THE GEOCHEMICAL BEHAVIOUR OF SELECTED CHALCOPHILE TRACE ELEMENTS IN SOILS FROM THE BLOEMFONTEIN REGION, SOUTH AFRICA

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In accordance with the requirements for the

M.Sc. degree

In the Department of Geology,

Faculty of Natural and Agricultural Sciences,

University of the Free State

February 2013

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Declaration:

I declare that the dissertation/thesis hereby handed in for the qualification of Master of Science in Geology at the University of the Free State, is my own independent work and that I have not previously submitted the same work for a qualification at/in another University/faculty.

John Herbert Attlee Clark June 2013

Motivational quote

“*It must be a strange world not being a scientist, going through life not knowing – or maybe not caring – about where the air came from, and where the stars at night come from, or how far they are from us. I want to know”*

Michio Kaku

Abstract

An early study was done on heavy metal contamination in the soils across the eastern portion of the city of Bloemfontein. One hundred and forty seven samples were collected for the study: there were 22 dust samples, 4 soil profiles, 112 urban soil samples and 9 background samples taken 10 km north, south, east and west of the power station.

Contamination was believed to be caused by the coal-burning power station found in Bloemfontein. Heavy metal/metalloids that were under investigation in the study area were the following: antimony, arsenic, bismuth, cadmium, mercury and selenium. Initial results from an earlier study indicated that there was no major issue with the metals/metalloids in the area and the project was abandoned. This is an update to that research.

The research indicates that there is a possible contamination of the soils with the heavy metals/metalloids. The ranges of concentrations for the different studied elements are as follows: antimony has a range of 3.44 ppm to 21.13, arsenic has a range of 1.33 ppm to 14.59 ppm, bismuth has a range of 0.12 ppm to 6.86 ppm, cadmium has a range of 0.11 ppm to 21.15, mercury has a range 0.06 ppm to 2.14 ppm, and selenium has a range 0.24 ppm to 1.22 ppm.

By comparing these concentrations to background levels found on Earth and comparing them to other areas that have been confirmed to have high amounts of contamination, it can be concluded that elements such as antimony, cadmium and mercury contain high enough concentrations to be considered contaminated. Arsenic and bismuth can be concluded to having very little to no contamination in the study area. Selenium concentrations indicate that there is a deficiency of the element in the area which may lead to other possible problems to the local population.

The possible sources for the contamination of the elements in the soils were blamed on the release of ash from the power station that may contain trace amounts of the elements. But because the highest concentration levels are found in the industrial areas of the study area, it can be concluded that the power station is a possible source for contamination but it can also be concluded that the industrial area is also a major source for the contamination.

Acknowledgements

For the completion of this thesis I would like to thank the following people and institutions for their assistance with this project:

Prof. Marian Tredoux and Prof. Cornie van Huyssteen for their constant help with making this thesis a possibility, guiding me through the entire duration of the project and for giving me so much more interest in the fields of environmental studies, geochemistry and soil sciences;

Inkaba yeAfrika and the National Research Fund (NRF) for the funding of this project and the chance to attend amazing international conferences;

A special thank you for Mr. Robert Kriger who fought tirelessly for me and my fellow Inkaba colleagues to obtain funding during the duration of our projects;

Mrs Bernice and Mr Attlee Clark for being the best parents a child could ever wish for, supporting me through thick and thin and giving me everything to make and have a successful varsity career;

Dr Thinus Cloete for organizing this project and going the extra mile to make sure I had all the samples and background information for this project to be a success;

Dr Freddie Roelofse for proof reading my thesis, obtaining climate information for my project, help with XRD work and for constant support with my project;

Mrs Huibrie Pretorius for helping me analyze XRD work and constant support through my project;

Prof. Willem van der Westhuizen for help with analyzing samples on the XRF machine;

Dr Charles Barker with help obtaining good quality GIS Maps for this study;

Mrs Rina Immelman and Mrs Petro Swart for sorting out all my admin work with a gracious smile every time;

Mr Andries Felix for helping me to obtain articles and willing to help me with any troubles I had;

Mr Jonas Choane for all the help he gave me with preparation work for XRD and XRF analysis;

Mrs Yvonne Dessels from the Soil Science Department for her constant help with all soil chemistry and analysis work;

Miss Louise Le Roux for all her help and keeping me company while doing all my soil chemistry experiments;

Mr Brenton Mabuza for helping me to take soil samples in the correct method;

For all my golfing friends in Newcastle; Mr Malcolm Gage, Mr Bernard Denny, Mr Filipe De Gouveia, Dr Quintin Hanson, Mr José Branco and Mr Mark Mckillop for always supporting me in doing my M.Sc. and for always chirping me that I should be writing up my thesis instead of being on the golf course because when I finish I'll have plenty of time to play golf;

To my fellow M.Sc. students: Miss Bianca Kennedy, Miss Megan Purchase and Miss Nequita Macdonald, thank for the support in the "dungeons" and keeping each other sane through the good times and the bad times. Good luck with the completion of your projects;

A special thank you to Miss Marike du Plessis for being the best friend anyone could ever ask for especially through the really tough times during the duration of this project. We're definitely going to run another Two Oceans half marathon in the near future;

Mr. Zander Fourie for all the support and lots of coffee every day during this project;

Finally to all my other friends especially to Dolf de Beer, Renier Koen and all who supported me through the entire duration of this project, thank you very much. All the support means a lot from all you guys. May all of you be a major success in the future!

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Chapter 1 Introduction

Over the last few decades, industrialization has increased by a significant margin as technologies have improved, but industrialization has caused a negative effect on the planet by causing heavy metal pollution on the environment (Ungaro et al., 2008). Technological advancement has caused a major influence on the natural environment due to an increase in pollution especially air pollution. Since a time when humans were becoming more civilized and were able to use simple stone tools and make fire for their own use, early pollution of the environment began as humans became increasingly dependent on products and artifacts produced from minerals. Evidence shows that early civilizations were already using metals. The burning of wood especially in caves contaminated the local environment with trace amounts of different elements (Wilson, 1998; Nriagu, 1996; Plant et al., 2003). As time progressed humans have been depending more on minerals than ever before. Human activities such as industrial and mining activities have caused a major disturbance in the natural distribution of metals in the environment. This has caused a potential increase of the metals in certain local regions causing contamination to the local environment (Nriagu, 1996; Ryan et al., 2000). Because of the massive population growth over the last few centuries and of economic development; pollution and land degradation has increased at a significant pace all over the world causing damage to the environment which must be slowed down significantly or stopped if at all possible. If this does not occur the consequences will lead to a possible global ecological disaster (Plant et al., 2001).

Environmental toxicology is a relatively new science that aims to aid with environmental problems by studying how toxic substances affect human health and the environment and ways on how to stop or slow down these processes from causing future damage (Duffus, 1980; Wright and Welbourn, 2002). Because of impractical methods by humans to dispose of hazardous material, contamination of the land, air and groundwater can develop. This results in humans, animals, aquatic and plant life being exposed to the hazardous materials. It can be extremely expensive to clean up contaminated areas, therefore certain areas don’t get restored properly which leads to a certain amount of residual contamination. This local contamination can lead to negative effects upon the local environment causing cancers and neurological disorders to the local human population. A risk assessment must be conducted to measure the potential harm the contaminated area has on the local environment (Watts and Teel, 2003).

Siderophile and the so-called “heavy metals” and metalloid type elements are of significant interest to human beings for many different reasons such as for their beauty (gold, silver), health reasons and their benefit in technological advances. But these elements can have a specific impact on the environment which can be detrimental to living organisms.

Heavy metals are defined as elements on the Periodic Table containing an atomic number of 21 and higher (e.g. mercury, cadmium) and having a density which is greater than 5 g/cm^3 (Duffus, 1980). The heavy metals are mostly associated with elements found in the transition elements section on the Periodic Table. An example of a heavy metal found in the transition elements group of the Periodic Table is cadmium. It forms part of a subset of trace elements that contain low concentrations in the crust of the Earth (Callender, 2003). Metalloids are defined as elements that can develop different chemical properties. The properties that develop cause the elements to show metallic as well as nonmetallic properties. The different states depend on different physico-chemical conditions. Changes in physical or chemical conditions can cause the element to form either an anion or a cation (e.g. arsenic, selenium, antimony) (Eby, 2004). During the 20th century many heavy metals such as cadmium, copper, nickel and lead were mined extensively for industrial uses (Callender, 2003).

There are 4 main sources found at the Earth’s surface – the hydrosphere, atmosphere, geosphere and the biosphere. The interaction between all the reservoirs determines the movement and the precipitation of metals/metalloids in an environment. Metals/metalloids are predominantly found in the geosphere but can be found temporarily in small concentrations in the other reservoirs through different chemical processes. Through natural or anthropogenic activities, parts of the Earth can become enriched with toxic metals/metalloids which can cause a detrimental effect to the local environment and to human health. Contamination of different environments is becoming more and more of a global problem (Siegel, 2002) and South Africa is no exception.

In nature, metals/metalloids are transported by geological activity such as volcanic processes, magmatic fluids and chemical weathering (Callender, 2003). As rocks break down, metals/metalloids can be released into the overlying soils through chemical weathering. Metals/metalloids can be deposited into surrounding water bodies through oxidation-reduction processes, and depending on the metal/metalloid, can move around in the atmosphere. If a metal such as mercury finds its way into the atmosphere, it can be spread far away from its original source and deposited somewhere else through wind and precipitation processes. The hydrosphere can transport or deposit metals/metalloids through many different oxidation-reduction processes and Eh-pH conditions, etc. (Siegel, 2002; Plumlee and Ziegler, 2003; Eby, 2004). Anthropogenic processes that release metals/metalloids into the environment are from industrial, smelting and mining activities, mineral processing techniques, construction processes, energy generation, release of emissions from smelters and from industrial effluent disposal and solid waste disposal. Buildings that collapse may release dusts into the environment that can lead to a health hazard in the local human population (Figure 1.1) (Siegel, 2002; Plumlee and Ziegler, 2003).

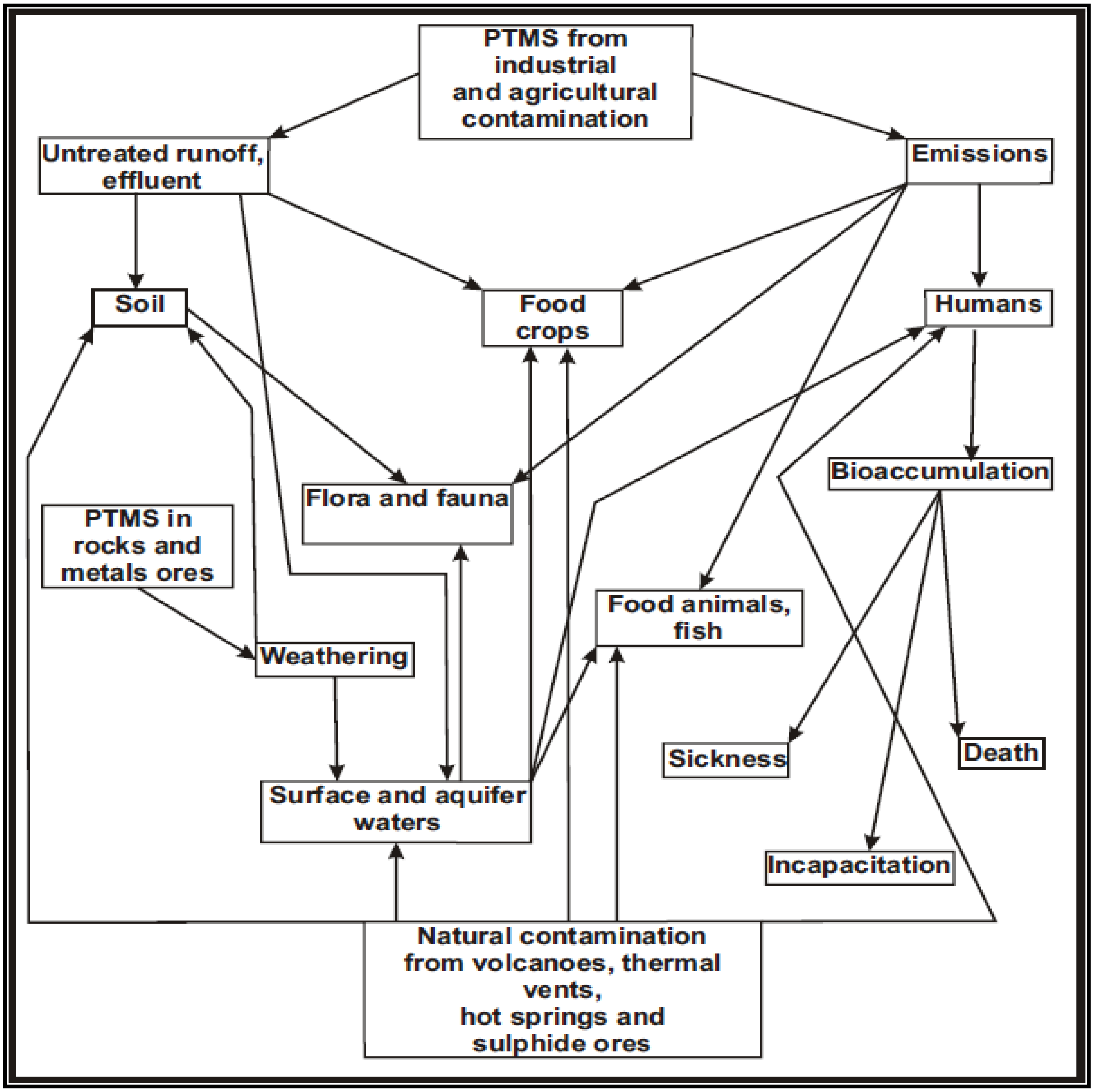


Figure 1.1 Anthropogenic and natural sources that may cause potential toxic metal pathways on the Earth (PTMS – pathway of toxic metal sources) (modified after Siegel, 2002).

This study was based in Bloemfontein, South Africa (Figure 3.1) around a coal-generated power station to obtain information of different metals/metalloids found in the soils surrounding the local area around the power station.

The aims of this study are to:

1. Determine the concentrations of the heavy metals in the samples taken for the study
2. Determine if the different elements are co-related.
3. Determine factors governing the spacial distribution of antimony, arsenic, bismuth, cadmium, mercury, and selenium around the Bloemfontein power station.
4. To investigate possible sources
5. Suggest action on areas that are identified as contaminated

Figure 1.2 Study area in Bloemfontein. The area shaded in blue is the sampling area with a total area of roughly 47 km^2. The points with numbers indicate the different sampling positions and the stars indicate the power station and sewage works, respectively.

Chapter 2 Literature study

2.1 Introduction

There are 6 heavy metal/metalloid elements in this study which are of considerable interest: the different elements that are under investigation are antimony, arsenic, bismuth, cadmium, mercury and selenium. There will be a discussion on each element describing chemical properties, the natural and anthropogenic sources of the element and their toxicity to humans. The elements will be discussed as follows: antimony, arsenic, cadmium, mercury and finally selenium. Bismuth will not be discussed here as there is little information compared to the other elements of interest, but all the elements will be commented on in the results, discussion and conclusion chapters. The elements under discussion all have negative impacts on human, animal and plant life if they occur in the environment at toxic levels. Because these elements can cause chronic or acute diseases to humans, these specific elements must be studied to prevent possible disasters in the future.

2.2 The Elements

2.2.1 Antimony

2.2.1.1 Chemical properties

Antimony is commonly referred to as a heavy metal but is chemically a non-metal and is defined as a metalloid element. It is the 63rd most abundant element found in the Earth's crust. Antimony and arsenic contain very similar chemical properties but antimony has a lower abundance in the crust by 1 order of magnitude compared to arsenic (Hamilton and Hardy, 1974; Gebel, 2000) but Reimann et al., (2010) concluded that antimony can also be chemically different from that of arsenic. Antimony and arsenic both show very similar oxidation states ranging between –III and V in environmental systems (Wilson et al., 2010), but antimony is mostly found in Sb (III) and Sb (V) states (Filella et al., 2002b). Table 2.1 gives the basic chemical properties of antimony.

2.2.1.2 General background

Antimony is a group 15 chalcophilic metalloid type element on the Periodic Table found below arsenic. It can form oxyanions in water bodies and because of this property it exhibits similar properties to arsenic (See sub-chapter 2.2.2) (Wilson et al., 2004a). It is found in trace amounts in the environment (Wilson et al., 2010) and because of its low concentrations, especially in natural waters (<1 µg/L), it is mostly an overlooked element in environmental issues (Filella et al., 2002a, 2007; Flynn et al., 2003). It is mostly an overlooked element for study purposes because it is difficult and expensive to analyze because antimony normally occurs at extremely low concentrations (Reimann et al., 2010). Compared to other toxic elements, antimony is the least studied and its potential toxicity in humans and animals physiologically is poorly understood (Shtangeeva et al., 2011).

There are nearly 200 different mineral species of antimony on Earth especially in sulfide forms. The main minerals bearing antimony, found in the environment are the sulphide minerals such as stibnite (Sb_2S_3). It is the ninth most mined metal or metalloid in the world and due to anthropogenic activities, it has caused much interest in the element (Roper et al., 2012). If a mineralizing solution is sulfur-deficient but contains a high concentration of antimony, antimony bearing oxide or silicate minerals can be produced (Roper et al., 2012). Lead, copper and silver ores are commonly associated with antimony minerals and it is also a common trace element in coal and petroleum bodies (Filella et al., 2002b). The concentration of antimony found in mesothermal gold deposits can be high enough to mine as a secondary ore (Wilson et al., 2004b) Table 2.1 gives general concentrations of antimony found in the crust, different rock types and world soils.

Table 2.1 The basic chemical properties and concentrations of antimony found on Earth. Wilson et al., 2004a[1], Filella et al., 2002a[2]; b[3]; Wilson et al., 2010[4], Rudnick and Gao, 2003[5], Koljonen, (1992)[6]*; Tauber (1998)[7*] Reimann et al., 2010[8], Sh and Liu, 2011[9]. * As cited in Reimann et al., 2010.

Chemical property		Crust/ Rock type/ Soil	
Geochemical classification	Chalcophilic Metalloid element[1]	Bulk continental crust	0.4 ppm[5]
Symbol	Sb	Mafic rocks	
		Ultra mafic	0.1 ppm[6]
		Mafic	0.2 ppm[6]
Periodic Table position	Group 15, Row 5	Felsic rocks	
		Granite	0.3 ppm[6]
Oxidation states	-III; 0; III; V[2, 3, 4]	Sedimentary rocks	
		Shale	1 – 2 ppm[6]
		Sandstone	0.05 ppm[3]
		Carbonates	0.15 ppm[3]
		Deep sea clays	1 ppm[3]
		Coal	2 ppm[7]
Atomic mass	121.76 amu	World soils	0.5 ppm[8] 1 ppm[9]

2.2.1.3 Natural sources

Antimony is found in soils from the natural breakdown of parent material rocks containing antimony, from soil forming processes and soil run-off (Smichowski, 2008; Reimann et al., 2010; Wilson et al, 2010). Antimony is released into the atmosphere from volcanic activity and it contributes approximately 3 – 5% of all global emissions into the environment. Other natural sources of antimony such as rock weathering and soil run-off have been identified (Smichowski, 2008). In mineralized zones, it is possible to find high concentrations of antimony present in the ore body (Tighe et al., 2005). Antimony can be found in geothermal fluids where it can be precipitated into the sulphide mineral stibnite. An example of antimony precipitation found in geothermal fluids occurs in New Zealand where it poses a major problem because the fluids are used in power stations for power production (Wilson et al., 2007).

2.2.1.4 Anthropogenic sources

In human history antimony has been used by many different civilizations as far back as 4000 BC (Smichowski, 2008). Evidence from a Swiss bog indicates anthropogenic activities occurred in Roman times dating as far back as 2000 years (Filella et al., 2002b). Anthropogenic activities from before the 18th century were from purifying precious metals such as gold from silver and copper ores. In the 20th century, anthropogenic activities included the use of antimony trioxides. These compounds were used as white pigments in paint (He et al., 2012).

Recent anthropogenic activities that release antimony into the environment which can pose a serious problem are from mining activities, chemical plants, coal combustion, pigments and semi-conductors. The main source of contamination of the environment from anthropogenic sources is from smelting plants (Filella et al., 2002b; Flynn et al., 2003; Tighe et al., 2005; Wilson et al., 2004a; Okkenhaug et al., 2011; Sh and Lui, 2011; Sh et al., 2012; Wu et al., 2011). An additional use for antimony in present times is in consumer products such as fire retardant materials and in brake pads of cars (Filella et al., 2002b).

Antimony is commonly enriched in coal deposits and through combustion for energy generation. It is vaporized and distributed into the surrounding regions around the power station (Miravet et al., 2006). There are still large amounts of coal reserves on Earth that will be consumed in the future because oil and gas prices are more expensive than coal. This poses a serious threat to the environment especially in China because high concentrations of antimony will be released into the environment from coal combustion (Tian et al., 2011). Soils can become contaminated with antimony when mining material is mixed into agricultural and residential soils. An example of soil contamination can be seen in Stahlberg, Germany (Hammel et al., 2000). Mines were in use for long periods of time and when they were closed, there were high concentrations of antimony in the mine dumps. Some of the mine dumps have now been reused for agricultural and residential purposes leading to a possible health hazard.

Areas downstream from abandoned antimony mines can contain enriched amounts of antimony at toxic levels that can affect aquatic life and possibly human populations. When the soils become highly contaminated the area has to be rehabilitated (Wilson et al., 2004b). Shooting ranges can have a major influence in the contamination of an area with antimony especially causing a serious potential risk for the contamination of groundwater in the surrounding areas (Wilson et al., 2010; Shtangeeva et al., 2011).

2.2.1.5 Toxicity

Because arsenic and antimony are found in the same group on the Periodic Table, they contain similar chemical and toxicological properties and, like arsenic, antimony is a possible carcinogenic metalloid (Gebel, 1997). Antimony is non-essential to living organisms and is potentially toxic to human health and living organisms (Sh et al., 2012).

Most trees and plants have difficulty taking up antimony but certain plant species can be used to identify possible antimony mineralization in an area (Reimann et al., 2010). Plants can accumulate antimony over time to toxic levels which can pose a threat to humans who eat the edible parts of the plants that contain the toxic levels (Hammel et al., 2000). It can be concluded that plants presently show indications of major toxicity to antimony greater than previous studies have shown (Shtangeeva et al., 2011).

There is little knowledge on the effects antimony has on human health and what is known is poorly understood (Shtangeeva et al., 2011), but what is known, is that it is most toxic in its natural elemental state opposed to any of its salts. The most toxic salt is in the Sb (III) state which is possibly carcinogenic (Gebel, 1997) and this is 10 times more toxic than in its Sb (V) state (Krachler et al., 2001; Smichowski, 2008). Sb (III) is easily taken up in red blood cells and sulfhydryl groups of cell constituents (Krachler et al., 2001) and exposure to acute concentrations of antimony through inhalation causes effects to the eyes and skin of humans (Qi et al., 2008).

2.2.2 Arsenic

2.2.2.1 Chemical properties

Arsenic is geochemically a chalcophilic element and is classified as a metalloid type element (Davies et al., 2005; Plant et al., 2003). Table 2.2 gives the basic physical and chemical properties of arsenic. In any environment it is rare for arsenic to be found in its native state because it has an affinity to bond easily with other elements and species. An exception to find arsenic in its native state will be in hydrothermal ores. When arsenic is found in an oxidizing environment it is in the As (V) state. Under a reducing environment arsenic is found in the As (III) state (Eby, 2004).

2.2.2.2 General background

Arsenic is a group 15 chalcophilic element and lies above antimony on the Periodic Table (Davies et al, 2005). It is ranked 20th most abundant element found in the Earth's crust (Mandal and Suzulki, 2002). Arsenic is found as a major constituent in well over 200 minerals. The types of minerals arsenic is mostly associated with are either ore type minerals or alteration product type minerals. The most common minerals containing arsenic are the sulphide minerals such as arsenopyrite (FeAsS), realgar (As_4S_4) and orpiment (As_2S_3).

Arsenic is odorless and tasteless and is known as the 'king of poisons' because it is highly toxic and was commonly used to poison humans and is ranked first in international hazardous substance lists (Dani, 2010; Camacho et al., 2011). People that suffer from arsenic poisoning are predominantly poisoned by contaminated drinking water (Gebel, 2000). The accumulation of arsenic in soil from natural or anthropogenic sources leads to the contamination of surface waters and groundwaters (Morin and Calas, 2006). On a global scale many countries have recorded cases of poisoning by arsenic from industrial processes, contamination of groundwater, and food and beverage contamination (Mandal and Suzuki, 2002). Table 2.2 gives the average concentrations of arsenic found in rocks and soil. Figure 2.1 and Figure 2.2 are examples of the arsenic cycle.

During reducing conditions and the addition of sulfur in the environment, arsenic will be incorporated into sulfide minerals. Arsenic can commonly bond with oxygen in the environment (O'Day, 2006). The different oxidation states produce different chemical forms: As (-III) produces arsine (H_3As), As (-I) produces arsenopyrite (FeAsS), As (0) forms elemental arsenic, As (III) forms arsenite ($H_2AsO_3^-$) and As (V) precipitates arsenate (AsO_4^{3-}) (Figure 2.2) (Plant et al., 2003; O'Day, 2006).

Besides native arsenic being the most rare form of arsenic to find, the gaseous arsine [As (-III)] form is rare to find and will only be found under extremely reducing conditions. Under oxidizing conditions, arsenate [As (V)] is the most prevalent type form and under anaerobic conditions, arsenite [As (III)] is the most dominant form to be found. Arsenic compounds can be soluble and dissolve in water causing a major problem to humans and animals that consume the water (Wang and Mulligan, 2006).

Table 2.2 The basic chemical properties and concentrations of arsenic found on Earth. Browning, 1969; Plant et al., 2003; Davies et al, 2005[1], Plant et al., 2003[2], Eby, 2004[3], O'Day, 2006[4], Garret, 2005[5]; Ng et al., 2003[6]; Lievremont et al., 2009[7]; Smedley and Kinniburgh, 2002[8]; Vaughan, 2006[9], Rudnik and Gao, 2003[10], Browning, 1969.

Physical and chemical properties		Crust/ Rock types and soils	Average concentration	Concentration range
Geochemical classification	Chalcophilic metalloid[1]	Crust	1.5 ppm[5, 6, 7, 8, 9]	
Symbol	As	Crust	Max – 4.8 ppm[10]	
Periodic Table position	Group 15, Row 4[2]	Mafic rocks Basalt	2.3 ppm[8]	0.18 – 113 ppm[8]
Atomic mass	74.9216 amu[2]	Felsic rocks Granite	1.3 ppm[8]	0.2–15 ppm[8]
Oxidation states	-III; -I; 0; III; V[2, 3, 4]	Sedimentary rocks Sandstone Coal	4.1 ppm[8] <5 ppm[6]	0.6 – 120 ppm[8] 0.3 – 35.000 ppm[9]
Electronegativity	2.18[2]	Soil	7.2 ppm[8]	15 – 600 ppm[11] 0.1 – 55 ppm[8]
Density	5.727[2]			
Melting point Boiling point	817ºC at high pressure 614ºC[2]			
Neutral configuration	[As] $3d^{10}4s^2 4p_x^1 4p_y^1 4p_z^1$ [4]			

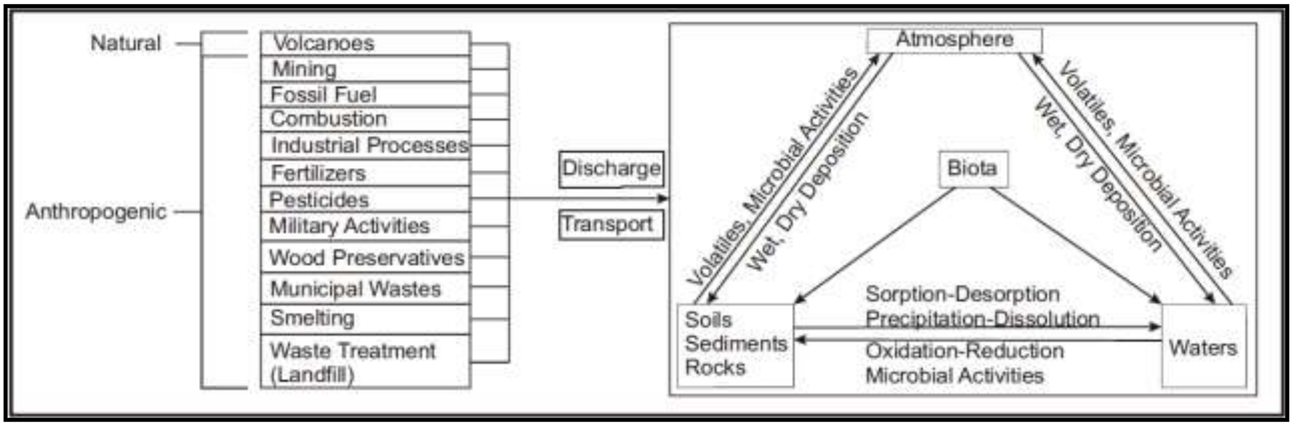


Figure 2.1 Simplified version of the arsenic cycle indicating the natural and anthropogenic sources and its movement between the different reservoirs on Earth (modified after Wang and Mulligan, 2006).

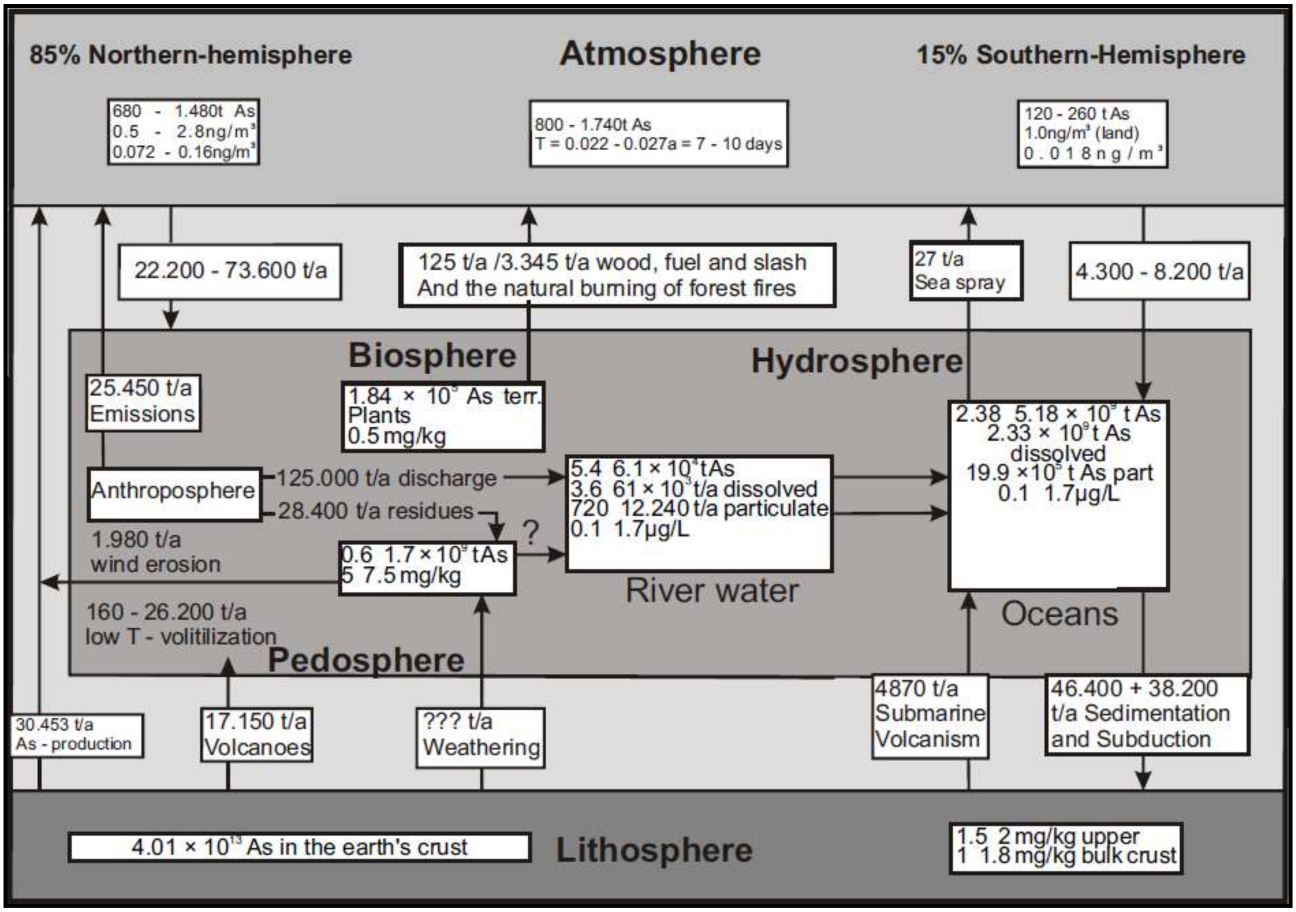


Figure 2.2 Detailed arsenic cycle showing the different sources on Earth and how much each hemisphere contributes to arsenic distribution (modified after Matschullat, 2000). t/a–tons per annum.

