502	18.859
Phosphorus	4669.694	3587.372	4451.484	4236.183
Lead	81.692	114.183	89.119	94.998
Praseodymium	0.000	0.000	0.000	0.000
Rubidium	86.869	67.666	80.468	78.334
Antimony	147.022	28.402	116.114	97.179
Selenium	29.176	6.405	21.349	18.977
Silicon	99384.480	93650.760	108940.680	100658.640
Tin	184.317	115.789	161.474	153.860
Sulphur	2334.915	1610.010	2162.700	2035.875
Strontium	347.537	345.001	346.692	346.410
Tantalum	0.000	0.000	0.000	0.000
Tellurium	120.725	14.391	89.544	74.887
Titanium	2798.918	2774.944	2834.878	2802.913
Vanadium	65.540	0.000	2.241	22.594
Tungsten	0.000	0.000	0.000	0.000
Yttrium	61.420	38.585	53.546	51.184
Zinc	188.799	171.124	182.372	180.765
Zirconium	501.197	283.543	406.436	397.058

Appendix 8: Sample C

Sample C				
	1st try	2nd try	3rd try	Average
Aluminium	19264.700	22069.725	23869.175	21734.533
Arsenic	19.692	0.000	0.000	6.564
Barium	663.677	0.000	0.000	221.226
Bismuth	45.746	40.365	15.249	33.787
Bromine	50.000	50.000	25.000	41.667
Calcium	261709.340	233654.740	234456.300	243273.460
Cadmium	51.826	51.826	8.784	37.478
Cerium	0.000	0.000	0.000	0.000
Chlorine	2600.000	2500.000	2030.000	2376.667
Cobalt	11.797	0.000	0.000	3.932
Chromium	0.000	0.000	0.000	0.000
Caesium	0.000	0.000	0.000	0.000
Copper	107.047	116.634	82.283	101.988
Iron	17275.921	17136.035	16856.263	17089.406
Gallium	22.318	0.000	0.000	7.439
Germanium	0.000	0.000	0.000	0.000
Iodine	100.000	102.000	12.000	71.333
Potassium	8384.515	8201.882	7014.768	7867.055
Lanthanum	246.425	0.000	0.000	82.142
Magnesium	12422.624	20443.056	14111.136	15658.939
Manganese	381.034	407.366	242.406	343.602
Molybdenum	18.663	18.663	2.666	13.331
Sodium	100151.100	135760.380	116472.020	117461.167
Niobium	31.457	30.758	8.388	23.534
Neodymium	0.000	0.000	0.000	0.000
Nickel	13.359	0.000	0.000	4.453
Phosphorus	3033.119	2779.995	3395.348	3069.487
Lead	62.197	71.481	94.689	76.122
Praseodymium	0.000	0.000	0.000	0.000
Rubidium	59.437	58.522	42.063	53.341
Antimony	124.467	119.455	30.073	91.332
Selenium	24.907	21.349	6.405	17.553
Silicon	63198.336	66256.320	87917.040	72457.232
Tin	162.262	157.536	117.364	145.721
Sulphur	1898.370	1750.185	1718.145	1788.900
Strontium	340.773	333.162	339.082	337.672
Tantalum	0.000	0.000	0.000	0.000
Tellurium	99.938	96.740	17.589	71.422
Titanium	1792.027	3044.647	1971.829	2269.501
Vanadium	73.382	0.000	0.000	24.461
Tungsten	0.000	0.000	0.000	0.000
Yttrium	49.609	48.034	25.198	40.947
Zinc	107.656	109.262	96.408	104.442
Zirconium	392.370	396.071	188.041	325.494

Appendix 9: Sample D

Sample D				
	1st try	2nd try	3rd try	Average
Aluminium	12913.700	13178.325	13919.275	13337.100
Arsenic	0.000	0.000	0.000	0.000
Barium	0.000	0.000	0.000	0.000
Bismuth	17.940	14.352	12.558	14.950
Bromine	31.000	30.000	28.000	29.667
Calcium	273331.960	270125.720	270526.500	271328.060
Cadmium	3.514	3.514	4.392	3.806
Cerium	0.000	0.000	0.000	0.000
Chlorine	1930.000	1880.000	1750.000	1853.333
Cobalt	0.000	0.000	0.000	0.000
Chromium	0.000	0.000	0.000	0.000
Caesium	0.000	0.000	0.000	0.000
Copper	74.294	54.322	50.328	59.648
Iron	11470.652	11610.538	11120.937	11400.709
Gallium	0.000	0.000	0.000	0.000
Germanium	0.000	0.000	0.000	0.000
Iodine	20.000	13.000	10.000	14.333
Potassium	5537.101	4665.443	4748.458	4983.667
Lanthanum	0.000	0.000	0.000	0.000
Magnesium	14834.784	16402.688	16221.776	15819.749
Manganese	157.215	147.147	124.688	143.017
Molybdenum	2.666	3.333	2.000	2.666
Sodium	113504.580	120181.320	114246.440	115977.447
Niobium	5.592	6.291	4.893	5.592
Neodymium	0.000	0.000	0.000	0.000
Nickel	0.000	0.000	0.000	0.000
Phosphorus	3945.237	3823.039	3919.052	3895.776
Lead	155.029	153.173	152.244	153.482
Praseodymium	0.000	0.000	0.000	0.000
Rubidium	32.919	32.919	30.176	32.004
Antimony	35.085	34.249	25.896	31.743
Selenium	6.405	4.981	5.693	5.693
Silicon	47526.168	47016.504	50902.692	48481.788
Tin	107.912	107.124	107.912	107.650
Sulphur	1638.045	1389.735	1457.820	1495.200
Strontium	501.435	508.200	502.280	503.972
Tantalum	0.000	0.000	0.000	0.000
Tellurium	23.985	21.587	18.389	21.320
Titanium	887.023	713.215	617.320	739.186
Vanadium	0.000	0.000	0.000	0.000
Tungsten	0.000	0.000	0.000	0.000
Yttrium	24.411	24.411	22.836	23.886
Zinc	136.578	127.741	130.954	131.758
Zirconium	88.838	89.579	74.032	84.150