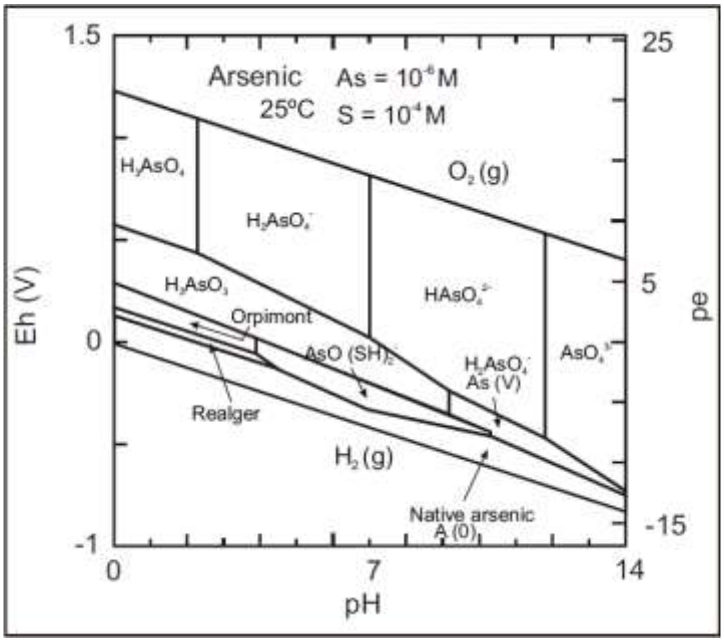


Figure 2.3 Eh-pH phase diagram of arsenic (modified after Plant et al., 2003).

2.2.2.3 Natural sources

The main natural process that brings arsenic to the surface of the Earth is mainly through volcanic activity (Matschullat, 2000; Dani, 2010). Geothermal fluids can contain elevated levels of arsenic (Wang and Mulligan, 2006). It is found in many different environments such as rocks, soil and all natural water sources. It can be found in hydrothermal, sulphidic or Fe^{3+}-oxyhydroxide-dominated and evaporative type environments (Lloyd and Oremland, 2006) Arsenic is found in coals in trace amounts and can be chemically found as pyritic, organic or arsenate types (Yudovich and Ketris, 2005a).

Lakes that contain arsenic tend to have lower concentrations compared to rivers and streams because arsenic is absorbed into iron oxides through neutral conditions (Duker et al., 2005) but can be significantly higher if there is little or no water flow (Smedley and Kinniburgh, 2002). Wind and water erosion processes break down rocks containing arsenic bearing minerals releasing arsenic into soils and water bodies (Smedley and Kinniburgh, 2002; Ungaro et al., 2008). Sea spray and forest fires are contributors of moving arsenic around the surface of the Earth (Lievremont et al, 2009). Biological activities can contribute to the aiding of arsenic enrichment in groundwater (Malik et al., 2009). An example of enrichment of arsenic in soils is found in Canada from the breakdown and weathering of arsenic bearing rocks (Wang & Mulligan, 2006). The most problematic causes of contamination of arsenic into the environment are from natural sources explained above (Smedley and Kinniburgh, 2002).

2.2.2.4 Anthropogenic sources

Anthropogenic processes that release arsenic into the environment are from the burning of fossil fuels (Dani, 2010) and from smelter plants around the world. Other main anthropogenic activities that cause an increase in arsenic concentrations in the environment are different mining activities, the use in herbicides, pesticides, and fertilizers, wood preservatives, in waste disposal, additives to livestock feeds, semi-conductor and glass industries, wood preservation and from different types of spillages that contain arsenic (Duffus, 1980; Gidhagen et al., 2002; Smedley and Kinniburgh, 2002; Chirenje et al., 2003; Camm et al., 2004; Duker et al., 2005; Lage et al., 2006; Morin and Calas, 2006). It was used in paint pigments, but was removed because if an area became damp where the paint was used, moulds that would form would convert arsenic to arsine, a highly toxic gas to humans (Vaughan, 2006).

In South America especially in Chile, copper and gold smelters are the major cause for releasing arsenic into the environment as fine particles that humans inhale (Gidhagen et al., 2002). Tailings of gold mining operations are the main anthropogenic processes found in North America especially in Canada (Wang and Mulligan, 2006).

In India, high amounts of arsenic are released into the environment through coal combustion at power stations because coal combustion is the primary source of generating electricity. The coal type found in India is sub-bituminous and arsenic concentrations in these coals are considerably higher than the world average concentration of the same coal type. World average concentrations are between 7.4 – 9.0ppm and in India the average concentrations are between 22.3 – 62.5ppm (Pandey et al., 2011). Many countries such as Russia, Great Britain, Ukraine, USA and Canada contain coals that have high concentrations of arsenic (Yudovich and Ketris, 2005a). Fly ash containing arsenic has been found to cause lung infections and skin diseases to humans in the Paula district of West Bengal, India. The animals and vegetation that are found in the region are covered with the fly ash. The animals feeding off of the contaminated plants developed skin and dental diseases (Pandey et al., 2011).

The body types that become contaminated by anthropogenic processes are mostly water bodies such as lakes, dams and groundwater which are often used for human and animal consumption (Lievremont et al., 2009). Main contributors to contamination are from insecticides and from solid waste deposits (Wang and Mulligan, 2006). In Bangladesh a severe case of arsenic contamination in groundwater exists that has been used for irrigation in agriculture and drinking purposes. The soils are becoming enriched in arsenic causing serious contamination of the environment which has lead to millions of people being exposed to high arsenic levels (Lievremont et al., 2009). This case is known as ‘the biggest arsenic calamity in the world’ (Alam et al., 2003) and described by the World Health Organization as the “the greatest mass poisoning in history” because an estimated 35 million people are affected by arsenic contamination (Vaughan, 2006).

2.2.2.5 Toxicity

The gas arsine (AsH_3) is the most toxic form of arsenic (Vaughan, 2006) and the inorganic forms of arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}) are the most toxic forms in nature (Camm et al., 2004). Arsenic is toxic to humans but elemental arsenic is less toxic than arsenic compounds because it is poorly absorbed into the body and is excreted unchanged. Arsenic affects many organs in the body but also causes severe damage to the immune system (Duker et al., 2005) and interestingly some compounds such as the arsenosugars are not toxic to humans at all (Vaughan, 2006).

Arsenic is a poison that accumulates in the body. It causes severe uncomfortable pains, and severe vomiting prior to death. It is known to be a carcinogenic metalloid to certain tissues of the body such as the mouth, bladder, larynx and oesophagus. High exposure to arsenic can also cause cancer growth especially skin cancer and can lead to internal organ failure (Lievremont et al, 2009). Because soils mainly contain higher concentrations than their parent rock material, arsenic in the soil can be taken up by plants through their roots and end up concentrating in certain edible parts of the plant that are then consumed by humans.

Arsenic poisoning may also lead to diseases such as vascular disease and diabetes, reproductive problems, neurological disorders and hypertension (Hopenhayn, 2006). It is of special interest that it is believed that arsenic poisoning can lead to dementia and Alzheimer's disease (Dani, 2010).

2.2.3 Cadmium

2.2.3.1 Chemical properties

Cadmium is a transition element found in group 12, row 5, on the Periodic Table which geochemically is a strong chalcophilic element. If there is a lowering of pH in groundwater, the cadmium concentration in the water can increase (Järup et al., 1998b). Table 2.3 presents the physical and chemical properties of cadmium.

2.2.3.2 General background

Cadmium is a group 12 transition metal on the Periodic Table. It is a rare element found on Earth being the 67th most abundant with a very low concentration of 0.1 mg/kg in the Earth's surface and is commonly associated with zinc (Callender, 2003; Nordberg and Cherian, 2005; Garrett, 2005). The metal was produced on a large scale during the 20th century until it was discovered to be a major pollutant. Production slowed down in the 1970s but gradually increased because of its demand in rechargeable batteries (Elinder and Järup, 1996). It is an element of great concern as it is toxic to humans and animals. Table 2.3 gives examples of average concentrations found in the crust, in different rock types and soils.

Table 2.3 The basic chemical properties and concentrations of cadmium found on Earth. Callender, 2003[1]; Wright and Welbourn, 2002[2]; Nordberg and Cherian, 2005[3]; Garrett, 2005[4].

Physical and chemical properties		Crust/ rock type/ soils	Concentration
Geochemical classification	Chalcophile[1]	Earth's surface	0.1 ppm[1, 3, 4]
Symbol	Cd	Mafic rocks Basalt	0.2 ppm[1]
Periodic Table	Transition elements Group 12, Row 5	Felsic rocks Granite	0.15 ppm[1]
Atomic mass	112.41 amu	Sedimentary rocks Shale Sandstone Coal	1.4 ppm[1] <0.03 ppm[1] 0.4 ppm[1]
Oxidation state	+II in aqueous solution. Under reducing conditions – forms sulphides in soils and sediments[2]	Soils	0.35 ppm[1]
Physical appearance	Metallic, ductile and soft No distinct taste or smell[1, 3]		
Colour	Silver-white with a bluish tinge[1, 3]		
Melting point	321ºC[1]		
Boiling point	765ºC[1]		

2.2.3.3 Natural Sources

Cadmium is found in low concentrations in all soil types and water bodies especially with underlying rocks that contain high concentrations of cadmium. Natural emissions such as volcanic activity and geological processes can release cadmium into the environment and atmospheric deposition deposits cadmium (Satarug et al, 2003; Olsson et al., 2005). Cadmium is associated with zinc and lead ores and many other sulphide minerals (Hamilton and Hardy, 1974). Bauxite soils may contain a possible enrichment of cadmium as can be seen in Jamaica where naturally high concentrations are found in the soils, where especially in the city of Manchester in the parish, concentrations of cadmium can be as high as 931 ppm (Lalor, 2008).

2.2.3.4 Anthropogenic Sources

Cadmium is associated with zinc and lead with many other nonferrous metals and is a common byproduct from mining and smelting of these ores (Hayes, 1997; Bi et al., 2009). Cadmium is released into the atmosphere and environment from the combustion of coal, waste incineration and in the manufacturing of alloys and electroplating (Wright and Welbourn, 2002, Satarug et al., 2003, Valerio et al., 1995). Other uses are in ceramics, engraving, colour pigments to plastics, cadmium coated materials and in rechargeable batteries (Valerio et al., 1995; Elinder and Järup, 1996; Hayes, 1997; Kirkham, 2006). In the agricultural world, phosphate fertilizers and the use of sewage sludge are contributors to cadmium concentrations increasing in arable lands (Lambert et al., 2003; Satarug et al, 2003).

The largest release of cadmium into the environment is from smelting plants, melting of cadmium metal and alloy manufacturing (Hamilton and Hardy, 1974). Modern worldwide production of cadmium is approximately 21,000 metric tons per year where approximately 7,000 metric tons is released into the atmosphere and environment. Airborne cadmium from smelters and metal manufacturing can be taken up by plants and ingested by animals which can later end up being consumed by human beings (Järup et al., 1998a).

In Europe different anthropogenic processes that lead to cadmium contamination in the environment are from industries such as smelters and metal accumulators (Bergbäck and Carlsson, 1995). Agricultural land can become contaminated with cadmium from phosphate fertilizer as can be seen in Sweden, where Salix (Salix vinimalis) phytoextraction is being used to minimize the contamination problem (Berndes et al., 2004). In the United States of America, humans are exposed to cadmium poisoning from industrial activities, waste management operations, tobacco products through smoking and eating contaminated food sources (Peters et al., 2010). In Asian countries such as China, smelters are also contributors to atmospheric and soil contamination (Bi et al., 2009). Contamination of soils in South Africa is on the rise due to excessive use of fertilizers and sewage sludge on arable land and from uncontrolled mining activities (Street et al., 2009).

2.2.3.5 Toxicity

In high concentrations in soil, cadmium can be easily taken up by plants and animals and it will concentrate in the tissues of both types. Trees and plants have the ability to take cadmium up into their systems more easily compared to animals but plants have a much higher toleration of cadmium compared to animals (Satarug et al, 2003). Cadmium accumulates in animals especially in organs such as the kidneys, reproductive organs and liver (Kirkham, 2006). For cadmium to be toxic to plants, the concentration must be considerably higher compared to animal absorption (Satarug et al, 2003). If mammals have a low calcium diet, cadmium is more easily absorbed into the body. Cadmium can be a significant environmental hazard in marine systems (Segovia-Zavala et al., 2004).

Cadmium builds up in the liver, kidneys and reproductive organs. The main way in which humans are exposed to cadmium poisoning is from contaminated food stuffs (contaminated plant foods, crustaceans and offal products), contaminated alcoholic beverages that are not regulated and contaminated tobacco used for smoking (Mena et al., 1996; Järup and Akesson, 2009). If humans are continuously exposed to cadmium poisoning, it will lead to heart enlargement, gastrointestinal disturbances, indigestion, liver and kidney damage, diarrhea and possible premature death. Cadmium is a plausible contributor to osteoporosis and cardiovascular diseases such as heart failure and strokes (Järup et al., 1998a; Peters et al., 2010). Cadmium in the blood can be positively identified as causing an elevated risk of hypertension in males but not females according to statistical studies done in Korea (Lee et al., 2011).

It is also known that cadmium is a possible contributor to lung cancer development (Hamilton and Hardy, 1974; Duffus, 1980; Plumlee and Ziegler, 2003; Waalkes, 2003), but the main damage cadmium causes to human beings is kidney damage (Nordberg and Cherian, 2005), and bone tissue damage (Olsen et al., 2005). Low level exposure of cadmium to humans has shown that cadmium can accumulate in any organ in the human body; therefore exposure must be at a minimum at all times (Saturug et al., 2010).

People who smoke tend to have a higher concentration of cadmium in their bodies compared to non-smokers, due to tobacco containing small amounts of cadmium from fertilizers that are used to produce the tobacco. Up to 50% of cadmium found in the tobacco products, when smoking is adsorbed onto the lungs (Olsen et al., 2005). A reference blood sample of a non-smoker will have a cadmium content of <0.2 µg/L compared to a smoker having a concentration of <1.4 µg/L (Nordberg and Cherian, 2005). Non-smokers tend to obtain increased concentrations of cadmium mostly from industry or from food that is contaminated with cadmium (Järup and Akesson, 2009).

An example of cadmium poisoning occurred in Japan in 1955 where cadmium accumulated in rice and soya beans. The cadmium poisoning originated from a metal mine where cadmium was discharged into a river and the river was used for irrigation purposes. The plants were contaminated and the people of the region became poisoned with cadmium. Human’s skeletons began to collapse because it was believed cadmium caused an increase in bone porosity, and the bones could not repair themselves causing extreme pain. The sickness was known as the Itai Itai (ouch ouch) disease (Mahara et al., 2007).

2.2.4 Mercury

2.2.4.1 Chemical properties

Elemental mercury [Hg (0)] is a heavy transition element. Through large Eh - pH condition ranges, mercury is found dominantly in its metallic state mostly as a liquid at room temperature. In its oxidized state mercury is soluble and in its elemental state it is insoluble in water. When oxidizing conditions are dominant, mercury will be found in the Hg (II) state or the aqueous product Hg (OH)$_2$. In a strongly reducing environment, mercury will react with sulfur to form cinnabar (HgS) (Eby, 2004). Mercury can form covalent bonds and is bioactive (Bergquist & Blum, 2009). Table 2.4 gives the basic chemical properties of mercury.

2.2.4.2 General background

Mercury is a group 12 transition metal on the Periodic Table. It is a natural metallic element with a silvery colour in its natural liquid state and is classified geochemically as a siderophile or a chalcogenic element (Fitzgerald and Lamborg, 2003; Davies et al, 2005) It can be found in different compounds on the Earth which can be highly toxic to human and animal life specifically in its methylated form. Table 2.4 gives average concentrations for mercury in the crust and different rock types.

Table 2.4 The basic chemical properties and concentrations of mercury found on Earth. Davies et al., 2005[1]; Fitzgerald and Lamborg, 2003[2]; Browning, 1969[3]; CICAD, 2003[4]; Bergquist & Blum, 2009[5]; Garrett, 2005[6] ; Rudnik & Gao, 2003[7]; Turekian and Wedepohl, 1961[8]*; World Bank Group, 1998[9]. * As cited by Fitzgerald and Lamborg, 2003.

Physical and chemical properties		Crust/ Rock types	Concentration
Geochemical classification	Siderophilic[1] Chalcophilic[2]	Crust	80 ppb[4, 5, 6, 7]
Symbol	Hg	Mafic rocks Ultramafic Basalt	 4 ppb[6] 0.09 ppm[2]
Periodic table	Transition element group Group 12, Row 6	Felsic rocks Granite	 39 ppb[6]
Atomic mass	200.59 amu	Sedimentary rocks Sandstone Shale Carbonates	 57 ppb[6] 270 ppb[6] 0.04 ppm[8*]
Most common form	Elemental mercury[3, 4]	Soil	0.05 – 0.08 ppm[9] Mostly < 0.1 ppm[9]
Oxidation states	0; I; II		
Density	15.534 g/cm^3 (4)		
Melting Point	-38.87ºC [4]		
Boiling Point	356.72ºC [4]		

The main types of mercury found on Earth are metallic mercury, inorganic and methylated mercury. In its elemental state it has a residence time of approximately 1 year in the atmosphere. Because the gaseous divalent state is highly soluble, it has a much shorter residence time of approximately a few days in the atmosphere (Seigneur et al., 2003). At room temperature, mercury is in liquid state. The gas phase of mercury is of geochemical importance because the element has high vapour pressures (Fitzgerald and Lamborg, 2003). The most common mineral to contain mercury is cinnabar (HgS) (Duffus, 1980). When humans are exposed to most forms of mercury especially in its organic state, it can cause a detrimental effect to human health which leads to a lower IQ, lower life expectancy, internal organ failure and may even lead to death in severe cases (CICAD, 2003; Bergquist & Blum, 2009).

2.2.4.3 Natural sources

Mercury is found at the surface of the Earth from natural geological activities such as volcanic processes, geothermal processes, the mineralization of base and precious metals and high crustal heat flow (Gustin et al., 2000). Volcanic activity is a major source of mercury emissions into the environment where an estimated amount of 93.2 tons is released into the environment on a yearly basis (Nriagu and Becker, 2003).

Other natural processes include distribution from fires, rivers, streams, lakes; ocean upwelling, burning of biomass set off by lightning, and biological processes (CICAD, 2003, Gustin et al., 2008). Soils and foliage contain small amounts of mercury. Studies by Gustin et al., (2008) indicate that mercury is moving through natural vegetation and soils almost permanently. This causes a problem identifying, assessing and understanding the different potential sources of mercury especially from anthropogenic contributors. Figure 2.4 gives an example of a mercury cycle indicating natural origins with anthropogenic sources.

Once mercury is introduced into an ecosystem, complex cycles of mercury begin to develop such as redox-oxidative reactions, biochemical reactions and valence changes that occur such as Hg (0) – Hg (II) (Bergquist & Blum, 2009). Areas on the Earth especially around active plate boundaries contain the highest natural concentrations of mercury (Figure 2.5) (Schluter, 2000).

2.2.4.4 Anthropogenic origins of mercury

Anthropogenic sources release large amounts of mercury into the atmosphere. There are two types of mercury release from anthropogenic processes namely – primary and secondary. The primary processes develop from a geological environment where mercury is released through direct and indirect mining activities. Mercury can be released directly through mining activities such as extracting minerals which contain, or are associated with mercury, or mercury containing minerals from a rock source. An indirect process in which mercury is released into the environment is from the burning of fossil fuels that were firstly mined containing trace amounts of mercury. Secondary processes develop from the intentional use of mercury as a product such as dental amalgams, industry and smelters (Pacyna et al., 2010).

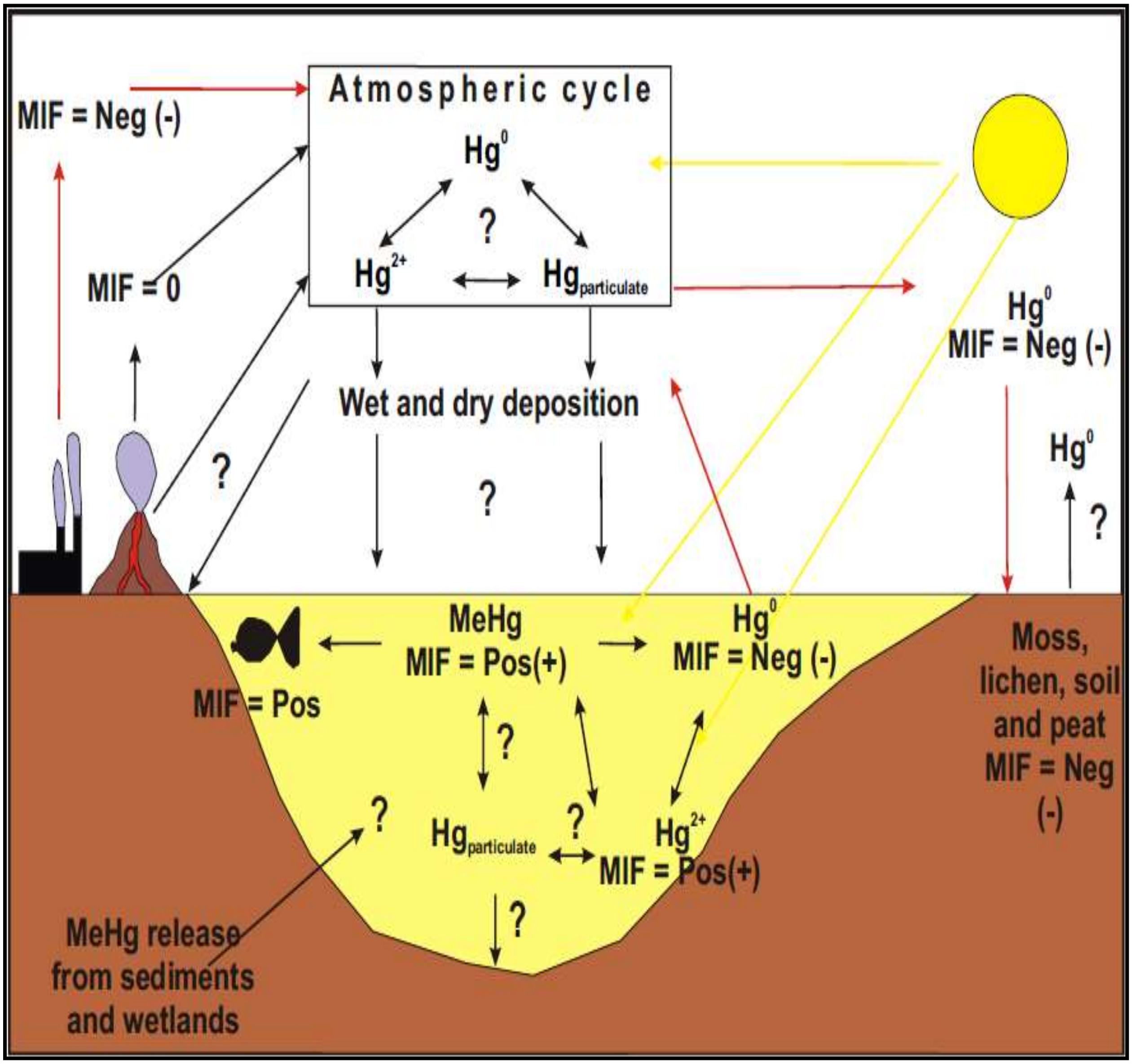


Figure 2.4 Simplified diagram of a mercury cycle (modified after Bergquist and Blum, 2009) (MIF – mass independent fraction, MeHg – methylmercury).

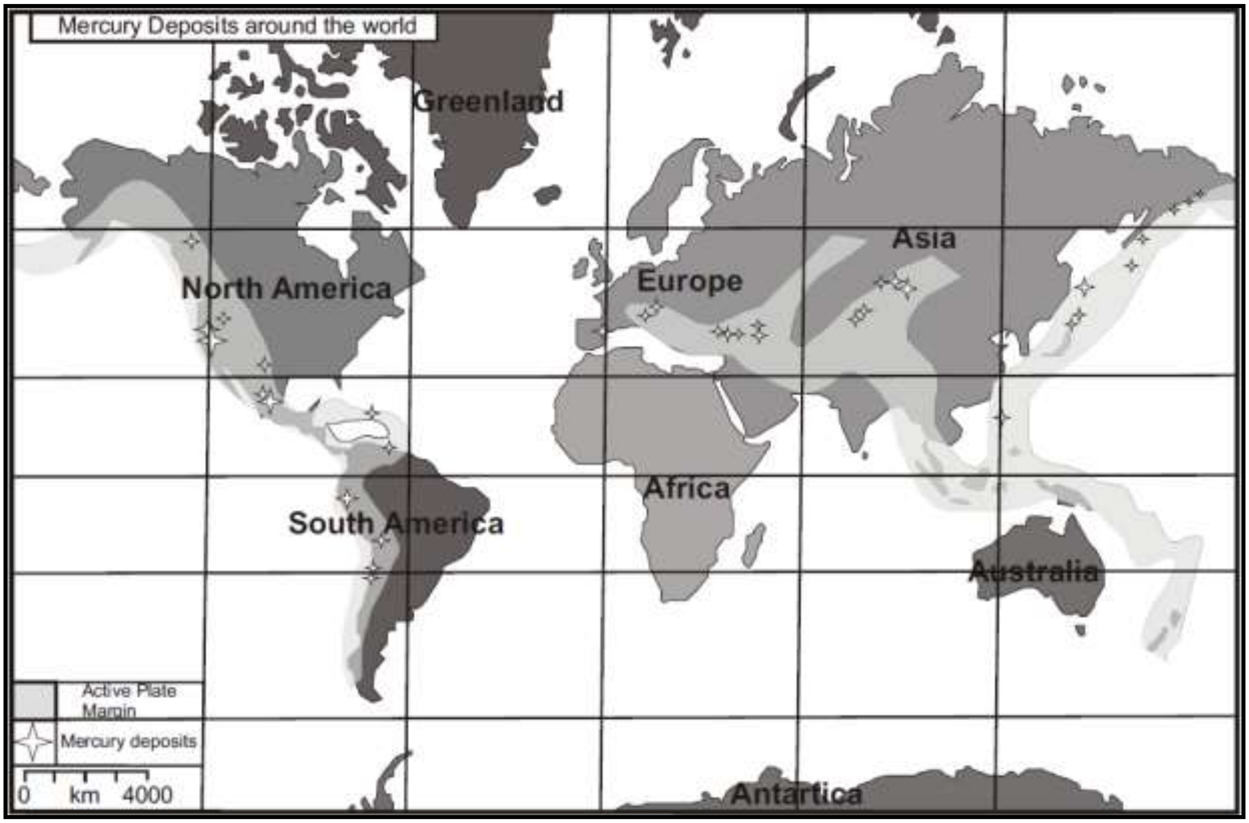


Figure 2.5 Mercury deposits and their association with active plate margins (modified after Kesler, 1994 as cited in Schluter, 2000; Fitzgerald and Lamborg, 2003).

Mercury's main use was in electrical apparatus production and in herbicides (Duffus, 1980). Mercury has many other different uses – in the textile and chemical industry, in mining especially in gold mining and in the manufacturing of scientific instruments such as thermometers and barometers. It is used in paper mills and in the production of mercury vapor lamps. In dentistry, mercury is used in amalgams with other elements such as gold, copper and silver. In the chemical industry, mercury is used to produce caustic soda and glacial acetic acid (Browning, 1969).

China is a high contributor to mercury being emitted into environment from anthropogenic processes. Emissions amounted to 539 (±236) tons being released in 1999. The main anthropogenic processes that lead to the release of mercury into the environment are coal combustion, steel production, artisanal gold mining and large scale industries such as acetic plants and chlor-alkali plants (Streets et al., 2005; Wong et al., 2006). The main reason for Asia, especially China, releasing such high amounts of mercury into the environment is from the industrial boom of the time causing a high production of minerals/metals on the continent. With the high production there were also poor pollution controls and this lead to high pollution rates in the Asia (Wong et al., 2006).

In Africa there has been an increase in mercury emissions from 1990 to 2000 from just under 200 tons in 1990 to over 400 Mg in 2000 (Figure 2.6). Table 2.5 gives an estimated by-product emission of mercury around the world by Pacyna et al. (2010). South Africa released the second highest amount of mercury into the environment in the world in 2000. An estimated 256.7 tons of mercury was released into the environment during the year 2000 through industrial activities (Pacyna, 2006).

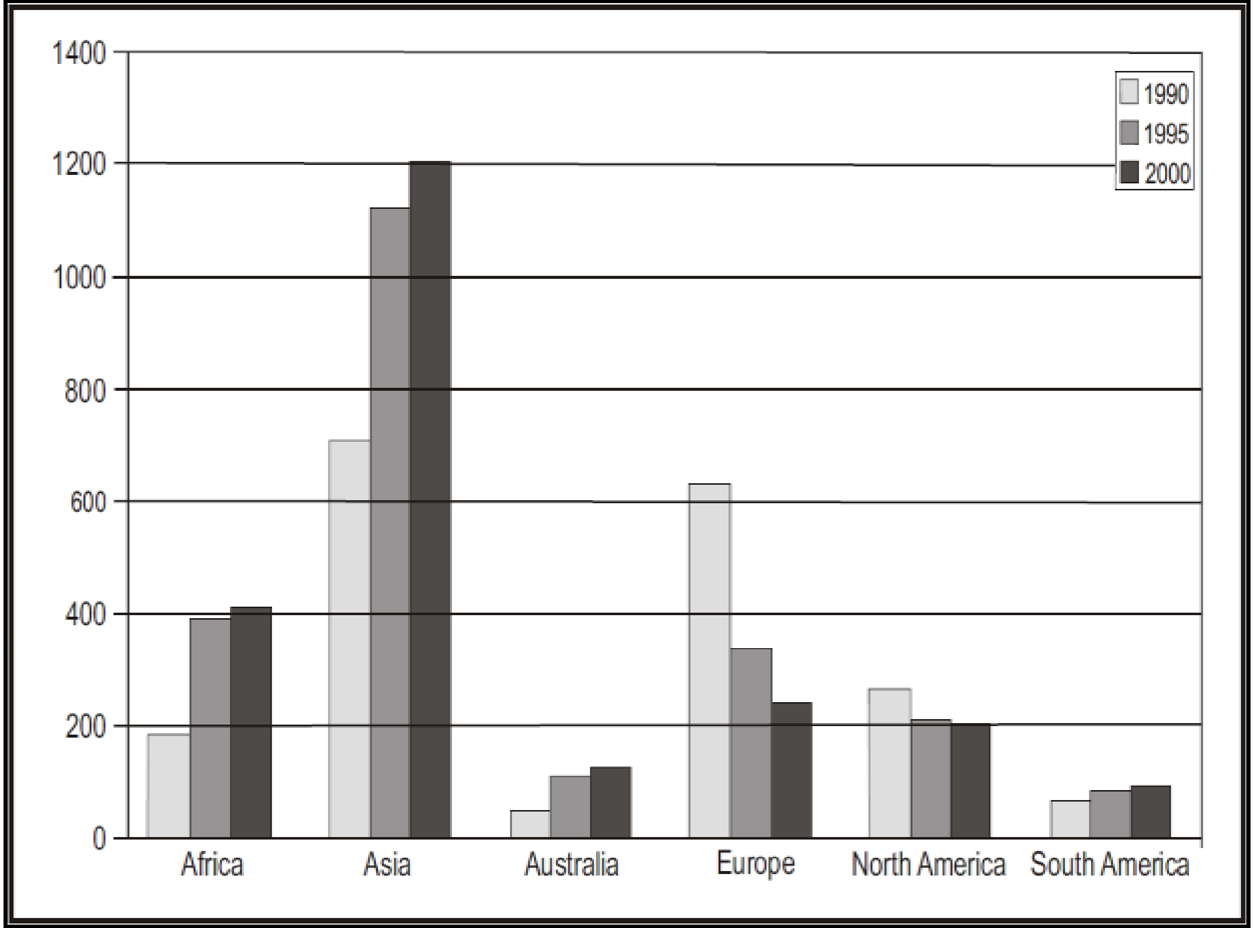


Figure 2.6 Global emission changes of mercury of different continents from 1990-2000 Africa, Asia, Australia and South America show increases over time. Europe and North America show decrease over time. All amounts in Mg (modified after Pacyna et al., 2006).

Mining activities, power plant usage, lead and zinc production, oil and wood combustion are many different anthropogenic processes found in North America and Europe which release mercury into the atmosphere. Lakes in North America that become acidified by anthropogenic processes, experience a bioaccumulation of mercury in the form of methylmercury in the aquatic organisms found in these lakes, especially in fish (Nordberg and Cherian, 2005). In the city Bydgoszcz in northern Poland, urban soils were compared to rural soils for mercury concentrations. It was found that mercury was considerably higher in the urban soils than the rural soils. The main contribution to the increase of mercury in the urban soils was from the burning of coal and from high traffic activity. Mercury is released from these activities in trace amounts and then redistributed onto the soils through atmospheric fall-out. Concentrations in urban soils are 2 – 9 times higher compared to rural areas (Dąbkowska-Naskręt and Różański, 2007).

Table 2.5 The global anthropogenic emissions of mercury produced by the different continents or specific countries on Earth. All amounts in tons (modified after Pacyna, et al., 2010). 1st – highest concentrations released by a continent, 7th – lowest concentrations released by a continent.

Continent	Mercury Production	Gold Production	Cement Production	Pig iron and steel production	Non – ferrous metals production	Caustic soda production	Stationary combustion	Total Mercury and rank
Africa	0.0	8.9	10.9	1.6	2.1	0.1	37.3	60.9 5th
North America	0.0	12.9	10.9	14.4	5.7	6.5	71.2	121.6 2nd
South America	0.0	16.2	6.4	1.8	13.6	2.2	8.0	48.2 6th
Europe (excluding Russia)	0.0	0.0	18.8	9.4	9.4	6.3	76.6	120.5 3rd
Asia (excluding Russia)	8.8	58.9	137.7	24.1	90.0	28.7	622.1	970.3 1st
Russia	0.0	4.3	3.9	2.6	5.2	2.8	46.0	64.8 4th
Oceania	0.0	10.1	0.4	0.8	6.1	0.2	19.0	36.6 7th
Total mercury emissions	8.8	111.3	189	54.8	132	46.8	880.2	1422.7 N/A

In Africa, industrial activity and the burning of fossil fuels such as coal and oil in power stations release mercury into the atmosphere (Wagner and Hlatshwayo, 2005; Pacyna et al., 2006; Veiga et al., 2006; Pone et al., 2007; Pacyna et al., 2010). 93% of all electricity produced in South Africa originates from the combustion of coal in power stations. Mercury concentrations in these coals are between 0.01 and 1.0 ppm (Pacyna et al., 2006). Mercury is released into the atmosphere through the burning of the coal (Mukherjee et al., 2008) and South Africa is regarded as the second highest emitter of mercury into the environment in the world (Dabrowski et al, 2008). In South Africa Masekoameng et al., (2010) estimated that roughly between 72 to 78% of anthropogenic mercury releases into the environment originate from power stations.

2.2.4.5 Toxicity

Most forms of mercury are toxic to human and animal life but the most toxic form of mercury is in the organic state namely, methylmercury. Methylmercury is the most dangerous and toxic because when it is taken up into living organisms, it bioaccumulates into certain organs especially in the human brain causing excessive damage to the organ and causing death in very severe cases (Nordberg & Cherian, 2005). Methylmercury is lipidophilic and accumulates in the fatty tissues in the human body. Mercury in its vapour state is the most dangerous form of inorganic mercury as it can be taken up in the lungs where it can move into the blood stream and possibly accumulate in the brain causing possible brain damage (Duffus, 1980) but it is mostly excreted from the human body by urine causing minimal damage.

Methylmercury is mostly found in fish and is a major source of exposure to humans around the world especially where mercury pollution is high around water sources. Mercury in its vapour state causes toxicity through dental amalgam fillings because the fillings contain more than 50% mercury with additional heavy metals such as copper and silver. The amalgams release mercury in the gaseous state which is absorbed through the lungs during inhalation.

An example of mercury poisoning on a large scale occurred in Japan in the 1960s. On the island known as Kyushu Island, in Minamata Bay, over 200 people suddenly died. It was later discovered that the fish and mollusks in the bay contained high amounts of mercury and these organisms were consumed by people. Consumption of these aquatic organisms caused the people to become sick and even pass away from the detrimental effects of the mercury found in the sea organisms. It was found that a chemical plant was releasing mercury into the nearby river as waste material and it was accumulating in the bay where it further became bioaccumlated in the sea organisms which the humans consumed. After this serious problem occurred, other cases around the world were also recognized (Malikova et al, 2011).

2.2.5 Selenium

2.2.5.1 Chemical properties

Selenium is a group 16, row 4 element found on the Periodic Table. Selenium has multiple oxidation states (Figure 2.7). It develops a Se (VI) state when it is in a strong oxidizing environment to form selenate (SeO_4^{2-}). At intermediate oxidizing conditions, selenium forms a Se (IV) state known as selenite ($HSeO_3^-$ and SeO_3^{2-}). In reducing conditions selenium can be found either in elemental form (Se 0) or in a Se (-II) state where it can form selenide (HSe^{-2}). Under reducing conditions and with the addition of sulfur, selenium will be incorporated into sulphide minerals (Bajaj et al., 2011; Eby, 2004). The selenium-oxy-anions are common in soils (Bajaj et al., 2011). Table 2.6 indicates the basic chemical properties for selenium.

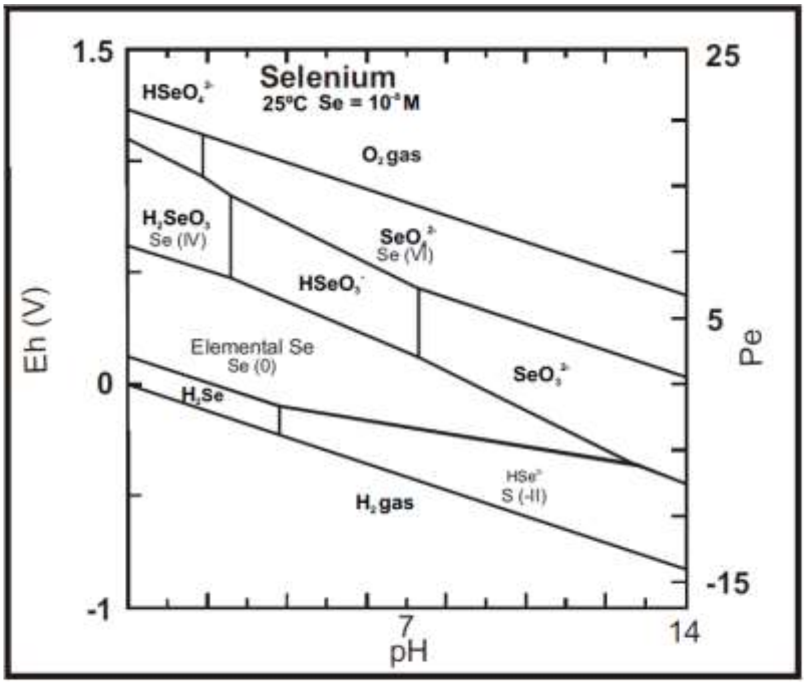


Figure 2.7 Eh-pH diagram of Selenium (modified after Plant et al., 2003).

2.2.5.2 General background

Selenium is a group 16 chalcofile element, found below sulfur on the Periodic Table. It forms part of the sulfur-group and displays chemical similarities to sulfur (Lenz and Lenz, 2009). It is theoretically not a metal but does contain metallic properties; it is described mostly as an element with properties intermediate between metals and nonmetals but is referred to as a nonmetal (Duffus, 1980, Plant et al., 2003). Selenium is a rare element as it is the 70th most abundant element on Earth with a continental crust average of 0.09 ppm (Rudnick and Gao, 2003). It is mostly found in a selenide form or in more rare cases associated with sulphides. The more common selenium minerals are berzelianite (Cu_2Se), naumannite (Ag_2Se) and tiemannite (HgSe). The metallic form of selenium mostly forms from residual mud found from the refining of copper ores, or in present times, in rare cases the roasting of the sulphide mineral pyrite (Compton, 1971).

The element's benefits on human health are completely different to other metal-like-elements such as arsenic and mercury. Trace amounts of selenium are beneficial to human health where trace amounts of arsenic can be toxic to human health, only doses of over 400 μg/day, selenium can cause toxicity to humans (Plant et al., 2003). Because of the consequences selenium has on human health, from either consuming too low (deficient) or too high (toxic) amounts, it needs to be consumed within certain limits (Hartikainan, 2005). Table 2.6 gives the average concentrations of selenium in different rocks, soils, surface waters and in the crust.

Table 2.6 The basic chemical properties and concentrations of selenium on Earth. Duffus, 1980[1]; Plant et al., 2003[2]; Wang and Gao, 2001[3]; Lemly, 2004[4]; Surai et al., 2008[5].

Physical and chemical properties		Rock type/ crust	Average
Geochemical classification	Intermediate element between a metal and nonmetal[1, 2]	Continental crust	0.09 ppm[2] 0.05 – 0.09 ppm[3] 0.2 ppm[4]
Symbol	Se	Felsic rocks Granite	0.01 – 0.05 ppm[2]
Periodic table	Group 16, Row 4[2]	Mafic rocks	0.05 ppm[2]
Atomic mass	78.96 amu[2]	Coal	1 – 20 ppm[2] 0.4 – 24 ppm[4]
Oxidation states	-II; 0; IV; V[2]	Mudstone	0.1 – 1500 ppm[2]
Boiling point	685ºC[2]	Soils (world general)	0.4 ppm[2] 0.1 and 2 ppm[5]
Melting point	220ºC[2]	Surface waters	0.2 μg/L[4]
Density (kg/m^3)	4.808[2]		

2.2.5.3 Natural sources

Selenium rich soils are produced from the breakdown of parent material containing selenium, and selenium transported from other areas through wind and water and topography (Bajaj et al., 2011). A high contributor of selenium into the environment is from volcanic activity especially from volcanoes that form from subduction zones. These volcanic types are extremely explosive and humans living around these active volcanoes are at high risk (Floor and Román-Ross, 2012). Calculations from Wen and Carignan (2007) indicate that natural processes are responsible for between 59.4% and 63.5 % of total selenium released into the atmosphere, which is more than anthropogenic processes.

2.2.5.4 Anthropogenic sources

There are many different types of anthropogenic processes that cause contamination of the environment. The different sources are coal mining, the combustion of coal, gold mining, silver mining, nickel mining, agricultural activities and irrigation, oil refining, oil transport and municipal landfalls (Hamilton, 2004; Lemly, 2004).

Selenium forms as a byproduct from the extraction of nickel, gold, copper or silver ores. Other uses of selenium are in the electronics field, as rubber compounds and in paints (Duffus, 1980). A major concern of selenium release into the environment is from coal mining and coal combustion. Coal contains a global average concentration of 0.4 – 24 ppm (dry weight basis) and waste material from the burning of coal could increase selenium concentrations as high as 500 ppm in fly ash (Lemly, 2004). An example of soils becoming contaminated from coal mining and coal combustion can be found in Xuzhou City, China, because the power plants do not have sufficient equipment to capture the waste materials, therefore releasing selenium into the environment (Shungsheng et al., 2009).

Selenium can be found in fertilizers and if a soil is deficient, selenium fertilizers are used to improve soil and food quality (Hartikainen, 2005). Agricultural activity could cause selenium accumulation especially in lakes as can be seen in Finland and in different parts of the USA such as California and North Carolina (Hamilton, 2004; Wang and Chen, 2003). An interesting use for selenium is in anti-dandruff shampoos for healthier hair (Lenz and Lenz, 2009).

2.2.5.5 Toxicity/benefits

Selenium is a micronutrient that the human body needs and a deficiency of selenium is detrimental. A selenium deficiency is a contributing factor in certain diseases and cancer development (Surai et al, 2008). A deficiency in selenium can result in liver necrosis and membrane dysfunction (Plumlee and Ziegler, 2003). Adequate Selenium concentrations of higher than 121 µg/L in the blood are necessary for natural protection against cancer. Selenium will help to minimize risk in cardiovascular disease and immunodeficiency (Hartikainen, 2005).

Selenium in the correct dosages has shown to improve the immune system of humans. It has been indicated that there can be a possible geographical link with HIV-AIDS cases. Areas with high HIV-AIDS incidence tend to have soils deficient in selenium and areas with adequate concentrations in soils tend to have a lower number of cases of HIV-AIDS infections. A geographical comparison example can be found between Southern Africa and Senegal. Senegal has a very low rate of HIV infection being about 1% and the soils in the country have adequate concentrations of selenium. Southern African soils are known to have a deficiency in selenium and the HIV infection rate is high. An explanation for this is that the HIV virus infects the immune system and selenium is found in the immune system and seems to defend against the virus attack causing a lower chance of infection (Davies and Mundalamo, 2010). Two random tests were done in the US on people that were HIV-positive by giving them 200 µg of selenium supplement per day and the results indicated that increased selenium content benefited the patients. Other benefits included decreased hospital admissions that were caused by infection (Raymon, 2012).

The main sources of selenium poisoning are edible plants that have taken it up from soils enriched with selenium at toxic levels for humans and animals. The enrichment of the soils can be either from natural or anthropogenic sources. Animals and humans may consume the contaminated plants, which leads to selenium poisoning (Shunsheng et al., 2009).

Selenosis in humans and animals is the result of toxic levels of selenium. People would lose their hair and nails. A good example occurs in the Daba Mountain area of China where there have been many cases of humans and pigs developing selenosis (Yonghua et al., 2008). Other selenium toxicity symptoms are the irritation of the eyes, nose and throat. In high concentrations, it can cause damage to the liver and aid in cancer development of the liver, it can degenerate the liver and kidneys which could lead to pneumonia, skin lesions and affects the central nervous system (Duffus, 1980; Plumlee and Ziegler, 2003). Studies have shown that selenium could have an ameliorative (repairs) effect on toxic levels of methyl mercury in the human body but was contradicted by studies done by Choi et al. (2008).

Hooved animals such as horses that consume plant material with toxic levels of selenium caused their hair to fall off, their growth was stunted, have poor reproduction and in severe cases the animals died (Hartikainen, 2005). Selenium can be toxic to aquatic life due to anthropogenic activities, that release selenium is released into rivers, dams and lakes. The selenium in its soluble state can start to bioaccumulate in aquatic organisms especially in fish causing a detrimental effect on the species and populations (Hamilton, 2004). Reproduction begins to diminish in sensitive fish such as bluegill, where concentrations as high as 6 µg/L can cause a 50% decrease in reproduction (Lemly, 2004).

2.3 Coal in South Africa

2.3.1 Introduction

Coal is a sedimentary rock that constitutes 50% mass and 70% volume of carbonaceous material. It is a primary energy resource; it has a major input in the metallurgical industry for the manufacturing of iron and steel, non-ferrous alloys and ferro-alloy through reducing reactions in the manufacturing process and is a major influence in the chemical industry (Snyman, 1998).

Countries around the world such as South Africa, Australia and Canada use coal domestically or export it to other countries to produce electricity and this consumption contributes to around 40% of the electricity generated on Earth. There are still large amounts of coal reserves found on Earth which can be consumed, therefore it is still a reliable resource for power generation for many countries across the globe (Vejahati et al., 2010). The main source of energy in the southern regions of Africa, such as South Africa, and its surrounding countries, such as Zimbabwe, are from the consumption of coal in power stations. Coal combustion in South Africa contributed 74% of the total electricity generated in the country (Cairncross, 2001) but can be as high as 93% in more recent times (NERSA, 2005). Through the burning of coal in power stations there is a potential for heavy metals such as mercury to contaminate the environment (Masekoameng et al, 2010). The quality of the coal that is found in South Africa can be of high or relatively poor quality. High quality coal that is mined in South Africa is mainly exported overseas to other developed countries giving the South African economy a significant boost. Local industry in South Africa uses the low quality coal for many different purposes but power generation is the primary user for the low grade coal (Mangena and Brent, 2006). South African coals are dominantly bituminous grade and the main coal used in South Africa is the low-grade, medium-rank C bituminous coals (Matjie et al., 2011). The coals found in the Mpumalanga Province region are classified as high volatile bituminous to sub-bituminous coals (Saghafi et al., 2008).

There are 3 main variables to classify coals which are grade, type and rank. Grade has an inverse correlation to the percentage of inorganic material found in coal. Grade is largely determined by the depositional stage when the plant materials were deposited with other clastic materials such as quartz and clay minerals. Type depends on the original plant material and the plant material’s degree of alteration during diagenesis of coal formation. Rank results in the degree of metamorphism of the deposited coal beds by temperature and pressure from newly formed overlying deposited sedimentary beds. The changes in metamorphism are responsible for physical-chemical properties of the coal. The rank of coal results from the properties of maceral vitrinite found in the coal (Snyman, 1998). Table 2.7 gives the rank of coal from the lowest quality being peat to the highest quality being meta-anthracite.

Coal is known to contain trace amounts of heavy metals and if coal has gone through diagenetic development, it can cause an enrichment of antimony, arsenic, mercury and selenium (He et al., 2002). Coals of the world and in South Africa all tend to contain trace amounts of heavy metals which poses a serious threat to the environment when the coal is used for electricity generation or for heat generation (Yudovich and Ketris, 2005a; b; Yudovich and Ketris, 2006).

Heavy metals such as mercury, cadmium, arsenic and selenium are of major concern during the utilization of coal (Vejahati et al., 2010). Sasol Synfields found in Mpumalanga Province uses coal to produce synthetic fuels and chemicals, and in poorer communities coal is used to generate heat to cook and keep warm especially during the winter months of the year (Wagner et al., 2008; Masekoameng et al., 2010) Approximately 16 million people living in South Africa in rural areas rely mostly on firewood and coal to survive leading them to live with the pollution that is generated when burning these materials (van Horen et al., 1996).

Table 2.7 The ranking of coal. Peat is poorly ranked and meta-anthracite the best ranked in terms of burning quality (modified after Orem and Finkelman, 2003).

Rank	Sub rank	Characteristics
Peat		Identifiable plant fragments, abundant cellulose
Lignite		Some identifiable plant fragments; only a residue of cellulose present; dehydration
Sub-bituminous	C B A	Gelification; no cellulose present; loss of methoxyl functionality on lignin
High volatile bituminous	C B A	Condensation of aromatic structures and loss of H and O; peak of oil; window from coal
Medium volatile bituminous		
Low volatile bituminous		
Semi-anthracite		
Anthracite		Condensation of aromatic structures and loss of H and O nearly complete; graphitization
Meta-anthracite		

2.3.2 Regional setting

During the formation of the Karoo Supergroup, sediments were the predominant rock forming constituents except for the Drakensberg Formation comprising of basalts (Figure 2.8). Later dolerite intrusions developed through the Karoo Supergroup. The Karoo Supergroup formed during the formation and the break-up of the supercontinent Gondwana. The age of the Karoo Supergroup ranges between Late Carboniferous (300Ma) to Middle Jurassic (180Ma). The cumulative thickness of the Karoo Supergroup is ~12km in the southeastern portion of the basin (Catuneanu et al, 2005; Johnson et al, 2006a). The southern region of the Karoo basin that formed was created by the formation of a subduction zone where the Dwyka, Ecca and the Stormberg Groups were created. The northern region formed within an extensional environment (Catuneanu et al, 2005).

All coal deposits that are found in South Africa are Karoo Supergroup hosted (Johnson et al, 2006a). The main coal deposits found in South Africa are associated with the midpart of the Ecca Group which formed during Permian times (Fabiańska and Kruszewska, 2003). Most coal seams are horizontal in the Karoo Basin except where disturbances, such as intrusions of dolerite sills and dykes into the seams, displaced and replaced the strata but also devolatilized the coal (Johnson et al, 2006a). Because of the dolerite intrusions and differences in geothermal gradients, there are different ranks of coal found in the Karoo Basin ranging from bituminous to anthracite quality coal (Table 2.7) (Catuneanu et al, 2005).

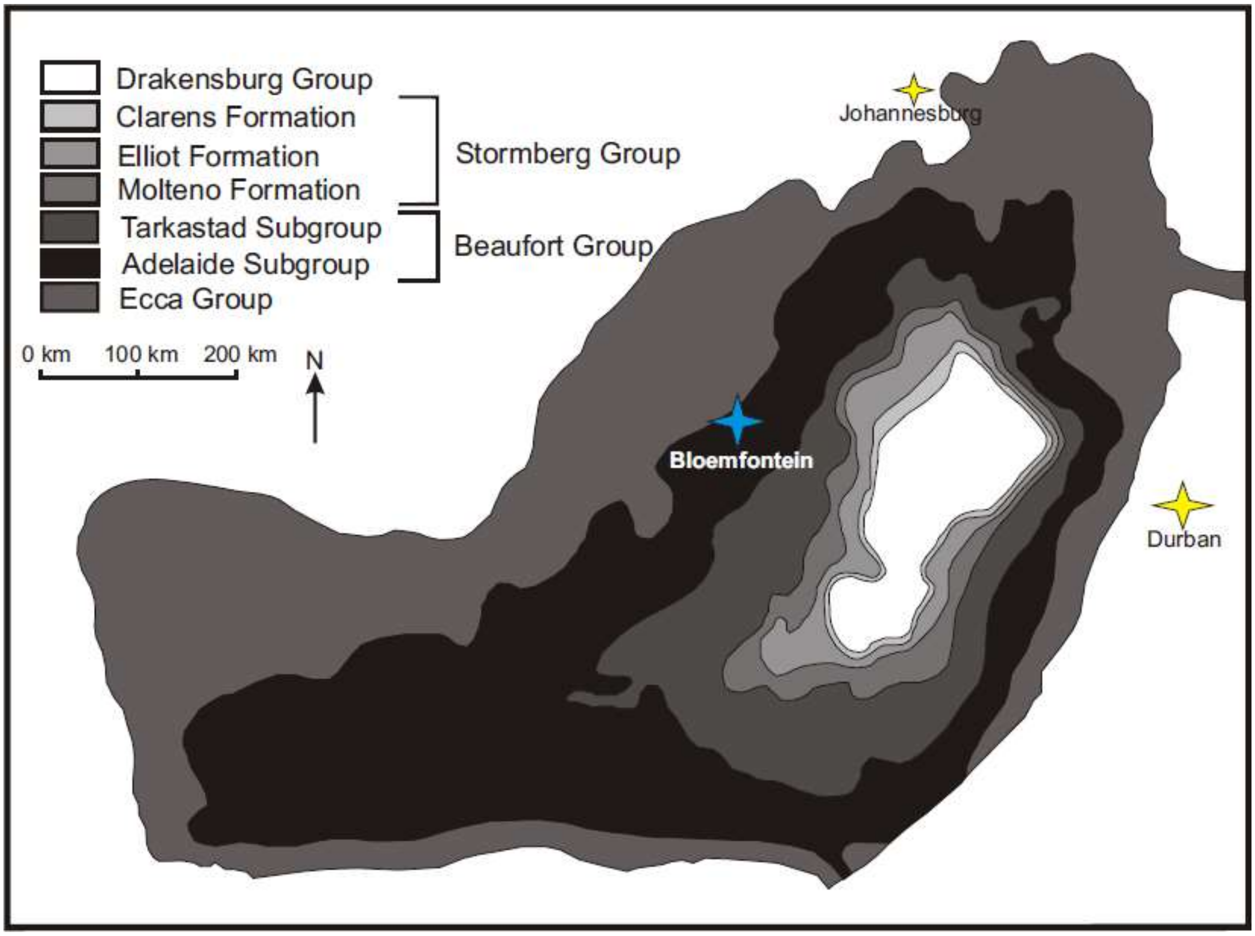


Figure 2.8 Geological map of South Africa indicating the Ecca, Beaufort, Stormberg and Drakensberg Groups of the Karoo Supergroup. Bloemfontein is situated overlying the Adelaide Sub-group (modified after Johnson et al., 1996).

The Vryheid Formation which is the midpart of Ecca Group (Bell et al, 2001) contains the main coal seams that are mined for human purposes such as domestic use. The main sediments containing coal are sandstones formed during the Early Permian, while mudstones are the predominant rock bearing sediments of the Late Permian during the formation of the coal seams

(Pone et al, 2007). Other rock types found in the Vryheid Formation are siltstones and shales (Bell et al, 2001).

There are 2 main coal deposit regions namely the Sasolburg coalfields and the Witbank coalfields. The deposits are located on the Northern margin of the Karoo Basin. The Witbank coalfields have 5 major seams and the Sasolburg coalfields have 3 major coal seams (Pone et al., 2007) (Figure 2.9).

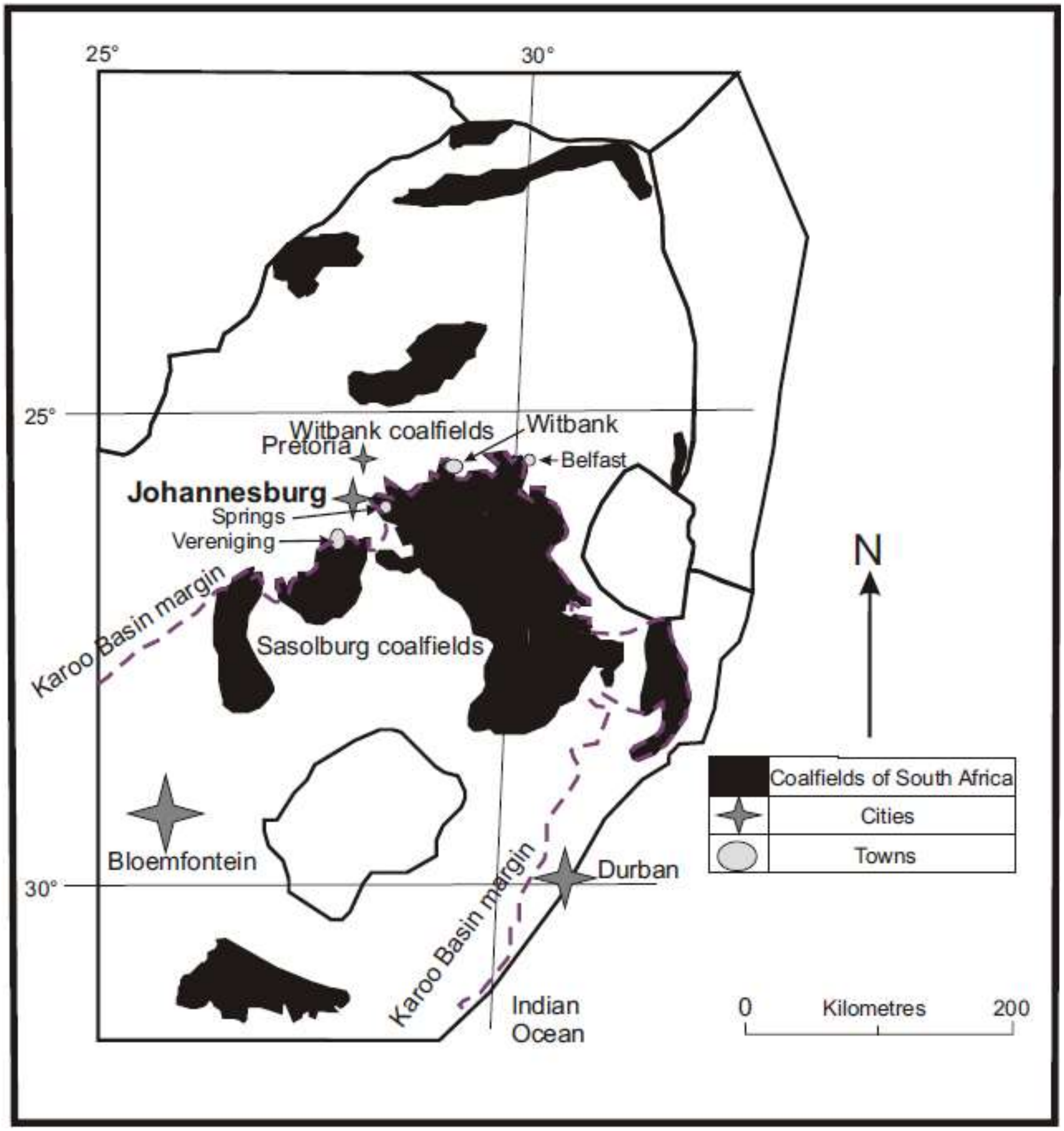


Figure 2.9 North east portion of South Africa where the Witbank coalfields are situated (modified after Pone et al, 2007).

2.3.3 Trace element geochemistry of coal

2.3.3.1 Introduction

Coal mostly consists of organic material but trace or even large concentrations of the different elements in the Periodic Table can be found in some coal deposits except for extremely rare elements such as actinium, astatine, protactinium, francium and polonium. Every element on the periodic table except the previously mentioned has been found in at least one coal deposit. The most common elements besides carbon, nitrogen, oxygen and hydrogen that can be found in coal are silicon, aluminium, calcium, sulfur and iron. These elements are commonly found in percent weight. Trace element concentrations in coal depend on many different criteria but mostly geology and geochemical processes govern trace element abundance in coal (Orem and Finkelman, 2003). World values and South African values of the trace elements under investigation in this study are found in Table 2.8.

2.3.3.2 Antimony and cadmium in coal

The concentrations of antimony and cadmium in coals is quite low with background values of less than 2 ppm for antimony and average values of 0.44 ppm for cadmium (Tauber, 1988 as cited in Reimann et al., 2010; Callender, 2003). Antimony is found in 2 different modes of occurrence normally being an accessory sulphide or less commonly found in organic association. Cadmium in coal is normally associated with the mineral sphalerite, in clay minerals or less likely in pyrite (Orem and Finkelman, 2003).

The average concentration of antimony and cadmium in South Africa in the Highveld Coalfield seam 4 is 0.32 and 0.44 ppm respectively. In the Witbank Coalfield seam 4 the average is 0.3 ppm for antimony and 0.5 ppm for cadmium (Wagner and Hlatshwayo, 2005 Bergh et al., 2011). Antimony concentrations are below world coal concentrations (2 ppm) for both the Highveld Coalfield seam 4 and the Witbank Coalfield seam 4, and cadmium shows the same type of concentration as world values (0.44 ppm) in the Highveld coal seams but lower concentrations in the Witbank coalfields.