Appendix 10: Sample E

	Sample E			
	1st try	2nd try	3rd try	Average
Aluminium	27468.075	27944.400	30961.125	28791.200
Arsenic	18.177	0.000	25.751	14.643
Barium	402.147	0.000	775.633	392.593
Bismuth	43.953	25.116	60.098	43.056
Bromine	69.000	55.000	81.000	68.333
Calcium	229646.940	189568.940	206802.480	208672.787
Cadmium	46.555	26.352	57.096	43.334
Cerium	0.000	0.000	0.000	0.000
Chlorine	3310.000	2810.000	3750.000	3290.000
Cobalt	0.000	0.000	0.000	0.000
Chromium	0.000	0.000	0.000	0.000
Caesium	0.000	0.000	139.763	46.588
Copper	93.467	79.886	131.812	101.722
Iron	26158.682	27487.599	26648.283	26764.855
Gallium	18.598	5.951	31.989	18.846
Germanium	7.636	2.083	0.000	3.240
Iodine	64.000	3.000	127.000	64.667
Potassium	11373.055	8882.605	14444.610	11566.757
Lanthanum	0.000	0.000	0.000	0.000
Magnesium	15317.216	23518.560	16945.424	18593.733
Manganese	526.633	495.654	616.470	546.252
Molybdenum	14.664	11.331	22.662	16.219
Sodium	91248.780	163951.060	97925.520	117708.453
Niobium	27.962	18.874	37.049	27.962
Neodymium	0.000	0.000	0.000	0.000
Nickel	23.574	0.000	44.005	22.526
Phosphorus	3927.780	3517.545	4756.978	4067.434
Lead	90.975	124.395	89.119	101.496
Praseodymium	0.000	0.000	0.000	0.000
Rubidium	79.554	71.324	89.612	80.163
Antimony	0.000	0.000	144.516	48.172
Selenium	21.349	9.251	30.600	20.400
Silicon	94924.920	89191.200	112763.160	98959.760
Tin	146.508	116.577	178.016	147.034
Sulphur	2635.290	2230.785	3204.000	2690.025
Strontium	347.537	368.677	351.765	355.993
Tantalum	0.000	0.000	0.000	0.000
Tellurium	71.156	6.396	114.329	63.960
Titanium	2810.905	3218.456	2906.799	2978.720
Vanadium	25.768	0.000	90.748	38.838
Tungsten	0.000	0.000	0.000	0.000
Yttrium	54.333	44.884	60.633	53.283
Zinc	183.175	187.192	199.243	189.870
Zirconium	406.436	312.415	532.290	417.047

Appendix 11: Southern Harbour Samples

	Southern Harbour																	
Sample Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Average
Element																			
Aluminium	23022.38	49908.28	39587.9	40699.33	32284.25	23128.23	27521	31331.6	34983.43	26727.13	48055.9	41387.35	26303.73	25033.53	45039.18	40540.55	39587.9	36147.78	35071.63
Arsenic	0	29.53821	9.08868	0	0	0	0	0.75739	9.08868	0	3.78695	0	0	12.11824	0	21.96431	0.75739	3.02956	5.007189
Barium	0	976.2585	136.1388	0	680.694	0	0	280.3385	206.8952	0	0	0	0	144.1997	0	768.4677	0	0	177.3885
Bismuth	18.83679	69.06823	26.9097	19.73378	44.8495	11.66087	18.83679	26.01271	26.01271	15.24883	27.80669	20.63077	14.35184	33.18863	30.49766	52.92241	20.63077	19.73378	27.60736
Bromine	53	83	40	25	52	19	25	29	30	22	36	31	23	33	35	59	34	29	36.55556
Caclium	229646.9	152296.4	216421.2	216020.4	218825.9	248082.8	227643	241670.3	227643	241269.6	181152.6	195580.6	232051.6	278542.1	175140.9	187164.3	197985.3	210008.7	215397
Cadmium	6.1488	57.9744	12.2976	13.176	57.096	8.784	3.5136	14.9328	12.2976	5.2704	14.0544	12.2976	7.0272	14.9328	11.4192	53.5824	8.784	8.784	17.9096
Cerium	0	0	0	0	0	0	0	0	0	0	0	0	0	79.77984	0	0	0	0	4.432213
Chlorine	2620	3430	2640	2630	2960	2600	2250	2350	2630	3080	2310	2980	2170	2310	2510	3070	3190	2820	2697.222
Cobalt	10.22424	0	0	0	0	0	0	0	35.3916	0	0	0	0	90.4452	0	0	0	0	7.558947
Chromium	0	71.841	0	0	0	0	0	0	0	0	134.1032	0	0	99.209	157.366	0	0	0	25.69551
Caesium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	140.6103	0	0	7.811683
Copper	92.66776	178.9446	140.5994	99.8575	117.4324	79.886	23.9658	243.6523	111.0415	19.17264	105.4495	68.70196	0	62.31108	71.09854	108.645	95.06434	94.26548	95.1531
Iron	16576.49	45323.06	29865.66	30914.81	24200.28	15317.52	17345.86	26018.8	20213.53	22731.48	38328.76	29166.23	17695.58	16086.89	32523.5	30425.21	24060.39	22381.76	25509.77
Gallium	0	48.35545	17.11039	9.67109	33.47685	0	0	17.11039	5.95144	0	19.34218	11.90288	0	20.08611	13.39074	29.7572	6.69537	4.46358	13.18409
Germanium	0	22.2144	7.6362	0	0	0	0	4.8594	0.6942	0	0	0	0	9.7188	0	14.5782	1.3884	0	3.393867
Iodine	2	132	12	10	103	4	4	1	35	10	7	2	10	36	12	117	15	17	29.38889