2.3.3.3 Arsenic in coal

World average concentration values for arsenic in coals tend to depend on the quality of the coal. Bituminous coals have an average (Clarke of As) of 9.0 ± 0.8 ppm and lignite values have an average value of 7.4 ± 1.4 ppm. Ash values of used coal indicate concentrations of 50 ± 5 ppm for bituminous and 49 ± 8 ppm for lignite. It can be deduced that arsenic has a strong affinity for coal therefore indicating it is a coalphile element. There are 3 different types of arsenic occurrences in coal namely sulfide form (arsenic in pyrite and arsenopyrite), in arsenate form and in organic association. The organic form of arsenic in coal has shown to exist but there is very little information with regard to the chemical nature of this type of arsenic (Orem and Finkelman, 2003; Yudovich and Ketris, 2005a). South African coals have an average concentration of 3.14 ppm and 4.7 ppm from the Highveld Coalfield seam 4 and the Witbank Coalfield seam 4, respectively (Wagner and Hlatshwayo, 2005; Bergh et al., 2011). These values are below the world average of 5 ppm (Ng et al., 2003). Bituminous coals have a world average concentration of 9.0 ppm and lignite coals have an average of 7.4 ppm which is higher than South African coals (Yudovich and Ketris, 2005a).

2.3.3.4 Mercury in coal

In general the mercury content in coal is low (Yudovich and Ketris, 2005b). The most common occurrence of mercury in coal is in a solid solution phase with pyrite, or the rare organic association (Orem and Finkelman, 2003). South Africa has been rated the second highest contributor to mercury emissions in the world with assumptions based on coal combustion and from gold mining. Coal combustion to produce electricity and for residential use is a major anthropogenic activity releasing mercury (Pacyna et al, 2001). The use of coal-fired electric utility boilers are also a source for mercury emissions during the combustion of the coal (Jongwana and Crouch, 2012). Even on a worldwide basis, mercury is found in trace amounts in coal, but because of the high consumption of coal for energy uses, it is a major anthropogenic contributor to contamination of the environment (Yudovich and Ketris, 2005b). It has been found that if there is a high selenium concentration in coal, it may lower mercury emissions during combustion due to selenium-mercury bonding (Yudovich and Ketris, 2005c).

Mercury that is found in the coals of South Africa is associated with pyrite, to lesser extent the organic fraction and the least of all with carbonate (Wagner and Hlatshwayo, 2005). Jongwana and Crouch, (2012) concluded from South African coal sample analyses that 96% of mercury was in the Hg (II) species and only a very small fraction was found in the organic fraction. World average values for mercury in coal are 0.3 ppm and South African coals, from the Highveld Coalfield seam 4 and the Witbank Coalfield seam 4 are 0.15 ppm and 0.2 ppm (Wagner and Hlatshwayo, 2005; Mukherjee et al., 2008; Bergh et al., 2011). These values are slightly below world average values.

2.3.3.5 Selenium in coal

Selenium has a strong affinity for coal matter therefore giving it a coalphile type element character similar to arsenic. Data indicating concentrations of selenium in coals are very limited due to the fact the concentrations of selenium in coal are mostly very low. Analytical equipment shows interference that may cause problems during analysis, and during ashing a large concentration of selenium can be lost. The 2 main types of selenium associated with coals are either in sulphide (mainly pyrite) or organic form (Orem and Finkelman, 2003; Yudovich and Ketris, 2006).

World average values for selenium concentrations in coal are 1.6±0.1 ppm and 1.0±0.15 ppm for hard coal and for brown coals, respectively. In the ash phase the values increase significantly to 9.9±0.7 and 7.6±0.6 ppm, respectively, indicating the strong affinity for coal matter (Yudovich and Ketris, 2006). Lemly (2004) gives an average value of 0.4-24 ppm for selenium in world coals. South African coal fields such as Highveld Coalfield seam 4 and Witbank Coalfield seam 4 values are 1.05 ppm and 1.2 ppm, respectively (Wagner and Hlatshwayo, 2005; Bergh et al., 2011). These concentration values are found in the lower range of the world average values for selenium.

Table 2.8 Concentrations of the different elements in worldwide coals and in South African coals. Tauber, 1988[1]; Wagner and Hlatshwayo, 2005[2]; Bergh et al., 2011[3]; Ng et al., 2003[4]; Callender, 2003[5]; Mukherjee et al., 2008[6]; Lemly, 2004[7]; Yudovich and Ketris, 2006[8]; Orem and Finkelman, 2003[9].

Element	World coals	South Africa (Highveld, Coalfield, seam 4)	South Africa (Witbank, Coalfield, seam 4)
Antimony	2 ppm(1)	0.32 ppm(2)	0.5 ppm(3)
Arsenic	<5 ppm(4)	3.14 ppm(2)	4.7 ppm(3)
Cadmium	0.44 ppm(5)	0.44 ppm(2)	0.3 ppm(3)
Mercury	0.3 ppm(6)	0.15 ppm(2)	0.2 ppm(3)
Selenium	0.4–24 ppm(7)	0.2–1.2 ppm(8) 1.05 ppm(2)	1.2 ppm(3)

2.4 Historical background of the Bloemfontein power station

The power station (Figure 2.10) on the eastern side of Bloemfontein's CBD (Figure 3.3) first came into use in the early 1950s. It was operational from 1953 to 1985 and then again from 1996 to 2006. The peak use of the power station came in 1998 to 1999 and 2002 when 16497 and 28900 tons of coal were used respectively to generate electricity for Bloemfontein. The coal was obtained through Anglo Coal from Kleinkoppje Colliery in Witbank, Mpumalanga. Operations ceased after 2006 because it was cheaper to obtain electricity from Eskom than to generate electricity from the power station (N. Swart, pers comm., 2010).

In 2005 coal cost R303.27 per ton via road transport and R384.61 per ton via railway transport to produce electricity for Bloemfontein at the power station. Clean sewage water from the sewage works was used for cooling the machinery. The water was never discharged and always recycled in the machines so no environmental impact occurred. When new roads were erected between the power station and the sewage works, the underground pipe lines that were used to transport the water were damaged and were never repaired and presently are not in use.

Figure 2.10 The power station in Bloemfontein.

2.5 Previous studies of the location

There has been one previous study of the area associated with mercury contamination in 2006 but was terminated due to the mercury levels being too low from a medical perspective. The present study will help update local knowledge of the heavy metal concentrations of antimony, arsenic, bismuth, cadmium, mercury and selenium to see if there is contamination or not, and if any contamination is identified, try to determine from where the contamination originates?

Chapter 3 Geography of the study area

3.1 Location

The study area is situated in the central part of the Free State in South Africa (Figure 3.1), in the city of Bloemfontein on the eastern side of the city (Figure 1.2). The co-ordinates of Bloemfontein are latitude 29º06' south and longitude of 26º18' east. Bloemfontein lies at an altitude of 1351 metres. The total area of the study area is roughly 47 km^2. The total area comprises of many different land use zones. The area comprises the eastern side of the Central Business District (CBD), an informal settlement, the Bloemfontein and Schoemanpark golf courses, the industrial area of Bloemfontein and a small rural area (Figure 3.2). The study area focuses around the power station found on the western part the study area and the sewage works on the eastern part of the study area.

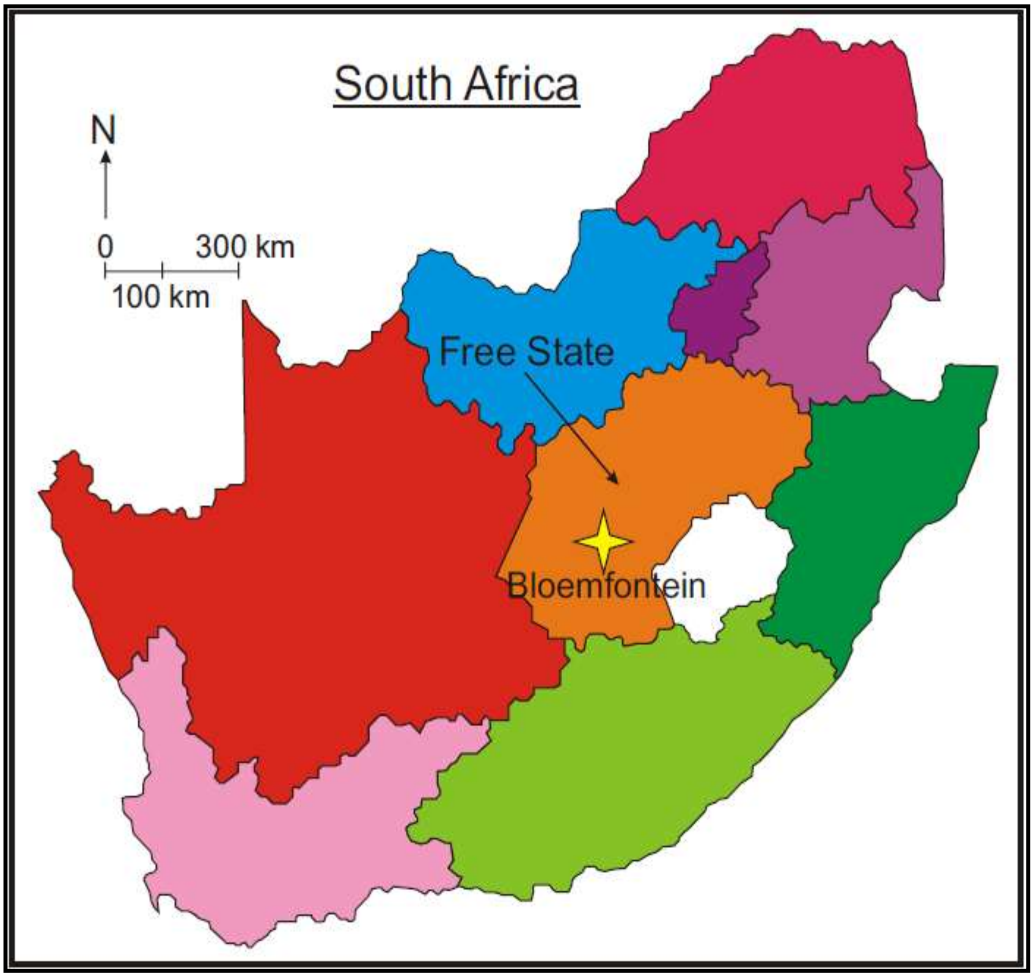


Figure 3.1 Map of South Africa showing the Free State and Bloemfontein. (Country and province borders modified after the geological map of Johnson et al., 2006b).

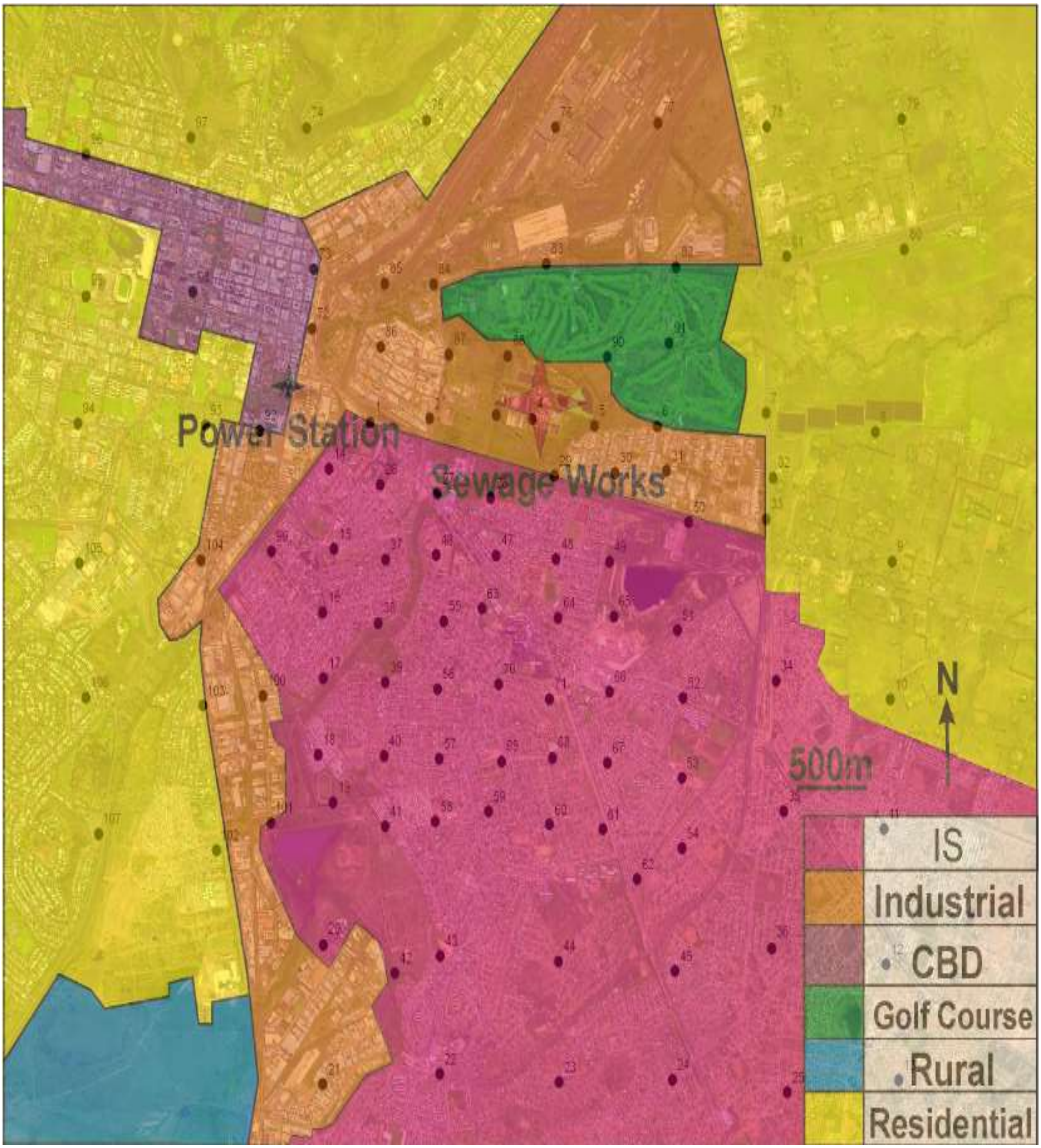


Figure 3.2 Study area of Bloemfontein indicating the different land use zones (IS – Informal settlement).

3.2 Climate of the Free State Province and Bloemfontein

3.2.1 Rainfall and evapotranspiration of the Free State and Bloemfontein

The climate of the Free State according to the aridity index criteria for bioclimatic zones gives an indication that the climate over most of the Free State is semi-arid (AI = rainfall/evaporation = 0.2–0.5). The extreme south western side of the province is classified as arid (AI = 0.03–0.2). Evaporation in the Free State ranges from 2000 mm in the east to a high of 2600 mm in the extreme west (Figure 3.3) (Hensley et al., 2006).

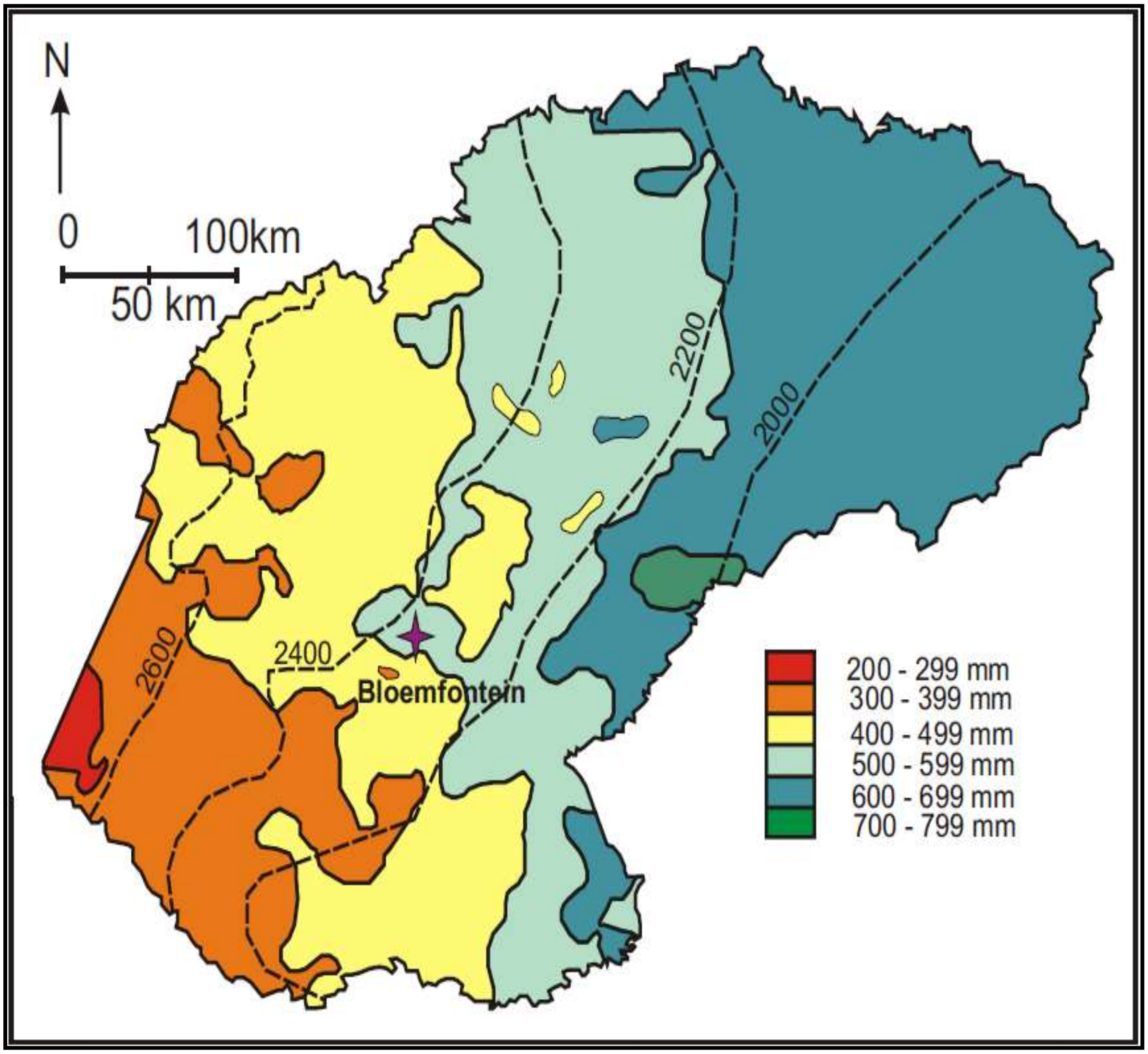
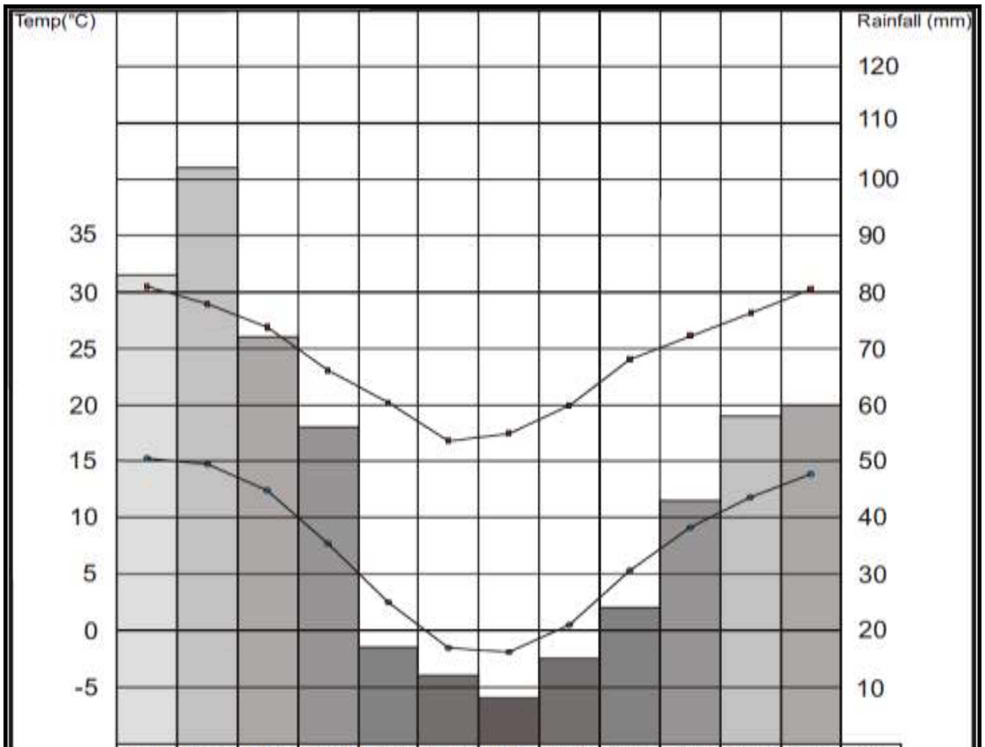


Figure 3.3 Annual rainfall and evaporation isoclines of the Free State (modified after Hensley et al, 2006 as cited in Department of Agricultural and environmental Affairs, 1995 and Schulze, 1997).

Bloemfontein normally receives roughly 559 mm precipitation per year, with most rainfall during the summer months with the heaviest being in February and March and the least rain falling in the winter months of June and July. Figure 3.4 indicates the average rainfall for Bloemfontein per month. Bloemfontein receives the highest average precipitation in February (111 mm) and the lowest in July (8 mm).

3.2.2 Temperature and wind direction

Bloemfontein has an average maximum temperature of 24.4ºC during the day and 7.5ºC during the night. The average monthly maximum temperatures during the day show that the average temperatures for Bloemfontein range from 16°C in June to 29.2°C in January. The average minimum temperatures range from 15.3°C in January to -1.9°C in July. The region is the coldest during July and the warmest during January (Figure 3.4). The South African Weather Service (SAWS) indicates the yearly average direction of wind in the Bloemfontein area is predominantly northerly to north easterly (Figure 3.5).



	Jan	Feb	Mar	April	May	June	July	Aug	Sep	Oct	Nov	Dec	Yr
Max Temp	30.8	28.8	26.6	23.1	20.1	16.8	17.4	20.0	24.0	26.1	28.1	30.1	24.4
Min Temp	15.3	14.7	12.4	7.7	2.5	-1.5	-1.9	0.5	5.2	9.1	11.7	13.8	7.5
Precipitation	83	111	72	56	17	12	8	15	24	43	58	60	559

Figure 3.4 Yearly figures of temperature and precipitation of Bloemfontein (South African Weather Service, 2011).

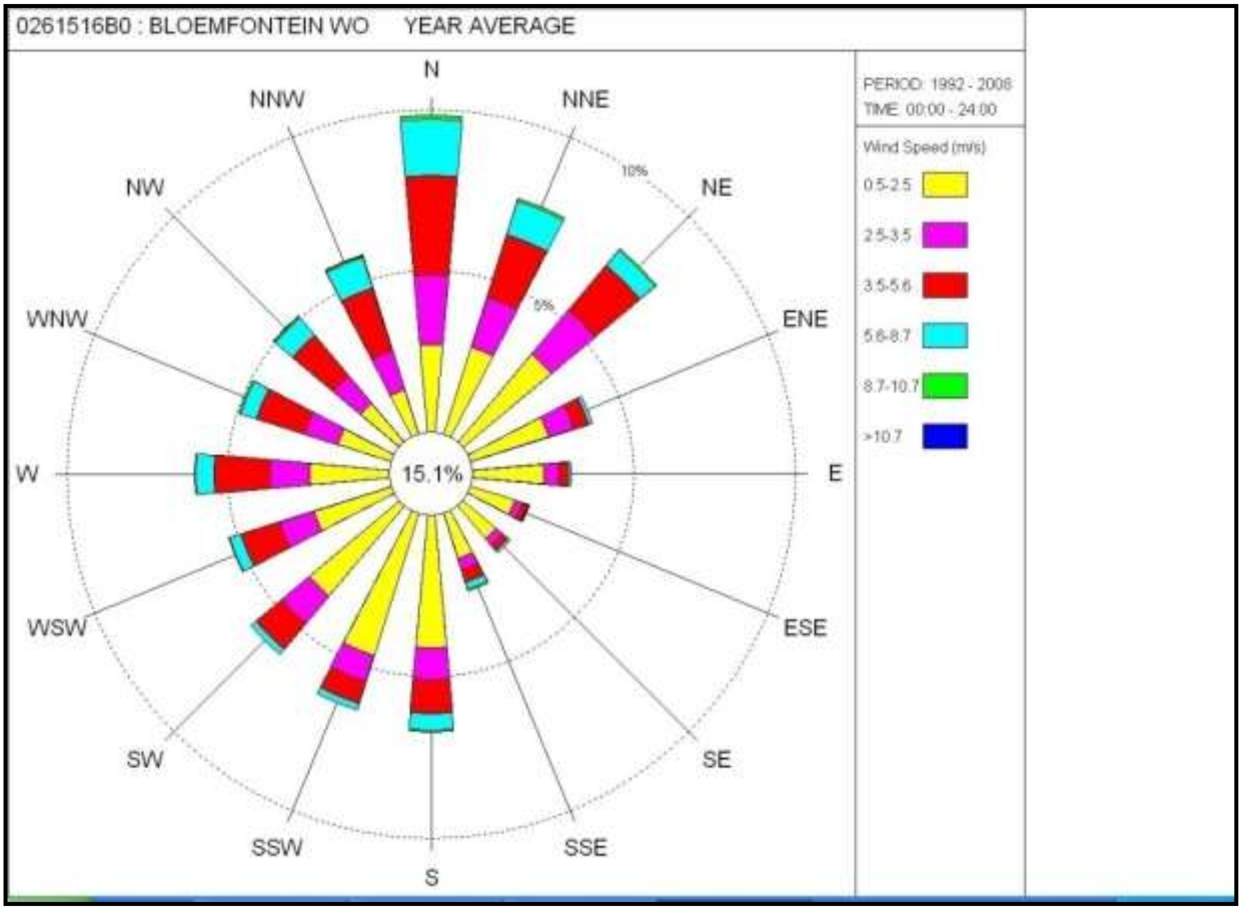


Figure 3.5 Wind rose indicating the average direction and speed of wind in Bloemfontein (South African Weather Service, 2011). The predominant wind direction with highest wind strength is mostly in the northerly direction and the least predominant wind direction and wind speed ranges between a south east direction and an east south east direction.

3.3 Geological background and soils of the Free State

The Geology of the Free State comprises Karoo sediments (Figure 2.8) with dolerite intrusive rocks (Johnson et al., 2006a). The Karoo Supergroup formed during the Late Carboniferous to the Middle Jurassic times. The Free State predominantly overlies the Beaufort Group and to the west of Bloemfontein, the older Ecca Group. The Beaufort Group contains 2 subgroups namely the Adelaide Subgroup and the Tarkastad Subgroup. Bloemfontein overlies the Adelaide Subgroup. The main rock types associated with the Adelaide subgroup are different grain-sized sandstones and red mudstone (Johnson et al., 2006b). In the eastern portion of the Free State, and in Lesotho, the rock types form part of the Karoo Igneous Province namely the Drakensberg Group classified as continental flood basalts and are of Mesozoic age (±180 Ma) (Catuneanu et al., 2005; Duncan and Marsh, 2006).

The Free State Province comprises a large area of South Africa, being 12.9 (11%) million ha while South Africa has a total area of 122.8 million ha. A large 11.8 (91%) million ha is used specifically for farming; therefore farming is a major economy for the province. The land is divided into different regions depending on how arable the land is. The land has a medium arable potential mostly on the eastern side of the province and decreases to non arable on the western side of the province. A small part on the north eastern portion is also classified as non arable and the land around Bloemfontein is mostly of low potential arable land (Figure 3.6) (Hensley et al., 2006).

There are many different soil types in the Free State. The types of soil that are found depend on 5 criteria such as parent material (geology), climate, topography, biological factors and time (Hensley et al., 2006). The parent materials associated with soil formation in the Free State are Karoo Supergroup sedimentary rocks of the Beaufort Group and Stormberg Group and dolerite igneous intrusions (Johnson et al., 2006a). The main rock types found in Bloemfontein are associated with the Beaufort Group (Figure 2.8) and the rock types are predominantly sandstone, shale and mudstones with many areas showing outcrops of dolerite intrusions. The main sources of parent material in the Bloemfontein area are from the Beaufort and Ecca sediments consisting of shale, mudstone and sandstone and dolerite intrusions. An overlying sand mantle that is believed to originate from Kalahari sands that have been blown over the region during dry seasons is another source of parent material for soil formation. Soils found in the area can be associated with underlying rocks, but in many locations this is not the case. Colluviation was the dominant process for transporting parent material of the many different soils in the region (Dohse, 1970).

The main soil types that are found in and around Bloemfontein have a texture classified between loamy-fine sand to fine sandy-loam. The sand fraction of soils in the Bloemfontein area are 70% between 0.250 mm and 0.088 mm indicating that the soils are well sorted and that aeolian action is a factor in the distribution of the sands (Dohse, 1970). The soils are of dark coloured clays with major shrink/swell properties. The breaking down of dolerite intrusive rocks by the local climate over time has been a major contributor to the soil forms in Bloemfontein. As dolerite weathers it forms 2:1 type clays causing the clays to swell upon wetting and to shrink upon drying causing the formation of cracks at the surface. As the mudstone and shale, rich in clay minerals, form the main geology of the area, break down due to the local climate, will further form 2:1 clay soils defined by montmorillonite clays.

The main dominant soil forms that are found in Bloemfontein are the Arcadia, Rensburg, Bonheim and Mayo soil forms (Hensley et al., 2006). Other noted forms described by Dohse (1970) are the Shortlands, Hutton, Willemsdal, Gemvale, Milkwood and the Mispah. The Soil Classification Working Group (1991) and MacVicar (1977) give a detailed description of each soil type. The Willemsdal and Gemvale soil forms are not classified in the Soil Classification Working Book Group (1991), and therefore they must be outdated soil forms. The Willemsdal form has similar properties to the Valsrivier comprising of an orthic A horizon overlying a pedocutanic B horizon. The Gemvale form has similar soil properties to a Glenrosa form comprising of an orthic A overlying a lithocutanic B horizon. Table 3.1 shows the different the sequences of diagnostic horizons that each profile contains.

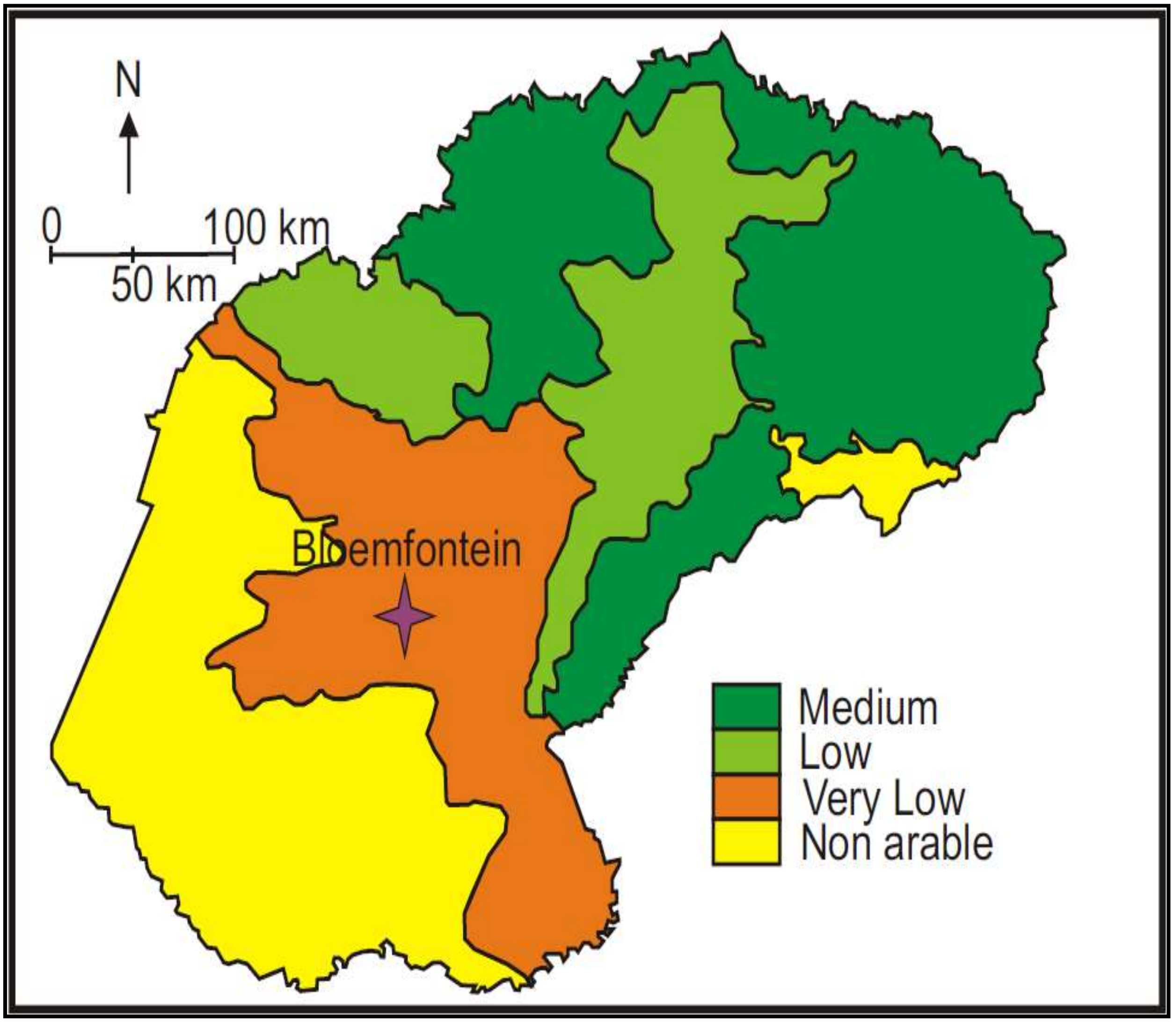


Figure 3.6 Arable agriculture potential of soils found in the Free State (modified after Hensley et al., 2006).

Table 3.1 The main dominant soil forms found in Bloemfontein (Dohse, 1970; Hensley et al., 2006; Soil Classification Working Group, 1991; MacVicar, 1977).

Soil Form	Diagnostic horizons
Arcadia	Vertic A horizon
Rensburg	Vertic A horizon G horizon
Bonheim	Melanic horizon Pedocutanic B horizon
Mayo	Melanic A horizon Lithocutanic B horizon
Shortlands	Orthic A horizon Red structured B horizon
Hutton	Orthic A horizon Red apedal B horizon Unspecified
Willemsdal (Valsrivier)	Orthic A horizon Pedocutanic B horizon
Gemvale (Glenrosa)	A horizon Lithocutanic B horizon
Milkwood	Melanic A horizon Hard rock
Mispah	Orthic A horizon Hard rock

Chapter 4 Materials and Methods

4.1 Sampling

4.1.1 Initial sampling

Initial sampling for a previous project began in May 2006 by people of the Council for Geoscience. The study was undertaken for medical research because of possible contamination of the area with mercury. However the results initially resulted in the research program being abandoned because initial conclusions were that there was no contamination. The Global Positioning System was used to identify the co-ordinates for each sampling position and the GPS MAP 60CSx data package was used. One hundred and forty seven samples were collected for the study: there were 22 dust samples, 4 soil profiles, 112 urban soil samples and 9 background samples taken 10 km north, south, east and west of the power station (Appendix 1). All the soil samples were collected at 500 m intervals from each other with the first sample being taken 500 m east of the coal-fired power station. The sample positions can be seen in Figure 3.2 and 3.3. The samples were all taken at depths of 0 - 5 cm; all had weights of approximately 500 g and were all stored in separate airproof plastic bags. A geological hammer and scoop were used to aid in obtaining the soil samples. The background samples were also collected at 0 - 5 cm depths with a scoop and were taken 10 km away of north, south, east and west of the power station and were also stored in separate airproof plastic bags (M. Cloete, pers comm., 2011).

Dust samples were collected with separate individual good quality soft bristle brushes to prevent cross-contamination of samples. The samples were approximately 1 g and were taken on top of refrigerators in tuckshops or on top of sewing cutting tables in sewing stores. The samples were stored in screw-cap polyethylene bottles. The first soil profile was taken approximately 50 m from the emission stacks and cooling towers of the power station. The samples were collected 0 - 20 cm, 20 - 40 cm and 40 – 60 cm depths (auger). The second profile was taken 500 m from the power station and the samples were collected at 0 - 20 cm, 20 - 40 cm and 40 - 60 cm depths with the use of a Thompson soil auger. All samples were analyzed for heavy metal content and results will be reported in Chapter 5.

4.1.2 Sudoku Sampling

Soil chemistry analysis was done on a random batch of the samples that were selected using the Sudoku type method (Hui-Dong and Ru-Gen, 2008). A grid was placed over the study area in the form of a Sudoku playing game which was completed with numbers appearing in the spaced blocks. Random numbers were selected and any sample falling into a block with a selected number, was analyzed further. In this study the numbers 6 and 8 were selected to obtain a sufficient amount of samples for further soil chemistry analysis (Figure 4.1).

Additional samples were taken from the original sampling session that were not part of the Sudoku sampling method and were also analyzed. The additional samples that were used were directly south of the power station because the wind direction for Bloemfontein is predominantly a northerly wind (Figure 3.5).

For soil characteristics, the samples were dried for 24 hours in a dying room at a temperature ranging between 40-60°C and they were sieved through a 2 mm sieve. The samples were then analyzed chemically, the mineralogy as well as texture were determined. All the references for all the specific methods except for texture can be found in The Non-Affiliated Soil analysis Work Committee (1990)

4.2 Texture

4.2.1 Introduction

Soil particles form the solid phase of soil and generally bond together as aggregates. The aggregates can be separated using chemical or mechanical techniques. By using these techniques particles can be separated and be divided into different sizes and shapes (Table 4.1). The texture methods that shall be described apply to the inorganic particles of soil.

Table 4.1 Particle sizes of soil and the different method types used to separate the particle sizes.

Class sizes	Diameter range (mm)	Method of separation
Gravel	> 2	Sieve
Coarse sand	2.0 – 0.5	Sieve
Medium sand	0.5 – 0.25	Sieve
Fine sand	0.25 – 0.106	Sieve
Very fine sand	0.106 – 0.05	Sieve
Coarse silt	0.05 – 0.02	Sedimentation
Fine silt	0.02 – 0.002	Sedimentation
Clay	< 0.002	Sedimentation

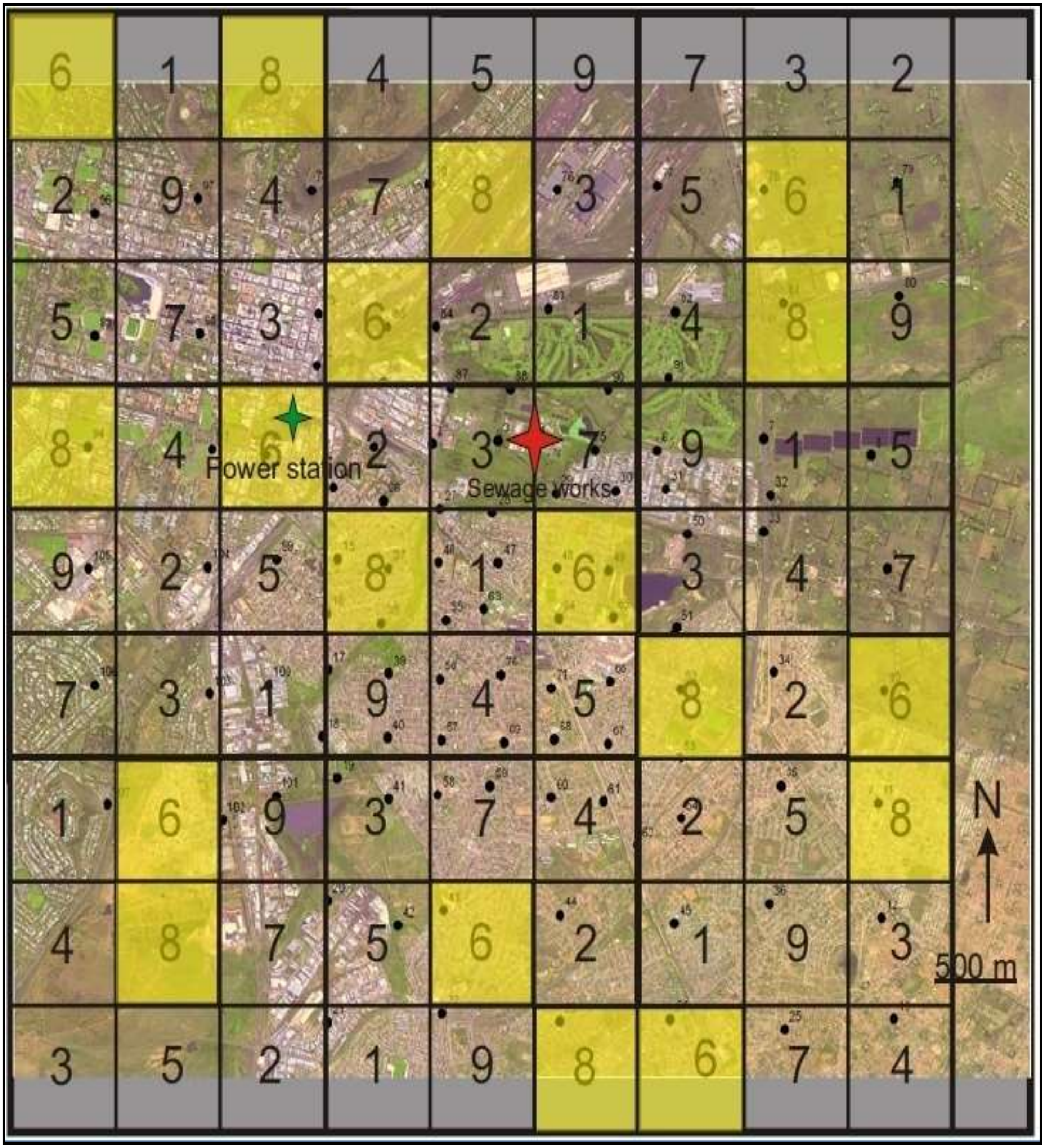


Figure 4.1 Sudoku grid map of the study area for random sample analysis. The image is the same image as Figure 3.2. The numbers used for selection for further analysis in the study were 6 and 8.

4.2.2 Apparatus

The different apparatuses that were used to obtain texture of the soils were the following: Glass sedimentation cylinders with a volume of 1 dm^3, a hand stirrer, a pipette stand and a Lowy pipette with a volume of 25 cm^3, sieves with a 100 mm diameter with different fractions (2.0 mm, 0.5 mm, 0.25 mm, 0.106 mm and 0.053 mm), a room that has a constant temperature. Other apparatus that is needed was a drying oven, hotplate, beakers, thermometer, high speed stirrer and crucibles.

The reagent that was used in the procedure was calgon dispersing solution. Calgon is made by dissolving 35.7 g sodium hexametaphosphate [$(NaPO_3)_6$] and 7.94 g sodium carbonate (Na_2CO_3) in 1 dm^3 de-ionized water.

4.2.3 Procedure

An amount of the sample was collected for measurement, and for this procedure 30 grams of a sample was used. 50 ml of calgon was added to the soil sample. The new sample was then transferred to a 250 cm^3 centrifuge bottle. De-ionized water was added to make a total volume of 150 cm^3 and then the sample was mixed for 5 minutes using an electric shaker.

The dispersed sample was then washed on a 0.053 mm sieve, causing the silt and clay particles to pass through a funnel into a 1000 cm^3 cylinder and the larger particles were left behind on the sieve. This procedure was done until the water moving through the sieve became clear. The remaining soil particles left in the sieve were transferred to a beaker and were dried at 105°C. After the sample was dried, the sample was transferred to a nest of sieves with different sizes (0.5; 0.25; 0.106; 0.053 mm and pan) on a sieve shaker where the sample was sieved for 10 minutes. The masses of each sieve with soil particles were then measured.

The clay and silt that was left in the cylinder was then determined. The cylinder was filled up to 1 dm^3 with de-ionized water and placed in a room with constant temperature. The sample was then stirred for 30 seconds in a vertical motion. The time was noted when the stirring ceased. A Lowy pipette was then placed at 10 cm depth into the cylinder and 25 cm^3 of sample was withdrawn and discharged onto an evaporating dish to determine the 0.05 mm fraction. The pipette was washed with de-ionized water to prevent contamination. The sample was dried at 105°C and the mass was determined. The procedure was repeated for the 0.02 mm fraction and 0.002 mm fractions at specific times. The times were 5 minutes 46 seconds for the 0.02 mm fraction (silt and clay) and 5 hours 34 minutes for the 0.002 mm fraction (clay) (USDA, 1972; Gee and Bauder, 1986).

4.3 Soil pH

4.3.1 Introduction

The pH of soil is very important to obtain, especially in the agricultural field because pH plays an important role in fertility of the soil. If a soil is acidic or alkaline, it will have a major influence on nutrient availability to plants for uptake. The optimal pH for a soil is between 5.5 and 7 because in this range most macro- and micronutrients are available for uptake by plants. At low pH values micronutrients such as iron and manganese and metals such as copper can become soluble to such an extent that the elements may become toxic to plants but at pH values which are highly alkaline, these micronutrients are very difficult to be taken up by plants (Brady and Weil, 2008).

4.3.2 Apparatus and preparation

The equipment needed to measure the pH of soil samples comprised a pH meter with combined-calomel electrode, dial scale 0 – 14 × 0.1 pH, 100 cm^3 beakers and 100 cm^3 measuring cylinders. The pH meter was turned on before the process began to warm up properly. It was then calibrated by rinsing the electrode with de-ionized water and then dipping it into a buffer solution with a known pH of 7.00. The calibration was completed using a buffered liquid of pH 4.00. After completing the calibration, the pH of a sample was determined.

4.3.3 Method

A 20 g soil sample was weighed and put into a 100 cm^3 glass beaker and 50 cm^3 of distilled water was added to the sample. The sample was stirred thoroughly with the use of a glass rod. After the sample had been stirred for a while it was left to stand for 30 minutes while the mixture was stirred from time to time. Another 20 g sample was measured in another glass beaker and 50 cm^3 of 1 M KCl solution was added to the sample. It was also stirred and left to stand for 30 minutes.

4.3.4 Measurements

The sample was stirred again after 30 minutes and the pH electrode was carefully dipped into the liquid. The tip of the pH electrode did not touch the precipitated soil in the beaker. The instrument was switched to “pH” and as soon as the instrument stabilized, the pH value was noted to 2 significant figures. When the pH was recorded, the electrode was removed from the solution and was then rinsed off with de-ionized water to prevent contamination. The same process was repeated with the second measurement containing the KCl suspension.

4.4 Organic carbon

The reagents that were used in the process were 0.167 N potassium dichromate solution ($K_2Cr_2O_7$), sulfuric acid (H_2SO_4), concentrated ortho phosphoric acid, 0.5 N ferro ammonium sulphate [$Fe(NH_4)_2(SO_4)_2$] solution and barium diphenylamine sulphonate indicator.

The Walkley and Black (1934) method with slight modifications was used for the organic carbon. Analysis of 1 g of soil was measured into a 500 cm^3 Erlenmeyer flask. 10 cm^3 of $K_2Cr_2O_7$ solution was added to the soil by use of a pipette. The contents were swirled in the flask to disperse the soil into the solution. 20 cm^3 of concentrated sulphuric acid (H_2SO_4) was added quickly to the contents. After the sample was cooled for 30 minutes, 150 cm^3 of de-ionized water and 10 cm^3 concentrated ortho phosphoric acid were added. When completed, the sample was analysed using titration.

1 cm^3 diphenylamine indicator was added and the excess $K_2Cr_2O_7$ was titrated using ferro-ammonium sulphate. The solution colour turned violet brown as the end point was approached. The ferro-ammonium sulphate was then added drop by drop until the colour changed green. The % C was then calculated using the following formula:

$\% C = \{[cm^3\ Fe(NH_4)_2(SO_4)_2\ blank - cm^3\ (Fe(NH_4)_2(SO_4)_2\ sample] \times M \times 0.3\} / soil\ mass\ in\ grams$. M is the normality of the ferro-ammonium sulphate solution being 0.5.

4.5 Phosphorus

The Bray I method was used for analysis. 2.5 g of soil was put into a plastic bottle with 50 ml $NaHCO_3$. It was mixed for 30 minutes after which 2 drops of superfloc were added to the sample. The sample was then filtered. 10 cm^3 of the filtered sample was then extracted and added to 8cm^3 of distilled water and a colour reagent. A colorimeter was used to determine light absorption at wave length 882 nm of the sample which was converted to determine the P concentration of the solution in mg/kg (ppm).

4.6 Nitrogen

The reagents that were used in the process were 8 N sodium hydroxide (NaOH), concentrated sulfuric acid (H_2SO_4), boric acid indicator and a catalyst.

2 g of soil was added to 0.1 g of catalyst in a 100 cm^3 digestion tube with an additional. 4 cm^3 of concentrated H_2SO_4 was pipetted into the tube for the entire sample to be mixed. The tube was heated for 1.5 hours until all the material in the tube was brought to a clear solution. After the sample cooled, de-ionized water was added to the tube with precaution to prevent any possible explosion from the acid in the tube due to heat produced from dilution. The tube was shaken carefully and the sample was rinsed out into a Kjeldahl flask. The tube was washed with 3 portions de-ionized water and it was all put in the Kjeldahl flask.

25 cm^3 of NaOH solution was added to the Kjeldahl flask and the released NH_3 was distilled in a saturated boric acid solution. The boric acid solution was then titrated with 0.01 N H_2SO_4 and the nitrogen was calculated as mg/kg^{-1} soil in the following way:
Titration in ml of sample – blank = T
mg N = standard N × 14 × T = 0.01× 14 × T = mg N / 2 g soil

4.7 Cation exchange capacity (CEC) and cations

The reagents that were used for the procedure were 60% ethyl alcohol, 1 Normal ammonium acetate pH 7, and sodium acetate.

A 10 g soil sample was placed into a 12 cm^3 folded Whatman #1 filter paper in a funnel. The funnel was placed over a 250 cm^3 volumetric flask. The soil was then leached with approximately 50 cm^3 of 60% ethyl alcohol. The alcohol was allowed to drain completely through the soil sample until 200 cm^3 of alcohol was completely filtered through. The flask was then filled with remaining alcohol to exactly the 250 cm^3 mark. The flask was shaken well and the liquid was poured into a plastic bottle marked A. This sample was used to determine the soluble calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na).

The soil that was on the funnel was leached again but with ammonium acetate into a 250 cm^3 volumetric flask. The ammonium acetate solution was drained through the soil completely and small portions were added repeatedly until the solution in the flask reached exactly 250 cm^3. The sample was shaken and poured into another plastic bottle marked B. This sample was used to determine the exchangeable Ca, Mg, K and Na. The soil was retained on the filter paper to determine the CEC of the soil.

The retained soil was then saturated with Na by leaching the soil with 1 N sodium acetate. The soil was leached with over 250 cm^3 of sodium acetate and the solution was discarded. The soil was now saturated with sodium. The soil was then leached with 60% ethyl alcohol till above 250 cm^3 to get rid of salts and the solution was also discarded. A volumetric flask was placed under the funnel and 1 N ammonium acetate was used to leach out the sodium. The sample is leached until the 250 cm^3 mark on the flask was reached. The sample was then shaken well and placed into a new bottle marked C. This sample was used to determine the CEC of the soil. All the samples are analyzed by means of an atomic absorption spectrometer.

4.8 XRD and XRF

4.8.1 Introduction

Milling equipment was cleaned beforehand to prevent contamination of the samples. A small amount of each sample was then put into the millers for a final pre-contamination and cleaned properly afterwards before the samples were finally milled. Small quantities of the samples were milled for 3 minutes to a fine powder that was then analyzed by x-ray diffraction (XRD) and x-ray fluorescence (XRF).

4.8.2 XRD

A small amount of the milled sample was mounted in a sample holder and was analyzed with a PANanalytical Emperyean model XRD instrument at the University of the Free State Geology Department.

4.8.3 XRF

4.8.3.1 Majors

Two sub samples were taken from the original sample to determine the major elements and the trace elements. The first sample was dried overnight to get rid of any traces of water. The sample was then heated to a temperature of 1000°C for 4 hours to obtain the loss of ignition in the sample. The sample was then reheated again to above 1000°C to obtain a melting point. After the sample was melted the sample was made into a fusion disc to analyze the major elements in the sample. The samples were analyzed at the University of the Free State Geology Department with the PANalytical Axios XRF machine.

4.8.3.2 Trace elements

Eight grams of the sample was mixed with 3 g of wax powder. The sample was mixed for at least 5 minutes so the mixture can be as homogonous as possible. The sample was then pressed into a pellet under 4 bar pressure. The pellet was then analyzed for trace elements. The samples were analyzed at the University of the Free State Geology Department with the PANalytical Axios XRF instrument.

4.9 Analysis for heavy metals

4.9.1 Introduction

The samples were prepared for analysis before sending it to China. The samples were sieved through a 75 µm sieve. The reasoning behind this choice were (a) that this size fraction during analysis is the most chemically absorbent and (b) the emissions from the power station will also have very fine sizes, therefore the 75 micron size was selected. As soon as the analysis was complete the sieved samples were returned to the original bag for any further chemical analysis. The reasons behind

4.9.2 Arsenic, antimony, mercury and bismuth

A 0.5 g sample was dissolved with aqua regia. The solution was diluted to 20% by adding de-ionized water and 10 ml was pipetted. Thiourea-ascorbic acid was added and the sample was reduced with KBH_4. The reduced solution of arsenic and antimony were analyzed using a hydride generation atomic fluorescence spectrometer (HG-AFS) with a detection limit of 0.2 µg/g for arsenic and 0.05 µg/g for antimony. The reduced solutions of bismuth and mercury were analyzed using the hydride generation-atomic fluorescence spectrometer (HG-AFS) with a detection limit of 0.05µg/g for bismuth and 0.005 µg/g for mercury.

4.9.3 Cadmium

A 0.2 g of the sample was dissolved with nitric acid, hydrofluoric acid and perchloric acid until the solution became clear. Diluted hydrochloric acid was added together with ammonium dihydrogen phosphate, thiourea and EDTA disodium salt matrix modifier. The sample was then analyzed with a graphite furnace-atomic adsorption spectrometry (GF-AAS) with a detection limit of 0.05 µg/g.

4.9.4 Selenium

A 0.25 g sample was dissolved with nitric acid, hydrofluoric acid and perchloric acid until the solution was clear. It was then heated to remove fluorine ions. Diluted 30% hydrochloric acid solution was added and the sample was then reduced with KBH_4. The sample was then analyzed using a hydride generation-atomic fluorescence spectrometry (HG-AFS) with a detection limit of 0.05 µg/g.

4.10 GIS mapping

Spatial distributions of the heavy metals were analyzed using Arc Map software to determine the concentration and enrichment factors to elucidate the spacial distribution of the heavy metals. Inverse Distance Weighting (IDW) was used to generate the maps from the analyzed point data.

Chapter 5 Results

5.1 Sudoku locality results

5.1.1 Locality positions

The analytical data of the samples that were selected through Sudoku sampling (Figure 4.1) appear in Table 5.1 – 5.9 with the exception of the dust sample results found in Table 5.8.

5.2 Texture

Measuring texture of a soil, recovery between 95% and 105% was needed for the information to be accurate. Of the 21 samples analyzed, 2 samples (A49, A64) fell in the range for acceptable accuracy. Some samples fell within the range but in the fine silt fraction a negative number appeared making the analyses worthless. Samples out of suitable range had a range of 89.2% up to 94.6% recovery. Table 5.1 gives the samples with their specific sand fraction and the percentage recovery.

5.3 Soil chemistry

5.3.1 Introduction

All samples that were selected using the Sudoku sampling method were analyzed for certain chemical analysis. The different analyses that were done on the samples were organic nitrogen, organic carbon, and phosphorous content, pH and cation exchange capacity. All results are presented in Table 5.2 and Table 5.3.

5.3.2 Organic nitrogen and carbon, phosphorus and pH

The organic nitrogen content of the selected samples ranged from 0.044% (436 mg/kg) to 0.211% (2112 mg/kg). The organic carbon of the selected samples ranged from 0.462% (4260 mg/kg) and 4.51% (45100 mg/kg). The values indicate very low to high amounts of organic carbon. The values of phosphorous of the selected samples ranged between 0.085 ppm and 1.06 mg P/kg soil. These values indicate very low phosphorous in the soil.

The pH_{water} of the samples ranged from 6.24 to 7.92. This indicates that the samples range between slightly acidic to a slightly alkaline. The pH_{KCl} values were significantly lower than the

pH_{water} values. The samples ranged between 5.7 and 7.45. The reason for the lower values is because the potassium in the KCl replaces the H^+ on the soil colloids and in turn the H^+ is increased in the solution causing the pH of the solution to drop. The samples were more acidic but still some samples remain slightly alkaline. Table 5.2 gives the organic nitrogen, carbon, accessible phosphorous and the pH and KCl values for each sample.

5.3.3 Cation exchange capacity

5.3.3.1 Introduction

The cation exchange capacity (CEC) as well as soluble and exchangeable calcium, magnesium, potassium and sodium results are given in Table 5.3.

5.3.3.2 Calcium

The soluble calcium ranged between a low 6.8 ppm and a high of 48.0 ppm. The exchangeable calcium ranged between a low of 955.0 ppm and a high of 4857.5 ppm.

5.3.3.3 Magnesium

The soluble magnesium ranged between a low of 2 ppm and a high of 14.3 ppm. The exchangeable magnesium ranged between a low of 45 ppm and a high of 967.5 ppm.

5.3.3.4 Potassium

The soluble potassium ranged between a low of 0.8 ppm and a high of 33.8 ppm. The exchangeable calcium ranged between a low of 87.5 ppm and a high of 647.5 ppm.

5.3.3.5 Sodium

The soluble sodium ranged between a low of 6.3 ppm and a high of 83 ppm. The exchangeable sodium ranged between a low of 14.5 ppm and a high of 102.5 ppm.

5.3.3.6 CEC

The CEC of the soil ranged between a low of 1250 ppm and a high 5625 ppm.

5.4 XRD

The Sudoku selected samples were analyzed for their clay mineralogy (Table 5.4). The XRD images are given in Appendix 3. Main minerals found were quartz, plagioclases, alkali feldspars, illite, augite, kaolinite, muscovite, montmorillonite, vermiculite and calcite.

5.5 XRF

The major element distribution of the Sudoku selected samples are given in Table 5.5. The sum concentration percentage's acceptable range must be between 98% and 102%. 9 samples fall out of the acceptable range. Table 5.6 show the trace element results of the selected samples.

5.6 Concentrations of the heavy metals

The concentrations of all the heavy metals in soils are given in Appendix A2.1. Table 5.7 gives the concentrations of the samples selected using the Sudoku method. All the results are indicated as parts per million (ppm) for antimony, arsenic, bismuth, cadmium, mercury and selenium. After completion the concentration values were put into the GIS to obtain concentration images of the study area. Table 5.8 gives all the concentrations of the samples. All the results are indicated as parts per million (ppm) for antimony, arsenic, bismuth, cadmium, mercury and selenium.

5.7 Enrichment factor values

The concentrations for each heavy metal element were used to calculate an enrichment factor. Appendix 3 indicates the enrichment factor results for all the soil samples and Table 5.9 gives the Sudoku samples. Table 5.10 gives the enrichment factor values for all the dust samples. The enrichment factor calculations were done by obtaining a background soil reference value and dividing the resultant concentration by the background value to achieve the enrichment factor. The resultant enrichment factor values for the soil samples were put into the GIS to obtain an enrichment factor image for each element of the study area.

Table 5.1 Soil texture in Sudoku soil samples (nd-not determined).

	Fraction %							
Sample number	Course sand	Medium sand	Fine sand	very fine sand	course silt	fine silt	clay	Total
A10	6.1	8.7	42.1	14.9	5.1	4.9	11.2	93.1
A11	4.2	6.0	46.7	19.6	6.3	6.2	4.5	93.6
A16	16.2	9.7	33.8	15.2	7.6	7.6	1.8	92.0
A23	8.1	4.0	15.7	12.8	7.6	17.8	18.7	84.7
A24	11.5	4.3	20.9	15.9	12.7	nd	nd	90.9
A37	22.8	10.5	30.6	14.7	6.4	5.5	4.1	94.6
A38	21.1	10.0	23.4	11.9	8.1	1.5	7.3	83.4
A43	20.7	11.1	22.4	11.7	8.1	11.9	7.2	93.2
A48	1.7	13.1	50.7	17.7	10.6	nd	1.9	95.1
A49	3.5	5.1	43.3	19.2	9.4	8.0	6.6	95.1
A52	13.3	10.2	43.9	15.5	4.9	nd	nd	96.8
A53	6.6	10.0	43.0	14.7	5.5	6.1	3.5	89.5
A64	3.2	11.9	51.4	17.7	5.8	4.2	1.6	96.0
A65	15.0	7.7	31.9	15.6	6.0	7.1	9.6	92.8
A78	1.8	3.6	24.9	14.1	7.9	9.1	28.0	89.2
A81	11.9	6.5	26.6	10.8	3.6	5.7	26.6	91.7
A85	15.1	31.1	31.2	6.7	4.4	nd	16.9	94.3
A86	7.9	10.0	31.8	14.2	7.8	12.5	6.8	91.1
A92	5.3	16.8	41.1	16.5	5.1	4.9	3.3	92.9
A94	2.1	5.0	31.4	13.7	5.8	7.1	27.2	92.3
A102	11.3	5.7	22.6	12.7	9.2	15.1	14.8	91.5

Table 5.2 Organic nitrogen, carbon, phosphorus and pH in Sudoku soil samples.

	Organic N	Organic C	Phosphorus	pH	
Sample	%	%	ppm	water	KCl
A10	0.09	1.29	0.67	6.56	6.08
A11	0.13	1.84	0.73	6.24	5.70
A14	0.21	3.44	0.67	7.34	7.02
A15	0.08	0.88	0.09	6.78	6.76
A16	0.10	1.87	0.69	7.52	7.18
A17	0.10	1.07	1.06	7.15	7.05
A18	0.17	4.22	0.54	6.94	6.42
A23	0.15	2.09	0.57	7.33	6.93
A24	0.10	1.25	0.66	7.22	6.76
A37	0.04	0.71	0.35	7.86	7.42
A38	0.05	0.64	0.42	7.86	7.27
A43	0.21	3.37	0.89	7.36	7.07

Table 5.2 continued: Organic nitrogen, carbon, phosphorus and pH for in Sudoku soil samples.