Potassium	7023.069	17931.24	10708.94	9712.755	9297.68	7222.305	7047.974	9546.725	10376.88	9131.65	12286.22	11456.07	8467.53	6632.899	10957.98	13448.43	12037.18	11207.03	10249.59
Lanthanum	0	414.4025	0	0	0	0	0	0	0	0	0	0	0	430.6034	0	0	0	0	46.94477
Magnesium	16643.9	15618.74	12905.06	14050.83	16824.82	0	14714.18	9347.12	11216.54	0	16161.47	14895.09	15377.52	10673.81	17126.34	16462.99	14050.83	11397.46	12637.04
Manganese	216.0743	1061.01	510.3691	494.8799	606.4022	221.4956	245.5038	500.3012	318.3031	329.92	679.9759	475.5184	236.2103	321.4009	581.6195	699.3374	430.5998	412.0127	463.3852
Molybdenum	3.99924	27.32814	6.6654	4.66578	19.32966	2.66616	2.66616	5.99886	5.99886	4.66578	5.33232	4.66578	1.99962	4.66578	11.33118	20.66274	3.3327	4.66578	7.81333
Sodium	128341.8	70031.58	69660.65	70254.14	111279	125374.3	111279	47033.92	77153.44	113504.6	67731.82	90506.92	114988.3	45401.83	94216.22	89023.2	87539.48	82346.46	88648.15
Niobium	6.29136	50.33088	16.07792	12.58272	33.55392	6.9904	8.38848	11.18464	13.28176	12.58272	16.77696	12.58272	7.68944	11.18464	23.06832	37.04912	11.88368	11.18464	16.8158
Neodymium	0	0	0	0	0	0	0	0	0	0	0	0	0	234.9139	0	0	0	0	13.05077
Nickel	17.2876	79.3658	33.7894	10.2154	0	0	0	25.1456	7.858	0	34.5752	18.0734	0	57.3634	30.6462	44.7906	0	0	19.95059
Phosphorus	4931.546	5848.028	4290.009	3443.354	3050.576	4145.99	3094.218	5760.744	4626.052	3508.817	3993.243	3059.304	3054.94	3006.934	4582.41	4844.262	5106.114	6109.88	4247.579
Lead	129.0365	181.0224	403.8192	299.8474	288.7075	194.9472	108.6134	828.9898	375.9696	181.9507	337.9085	263.6429	100.2586	66.83904	138.3197	97.4736	253.4314	240.4349	249.5118
Praseodymium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Rubidium	39.31963	151.7921	70.40957	72.23839	76.81044	35.66199	45.7205	63.09429	57.60783	60.35106	101.4995	76.81044	49.37814	44.80609	89.61218	100.5851	67.66634	64.0087	70.40957
Antimony	0	149.5277	30.90795	26.7312	118.6197	23.3898	0	26.7312	55.96845	34.24935	0	18.3777	25.89585	0	22.55445	136.9974	0	33.414	39.07582
Selenium	7.82782	34.15776	9.25106	5.69296	25.61832	4.98134	7.1162	9.96268	9.96268	5.69296	9.25106	7.1162	4.26972	14.94402	10.6743	27.04156	6.40458	7.82782	11.54406
Silicon	78997.92	178382.4	119771	119771	93650.76	73264.2	97473.24	115311.5	112763.2	81546.24	156084.6	132512.6	87917.04	80909.16	149713.8	138246.4	136335.1	129964.3	115700.8
Tin	97.67232	192.9816	152.8099	128.3918	167.7758	107.1245	109.4875	144.1454	141.7824	131.5426	122.0904	109.4875	105.5491	115.0013	118.152	185.1048	115.789	122.8781	131.5426
Sulphur	2975.715	2695.365	2270.835	1794.24	1970.46	2122.65	1778.22	1950.435	2086.605	2262.825	1589.985	1930.41	1597.995	1742.175	2286.855	3011.76	2126.655	2018.52	2122.873
Strontium	292.5741	260.4417	307.7948	239.302	273.9712	300.1845	339.9272	329.7801	292.5741	261.2873	253.677	268.8976	335.6992	335.6992	275.6623	279.0447	302.7212	266.3609	289.7555
Tantalum	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tellurium	11.9925	126.321	16.7895	14.391	104.7345	19.188	17.589	20.787	45.5715	25.584	7.995	7.995	19.188	0	27.183	109.5315	10.3935	18.3885	33.53458
Titanium	2001.796	4626.905	2936.766	3416.238	2217.558	1726.099	2145.637	2709.017	2187.591	2391.367	3560.08	3745.875	1989.809	2085.703	3626.007	3158.522	2996.7	2529.215	2780.605
Vanadium	0	219.0265	0	0	0	0	0	0	0	0	0	0	0	16.8051	0	99.71026	0	0	18.64121
Tungsten	0	0	0	0	0	0	0	0	0	0	0	0	0	22.20316	0	0	0	0	1.233509
Yttrium	22.04832	66.9324	24.41064	23.6232	43.3092	18.89856	26.77296	16.53624	22.04832	22.04832	28.34784	22.83576	25.19808	27.5604	45.67152	58.27056	20.47344	22.04832	29.83523
Zinc	215.3112	538.278	249.8574	180.765	185.5854	194.4228	99.6216	988.182	238.6098	114.8862	310.9158	185.5854	85.9638	75.5196	175.9446	220.935	228.969	234.5928	251.3303
Zirconium	111.7883	683.3154	254.6701	245.0459	422.7227	127.335	202.8477	235.4218	210.9912	210.2509	362.0165	273.1781	180.6381	168.0526	351.652	495.2741	234.6814	253.9298	279.1006