	Organic N	Organic C	Phosphorus	pH	
Sample	%	%	ppm	Water	KCl
A48	0.11	1.73	0.61	6.40	6.15
A49	0.05	0.55	0.10	7.11	6.26
A52	0.05	0.43	0.14	7.92	7.45
A53	0.05	0.56	0.24	7.71	7.43
A64	0.11	1.74	0.79	6.30	6.04
A65	0.09	2.27	0.44	7.45	6.84
A78	0.09	1.16	0.15	7.53	7.20
A81	0.09	1.08	0.20	7.09	6.46
A85	0.11	4.51	0.33	7.37	6.80
A86	0.13	3.51	0.74	7.45	7.07
A92	0.10	2.49	0.63	6.40	6.02
A94	0.11	1.53	0.40	7.60	7.35
A102	0.07	0.78	0.28	7.81	7.37

Table 5.3 Cation exchange capacity as well as soluble and exchangeable calcium, magnesium, potassium and sodium in Sudoku soil samples.

	Cations								CEC
	Soluble				Exchangeable				
Solution	Ca	Mg	K	Na	Ca	Mg	K	Na	Na
Label	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
A10	12.3	4.5	5.5	6.3	1263	248	310	17.3	2150
A11	15	7.3	14.8	11	1403	293	408	21.8	2900
A14	41	14.3	33.8	30	2938	313	515	42	3275
A15	16.5	6.3	15.5	13.3	1090	258	525	24.5	1925
A16	31.5	8.3	5	12.8	3883	313	298	24.8	4550
A17	6.8	2	2.5	22.5	2413	588	305	77.5	4200
A18	29	8.8	11.8	16.5	3923	320	395	40	2525
A23	20.5	7	2	20.8	3688	693	165	45	5475
A34	27.3	7	8.3	42.3	3100	485	213	60	4200
A37	48	8.8	2.5	83	2873	398	160	102.5	2550
A38	26.8	6.5	1.3	49	3588	398	118	72.5	3175
A43	17.3	7.5	9.8	20.3	4080	530	648	40	1675
A48	15.5	4.3	8	11.5	1125	100	200	17.5	1625
A49	11.8	2.3	0.8	6	955	45	87.5	14.5	1500
A52	17	4.5	12.8	10.8	2175	248	245	17	1250

Table 5.3 continued: Cation exchange capacity as well as soluble and exchangeable calcium, magnesium, potassium and sodium in Sudoku soil samples.

	Cations								CEC
	Soluble				Exchangeable				
Solution	Ca	Mg	K	Na	Ca	Mg	K	Na	(Na)
Label	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
A53	25.5	5.8	7.3	9.5	2795	200	303	37.5	1925
A64	17.8	5.5	7.3	14.8	1108	148	283	37.5	1675
A65	15.3	5.3	3.5	12.5	2303	478	335	37.5	3675
A78	24.8	6.5	2.3	9.8	4858	880	550	37.5	5625
A81	14.8	5.8	2.5	9.5	2495	653	448	32.5	4450
A85	10	2.8	7	6.3	1303	173	200	25	1925
A86	15.8	5	5.3	15.3	4633	448	450	40	4150
A92	13	3.8	13.5	8.3	1493	163	430	32.5	2325
A94	22	11.3	5.5	14.3	3160	968	483	32.5	4500
A102	26	7.8	7.8	7	3965	583	620	27.5	4150

Table 5.4 XRD results of the selected samples containing minerals found in Sudoku soil samples.

Sample #	Mineralogy
A10	Quartz, plagioclase, alkali feldspar, illite
A11	Quartz, plagioclase, muscovite, illite, montmorillonite
A14	Quartz, plagioclase, muscovite
A15	Quartz, plagioclase, alkali feldspar, muscovite
A16	Quartz, plagioclase, alkali feldspar, muscovite, montmorillonite, kaolinite
A17	Quartz, plagioclase, muscovite, vermiculite
A18	Quartz, plagioclase, muscovite, montmorillonite
A23	Quartz, plagioclase, illite, montmorillonite, kaolinite
A24	Quartz, plagioclase, muscovite, montmorillonite
A37	Quartz, plagioclase, muscovite, montmorillonite, kaolinite
A38	Quartz, plagioclase, muscovite, vermiculite
A43	Quartz, plagioclase, muscovite, vermiculite
A48	Quartz, plagioclase, muscovite, muscovite, vermiculite
A52	Quartz, plagioclase, annite, augite
A53	Quartz, plagioclase, muscovite, montmorillonite, kaolinite
A64	Quartz, plagioclase, muscovite
A65	Quartz, plagioclase, augite, muscovite
A78	Quartz, plagioclase, muscovite, calcite
A81	Quartz, plagioclase, muscovite, montmorillonite
A85	Quartz, plagioclase, montmorillonite
A86	Quartz, plagioclase, muscovite, montmorillonite
A92	Quartz, plagioclase, muscovite
A94	Quartz, plagioclase, muscovite, montmorillonite
A102	Quartz, plagioclase, muscovite, montmorillonite, kaolinite

Table 5.5 XRF major element oxide (in %) results of the Sudoku soil samples. LOI – Loss of ignition (%).

	A10	**A11**	**A14**	**A15**	**A16**	**A17**	**A18**	**A23**	
SiO_2	83.7	72.13	61.76	75.57	61.38	66.64	60.32	65.43	
Al_2O_3	5.54	8.78	8.80	4.47	11.58	13.80	12.20	12.30	
Fe_2O_3	3.38	5.13	5.20	2.69	7.64	4.70	8.79	6.60	
MnO	0.37	2.09	4.37	0.55	6.81	1.59	6.44	2.71	
MgO	0.50	1.64	2.22	0.50	5.05	2.67	6.27	1.99	
CaO	0.06	0.09	0.10	0.048	0.13	0.16	0.15	0.12	
Na_2O	0	0	0.08	0	0.87	0.06	1.30	1.99	
K_2O	1.16	1.14	1.09	0.79	0.67	2.36	1.04	1.23	
TiO_2	0.12	0.16	0.31	0.06	0.15	0.14	0.24	0.18	
P_2O_5	0.65	0.68	0.71	0.57	0.78	0.60	0.94	0.83	
H_2O	0.01	0.02	0.01	0.01	0.01	0.02	0.002	0.031	
LOI	4.03	7.37	8.11	3.17	4.22	4.28	1.14	7.97	
total	99.52	99.25	92.78	88.42	99.29	97.01	98.84	101.40	
	A24	**A37**	**A38**	**A43**	**A48**	**A49**	**A52**	**A53**	
SiO_2	59.95	65.77	65.49	53.58	59.41	68.49	77.82	72.68	
Al_2O_3	10.76	9.51	13.90	10.92	12.11	10.21	6.55	7.93	
Fe_2O_3	6.73	6.78	5.83	6.63	7.35	7.62	4.89	5.92	
MnO	4.45	4.95	2.86	6.08	6.74	5.71	2.34	3.26	
MgO	3.19	3.59	2.04	2.89	3.21	4.31	2.19	3.58	
CaO	0.12	0.12	0.13	0.12	0.14	0.13	0.08	0.09	
Na_2O	0.20	0.15	0.95	0.30	0.33	0.64	0.43	0.07	
K_2O	0.96	0.73	2.23	0.88	0.98	0.98	0.87	0.86	
TiO_2	0.27	0.14	0.14	0.36	0.41	0.27	0.068	0.07	
P_2O_5	0.80	0.74	0.74	0.83	0.93	0.77	0.84	0.8	
H_2O	0.02	0.01	0.02	0.02	0.01	0.02	0.01	0.01	
LOI	4.94	3.70	4.19	14.91	5.93	5.68	2.09	2.85	
total	92.39	96.19	98.52	97.53	97.54	99.13	98.17	98.15	
	A64	**A65**	**A78**	**A81**	**A85**	**A86**	**A92**	**A94**	**A102**
SiO_2	77.80	67.20	73.32	63.97	75.06	72.78	63.90	63.06	61.90
Al_2O_3	5.35	10.43	9.01	12.77	5.55	8.03	9.37	9.53	12.93
Fe_2O_3	3.47	6.06	4.95	7.37	3.16	4.66	8.32	4.97	8.01
MnO	0.92	2.76	1.78	4.79	1.32	2.38	5.03	1.70	4.72
MgO	0.79	2.08	1.02	3.60	1.13	1.53	4.60	1.59	4.64
CaO	0.07	0.13	0.09	0.11	0.08	0.10	0.13	0.07	0.11
Na_2O	0	0.06	0	2.31	0.62	0	0.31	0.55	0.29
K_2O	1.06	1.14	1.20	1.05	0.30	1.05	0.74	1.11	1.09
TiO_2	0.18	0.14	0.05	0.10	0.22	0.17	0.16	0.07	0.08
P_2O_5	0.70	0.81	0.88	0.78	0.29	0.78	0.87	0.68	0.74

Table 5.5 continued: XRF major element oxide (in %) results of the Sudoku soil samples. LOI – Loss of ignition (%).

	A64	**A65**	**A78**	**A81**	**A85**	**A86**	**A92**	**A94**	**A102**
H_2O	0.01	0.03	0.05	0.02	0.01	0.02	0.01	0.04	0.03
LOI	3.88	6.33	6.53	4.62	11.42	6.38	6.30	6.77	5.26
	94.22	97.20	98.9	101.50	99.17	97.88	99.75	90.15	99.81

Table 5.6 XRF trace element results for the Sudoku soil samples.

#	Sum of conc. (%)	CaO Ca (ppm)	Sc Sc (ppm)	TiO_2 Ti (ppm)	V V (ppm)	Cr Cr (ppm)	Fe_2O_3 Fe (ppm)	Co Co (ppm)	Ni Ni (ppm)	Cu Cu (ppm)	Zn Zn (ppm)	Br Br (ppm)	Rb Rb (ppm)
A10	4.19	3954	7	6555	51	97	30205	6	19	17	121	5	34
A11	7.20	17779	12	7398	77	135	45570	12	33	36	118	6	34
A14	9.78	42736	12	7484	79	134	45904	14	33	29	182	5	34
A15	4.09	6141	7	6397	51	91	27474	6	21	19	38	6	25
A16	13.33	61148	18	7929	111	275	62739	21	74	45	139	5	15
A17	6.25	11658	10	6504	71	73	41324	12	26	21	78	3	93
A18	12.58	50815	16	8664	109	280	64722	27	85	59	148	4	24
A23	8.59	20811	11	7868	92	156	55707	17	46	45	142	11	36
A24	10.34	34407	16	8643	107	176	58953	16	50	43	89	7	29
A37	11.22	42568	18	8132	106	172	60084	18	46	45	94	5	19
A38	8.12	21180	14	7516	80	87	50727	15	34	30	101	5	71
A43	11.60	53564	17	7843	867	175	52995	16	42	53	185	10	23
A48	11.78	47155	20	7743	112	280	61321	18	53	34	161	6	29
A52	7.23	21221	10	8146	75	156	41728	12	44	26	43	4	23
A53	7.71	23572	11	7251	73	187	45065	15	55	301	39	5	24
A64	4.77	7862	5	7434	53	93	31137	6	22	18	109	6	38
A65	8.34	21740	14	8210	96	136	51674	16	43	40	143	6	36
A78	7.16	18933	12	7783	87	150	43599	9	43	26	39	11	40
A81	10.22	32107	18	7438	107	210	61364	17	59	44	49	9	28
A85	4.86	14326	5	3708	27	88	29120	8	18	63	103	5	6
A86	7.19	21894	13	7917	73	140	40531	14	37	44	162	6.	29
A92	11.75	40727	20	8927	117	277	65715	22	115	146	196	14	18
A94	7.23	15511	7	7114	74	140	48399	11	47	26	61	15	47
A102	10.92	33956	17	7441	107	301	66416	21	81	38	49	7	32

Table 5.6 Continued: XRF trace element results for the Sudoku soil samples.

#	Sr	Y	Zr	Nb	Mo	Ag	Sn	Ba	Tl	Pb	Th	U
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
A10	39	18	334	9	0	104	12	262	2	19	9	0.6
A11	68	21	295	4	0	98	16	315	0	22	11	1
A14	185	23	369	0	0	103	17	463	0	36	7	1
A15	35	16	271	11	0	104	15	217	0	11	17	0.1
A16	126	22	233	0	0	107	11	278	0	23	10	0.8
A17	185	30	739	0	0	103	14	1523	0.8	17	17	3
A18	112	23	248	0	0	101	18	343	1	27	13	0.7
A23	135	24	315	0	0	94	14	411	1	28	10	1
A38	135	30	410	0	0	98	16	655	1	24	15	2
A43	144	22	286	0	0	105	10	414	0	79	0.3	2
A48	92	22	284	2	0	103	12	374	0	35	8	2
A52	51	17	314	7	0	106	14	248	1	34	8	0.7
A53	59	19	296	5	0	102	11	256	2	11	8	0.7
A64	58	19	379	7	0	105	13	312	1	37	12	0.1
A65	193	26	392	0	0	96	23	541	2	32	14	2.
A78	43	24	377	8	0	93	12	357	1	8	12	0.5
A81	81	24	226	4	0	98	11	283	0	12	14	1
A85	197	23	281	0	0	99	63	467	0	85	19	1
A86	103	21	331	1	0	99	31	389	0.1	93	8	0.4
A92	109	17	251	0	0	106	37	350	0.4	370	0	2
A94	57	28	329	8	0	98	9	347	0	23	17	1
A102	63	26	230	3	0	103	16	275	0	8	5	0.8

Table 5.7 Concentration values of the different heavy metals found in the Sudoku soil samples.

Sample	Sb	As	Bi	Cd	Hg	Se
	ppm	ppm	ppm	ppm	ppm	ppm
A10	0.54	3.27	0.32	0.16	0.035	0.12
A11	0.58	3.74	0.35	0.17	0.039	0.13
A14	1.32	5.40	0.33	0.25	0.110	0.15
A15	0.47	2.52	0.18	0.13	0.029	0.13
A16	1.44	4.15	0.27	0.28	0.145	0.18
A17	1.60	7.18	0.36	0.48	0.082	0.13
A18	1.22	6.67	0.18	21.15	0.030	0.49
A23	0.82	3.14	1.35	0.23	0.191	0.19
A24	0.75	2.40	0.27	0.21	0.041	0.14
A37	0.69	2.83	0.20	0.18	0.050	0.11
A38	1.24	5.67	0.30	0.23	0.047	0.13
A43	1.50	3.23	0.46	0.71	0.111	0.21
A48	0.96	2.42	0.25	1.86	0.040	0.14
A49	0.38	3.26	0.26	0.12	0.040	0.27
A52	0.52	2.66	0.16	0.16	0.021	0.12
A53	0.43	3.34	0.26	0.13	0.038	0.27

Table 5.7 continued: Concentration values of the different heavy metals in the Sudoku soil samples.

Sample	Sb	As	Bi	Cd	Hg	Se
	ppm	ppm	ppm	ppm	ppm	ppm
A64	0.79	2.23	0.29	0.22	0.048	0.15
A65	2.56	6.34	0.43	0.30	0.168	0.19
A78	0.26	2.65	0.18	0.11	0.026	0.19
A81	0.60	4.60	0.19	0.11	0.031	0.23
A85	21.31	10.45	0.53	0.32	0.107	0.30
A86	4.12	5.64	0.32	0.34	0.095	0.25
A92	8.38	4.10	0.37	0.52	0.116	0.30
A94	0.48	3.57	0.25	0.12	0.051	0.25
A102	0.39	3.66	0.23	0.12	0.051	0.18

Table 5.8 Concentration values of the different heavy metals in dust samples.

Sample	Sb	As	Bi	Cd	Hg	Se
	ppm	ppm	ppm	ppm	ppm	ppm
D004	3.36	48.15	0.48	312	83.12	1.00
D010	5.28	4.98	0.28	1.05	0.09	0.35
D014	3.20	6.73	0.29	2.22	0.23	0.50
D027	7.51	5.50	0.40	6.4	0.12	0.45
D033	4.10	1.65	0.60	2.85	0.06	0.36
D038	2.36	2.75	0.42	3.25	0.40	0.50
D040	1.64	3.62	0.31	1.75	0.08	0.20
D042	2.52	2.58	0.29	2.2	0.82	0.44
D052	9.15	3.85	0.23	1.7	0.21	0.24
D056	3.65	4.17	0.35	2.6	0.24	0.50
D062	2.54	3.89	0.24	0.57	0.05	0.29
D092	26.14	5.19	0.71	1.85	0.13	0.89
D095	5.35	3.13	0.86	1.55	0.17	0.45
D099	2.55	4.30	0.77	5.15	0.37	0.68
D100	5.64	3.73	0.36	1.12	0.08	0.34
D106	27.13	1.68	0.58	3.3	0.21	0.43
DD01	8.55	5.41	0.20	3.6	0.42	0.36
DD02	6.97	4.85	1.10	3.5	0.20	0.49
DD03	8.64	4.28	0.30	2.25	0.20	0.38
DD04	2.01	6.26	0.24	No value	0.14	No value
DD05	3.39	2.82	0.67	2	0.13	0.47
DD06	1.95	3.27	0.34	No value	0.11	No value

Table 5.9 Enrichment factor values of the Sudoku soil samples. Sh and Liu, 2011[1]; Smedley and Kinniburgh, 2002[2]; Callender, 2003[3]; World Bank Group, 1998[4]; Plant et al., 2003[5].

	Sb	As	Cd	Hg	Se
Background value	1 ppm[1]	7.2 ppm[2]	0.35 ppm[3]	0.05 ppm[4]	0.4 ppm[5]
A10	0.54	0.5	0.4	0.72	0.3
A11	0.58	0.5	0.5	0.79	0.3
A14	1.32	0.4	0.7	2.2	0.4
A15	0.47	0.3	0.4	0.59	0.3
A16	1.44	0.6	0.8	2.92	0.5
A17	1.60	1	1.4	1.65	0.3
A18	1.22	0.9	60.1	0.6	1.2
A23	0.82	0.4	0.6	3.83	0.5

Table 5.9 continued. Enrichment factor values of the Sudoku samples.

	Sb	As	Cd	Hg	Se
A24	0.75	0.3	0.6	0.83	0.4
A37	0.69	0.4	0.5	1.01	0.3
A38	1.24	0.8	0.7	0.95	0.3
A43	1.50	0.4	2	2.22	0.5
A48	0.96	0.3	5.3	0.82	0.4
A49	0.38	0.5	0.3	0.81	0.7
A52	0.52	0.4	0.5	0.44	0.3
A53	0.43	0.5	0.4	0.76	0.7
A64	0.79	0.3	0.6	0.97	0.4
A65	2.56	0.8	0.9	3.38	0.5
A78	0.26	0.4	0.3	0.52	0.5
A81	0.60	0.6	0.3	0.63	0.6
A85	21.31	1.5	0.9	2.15	0.8
A86	4.12	0.8	1	1.91	0.6
A92	8.38	0.6	1.5	2.33	0.7
A94	0.48	0.5	0.3	1.04	0.6
A102	0.39	0.5	0.4	1.03	0.5

Table 5.10 Enrichment factor values of the dust samples. Sh and Liu, 2011[1]; Smedley and Kinniburgh, 2002[2]; Callender, 2003[3]; World Bank Group, 1998[4]; Plant et al., 2003[5]

	Sb	As	Cd	Hg	Se
Background value	1 ppm[1]	7.2 ppm[2]	0.35 ppm[3]	0.05 ppm[4]	0.4 ppm[5]
D004	3.36	6.69	891.43	3613.72	2.50
D010	5.28	0.69	3.00	3.71	0.88
D014	3.20	0.94	6.34	9.96	1.25
D027	7.51	0.76	18.29	5.25	1.13
D033	4.10	0.23	8.14	2.69	0.90
D038	2.36	0.38	9.29	17.28	1.25
D040	1.64	0.50	5.00	3.70	0.50
D042	2.52	0.36	6.29	35.59	1.10
D052	9.15	0.53	4.86	9.13	0.60
D056	3.65	0.58	7.43	10.22	1.25
D062	2.54	0.54	1.67	2.24	0.73
D092	26.14	0.72	5.29	5.84	2.23
D095	5.35	0.44	4.43	7.45	1.13
D099	2.55	0.60	14.71	16.21	1.70
D100	5.64	0.52	3.19	3.34	0.85
D106	27.13	0.23	9.43	9.13	1.08
DD01	8.55	0.75	10.29	18.40	0.90
DD02	6.97	0.67	10.00	8.73	1.23
DD03	8.64	0.60	6.43	8.50	0.95
DD04	2.01	0.87	No value	5.92	No value
DD05	3.39	0.39	5.71	5.55	1.18
DD06	1.95	0.45	No value	4.61	No value

Chapter 6: Discussion

6.1 Introduction

The samples were analyzed for many different criteria such as texture, soil chemistry, XRD and XRF. Each shall be discussed separately. Heavy metal concentrations for antimony, arsenic, bismuth, cadmium and selenium concentrations were analyzed. Table 5.5 gives the Sudoku selected sample concentrations for the heavy metals and Appendix 2.1 gives all the concentrations of all elements for each sampling position. The concentrations were put into a GIS, using the IDW tool to obtain a spatial distribution of the elements in the different positions.

6.2 Physical and chemical properties

6.2.1 Texture

Only the results of 2 of the samples analyzed fell into the acceptable range for soil texture analysis. The other samples can be regarded as out of range and not acceptable. But from previous work done on the Bloemfontein area by Dohse (1970), it can be concluded that the main texture type found in the Bloemfontein area is loamy fine sand to fine sandy loam with the main soil fraction being between 0.250 mm and 0.888 mm meaning the soils are well sorted.

6.2.2 pH

The main pH range for optimal crop growth is between pH 5.5 to 7.0 which in some cases can be found in this study except with the samples that range above 7.0 (Brady and Weil, 2008). pH plays an important role in the chemistry of heavy metals in soils. An increase in soil acidity generally causes micronutrients to be more readily available to plants and it can cause toxicity in such cases. Cadmium in its Cd (II) is available to plants, and retention of the element is independent of pH. As pH increases elements such as mercury in its ion state Hg (II) becomes less available to plants. The exception to the increase of pH on plant take up occurs with arsenic (Bohn et al., 2001). Because the pH values of this study are slightly acidic to slightly alkaline, the heavy metals are less likely to become available compared to soils that are much more acidic.

6.2.3 Nitrogen, carbon and phosphorous

Nitrogen is a major part of many essential plant compounds. A large concentration of nitrogen in the soil helps plants to grow. Nitrogen forms part of the amino acids and in chlorophyll which is the main reason for photosynthesis to work (Brady and Weil, 2008).

The higher the carbon content the higher the nutrient cations such as calcium, potassium and magnesium that can be found in exchangeable form (Brady and Weil, 2008), because these cations are present in the organic matter. Soils in South Africa have 3 main ranges of organic matter content. In general the soils are mostly low in organic carbon with 58% of South African soils containing less than 0.5% organic carbon. 38% of soils range between 0.5% and 2% and only a low 2 percent of South African soils contain organic carbon higher than 2%. The organic carbon in the sampled soils mostly falls into the 38% category. 1 sample falls below the 0.5% range (A52) and 8 samples range above 2% (A14, A18, A23, A43, A65, A85, A86 and A102) which indicates very high amounts of organic carbon in the soils (The Fertilizer Society of South Africa, 2003). A14, A85, A86 and A102 are found in the industrial area of Bloemfontein and A18, A23, A43 and A65 are found in the residential areas south east of the power station.

The phosphorus content from the Sudoku selected samples range between 0.085 ppm and 1.06 ppm. Soils naturally contain total phosphorus concentrations in the range of 0.1 to 3.0 g/kg, but plant available phosphorus is normally very low due to the low suitability of phosphorus in soils (The Fertilizer Society of South Africa, 2003).

6.2.4 CEC and cations

6.2.4.1 Calcium

Calcium and magnesium are common in the Earth’s crust, but can have substantially different concentrations in soils. Calcium is the more dominant cation in soils and rarely does a soil have a deficiency in calcium. Calcium deficiencies can be expected with soils that contain a low pH and toxic levels of aluminium and manganese. The reason for the toxic levels of aluminium is because under highly acidic conditions in soil, the soil becomes stripped of its silica and base metals such as calcium and aluminium hydroxides remain causing toxicity (The Fertilizer Society of South Africa, 2003). The pH of the sampled soils are slightly acidic to alkaline, therefore no deficiency of calcium is expected in these soils.

6.2.4.2 Magnesium

Magnesium is the less dominant cation compared to calcium in the soil. When it comes to deficiencies of magnesium in the soils, it has similar characteristics compared to calcium. A low pH and toxic levels of aluminium can indicate a deficiency in soils but because the pH of the sampled soils is slightly acid to alkaline, no deficiency is expected in these soils (The Fertilizer Society of South Africa, 2003).

6.2.4.3 Potassium

Potassium is a common element occurring in the Earth's crust. It forms about 2.3% of the crust. Clay minerals and rocks containing potassium rich minerals are the main source for potassium in soils. Potassium can be fixed in soils by certain clays which make it difficult for plants to take it up.

6.2.4.4 Sodium

The soluble sodium ranges between a low value of 6.3 ppm and a high value of 83 ppm. The exchangeable sodium ranges between a low value of 14.5 ppm and a high value of 102.5 ppm.

6.2.4.5 CEC

The CEC ranges between a low value of 1250 ppm and a high value 5625 ppm. The soluble sodium and the exchangeable sodium show similar concentration ranges for both fields.

6.3 XRF

6.3.1 Majors

All the samples contained high percentages of silica. Sodium, manganese, potassium and phosphorus contents were low. Calcium, aluminium and iron show low to medium concentration from the XRF analysis. The reason for this could originate from the underlying rock types of sandstones and dolerites. Sandstones are rich in quartz, and dolerites are rich in plagioclase and pyroxenes indicating a higher amount of calcium and iron and low amounts of sodium in the soils.

The soils of the area overlie sediments of the Karoo Supergroup and there is plenty of dolerite intrusions found in the Bloemfontein area. The major chemistry of these rock types should therefore be depicted in the soils. Main minerals to be found should be quartz, feldspars such as the potassium rich feldspars and possibly the calcium rich plagioclases and smectite clay minerals such as vermiculite. By obtaining the major chemical composition and using XRD analysis of the samples should give the mineralogy of the soils.

6.3.2 Trace elements

The concentration values for the Sudoku selected samples indicate high values of calcium, iron and titanium. The traces have in most cases low values for each element. Values of silver, zirconium and zinc indicate higher values compared to the other trace elements.

6.4 XRD

The main minerals that were found in the soil samples are dominantly quartz and plagioclases. Other minerals that were found were augite, alkali feldspars, micas such as the biotite end-member annite (Fe^{2+} end-member) and muscovite and clay minerals such as illite, montmorillonite, vermiculite and kaolinite were also found (Table 5.4).

6.5 Heavy metal and enrichment factors in soils

6.5.1 Antimony

6.5.1.1 Antimony concentration values

The concentrations found in the soil samples ranged between a low of 0.26 ppm, a high of 21.31 ppm and an average of 0.21 ppm (Table 6.4). Figure 6.4 represents the concentration values with red indicating the highest concentrations and dark green the lowest concentrations. The highest concentrations were situated north-east and south east of the power station in the industrial areas as can be seen from Figure 3.3.

6.5.1.2 Antimony enrichment factor values

The antimony enrichment factors have the same values as the metal concentrations in the soil because the background value for soils containing antimony is 1 ppm (Sh and Liu, 2011). The enrichment factor values ranged between a low 0.26, a high 21.31 and an average value of 1.64 (Table 6.5). Table 6.1 indicates enrichment factors of the samples with enrichment factor values of antimony being 2 or higher. Figure 6.5 represents enrichment factor values with red indicating enrichment above 2.5 and green below 1. Figure 6.6 represents the enrichment factors where red indicates the highest enrichment and dark green the lowest enrichment.

Most of the samples (65%) were well below the average soil background value except for 17 samples that had enrichment values of 2.0 or higher. These positions were suspected to be contaminated with antimony especially A27, A28, A31, A61, A83, A85, A92 and A99 having values above 5.0. Position A85 had an enrichment factor of 21.13 and should be considered highly contaminated compared to background values of 1 ppm (Sh and Liu, 2011).

Table 6.1 Enrichment factor classes for antimony.

Enrichment factors	2 < x < 5	5 < x < 10	>10
Samples	A2; A19; A30; A39; A55; A59; A65; A72; A73; A76; A77; A86; A100	A27; A28; A31; A61; A92	A85; A99

6.5.1.3 Discussion of antimony soil concentration values

Comparisons to sediments of a study area in New Zealand at a historic smelter site show that in this study, the antimony values are way below the values found there. The concentration values found in the sediments surrounding the smelter have a concentration range from 18 ppm up to 243 ppm. An extremely high value can be seen in a soil sample at the smelter plant that had an antimony concentration of 80200 ppm (Wilson et al., 2004a). This value showed an extremely high contamination compared to this study area.

An example of soils being contaminated in Germany occurred in the Palatinate Forest where mining over the last 500 years which ceased since the 1930s, shows massive contamination of the soils. Antimony concentrations were found to be as high as 500 ppm (Hammel et al., 2000). An example of soils around a mining area in China such as the De'an antimony mine which is found in the Jiangxi Province had average antimony concentrations of 362 ppm with a maximum value of 593 ppm. A smaller scale antimony smelting plant found in the Guizhou Province showed soils with antimony concentration values that are higher than 35.6 ppm (He et al., 2012).

Comparison to a permissible standard of 3.5 ppm in soils for countries like the Netherlands (Crommentuijn et al, 2000) these values are way above the indicated permissible value. This indicates that the areas are fairly contaminated to extremely contaminated with antimony. Concentration values of 3.5 ppm and higher can be seen in this study; the concentration values were not as high as other study areas but it can be concluded that the soils in this study can be considered contaminated.

6.5.2 Arsenic

6.5.2.1 Arsenic concentration values

The concentrations found in the soil samples ranged between a low of 1.33 ppm, a high of 14.59 ppm and an average 4.21 ppm (Table 6.4). Figure 6.7 represents the concentrations where red indicates the highest concentrations and dark green the lowest concentrations. The higher concentrations are situated east and south east of the sewage works with values ranging from 5 ppm up to 14.59 ppm.

6.5.2.2 Arsenic enrichment factor values

The levels for arsenic were mostly below background values, giving an indication that the study area was not contaminated by arsenic. The enrichment factor values ranged between a low 0.2, a high 2.0 and an average value of 0.58 (Table 6.5). Localities A80 (EF–2) and A50 (EF–1.6) should maybe receive some attention because they are slightly above the background values, possibly indicating contamination, but it is only a slight contamination at the present time compared to background values of 7.2 ppm (Smedley and Kinniburgh, 2002). Figure 6.8 represents enrichment factor values with yellow indicating enrichment between 1 and 2.5 and green lower than 1. Figure 6.9 represents the enrichment factors where red indicates the highest enrichment and dark green the lowest enrichment.

6.5.2.3 Discussion of arsenic concentration values

An example of arsenic in the soil having concentrations that can be considered contaminated can be seen in the Brenta Plain, Italy where arsenic concentrations in the topsoil ranged between a low of 3.72 ppm and reaches values as high as 49.3 ppm. Values that are higher than 20 ppm in soils can be considered contaminated (Ungaro et al., 2008).

Arsenic ranges between 4.8 ppm and 13.6 ppm in the natural environment in Canada which shows very similar concentrations found in this study area. Some areas in Canada had ranges that were extremely high with concentrations of 172000 ppm in places such as Bowen Island, BC (Wang and Mulligan, 2006). From mining activities found in the Salmanca Province, Spain, showed soils were highly contaminated with arsenic. In the contaminated regions around the mine tailings, arsenic values ranged between 59.1 ppm to an extremely contaminated value of 4900 ppm (Garcia-Sanchez and Alvarez-Ayuso, 2003). In Cornwall, United Kingdom, there was widespread contamination of arsenic due to mining of polymetallic and calcination ores. In West

Cornwall, soil samples showed arsenic concentrations exceeding 100 ppm. A study of a calciner stack in an area near Camborne, named the New Mill site, showed extremely high values of arsenic in the soils. Some samples showed values exceeding 4000 ppm adjacent to the calciner and values of around 500 ppm occurred near the stack. These areas showed massive contamination (Camm et al., 2004).