Appendix 12: Northern Harbour Samples

Northern Harbour

Sample Number	19	20	21	22	23	24	25	26	27	28	29	30	Average
Element													
Aluminium	30273.1	20587.83	36888.73	33025.2	28685.35	28579.5	47738.35	30326.03	26674.2	28949.98	31966.7	21275.85	30414.23
Arsenic	0	0	0	0	0	15.90519	0	0	0	0	0	0	1.325433
Barium	0	0	0	102.1041	0	459.4685	0	0	0	0	0	0	46.79771
Bismuth	17.9398	16.14582	20.63077	18.83679	27.80669	40.36455	45.74649	17.04281	18.83679	19.73378	19.73378	19.73378	23.54599
Bromine	23	20	27	29	50	45	61	24	26	30	36	30	33.41667
Caclium	221230.6	241269.6	205600.1	239265.7	245277.4	236460.2	149891.7	220429	248884.4	228845.4	230849.3	260507	227375.9
Cadmium	12.2976	5.2704	12.2976	20.2032	14.9328	40.4064	63.2448	1.7568	1.7568	10.5408	10.5408	7.0272	16.6896
Cerium	0	0	0	0	0	0	0	0	0	0	0	0	0
Chlorine	2300	2340	2520	2430	3490	2680	2850	2250	2090	2250	2840	2310	2529.167
Cobalt	0	0	0	0	0	0	0	0	0	0	0	0	0
Chromium	0	0	21.2102	103.9984	60.2096	0	77.9988	0	0	0	0	0	21.95142
Caesium	0	0	0	0	0	0	0	0	0	0	0	0	0
Copper	36.74756	64.70766	71.09854	97.46092	0	16.77606	92.66776	27.9601	139.8005	0	0	0	45.60159
Iron	23990.45	13708.83	24130.34	25878.91	24130.34	25459.25	37419.51	18325.07	14827.92	17975.35	21822.22	13568.94	21769.76
Gallium	0	0	0	11.90288	0	14.8786	37.94043	0	0	0	0	0	5.393493
Germanium	0	0	0	0	0	4.1652	11.1072	0	0	0	0	0	1.2727
Iodine	0	11	3	20	0	78	117	19	21	10	20	9	25.66667
Potassium	7072.878	6765.723	9214.665	9380.695	8093.963	9214.665	13282.4	8027.551	7695.491	7911.33	9629.74	6400.457	8557.463
Lanthanum	0	0	0	0	0	528.6616	0	0	0	0	0	0	44.05513
Magnesium	13568.4	15377.52	15618.74	12663.84	11457.76	12784.45	26473.46	15980.56	13447.79	13266.88	0	15799.65	13869.92
Manganese	396.5235	218.3977	401.9447	520.4371	375.6131	439.1188	813.183	230.7891	272.6099	230.7891	293.5203	224.5934	368.1267
Molybdenum	2.66616	1.33308	4.66578	1.99962	4.66578	13.99734	21.32928	1.99962	1.99962	1.99962	4.66578	5.33232	5.5545
Sodium	102376.7	114988.3	81604.6	49036.95	77153.44	86797.62	129083.6	117213.9	80862.74	113504.6	102376.7	98667.38	96138.87
Niobium	11.18464	5.59232	12.58272	6.9904	13.28176	30.75776	37.04912	6.9904	6.9904	8.38848	12.58272	9.78656	13.51477
Neodymium	0	0	0	0	0	0	0	0	0	0	0	0	0
Nickel	0	0	0	29.8604	0	0	0	0	0	0	0	0	2.488367
Phosphorus	3229.508	5629.818	5586.176	5367.966	1750.044	1946.433	3914.687	3124.767	5324.324	1942.069	2797.452	2278.112	3574.28
Lead	65.91072	129.0365	199.5888	246.9331	87.26208	52.91424	103.0435	103.0435	113.255	77.97888	81.69216	110.4701	114.2607
Praseodymium	0	0	0	0	0	0	0	0	0	0	0	0	0
Rubidium	66.75193	37.49081	61.26547	61.26547	65.83752	81.38249	116.1301	46.63491	44.80609	53.95019	65.83752	39.31963	61.72268
Antimony	0	31.7433	27.56655	0	30.90795	98.5713	126.9732	0	26.7312	29.23725	0	25.0605	33.06594
Selenium	5.69296	4.98134	6.40458	5.69296	9.25106	19.92536	23.48346	6.40458	7.1162	7.1162	5.69296	7.82782	9.132457
Silicon	107029.4	80909.16	132512.6	113400.2	95562	95562	138246.4	98110.32	91739.52	94287.84	103844	68167.56	101614.3
Tin	101.6107	118.9397	126.0288	132.3302	103.9738	137.844	174.0773	101.6107	107.9122	104.7614	108.6998	95.30928	117.7582
Sulphur	1501.875	1766.205	2202.75	2054.565	1493.865	1814.265	2306.88	1790.235	1778.22	1593.99	2122.65	1481.85	1825.613
Strontium	317.0963	441.398	312.0227	324.7066	323.861	310.3315	251.1402	301.03	317.9418	397.4273	377.9787	409.2656	340.35
Tantalum	0	0	0	0	0	0	0	0	0	0	0	0	0
Tellurium	18.3885	23.985	19.9875	23.1855	17.589	85.5465	97.539	23.1855	0	19.188	18.3885	0	28.91525
Titanium	2463.287	1384.475	2816.898	2858.852	2223.551	2996.7	5495.948	1959.842	1528.317	2181.598	2505.241	1516.33	2494.253
Vanadium	0	0	0	0	0	124.9179	0	0	0	0	0	0	10.40983
Tungsten	0	0	0	0	0	0	0	0	0	0	0	0	0
Yttrium	30.71016	25.98552	34.64736	28.34784	29.92272	42.52176	54.33336	19.686	19.686	21.26088	22.83576	17.32368	28.93842
Zinc	117.2964	163.8936	200.0466	278.7798	447.4938	63.4686	178.3548	92.391	187.9956	60.255	62.6652	71.5026	160.3453
Zirconium	231.7202	128.8157	276.8797	255.4104	246.5266	434.5678	585.5931	142.1414	133.9979	180.6381	222.8363	143.6221	248.5624