Comparing this study’s concentrations to other studies indicates that because there are no samples with concentrations above 20 ppm in this study area (Ungaro et al., 2008), there is little or no contamination of arsenic in the study area.

6.5.3 Bismuth

6.5.3.1 Bismuth concentration values

The concentrations found in the soil samples ranged between a low 0.12 ppm, a high 6.86 ppm and an average of 0.47 ppm (Table 6.4). Figure 6.10 represents the concentrations where red indicates the highest concentrations and dark green the lowest concentrations. The highest concentrations were situated at the sewage works with concentrations being 5.65 ppm. Other possible hotspots are situated west of the power station (Figure 6.10).

6.5.3.2 Discussion of bismuth values

Compared to a study done on soils at the Dalsung copper-tungsten mine in Korea, the concentrations show higher concentrations ranging between 42 ppm and 1510 ppm. The average concentration in the soil was 436 ppm. These values indicated that the area was contaminated with bismuth (Jung et al., 2002). The values found at this mine were high to extremely high compared to this study with the highest concentration in this study being 5.65 ppm.

6.5.4 Cadmium

6.5.4.1 Cadmium concentration values

The concentrations found in the soil samples ranged between a low 0.11 ppm, a high 21.15 ppm and an average of 0.56 ppm (Table 6.4). Figure 6.11 represents the concentrations where red indicates the highest concentrations and dark green the lowest concentrations. The highest concentration of 21.15 ppm is situated directly south of the power station with another hotspot situated directly north of the sewage works (Figure 6.11). Both hotspots are situated in industrial areas of Bloemfontein (Figure 3.3).

6.5.4.2 Cadmium enrichment factor values

The background cadmium concentration that was used to obtain the enrichment factor values for cadmium was 0.23 ppm (Callender, 2003). The enrichment factor values ranged between a low 0.28, a high 60.1 with an average value of 1.61 (Table 6.5). Figure 6.12 represents enrichment factor values with red indicating enrichment above 2.5 and green below 1. Figure 6.13 represents the enrichment factors where red indicates the highest enrichment and green the lowest enrichment. 24 samples indicated enrichment factors of 1 or higher, 9 showed enrichment factors above 2, with 4 samples showing values of enrichment of 7 or higher with the highest being 60.1 (Table 6.2).

Most samples indicated levels below background values, but the localities that had enrichment values above 2 should be considered fairly contaminated to extremely contaminated, depending on the enrichment factor value. The localities that show values above 7 (A47, A61 and A77) should be regarded as contaminated and locality A18 with an enrichment factor value of 60.1 should be regarded as extremely contaminated compared to the average background soil value of 0.35 ppm (Callender, 2003).

Table 6.2 Enrichment factor classes for cadmium.

Enrichment factors	2 < x < 5	5 < x < 10	>10
Samples	A19; A43	A30; A47; A48; A77	A18; A61

6.5.3.2 Discussion of cadmium concentration values

An accumulator factory, in Fliseryd, southeast Sweden was under investigation for contamination. It manufactured nickel-cadmium accumulators and was a smelter for lead accumulators. The factory was in use from 1910 and ceased cadmium production in 1976. Soils containing high organic matter in certain parts of the accumulator plant were analyzed for cadmium concentrations and the concentrations for cadmium ranged between a low 0.64 ppm and a high 39.6 ppm. The highest concentrations occurred close to the factory and decreased away from the factory (Bergbäck and Carlsson, 1995). The higher concentrations were higher than this study but the lower concentrations were similar to this study.

An example of extremely high concentrations of cadmium in soils occurred in the West Indies in Jamaica. In some of rural regions of Central Jamaica, concentration values of cadmium in the soils reached values as high as 400 ppm indicating extremely high contamination but the interesting fact was that the high concentrations originated from bird guano during the Late-Miocene or Pliocene (Garret et al., 2008).

A large study was done on agricultural lands in Chenzhou City, China where soils were analyzed for cadmium. The maximum concentrations of cadmium reached a high of 48.33 ppm and a low 0.01 ppm. By comparing the values to maximum permitted levels (MPL) in agricultural soils by using the Chinese MPL of 0.6 ppm, more than 80% of the soil exceeded the normal limits. When using other MPLs of other countries such as the Netherlands (1 ppm) and Australia (3 ppm) the values decreased the contaminated levels to just over 60% (Limei et al., 2008).

6.5.5 Mercury

6.5.5.1 Mercury concentration values

The concentrations found in the soil samples ranged between a low 0.02 ppm, a high 2.14 ppm and an average of 0.13 ppm (Table 6.4). Figure 6.14 represents the concentrations where red indicates the highest concentrations and dark green the lowest concentrations. The hotspot with the highest concentration value being 2.14 ppm was situated at the sewage works (Figure 6.1 and 6.2). Other possible hotspots were situated west of the power station.

6.5.5.2 Mercury enrichment factor values

The background mercury concentration value that was used to calculate the enrichment factors was 0.05 ppm (World Bank Group, 1998). The enrichment factor values ranged between a low 0.41, a high 42.78 and an average value of 2.26 (Table 6.5). Figure 6.15 represents the enrichment factors where red indicates values above 2.5 and green values below 1. Figure 6.16 represents the enrichment factors where red indicates the highest enrichment and dark green the lowest enrichment. Like the concentration map (Figure 6.14), high enrichment was found at the sewage works facility (Figure 6.1 and 6.2).

Table 6.3 Enrichment factor classes for mercury.

Enrichment factors	2 < x < 5	5 < x < 10	> 10
Samples	A7; A14; A16; A23; A28; A43; A55; A56; A58; A59; A65; A68; A70; A72; A85; A90; A98; A23	A27; A30; A31; A88; A92; A100; A106	A4; A95

Figure 6.1 The sewage works in Bloemfontein (a).

Figure 6.2 The sewage works in Bloemfontein (b).

6.5.5.3 Discussion of mercury concentration values

Soils analyzed for mercury in Altai Territory, West Siberia show in the A horizon of the soil profile to have concentrations that range between 0.006 and 0.78 ppm. These values range within background values used which range between 0.003 and 0.4 ppm depending on the area in the Altai territory. Causes of contamination were from atmospheric mercury fallout and from local gold recovery factories and tailing sites (Malikova et al., 2011).

Studies were done on soils in an urban area of Bydgoszcz, northern Poland. The concentration of mercury ranged from 0.05 ppm to 0.29 ppm in the top soils which was higher than background values of the rural area (Dąbkowska-Naskręt and Różański, 2007).

An area in eastern Guizhou, China suffers from heavily polluted air. Mercury found in the soils was extremely high ranging between a low 1 ppm and an extremely high 743.5 ppm in polluted areas. The areas were considered extremely polluted with mercury and the air in the region was also extremely polluted. The main cause of the pollution was from the Wanshan mercury mining area (Wang et al., 2007).

A chlor-alkali plant in Estarreja in north-west Portugal had studies done on soil, water, vegetables, fish and feedstuffs for mercury contamination. The results of the analyzed soils revealed concentrations that were highly variable, ranging between a low 1 ppm value and a high 90.8 ppm. The very high values are limited with the mean being 5.4 ppm. Effluents from the chlor-alkali plant were dumped into the Ria de Aveiro until it was stopped, but because of mercury persistence, high mercury levels can still be seen in the soils (Reis et al., 2009).

6.5.6 Selenium

6.2.6.1 Selenium concentration values

The concentrations found in the soil samples range between a low 0.24 ppm, a high 1.22 ppm and an average of 0.21 (Table 6.4). The peak hotspots are directly south of the power station and directly north of the sewage works (Figure 6.17).

6.5.6.2 Selenium enrichment factor values

Figure 6.18 shows the enrichment factors of selenium in the soils by using the background value of 0.4 ppm (Plant et al., 2003). The enrichment factor values ranged between a low 0.24, a high 1.22 and an average value of 0.5 (Table 6.5). Figure 6.18 represents enrichment factor values with yellow indicating enrichment between 1 and 2.5 and green lower than 1. Most enrichment factor values were below 1.0 except for 3 samples that have a range between 1 and 1.22 (Figure 6.19). There was very little to no contamination found in the study area. In actual fact some values are extremely low compared to background values indicating a possible deficiency of selenium in the area. There are many “cold spots” in the study area showing low concentrations which can possibly lead to a deficiency in the element (Figure 6.19). This can have a negative effect on people and animals that may eat edible plants growing in the study areas. The people and animals will not obtain sufficient amounts of selenium in their systems which can lead to a weaker immune system (Plumlee and Ziegler, 2003; Hartikainen, 2005).

6.5.6.3 Discussion of selenium concentration values

Soils in the Xuzhou District, China were analyzed for selenium contamination. Values ranged between 0.21 ppm to 4.08 ppm (Shunsheng et al., 2009). According to Shungshen et al. (2009), selenium concentrations in the 100 cm – 200 cm depth were used as background values, which were 0.08 ppm. The reason for this was that the soils at depth were not disturbed by human activity. This indicated high amounts of contamination.

In Yutangba, China, the soils were analyzed for selenium. This region of China is known for high concentrations of selenium where selenium poisoning has been reported. Selenium concentrations ranged between 0.42 ppm and 42.3 ppm. The soils with concentration values above 1.4 ppm were considered contaminated with the very high values being highly contaminated (Zhu et al., 2008).

In the northern regions of the world such as northern Europe and northern Asia, selenium concentrations are less than 0.5 ppm in the soils. According to Ermakov and Jovanović (2010) these values in soils are lower than 0.5 ppm and this could be a cause for concern because there is a possibility for selenium deficiency in the soil and negative health effects on humans and animals are possible.

Selenium concentrations of this study area are well below some of the concentrations found in other study areas (Shunsheng et al., 2009; Zhu et al., 2008). Values of selenium found in this study are less than 0.5 ppm. It can be concluded that there is no contamination of selenium in the study area and in fact there is a possible deficiency of selenium in soils which can possibly have a negative effect on human and animal health.

6.6 Heavy metal concentrations and enrichment factors in dust samples

6.6.1 Origin and health risks of hazardous dust

There are many different pathways that can occur to cause an increase in heavy metal concentrations in dust samples. Examples of different pathways that can occur to increase concentrations in dust develop from water transported material from erosion of slopes and soils, particles deposited from atmospheric fallout that accumulate on streets, in residential areas, gardens and schools. Other sources are biological inputs, degradation of road paint, tires, brakes and other vehicle materials that break down over time and vehicle emissions (Zheng et al., 2010; Ma and Singhirunnusorn, 2012).

Dust particles are an important pathway exposing humans to heavy metals (Zheng et al., 2010). Street dust often contains increased concentrations of heavy metals and this can cause a health risk to people especially with a low immunity system. This occurs especially in young children because their immune systems are not fully developed and they are more susceptible to ingestion of dirt and dust compared to the rest of human population (Banerjee, 2003).

6.6.2 Sample concentrations

6.6.2.1 Antimony

Antimony concentrations in dust samples ranged between 1.64 ppm and 27.13 ppm and the average dust sample concentration was 6.53 ppm (Table 6.4). The 2 samples with the highest concentrations were found in an industrial area (D092) and in a Multisave supermarket just outside the industrial area (D106) (Figure 6.20).

6.6.2.2 Arsenic

Arsenic concentrations in dust samples ranged between 1.65 ppm and 48.15 ppm and the average concentration was 6.04 ppm (Table 6.4). This included the high arsenic concentration of 48.15 ppm found at D004 (Figure 6.21). Without including sample D004, the average concentration for arsenic in the dust samples was 4 ppm.

6.6.2.3 Bismuth

Bismuth concentrations in dust samples ranged between 0.2 ppm and 1.10 ppm and the average concentration was 0.46 ppm (Figure 6.22 and Table 6.4).

6.6.2.4 Cadmium

Cadmium concentrations in dust samples ranged between 0.59 ppm and 312 ppm and the average dust sample was 18.05 ppm (Table 6.4). This included the high cadmium concentration of 312 ppm found at D004 (Figure 6.23). Without including sample D004, the average concentration for cadmium in the dust samples was 2.58 ppm.

6.6.2.5 Mercury

Mercury concentrations in dust samples ranged between 0.05 ppm and 83 ppm and the average dust sample was 3.9 ppm (Table 6.4). This included the high mercury concentration of 83 ppm found at D004 (6.24). Without including sample D004, the average concentration for mercury in the dust samples was 0.2 ppm.

6.6.2.6 Selenium

Selenium concentrations in dust samples ranged between 0.2 ppm and 1.00 ppm and the average concentration was 0.46 ppm (Figure 6.25 and Table 6.4). All these elements excluding bismuth and antimony had extremely high concentrations at locality D004 which is found at the sewage works compared to all the other sampling localities.

6.6.3 Enrichment factors

6.6.3.1 Antimony

Enrichment factor values ranged between a low 1.65 and a high 27.13 (Table 6.5). The highest enrichment factor values were found part of the industrial area and just outside the industrial area. All the dust samples had enrichment factor values above 1 and the average enrichment factor value for antimony in the dust samples was a moderately high 6.53.

6.6.3.2 Arsenic

Enrichment factor values ranged between a low 0.23 and a high 6.69 (Table 6.5). The highest enrichment factor value was found at the sewage works and it was the only sample with an enrichment factor value above 1 (D004). All the other dust samples had enrichment factors below 1 and the average enrichment factor value for arsenic in the dust samples was a low 0.84.

6.6.3.3 Cadmium

Enrichment factor values ranged between a low 1.67 and an extremely high value of 891.43 (Table 6.5). All the dust samples had enrichment factor values above 1 with the sewage works sample (D004) having the extremely high enrichment factor value of 891.43. The average enrichment factor value for cadmium in the dust samples was a high 51.56. Excluding the extremely high value found at the sewage works the enrichment factor value decreased to a much lower 6.99 which is still moderately high.

6.6.3.4 Mercury

Enrichment factor values ranged between a low 0.60 and an extremely high value of 3613.72 (Table 6.5). All the dust samples had enrichment factor values were above 2 with the sewage works sample (D004) having the extremely high value of 3613.72. The average enrichment factor value for mercury in the dust samples was an extremely high 173.05. Excluding the extremely high value found at the sewage works the enrichment factor value decreased excessively but was still a moderately high 9.21

6.6.3.5 Selenium

Enrichment factor values ranged between a low 0.5 and a high 2.50 (Table 6.5). Most of the samples ranged around 1 with 3 samples having enrichment factor values above 1.7. The 2 samples that had enrichment factor values above 2 were found at the sewage works (D004) and the industrial area (D092).

6.6.4 Comparisons between soil sample concentrations and dust sample concentrations

Soil samples compared to dust samples indicate that there were differences and similarities between the different elements. Major differences were seen with mercury, arsenic and cadmium. The highest soil concentration for mercury was 2 ppm and the highest dust concentration was 83 ppm. The highest soil concentration for cadmium in soil was 21.15 ppm and the highest dust sample was 312 ppm. The highest concentration in soil for arsenic was

14.59 ppm, and the highest dust sample was 48.15 ppm. The concentrations for antimony in soil samples were similar to the dust samples but 2 dust samples showed slightly higher concentrations compared to the highest soil concentration. The highest soil concentration was 21.77 ppm where the highest dust sample was 27.13 ppm (D106). Comparing bismuth soil concentrations to dust samples indicate that the highest dust concentration was lower than the highest soil sample. The highest dust concentration was 1.1 ppm and the highest soil concentration was 6.86 ppm. Comparing selenium soil concentrations and dust concentrations indicate very similar concentrations with the highest soil concentration being 0.49 ppm and the highest dust sample was 1 ppm. The mean and ratios for the different elements can be seen in Table 6.4. Figure 6.2 gives the ratios of the different elements.

The dust/soil ratios indicate large differences in cadmium and mercury. The ratios for cadmium and mercury are 32.5 and 30. Antimony and selenium are slightly higher than 1 being 4.1 and 2.2. Arsenic and bismuth are around 1 indicating very similar means between soil and dust samples.

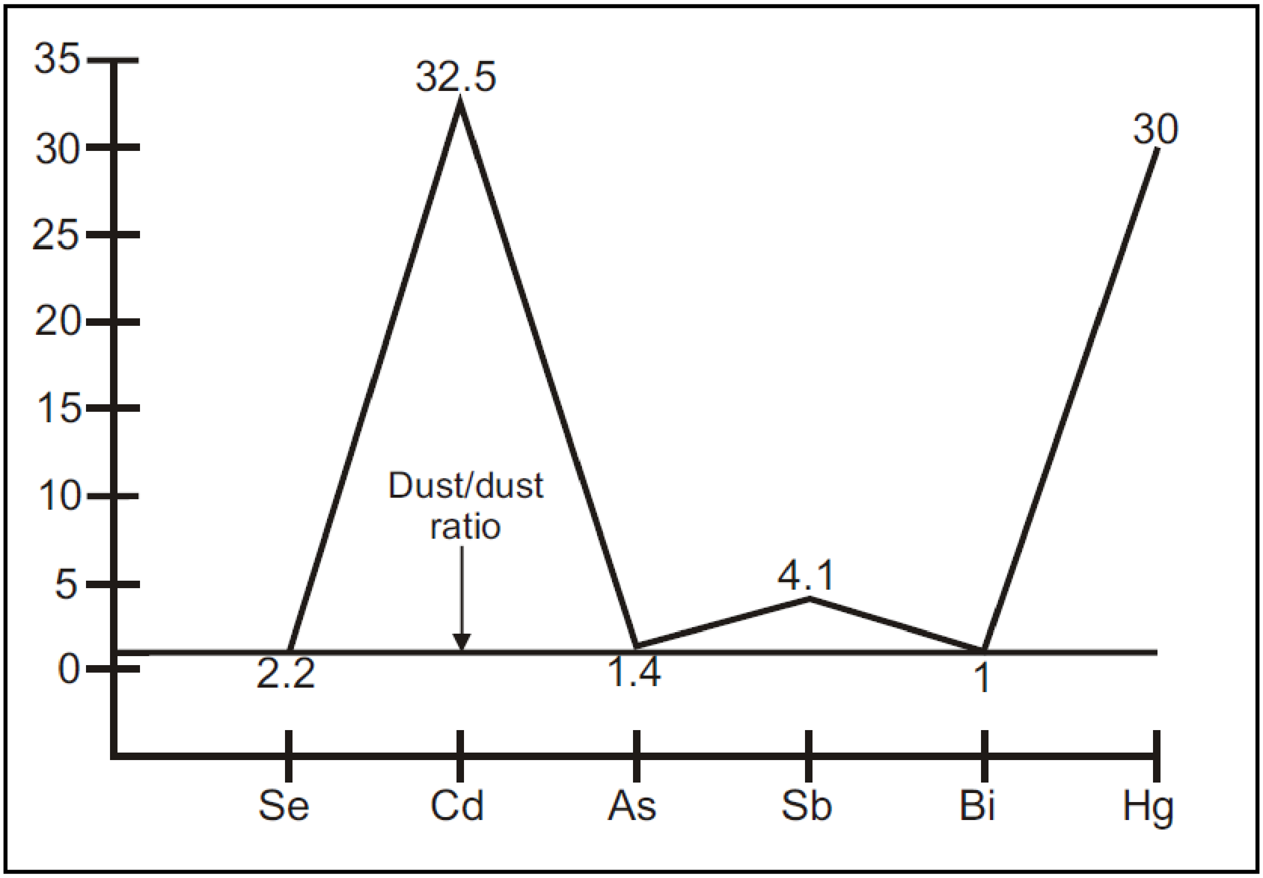


Figure 6.3 Mean dust/soil ratios of the different elements. Elements follow ascending atomic number.

Table 6.4 Minimum, maximum and the mean soil and dust sample concentrations and dust/soil ratios for the different elements.

Soil samples (concentrations)	Se (ppm)	Cd (ppm)	As (ppm)	Sb (ppm)	Bi (ppm)	Hg (ppm)
Minimum	0.10	0.08	1.31	0.26	0.13	0.02
Maximum	0.49	21.15	14.61	21.31	5.70	2
Mean	0.21	0.56	4.21	1.61	0.47	0.13
Dust samples (Concentrations)	**Se (ppm)**	**Cd (ppm)**	**As (ppm)**	**Sb (ppm)**	**Bi (ppm)**	**Hg (ppm)**
Minimum	0.20	0.59	1.65	1.64	0.20	0.05
Maximum	1.00	312.00	48.15	27.13	1.10	83
Mean	0.47	18.05	6.04	6.53	0.46	3.9
Dust/soil ratio	2.2	32.5	1.4	4.1	1	30

Table 6.5 Minimum, maximum, mean of soil and dust sample enrichment factor values for the different elements.

Soil samples (EF)	Se	Cd	As	Sb	Hg
Minimum	0.24	0.28	0.2	0.26	0.41
Maximum	1.22	60.1	2.0	21.31	42.78
Mean	0.5	1.61	0.58	1.64	2.26
Dust samples(EF)					
Minimum	0.5	1.67	0.23	1.64	0.60
Maximum	2.50	891.43	6.69	27.13	3613.72
Mean	1.17	51.56	0.84	6.53	173.05
Mean (without sample D004)	1.04	6.99	0.56	6.68	9.21

6.7 Conclusions

6.7.1 Soil samples

The concentrations can be found in Appendix 2.1. There are different ranges that are found in soils with regard to the different heavy metals of this study. Certain heavy metals indicate contamination in certain regions of the study area namely antimony, cadmium and mercury; certain heavy metals such as arsenic have a range that is the same or just above the background concentrations in soil and one element namely selenium actually shows a deficiency in the soils.

Cadmium with values as high as 21.15 ppm, antimony with values as high as 21.17 ppm and mercury having values as high as 2.13 ppm indicate that there is contamination in the soils from these heavy metals in the study area.

Arsenic concentration values are below or slightly above the background values that were used in this study. This indicated that there are normal concentrations of arsenic found in the area and there is not a high concern for arsenic or its potential for it to be a health hazard. Only with places that have an enrichment factor higher than 2 should receive further investigation on why it has higher than background values but at present it is not a major concern.

Selenium concentrations in the soils have a range that borders normal background values to being deficient in certain areas. This deficiency can possibly lead to a lowered immune system in humans and animals alike that use the land to grow crops for food.

There appears to be no co-relation between the elements. If there is a possibility of a co-relation it will probably be between mercury and bismuth as can be seen with both elements, the hotspots for both elements are almost coincidental (Figure 6.8 and 6.12). Between the other elements there appears to be no co-relation.

6.7.1.1 Antimony and cadmium

Both elements contain high concentrations south of the power station and could be possibly related to wind if the primary source for contamination comes from the power station. The dominant wind in the Bloemfontein area is northerly therefore areas south of the power station would have elevated concentration values if the power station is the primary source for contamination. But because the hotspots are found in the industrial area of Bloemfontein it is possible that the distribution of these elements can originate from industrial activities.

In Figure 6.2 and 6.9 it can also be seen that there are high concentrations north-east of the power station in the north-eastern part of the industrial area of Bloemfontein. Because the dominant wind direction is northerly to north-easterly (Figure 3.6) it can therefore not be possible for the power station to be a major contributor to the high concentrations found in those specific areas.

6.7.1.2 Mercury

Mercury’s main hotspot was found in the sewage works of Bloemfontein area. The main contributor to this possible high concentration can be from the power station when it was still working. As stated in Chapter 2 about the chemistry of coal, coal contains trace amounts of mercury and when it is combusted at power stations, it is released into the atmosphere. It could possibly return to the surface of the earth with dust particles. The possible reason for the high concentration to be found at the sewage works is because as the dust, containing possible traces of mercury, settles on people's cupboards, window sills, tables, chairs, and equipment etc., people clean their equipment and apparatus from the dust with cloths, then they wash this dust down their sinks. When this occurs the dust moves towards the sewage works and accumulates there causing the high concentration.

6.7.1.3 Selenium

Selenium has low concentrations in the study area. The areas with the highest concentrations are north-east and south of the power station in the industrial areas. Soils of southern Africa tend to have a deficiency in selenium (Davies and Mundalamo, 2010). The possible reason for the higher concentrations found especially in the industrial areas could be from industrial sources, but the concentrations are still low enough to have little concern for contamination.

6.7.1.4 Arsenic

Arsenic concentration levels are not of major concern because they are slightly above or below background values with no real threat of contamination. The distribution of the arsenic could be geological as the main rock types such as sandstone are dominant in the area. World average concentrations of arsenic in sandstone are 4.1 ppm and in soils are 7 ppm (Smedley and Kinnibergh, 2002). The soils of the study area contain similar concentrations. Elevated concentrations of arsenic can be seen in the industrial areas, meaning that there could be a small contribution of arsenic coming from these areas and maybe from the power station when it was in use. Another area that may have slightly elevated levels of arsenic was found at the race course (A80) east of the sewage works. A possible reason for a higher elevated level of arsenic could be from the use of arsenic containing compounds to wash horses, the stables or injections to improve the health of the horses. An example of a possible arsenic containing compound that can be used is a Jurocyl injection that contains sodium arsanilate. It is used to improve the coat, body condition and appetite of horses (http://www.ceva.com.au).

6.7.2 Dust samples

Certain areas showed extremely high concentrations of the elements in certain areas. The main locality that shows the greatest anomaly was sample D004 which was situated at the sewage works. Arsenic, cadmium, mercury and selenium showed high to extremely high concentrations compared to the other sampling localities. For antimony, the main anomalous areas were found at sampling localities D092 and D196 which are found south of the power station which showed extremely high concentrations compared to the other sampling localities. Bismuth showed similar concentrations to soil samples and was found to have a small range of different concentrations in the dust samples compared to all the other elements.

Bismuth and arsenic showed similar means to the soil samples where all the other elements means for the dust samples were much higher compared to the soil samples. The selenium dust sample mean was double the soil sample mean, the antimony dust sample mean was 4 times higher than the soil sample mean and the dust sample means for mercury and cadmium were 30 and 32.5 times higher than the soil sample means respectively.

Reasons for the extremely elevated concentrations found at the sewage works could possibly be from a collection area meaning from atmospheric fall-out, dust settles on roads and during rainy days, the dust can be washed down storm water drains and eventually end up at the sewage works. Dust in houses and buildings can also be washed down drains and eventually end up at the sewage works. But another possibility for such high concentrations is that there could be contamination at the lab where the dust sample was taken. After experiments were done, the lab might not have been cleaned properly leading to elevated levels of the different elements. An example of contamination could be that a thermometer containing mercury was broken, increasing the concentration of mercury in local area. The mercury could evaporate and then precipitate with dust fall-out causing an increase in concentration in the dust in and around the lab.

6.8 Possible sources for the contamination

It was hypothesized that the power station was the main source for the contamination of the soils found in the Bloemfontein study area. It can be said that it could possibly be the source but by looking at the trace elements found in South African coals that were used in the power station to produce electricity, the heavy metal concentrations are much lower compared to average world coal with the exception that cadmium has the same or slightly lower values compared to world coals (Table 2.8). Because the coal that was used contained trace amounts of these heavy metals, the power station can lead to the addition of the heavy metals found in the soils over a period of time since it was operational but more importantly it could have possibly lead to elevated levels in dusts compared to the soil samples. It has been in operation for 42 years since the 1950s (1953-1985 and 1996-2006). But because the power station has not been operational for 18 years (1985-1996, 2006-2013) also means that it was not a source during those periods when it was not in use, so there must be other sources for contamination.

By looking at the concentration maps found in Chapter 6 and overlaying them over Figure 3.3 to show the different land use areas, most of the hotspots are found in industrial areas such as south of the power station (cadmium), east of the power station in the industrial area and sewage works (mercury, bismuth) and north east of the power station (antimony, cadmium) with the exception of mercury and bismuth that can be found in higher concentrations than normal west of the power station around the Loch Logan Waterfront. The reason for mercury to be found in elevated levels at the Loch Logan Waterfront could be from atmospheric fall-out where the mercury could have possibly collected in and around the Loch Logan Waterfront. There has been a lot of building that has been going on at the Waterfront for the past few years and presently, there is still a continuous building operation that is found there. The building material can be a possible source. Because the Bloemspruit River flows through the Loch Logan Waterfront and the area is dammed up, the source for mercury could also originate from upstream somewhere and collect at the Loch Logan Waterfront.

Dust samples show extremely high values of the heavy metals at the sewage works compared to other dust samples except for antimony showing only elevated levels at other localities. It can be concluded that there is possibly a contamination in the lab where the dust sample was taken which in this case showed extremely high levels of the heavy metals especially mercury and cadmium.

It can be concluded that while the power station was a source of contamination in the area while it was still in use, activities in the industrial areas of Bloemfontein can also be sources of contamination in the area.

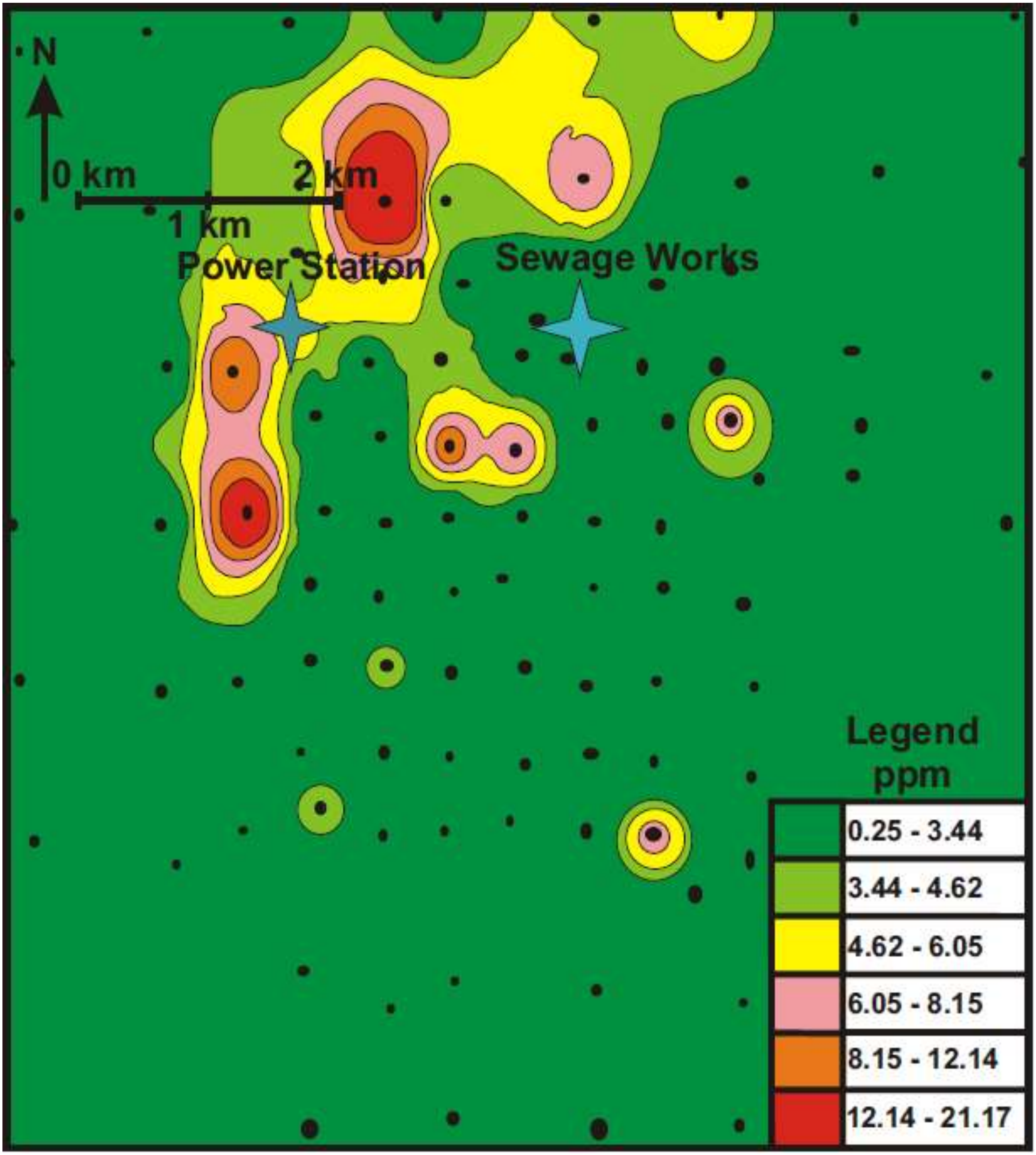


Figure 6.4 IDW concentration map of antimony with red indicating areas with the highest concentrations and dark green with the lowest concentrations.