Appendix 13: South-Eastern District Samples

	South Eastern																							
Sample Number	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	Average
Element																								
Aluminium	27415.15	30326.03	28632.43	31490.38	27256.38	37735.53	39323.28	30855.28	46891.55	38211.85	51760.65	36306.55	32072.55	54512.75	21328.78	52025.28	47897.13	54512.75	36994.58	56629.75	26515.43	29955.55	29743.85	37756.23
Arsenic	0	0	0	0	0	0	0	0	3.78695	0	7.5739	4.54434	0	21.96431	0	24.23648	21.20692	28.78082	21.20692	5.30173	0	15.90519	0	6.71772
Barium	0	0	0	0	669.9462	724.5809	72.54765	0	57.3216	0	173.7561	171.9648	0	710.2505	0	1379.301	967.302	866.0936	779.2155	0	0	459.4685	0	305.7282
Bismuth	17.9398	17.04281	17.9398	17.9398	43.05552	45.74649	15.24883	15.24883	29.60067	38.57057	26.9097	21.52776	41.26154	50.23144	21.52776	50.23144	46.64348	60.99532	49.33445	28.70368	17.9398	41.26154	43.05552	32.95463
Bromine	27	24	38	26	49	57	35	19	36	50	35	42	48	46	24	58	52	58	49	36	28	44	51	40.52174
Caclium	224436.8	220429	221230.6	232452.4	234857.1	193176	196382.2	230448.5	185561.1	187565	167125.3	209207.2	224837.6	156705	243674.2	156705	170331.5	150693.3	207604	147887.8	247682	224036	222833.7	202428.8
Cadmium	2.6352	1.7568	7.0272	7.0272	46.5552	55.3392	14.0544	7.0272	12.2976	59.7312	16.6896	12.2976	52.704	43.0416	5.2704	53.5824	52.704	57.096	50.9472	10.5408	11.4192	34.2576	51.8256	28.94901
Cerium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Chlorine	2330	2250	3110	2460	3000	2920	2760	2270	2520	3130	2890	5130	2850	2940	2200	3000	3220	3040	2940	2380	2300	2860	2990	2847.391
Cobalt	0	0	0	20.44848	25.16736	0	0	0	0	0	127.4098	0	0	0	0	0	0	0	0	0	25.16736	0.78648	0	8.65128
Chromium	0	0	0	0	14.3682	0	199.7864	0	125.8928	0	111.5246	0	0	93.7354	0	140.261	95.788	38.3152	0	236.7332	0	0	0	45.93064
Caesium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	134.681	0	0	0	0	5.855693
Copper	0	27.9601	19.17264	48.73046	111.0415	61.51222	75.8917	23.9658	88.67346	82.28258	71.09854	123.0244	88.67346	98.25978	0	108.645	180.5424	154.18	71.09854	92.66776	45.53502	59.9145	0	70.99434
Iron	16996.15	18325.07	19234.33	23500.85	24829.77	30145.43	6994.3	18814.67	39238.02	27977.2	47631.18	28676.63	24899.71	49379.76	16296.72	46162.38	34901.56	44693.58	26648.28	51757.82	23151.13	22661.53	19723.93	28810.43
Gallium	0	0	0	0	21.57397	32.73292	9.67109	0	19.34218	0	23.06183	14.13467	0	32.73292	0	41.66008	35.70864	41.66008	26.03755	25.29362	0	16.36646	0	14.78157
Germanium	0	0	0	0	11.1072	0	0.6942	0	0	0	5.5536	0	0	11.1072	0	11.8014	0	18.0492	0	6.2478	0	0	0	2.806983
Iodine	28	19	31	15	97	96	0	14	8	90	2	17	97	94	1	115	105	124	124	0	18	68	72	53.69565
Potassium	7288.717	8027.551	8259.993	8160.375	8882.605	10127.83	8152.073	6699.311	9463.71	11871.15	10459.89	10957.98	10459.89	12867.33	4897.885	12286.22	14859.69	17433.15	10791.95	10127.83	7604.174	10210.85	9546.725	9975.516
Lanthanum	0	0	0	0	303.5541	0	0	0	0	0	0	0	0	0	0	0	0	370.9158	0	0	0	0	0	29.32478
Magnesium	17246.94	15980.56	11337.15	9528.032	13327.18	17669.07	14292.05	15437.82	16342.38	17548.46	14533.26	15256.91	17307.25	14593.57	15618.74	0	18151.5	15679.04	15437.82	21588.83	15136.3	14774.48	16643.9	14931.79
Manganese	211.4276	230.7891	288.0991	390.3278	530.5051	684.6226	606.4022	278.8056	740.3838	622.6658	952.5858	500.3012	559.1601	890.629	228.4657	937.0966	913.8628	1061.01	637.3806	921.6074	388.0045	427.5019	491.7821	586.6703
Molybdenum	1.33308	1.99962	5.33232	3.99924	18.66312	19.32966	9.33156	3.3327	9.9981	17.99658	5.99886	4.66578	17.99658	19.9962	1.33308	21.32928	17.99658	25.99506	18.66312	11.99772	3.99924	12.66426	18.66312	11.85282
Sodium	120181.3	117213.9	117213.9	88281.34	100893	110537.1	109795.3	104602.3	69289.72	114988.3	66693.21	74927.86	106086	75669.72	123148.8	123148.8	89023.2	67064.14	86797.62	82346.46	89765.06	91990.64	110537.1	97399.77
Niobium	8.38848	6.9904	9.08752	11.18464	30.75776	34.952	18.17504	9.08752	21.67024	32.85488	20.9712	12.58272	35.65104	42.64144	9.08752	39.14624	33.55392	46.13664	32.15584	30.05872	11.88368	24.4664	32.15584	24.07129
Neodymium	0	0	0	0	0	0	0	0	0	0	36.0087	0	0	0	0	121.7437	0	0	0	264.9212	0	0	0	18.37711
Nickel	0	0	0	0	19.645	0	35.361	0	45.5764	0	52.6486	26.7172	0	55.006	0	62.864	51.077	61.2924	23.574	58.1492	0	11.787	0	21.8999
Phosphorus	2801.816	3124.767	3286.243	2745.082	3185.866	2675.255	3727.027	3404.076	4167.811	3395.348	2937.107	3692.113	2862.915	3207.687	2151.551	3351.706	6066.238	4582.41	3722.663	4124.169	2806.181	3809.947	3242.601	3437.851
Lead	92.832	103.0435	101.1869	134.6064	187.5206	76.12224	192.1622	119.7533	225.5818	141.1046	159.671	278.496	122.5382	195.8755	140.1763	188.449	126.2515	169.8826	81.69216	312.8438	170.8109	75.19392	61.26912	150.3071
Praseodymium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Rubidium	48.46373	46.63491	50.29255	62.17988	69.49516	96.01305	79.55367	51.20696	96.92746	87.78336	117.0445	66.75193	84.12572	144.4768	48.46373	127.103	107.9004	145.3912	84.12572	133.5039	61.26547	71.32398	68.58075	84.72207
Antimony	23.3898	0	38.4261	31.7433	124.4672	122.7965	20.0484	30.90795	38.4261	0	23.3898	30.90795	116.949	109.4309	0	138.6681	129.4793	139.5035	134.4914	25.0605	0	95.2299	0	59.70937
Selenium	6.40458	6.40458	6.40458	5.69296	22.77184	25.61832	4.26972	4.98134	10.6743	22.77184	7.82782	9.96268	23.48346	24.19508	8.53944	25.61832	23.48346	30.59966	26.32994	9.96268	6.40458	19.92536	24.19508	15.50094
Silicon	93650.76	98110.32	101295.7	103844	85368.72	121045.2	112126.1	93013.68	149076.7	124867.7	168189.1	128690.2	87279.96	168189.1	73901.28	146528.4	147802.6	182204.9	122319.4	168189.1	78997.92	105755.3	95562	119826.4
Tin	101.6107	101.6107	115.789	115.789	156.7483	162.2621	109.4875	115.789	123.6658	163.0498	137.0563	140.9947	159.899	173.2896	103.1861	187.4678	167.7758	189.8309	175.6526	128.3918	121.3027	148.8715	146.5085	141.1317
Sulphur	1630.035	1790.235	1942.425	1602	2358.945	1914.39	2366.955	1630.035	1758.195	2266.83	2094.615	2158.695	2058.57	2094.615	1241.55	2286.855	2443.05	2170.71	2382.975	1461.825	1878.345	2102.625	2102.625	1988.57
Strontium	350.9199	301.03	341.6184	269.7432	245.2211	245.2211	220.699	293.4197	251.1402	230.8461	208.8607	323.0154	257.0594	236.7652	414.3391	252.8314	265.5153	261.2873	269.7432	203.7872	331.4713	302.7212	275.6623	276.2138
Tantalum	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tellurium	18.3885	23.1855	25.584	21.5865	97.539	92.742	14.391	18.3885	20.787	85.5465	2.3985	21.5865	103.1355	94.341	15.99	99.9375	105.534	119.925	113.529	15.99	18.3885	0	83.9475	52.73224
Titanium	1816	1959.842	2259.512	2559.182	2589.149	2990.707	3230.443	1618.218	4003.591	2960.74	5076.41	2996.7	2085.703	5070.416	1744.079	5711.71	4063.525	4920.581	2906.799	4141.439	2553.188	2481.268	2049.743	3121.258
Vanadium	0	0	0	0	92.42805	0	67.2204	0	0	0	95.2289	0	0	243.674	0	683.4074	0	196.0595	99.71026	0	0	0	0	64.24906
Tungsten	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Yttrium	20.47344	19.686	30.71016	29.92272	43.3092	55.1208	38.58456	27.5604	51.1836	49.60872	55.1208	25.98552	48.03384	70.8696	24.41064	62.9952	51.97104	64.57008	50.39616	66.14496	24.41064	40.15944	45.67152	43.34344
Zinc	62.6652	92.391	80.34	120.51	231.3792	97.2114	274.7628	100.425	200.85	159.8766	183.9786	235.3962	201.6534	215.3112	96.408	206.4738	277.173	245.8404	145.4154	262.7118	196.833	175.1412	103.6386	172.4516
Zirconium	159.9091	142.1414	179.8978	219.1347	406.4357	498.9757	313.1554	171.7542	410.1373	481.208	538.2126	284.2829	383.4858	578.9302	174.7155	673.6912	550.0578	728.4749	502.6773	532.2901	198.4058	355.3536	446.413	388.2496

Appendix 14: Western District Samples

	Western																		
Sample Number	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	Average
Element																			
Aluminium	46997.4	46256.45	43821.9	40646.4	53454.25	41969.53	23392.85	68273.25	39587.9	24345.5	31755	29955.55	36200.7	34612.95	16565.53	44086.53	33607.38	30378.95	38106
Arsenic	2.27217	9.84607	10.60346	0	22.7217	19.69214	0	23.47909	0	0	0	15.90519	5.30173	0	0	0	0	16.66258	7.026896
Barium	0	0	453.1989	0	770.259	738.0156	0	904.6065	0	0	0	459.4685	188.0865	0	0	0	0	526.6422	224.4598
Bismuth	21.52776	29.60067	38.57057	19.73378	36.77659	48.43746	14.35184	42.15853	18.83679	17.9398	17.9398	41.26154	27.80669	16.14582	19.73378	13.45485	62.7893	42.15853	29.40134
Bromine	29	25	39	39	46	48	18	61	24	26	22	44	25	26	18	25	69	41	34.72222
Caclium	193576.7	186362.7	193176	169129.2	133059	197985.3	258102.3	115424.6	218024.3	236861	206802.5	224036	209607.9	207203.3	260106.2	194378.3	189568.9	225238.4	201035.7
Cadmium	8.784	18.4464	41.2848	9.6624	49.1904	45.6768	7.9056	56.2176	14.9328	4.392	7.0272	34.2576	19.3248	10.5408	6.1488	5.2704	66.7584	38.6496	24.6928
Cerium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Chlorine	2820	2480	3060	2580	2860	2810	3150	3120	2310	2250	2370	2860	2730	2620	1680	2500	3350	2750	2683.333
Cobalt	0	0	0	14.15664	0	0	0	0	0	0	0	0.78648	0	0	52.69416	0	0	0	3.757627
Chromium	0	192.9444	7.5262	0	0	22.5786	0	0	0	0	0	0	0	0	0	0	0	0	12.39162
Caesium	0	0	0	0	0	119.4341	0	0	0	0	0	0	0	0	0	0	0	0	6.635225
Copper	65.50652	79.886	71.8974	25.56352	55.9202	165.364	0	63.9088	44.73616	85.47802	34.35098	59.9145	105.4495	19.9715	52.72476	131.8119	121.4267	87.8746	70.65473
Iron	34831.61	40916.66	28396.86	29865.66	51408.11	35391.16	14618.09	58052.69	28256.97	17136.04	22591.59	22661.53	21682.33	25459.25	10001.85	27067.94	25599.14	24410.11	28797.09
Gallium	13.39074	23.06183	22.3179	0	34.96471	29.01327	0	42.40401	13.39074	0	0	16.36646	8.92716	0	13.39074	0	45.37973	19.34218	15.66386
Germanium	2.7768	6.942	9.0246	0	0	11.8014	0	0	0	0	0	0	2.0826	0	4.8594	0	0	0	2.0826
Iodine	11	0	64	0	102	100	19	127	10	5	16	68	34	3	0	10	134	81	43.55556
Potassium	12784.31	10625.92	14278.58	9629.74	15689.84	13531.45	8201.882	20670.74	6931.753	6275.934	7172.496	10210.85	11622.1	7878.124	3013.445	10957.98	10791.95	10957.98	10623.61
Lanthanum	0	0	0	0	0	46.8974	0	0	0	0	0	0	0	0	0	0	0	92.08944	7.721491
Magnesium	16040.86	14472.96	16583.6	21528.53	18995.76	14593.57	0	20985.79	13930.22	15920.26	15437.82	14774.48	15618.74	11759.28	19297.28	14653.87	20623.97	14774.48	15555.08
Manganese	646.6741	836.4168	633.5083	518.1137	991.3088	789.9492	218.3977	1231.391	528.9562	254.7973	353.1538	427.5019	397.298	409.6893	134.756	492.5566	750.4517	478.6163	560.7521
Molybdenum	3.99924	3.3327	15.33042	2.66616	19.9962	16.6635	3.99924	17.33004	3.3327	1.99962	2.66616	12.66426	7.33194	5.99886	1.33308	7.33194	24.66198	11.33118	8.99829
Sodium	83088.32	91248.78	86055.76	160983.6	129825.5	77895.3	109053.4	86797.62	54897.64	114246.4	112020.9	91990.64	78637.16	126116.2	118697.6	99409.24	126116.2	90506.92	102088.2
Niobium	13.9808	13.9808	25.86448	9.08752	39.14624	32.15584	6.29136	45.4376	9.78656	7.68944	9.78656	24.4664	15.37888	12.58272	4.89328	14.67984	41.9424	25.16544	19.57312
Neodymium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Nickel	19.645	39.29	28.2888	0	41.6474	23.574	0	56.5776	0	0	0	11.787	8.6438	0	43.219	0	0	16.5018	16.06524
Phosphorus	3015.662	2448.316	4407.842	2910.921	2378.489	3438.99	4058.706	2478.866	2452.68	4669.694	3840.496	3809.947	5498.892	1606.026	2422.131	4495.126	5018.83	4931.546	3549.064
Lead	100.2586	117.8966	109.5418	90.97536	73.33728	179.1658	81.69216	58.48416	145.7462	197.7322	61.26912	75.19392	194.0189	70.55232	74.2656	100.2586	91.90368	109.5418	107.3241
Praseodymium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Rubidium	91.441	117.0445	90.52659	69.49516	152.7065	117.0445	31.08994	182.882	68.58075	46.63491	64.0087	71.32398	63.09429	67.66634	29.26112	65.83752	91.441	77.72485	83.21131
Antimony	22.55445	20.88375	0	15.87165	120.2904	125.3025	30.90795	137.8328	32.57865	0	31.7433	95.2299	58.4745	0	21.7191	22.55445	139.5035	101.9127	54.29775
Selenium	8.53944	10.6743	0	6.40458	19.21374	22.77184	5.69296	20.63698	5.69296	7.1162	5.69296	19.92536	11.38592	5.69296	9.96268	3.5581	34.15776	19.92536	12.05801
Silicon	128053.1	131875.6	132512.6	110214.8	154810.4	129964.3	71352.96	187301.5	137609.3	82183.32	117859.8	105755.3	129327.2	105118.2	62816.09	125504.8	114674.4	100658.6	118199.6
Tin	118.9397	114.2136	152.0222	100.823	166.9882	168.5635	116.5766	181.9541	124.4534	118.9397	100.823	148.8715	133.9056	104.7614	90.5832	105.5491	174.865	147.2962	131.6738
Sulphur	1830.285	1614.015	2198.745	2090.61	1878.345	1970.46	2194.74	2234.79	1513.89	1618.02	1618.02	2102.625	2378.97	1666.08	841.05	1914.39	2499.12	2354.94	1917.728
Strontium	209.7063	222.3902	209.7063	154.743	195.3313	234.2284	207.1696	163.1989	312.8683	324.7066	300.1845	302.7212	311.1771	309.4859	706.9132	166.5812	273.1256	286.655	271.7163
Tantalum	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tellurium	18.3885	0	84.747	7.995	95.94	94.341	23.985	107.133	23.1855	14.391	24.7845	0	47.1705	15.99	12.792	13.5915	112.7295	86.346	43.52833
Titanium	3464.185	4501.043	3008.687	2816.898	4231.34	3679.948	1438.416	5555.882	3170.509	1666.165	2463.287	2481.268	2655.076	2906.799	463.2898	2828.885	2571.169	2409.347	2906.233
Vanadium	0	0	70.58142	0	174.773	126.0383	0	312.5749	0	0	0	0	0	0	0	0	0	62.17887	41.45258
Tungsten	0	0	0	0	0	0	0	0	0	0	0	0	0	0	15.8594	0	0	0	0.881078
Yttrium	20.47344	26.77296	33.85992	17.32368	53.54592	45.67152	12.59904	55.90824	25.98552	20.47344	27.5604	40.15944	27.5604	29.13528	14.17392	20.47344	56.69568	37.79712	31.45385
Zinc	163.0902	176.748	149.4324	130.9542	124.527	241.8234	102.0318	123.7236	110.0658	179.9616	108.459	175.1412	228.969	62.6652	106.0488	231.3792	187.9956	255.4812	158.8054
Zirconium	219.1347	299.0893	331.6634	193.2235	541.1739	432.3469	71.81104	631.493	333.144	154.7269	225.7976	355.3536	281.3216	262.0733	59.96592	231.7202	527.8482	312.415	303.5723

Appendix 15: Northern District Samples

	Northern															
Sample Number	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	Average
Element																
Aluminium	38476.48	43821.9	75153.5	31172.83	32601.8	43874.83	40752.25	18682.53	31172.83	21540.48	36041.93	30326.03	45197.95	17465.25	47262.03	36902.84
Arsenic	21.96431	0	0	0	27.26604	22.7217	0	0	0	0	19.69214	0	27.26604	0	0	7.927349
Barium	757.7199	34.0347	0	0	728.1635	0	0	0	0	0	667.2593	0	804.2937	0	777.4242	251.2597
Bismuth	53.8194	21.52776	4.48495	14.35184	61.89231	43.05552	40.36455	8.07291	17.04281	13.45485	47.54047	19.73378	59.20134	31.39465	45.74649	32.11224
Bromine	52	32	12	29	112	59	46	82	35	17	52	27	75	35	52	47.8
Caclium	195580.6	184759.6	130654.3	217623.5	208004.8	181954.1	183156.5	236059.4	213215	261308.6	212012.6	218024.3	173938.5	287359.3	110214.5	200924.4
Cadmium	53.5824	10.5408	0	3.5136	57.096	48.312	55.3392	11.4192	9.6624	7.0272	46.5552	12.2976	54.4608	27.2304	54.4608	30.09984
Cerium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Chlorine	2720	2870	4230	2230	3280	2790	2960	2640	2350	1990	2890	2370	4290	2680	3010	2886.667
Cobalt	0	0	0	0	0	0	0	0	0	0	0	0	0	0	64.49136	4.299424
Chromium	0	0	87.5776	0	2.0526	94.4196	51.9992	0	0	0	0	0	35.5784	0	10.263	18.79269
Caesium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Copper	136.6051	31.9544	5.59202	0	84.67916	229.2728	0	0	18.37378	9.58632	48.73046	0.79886	177.3469	36.74756	43.9373	54.90831
Iron	34062.24	37909.11	24200.28	19234.33	31124.64	36300.42	31894.01	13149.28	23500.85	13708.83	29376.06	23990.45	37769.22	9861.963	44693.58	27385.02
Gallium	31.24506	17.11039	2.97572	0	36.45257	33.47685	0	0	0	0	23.80576	0	40.91615	6.69537	29.7572	14.829
Germanium	13.884	4.1652	0	0	18.7434	0	0	0	0	0	9.7188	0	19.4376	0	0	4.3966
Iodine	116	10	0	10	134	91	108	14	0	7	105	15	130	79	114	62.2
Potassium	14361.6	12120.19	23161.19	9463.71	13531.45	13365.42	13863.51	6350.648	7072.878	6857.039	10044.82	8550.545	17848.23	7106.084	15025.72	11914.87
Lanthanum	0	0	0	0	498.8178	0	0	0	0	0	254.0986	0	0	0	0	50.19443
Magnesium	15558.43	16040.86	0	16945.42	14834.78	16101.17	18694.24	15196.61	10553.2	6030.4	14231.74	13206.58	16583.6	0	16161.47	12675.9
Manganese	655.1932	480.9397	324.4987	171.1557	591.6874	875.1398	476.2929	168.0578	406.5915	145.5985	593.2364	361.6728	983.5642	133.2071	944.8412	487.4451
Molybdenum	20.66274	2.66616	17.33004	0.66654	21.32928	15.99696	16.6635	0	3.3327	3.99924	19.9962	5.99886	23.99544	5.33232	23.3289	12.08659
Sodium	93474.36	83830.18	0	117213.9	79379.02	79379.02	105344.1	153565	121665	83088.32	86797.62	109053.4	75669.72	80120.88	189916.2	97233.12
Niobium	37.74816	15.37888	34.25296	8.38848	39.14624	33.55392	34.952	6.29136	11.18464	7.68944	35.65104	13.9808	50.33088	12.58272	46.83568	25.86448
Neodymium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Nickel	34.5752	0	0	0	38.5042	45.5764	0	0	0	0	18.8592	0	49.5054	0	0	12.46803
Phosphorus	2976.384	2683.983	4626.052	2321.754	3709.57	5542.534	2675.255	3041.847	3046.212	4756.978	3308.064	3478.267	4451.484	3962.694	2710.168	3552.75
Lead	70.55232	64.05408	55.6992	49.20096	73.33728	107.6851	28.77792	62.19744	77.05056	124.3949	97.4736	64.9824	68.69568	35.27616	67.76736	69.80966
Praseodymium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Rubidium	110.6436	104.2427	76.81044	50.29255	95.09864	106.986	109.7292	31.08994	60.35106	37.49081	85.95454	62.17988	123.4454	35.66199	143.5624	82.23594
Antimony	137.8328	27.56655	0	0	131.15	108.5955	120.2904	17.54235	0	0	117.7844	0	140.3388	85.2057	112.7723	66.60524
Selenium	27.75318	7.82782	1.42324	4.98134	33.44614	21.3486	22.77184	2.13486	5.69296	5.69296	25.61832	6.40458	32.73452	15.65564	19.21374	15.51332
Silicon	124867.7	143980.1	282863.5	100658.6	125504.8	145891.3	133149.7	61796.76	105118.2	86642.88	115948.6	105118.2	154173.4	63070.92	155447.5	126948.8
Tin	175.6526	107.1245	81.13104	101.6107	171.7142	170.9266	163.8374	100.823	100.0354	111.0629	156.7483	114.2136	193.7693	126.8165	166.9882	136.1636
Sulphur	1994.49	1718.145	2346.93	1686.105	2803.5	2182.725	1706.13	2843.55	2026.53	1565.955	2098.62	1630.035	2354.94	2010.51	1902.375	2058.036
Strontium	317.0963	284.1182	103.162	171.6548	220.699	258.7505	388.1258	289.1918	276.5079	377.1331	271.4344	317.9418	209.7063	454.0818	259.5961	279.9467
Tantalum	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tellurium	115.128	11.193	35.178	20.787	120.7245	94.341	103.1355	19.188	14.391	0	99.9375	0	127.1205	76.752	110.331	63.2138
Titanium	3440.212	3679.948	1804.013	1798.02	2888.819	4453.096	3086.601	1288.581	2505.241	1402.456	3374.284	2643.089	4824.687	1096.792	4740.779	2868.441
Vanadium	82.90516	16.8051	0	0	146.7645	0	0	0	0	0	124.9179	0	164.69	0	229.1095	51.01281
Tungsten	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Yttrium	50.39616	22.04832	25.19808	11.8116	44.88408	59.058	37.79712	8.66184	27.5604	18.89856	51.97104	26.77296	51.97104	23.6232	60.63288	34.75235
Zinc	232.986	107.6556	59.4516	49.8108	498.9114	447.4938	106.0488	36.9564	93.9978	167.1072	130.9542	90.7842	359.1198	110.8692	110.0658	173.4808
Zirconium	513.7821	259.8523	404.2147	133.9979	460.479	520.445	402.7341	102.9045	236.9024	119.9318	501.1966	265.0346	594.477	142.1414	680.3541	355.8965

Appendix 16: Gozo and Comino District

Gozo& Comino

Sample Number	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	Average
Element																
Aluminium	18417.9	44880.4	30378.95	32019.63	23657.48	14713.15	34718.8	32548.88	45833.05	29108.75	31543.3	45092.1	35724.38	31860.85	25562.78	31737.36
Arsenic	0	18.93475	0	0	0	0	0	0	0	0	16.66258	12.11824	0	15.1478	0	4.190891
Barium	0	846.3893	0	0	0	0	0	0	0	0	369.0078	0	0	388.7121	0	106.9406
Bismuth	41.26154	60.09833	16.14582	18.83679	23.32174	23.32174	42.15853	21.52776	13.45485	17.04281	41.26154	31.39465	17.9398	39.46756	15.24883	28.16549
Bromine	44	49	17	19	39	24	52	30	29	37	45	43	22	40	22	34.13333
Calcium	199187.7	181954.1	214417.3	210008.7	262110.1	323429.5	215619.6	237662.5	146284.7	223635.2	220829.8	175140.9	195580.6	217222.8	224837.6	216528.1
Cadmium	27.2304	61.488	7.0272	7.9056	5.2704	7.0272	57.9744	12.2976	17.568	7.0272	42.1632	34.2576	9.6624	42.1632	1.7568	22.72128
Cerium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Chlorine	3580	2970	2440	2410	4630	1850	2860	2230	3050	2500	2720	2860	2540	2860	2390	2792.667
Cobalt	0	0	0	45.61584	43.2564	41.68344	0	0	0	0	0	0	50.33472	29.88624	26.74032	15.83446
Chromium	134.7874	0	0	0	0	0	0	0	0	0	0	0	0	0	0	8.985827
Caesium	0	0	0	0	0	0	0	0	0	0	0	0	0	82.16385	0	5.47759
Copper	93.46662	130.2142	0	0	24.76466	25.56352	103.8518	47.13274	13.58062	0	67.10424	24.76466	0	26.36238	37.54642	39.62346
Iron	29585.89	39377.91	22451.7	35810.82	15667.23	12100.14	31684.18	27837.31	37069.79	23151.13	24759.82	37559.39	27207.83	30984.75	19024.5	27618.16
Gallium	12.64681	40.91615	0	0	8.92716	7.4393	0	0	7.4393	0	17.85432	13.39074	0	14.8786	0	8.232825
Germanium	0	0	0	0	3.471	0	0	0	0	0	0	0	0	0	0	0.2314
Iodine	0	143	12	10	9	15	98	10	0	8	84	52	11	69	6	35.13333
Potassium	9214.665	17101.09	9463.71	10625.92	7878.124	5429.181	11622.1	10376.88	11871.15	10044.82	10791.95	13863.51	11290.04	10791.95	10293.86	10710.6
Lanthanum	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Magnesium	0	17849.98	18814.85	14895.09	12784.45	20503.36	16704.21	15015.7	24423.12	16101.17	17669.07	22975.82	19659.1	18392.72	18935.46	16981.61
Manganese	535.1519	591.6874	189.7427	301.2649	171.1557	149.4708	624.9892	359.3494	421.3062	363.9962	464.676	556.8367	264.0909	394.2001	232.338	374.6837
Molybdenum	0	22.66236	1.33308	4.66578	1.99962	3.3327	17.99658	0	5.33232	1.99962	11.99772	13.3308	2.66616	11.99772	2.66616	6.798708
Sodium	200302.2	92732.5	116472	109053.4	61500.19	0	101634.8	61648.57	143179	108311.6	93474.36	97183.66	111279	96441.8	112762.7	100398.4
Niobium	16.77696	39.84528	6.9904	13.28176	5.59232	5.59232	32.15584	9.08752	16.07792	8.38848	23.76736	27.9616	9.08752	23.76736	6.29136	16.31093
Neodymium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Nickel	0	60.5066	0	0	13.3586	0	0	0	0	0	0	11.787	0	0	0	5.710147
Phosphorus	5324.324	4931.546	3622.286	2788.724	3260.057	3543.73	2653.434	3308.064	3107.31	3809.947	5848.028	4495.126	3836.132	3434.625	5411.608	3958.329
Lead	182.879	49.20096	42.70272	61.26912	35.27616	50.12928	132.7498	63.12576	56.62752	39.91776	37.1328	37.1328	52.91424	46.416	46.416	62.25933
Praseodymium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Rubidium	92.35541	128.0174	63.09429	84.12572	46.63491	36.5764	82.2969	72.23839	97.84187	60.35106	75.89603	103.3283	71.32398	74.98162	51.20696	76.01795
Antimony	0	152.8691	29.23725	40.93215	31.7433	31.7433	0	0	0	0	0	0	20.88375	0	0	20.49392
Selenium	14.94402	0	4.98134	5.69296	9.25106	9.96268	23.48346	7.82782	4.26972	5.69296	21.3486	13.52078	4.98134	19.21374	6.40458	10.105
Silicon	73264.2	127416	99384.48	103207	86005.8	57783.16	96836.16	105755.3	142705.9	93650.76	100658.6	134423.9	119771	100658.6	90465.36	102132.4
Tin	133.9056	184.3171	101.6107	113.4259	101.6107	109.4875	155.9606	111.0629	107.1245	100.0354	140.9947	126.8165	104.7614	144.1454	96.88464	122.1429
Sulphur	2631.285	2174.715	1650.06	1401.75	5607	1373.715	1878.345	1638.045	2018.52	2066.58	2310.885	2250.81	1754.19	2130.66	2394.99	2218.77
Strontium	397.4273	302.7212	533.5673	372.0596	766.1045	677.3176	239.302	379.6699	273.9712	328.9345	309.4859	349.2287	576.6924	484.5231	517.5011	433.9004
Tantalum	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tellurium	23.985	143.91	23.1855	22.386	19.9875	21.5865	91.143	23.985	7.1955	11.9925	79.95	63.96	21.5865	74.3535	15.99	43.0131
Titanium	2876.832	3272.396	1863.947	2517.228	1288.581	1120.766	2679.05	2175.604	4153.426	2139.644	1941.862	3356.304	2253.518	2061.73	1702.126	2360.201
Vanadium	0	161.329	0	0	0	0	0	0	0	0	0	0	0	0	0	10.75526
Tungsten	0	0	0	0	0	2.37891	0	0	0	0	0	0	0	0	0	0.158594
Yttrium	31.4976	44.88408	21.26088	26.77296	17.32368	29.13528	40.94688	24.41064	22.04832	22.04832	36.22224	44.88408	20.47344	39.372	22.04832	29.55525
Zinc	264.3186	326.1804	77.1264	81.1434	72.306	67.4856	147.8256	101.2284	95.6046	104.442	179.9616	119.7066	85.1604	87.5706	111.6726	128.1155
Zirconium	191.0026	380.5245	118.4512	167.3123	92.54	88.09808	373.8616	177.6768	269.4765	170.2736	300.5699	325.7408	139.1802	287.9845	99.9432	212.1757

Appendix 17: Example of XRF graph with a chromium peak but a 0 ppm value