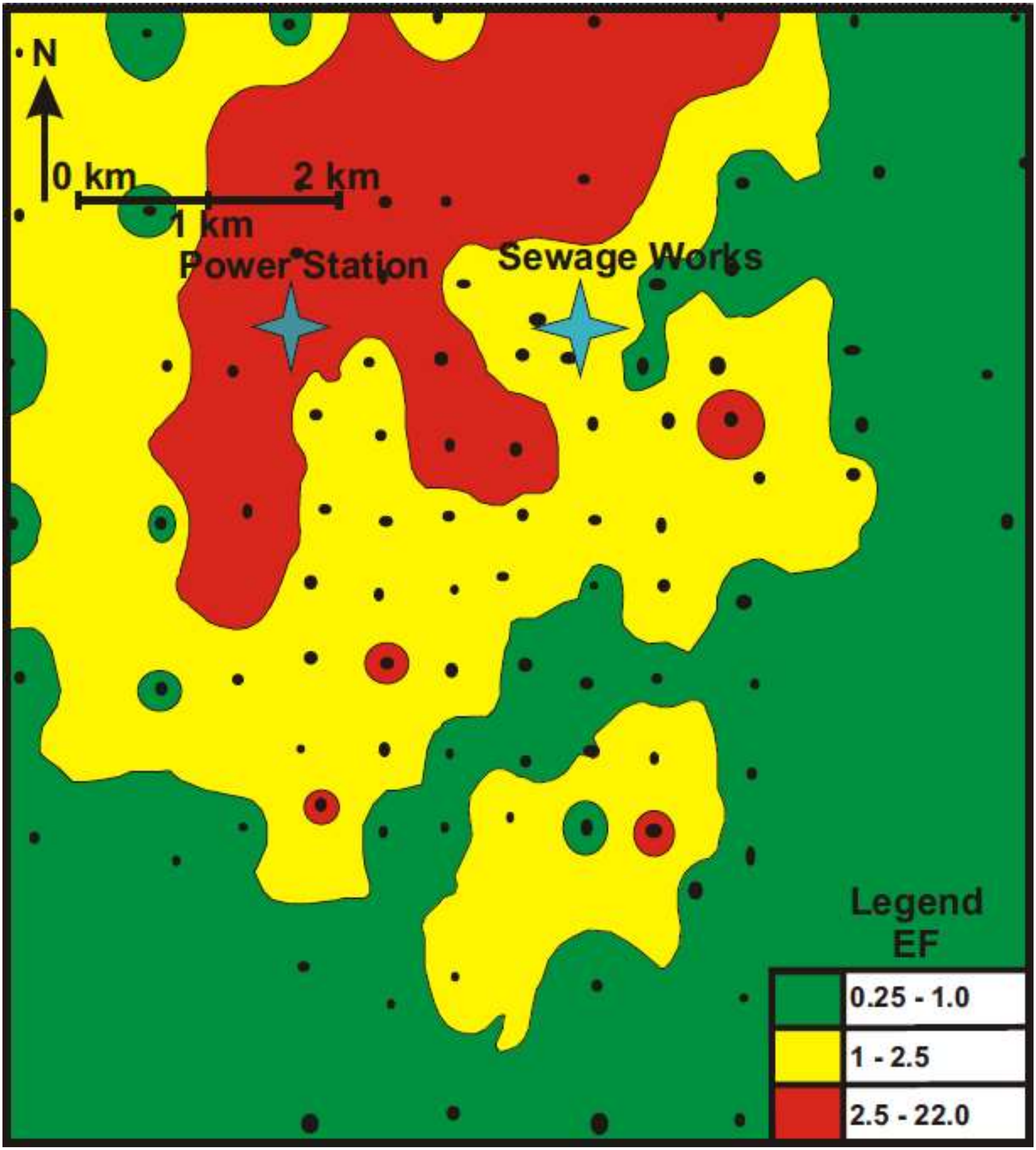


Figure 6.5 IDW enrichment factor map of antimony with red indicating possible contamination, yellow is moderate and green is below background values.

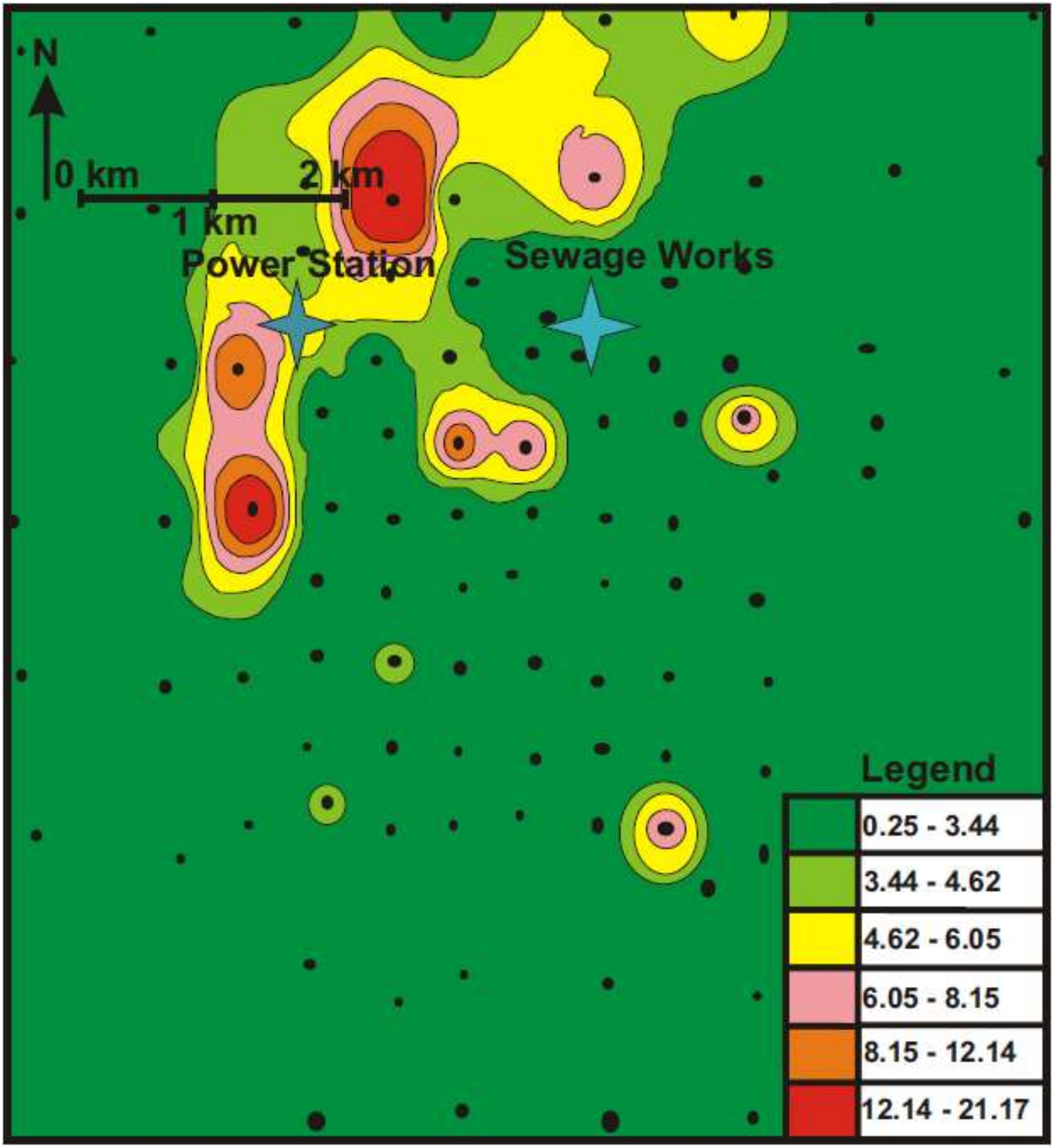


Figure 6.6 IDW detailed enrichment factor map of antimony with red indicating the highest enrichment factor values and dark green the lowest enrichment factor values.

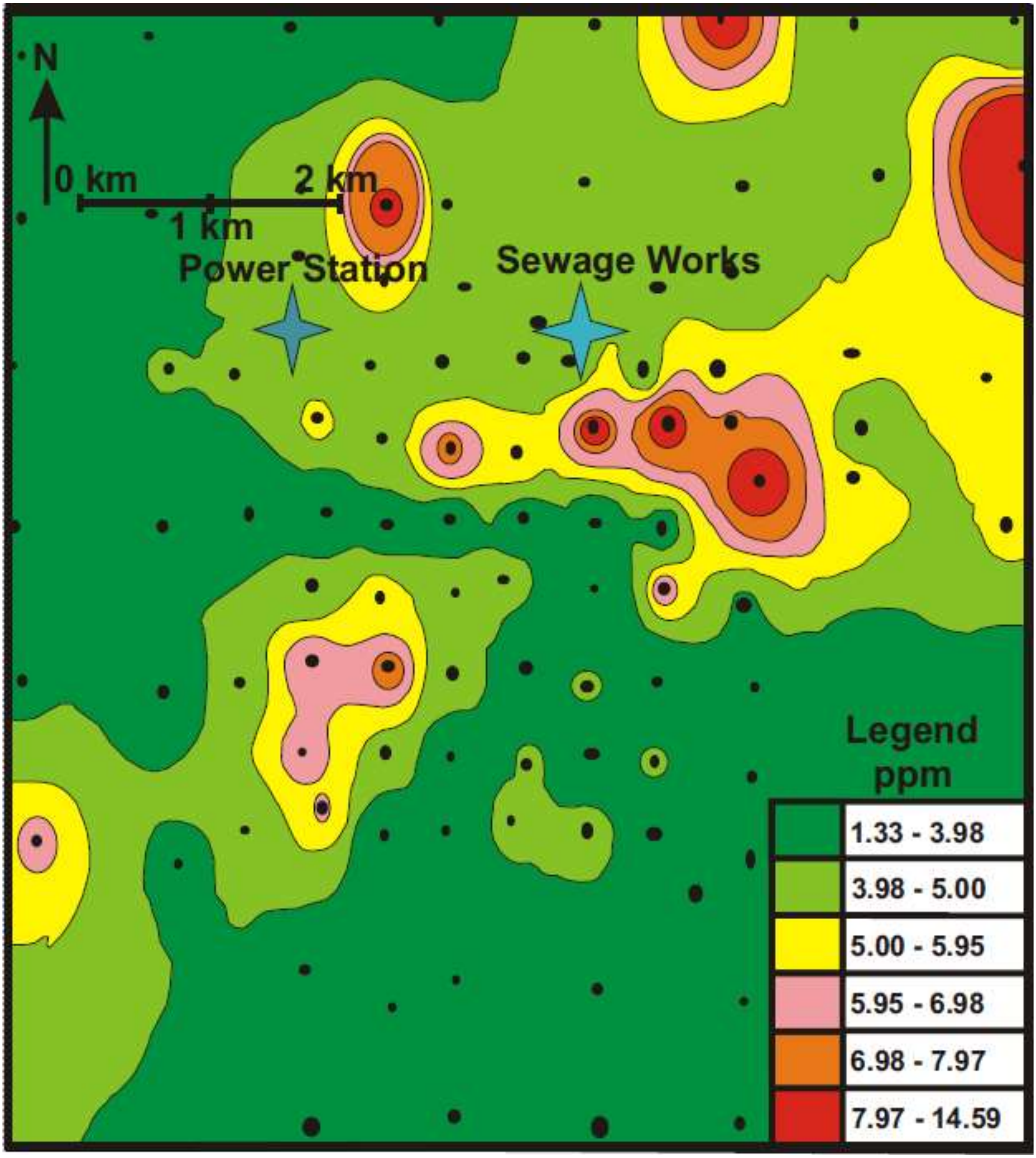


Figure 6.7 IDW concentration map of arsenic with red indicating areas with the highest concentrations and dark green with the lowest concentrations.

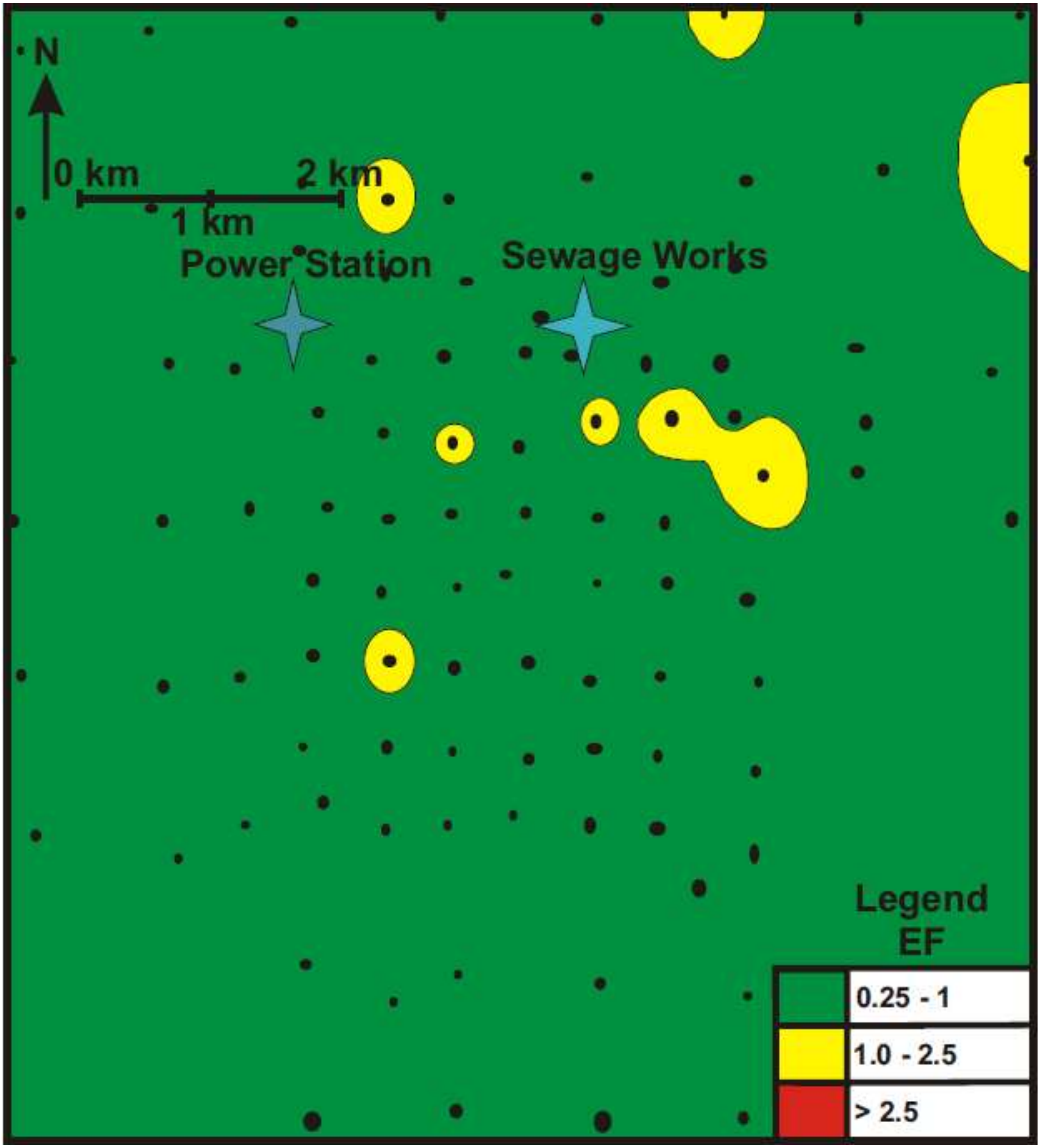


Figure 6.8 IDW Enrichment factor map of arsenic with the yellow hotspots indicating moderate enrichment factors and green below background values.

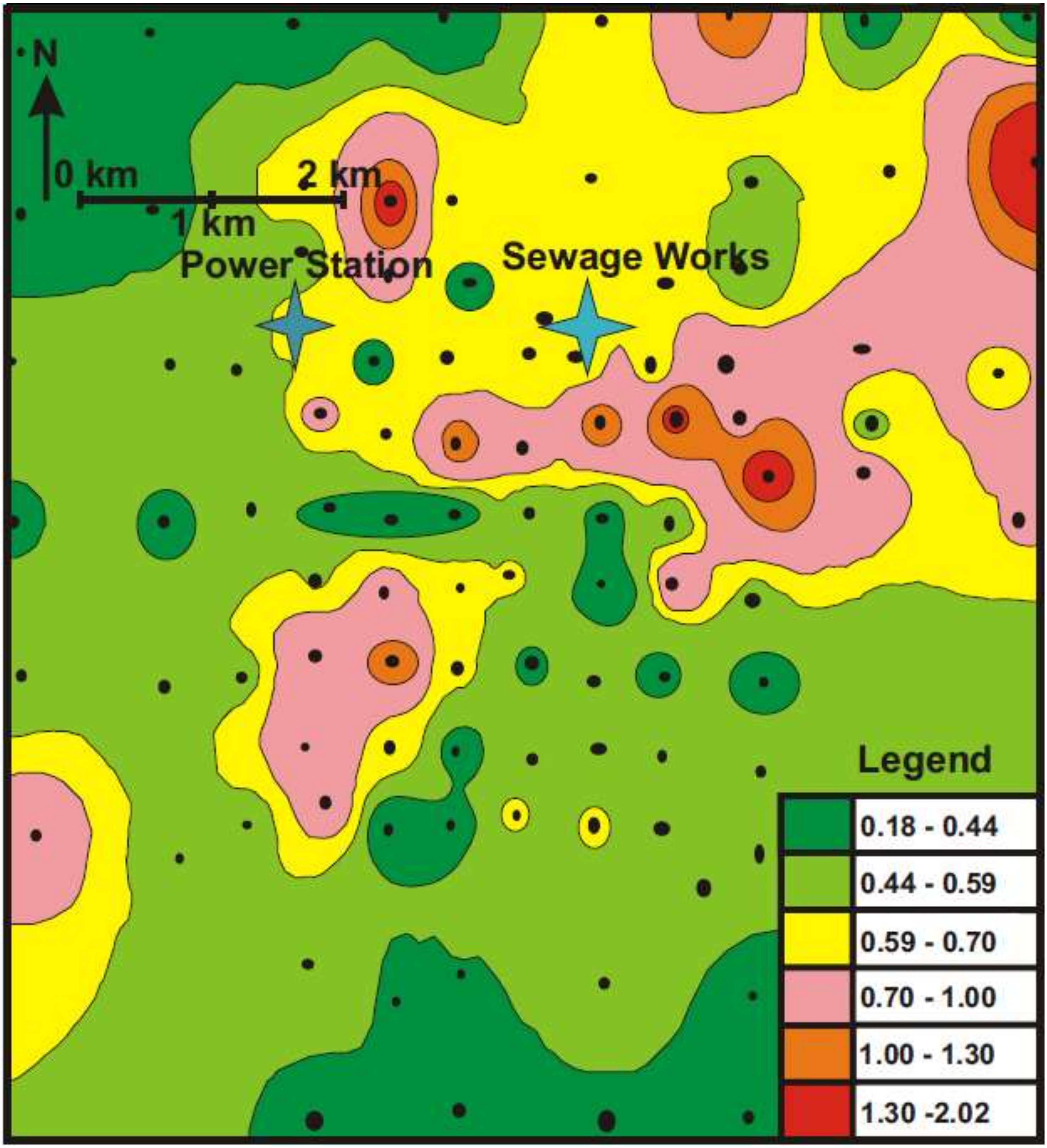


Figure 6.9 IDW detailed enrichment factor map of arsenic with red indicating the highest enrichment factor values and dark green the lowest enrichment factor values.

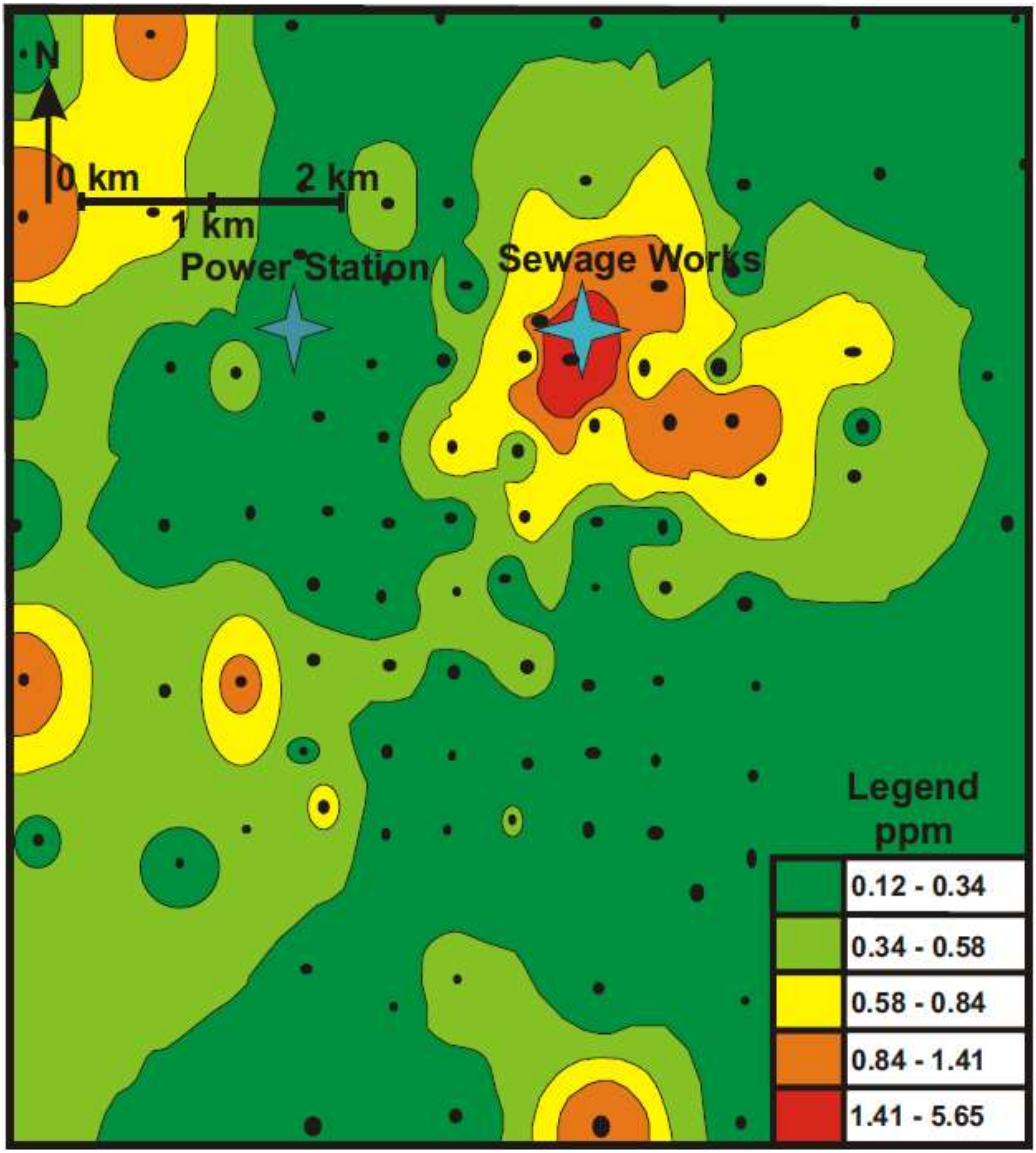


Figure 6.10 IDW concentration map of bismuth with red indicating areas with the highest concentrations and dark green with the lowest concentrations.

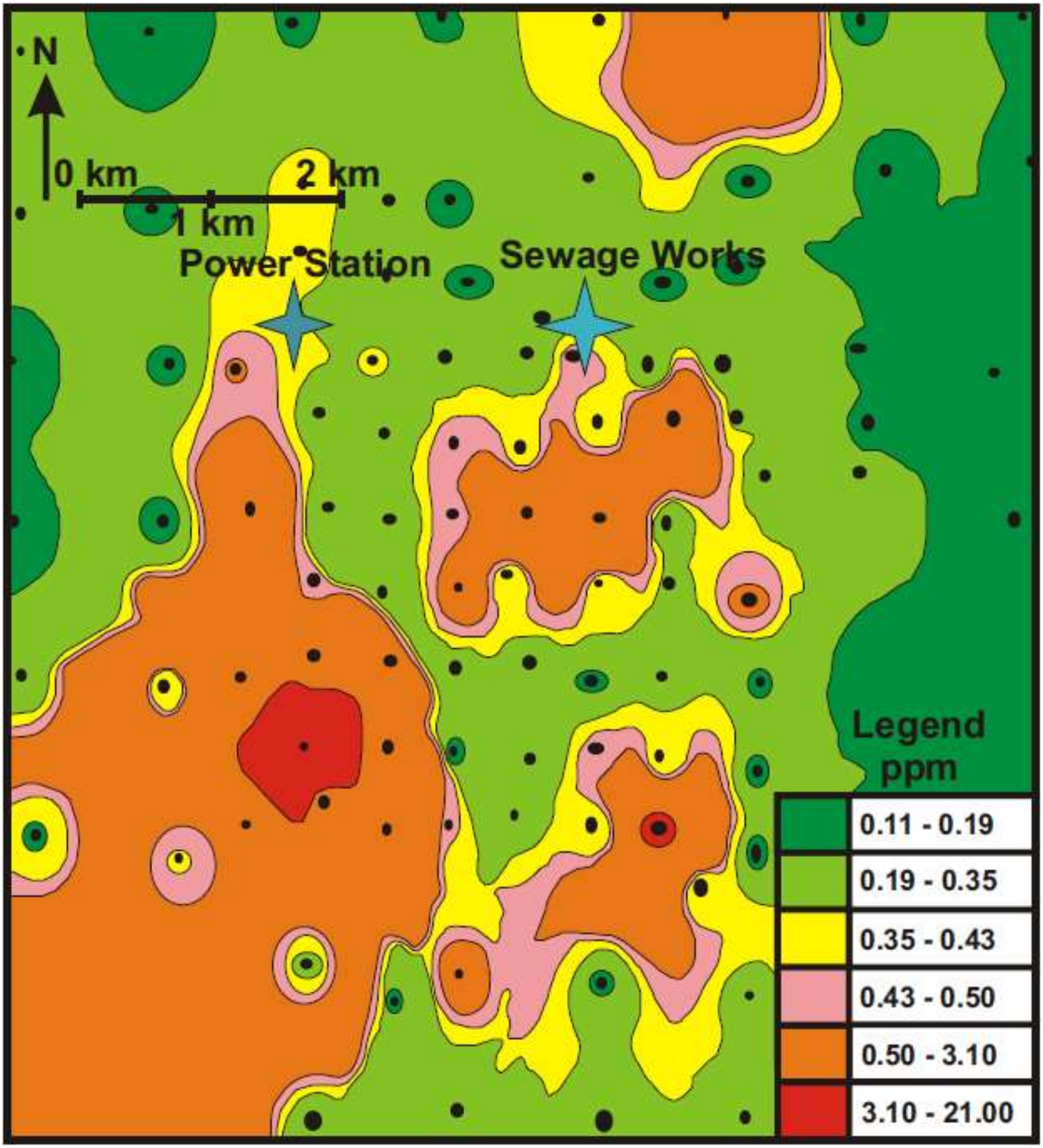


Figure 6.11 IDW concentration map of cadmium with red indicating areas with the highest concentrations and dark green with the lowest concentrations.

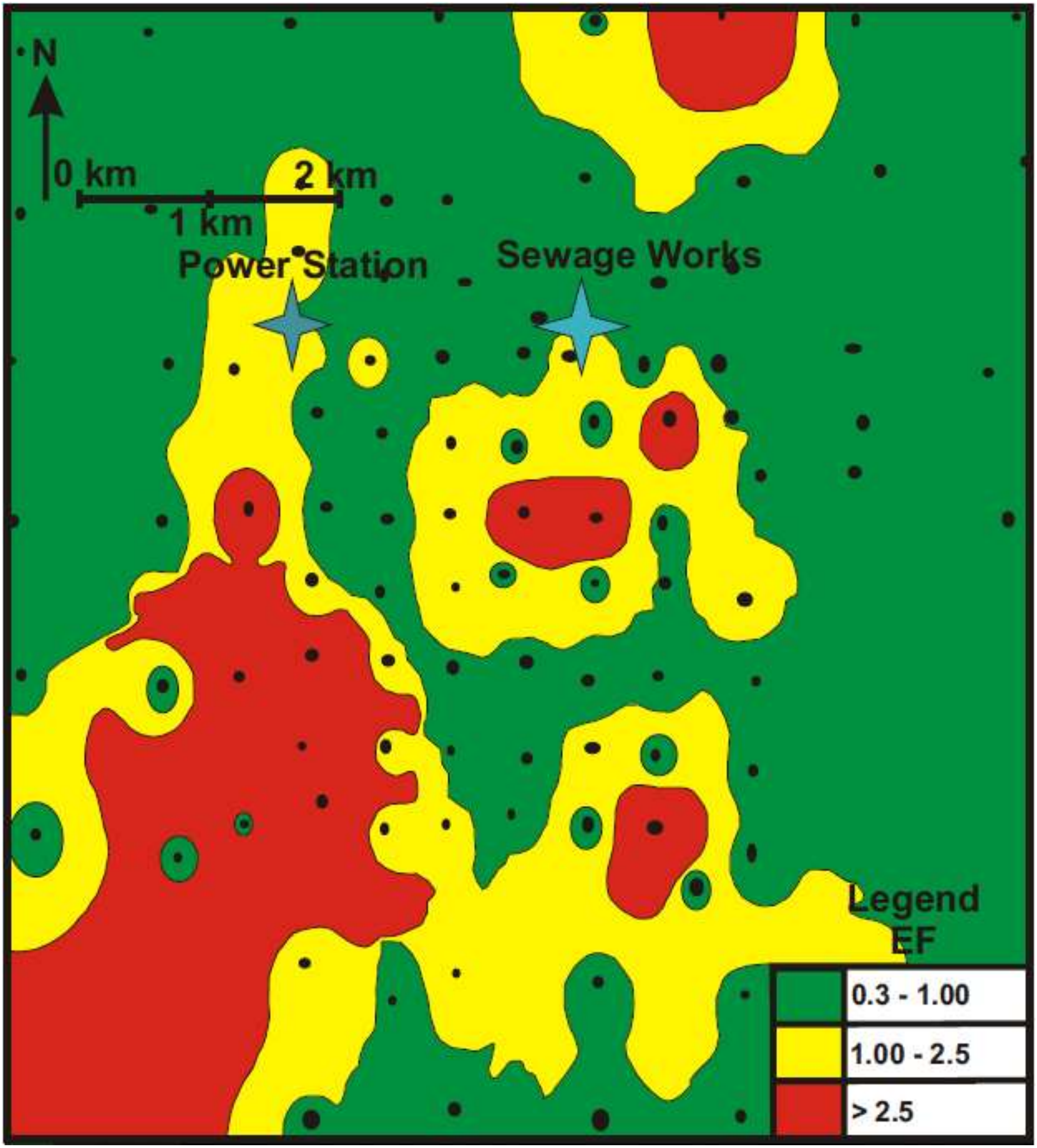


Figure 6.12 IDW enrichment factor map of cadmium with red indicating possible contamination, yellow is moderate and green is below background values.

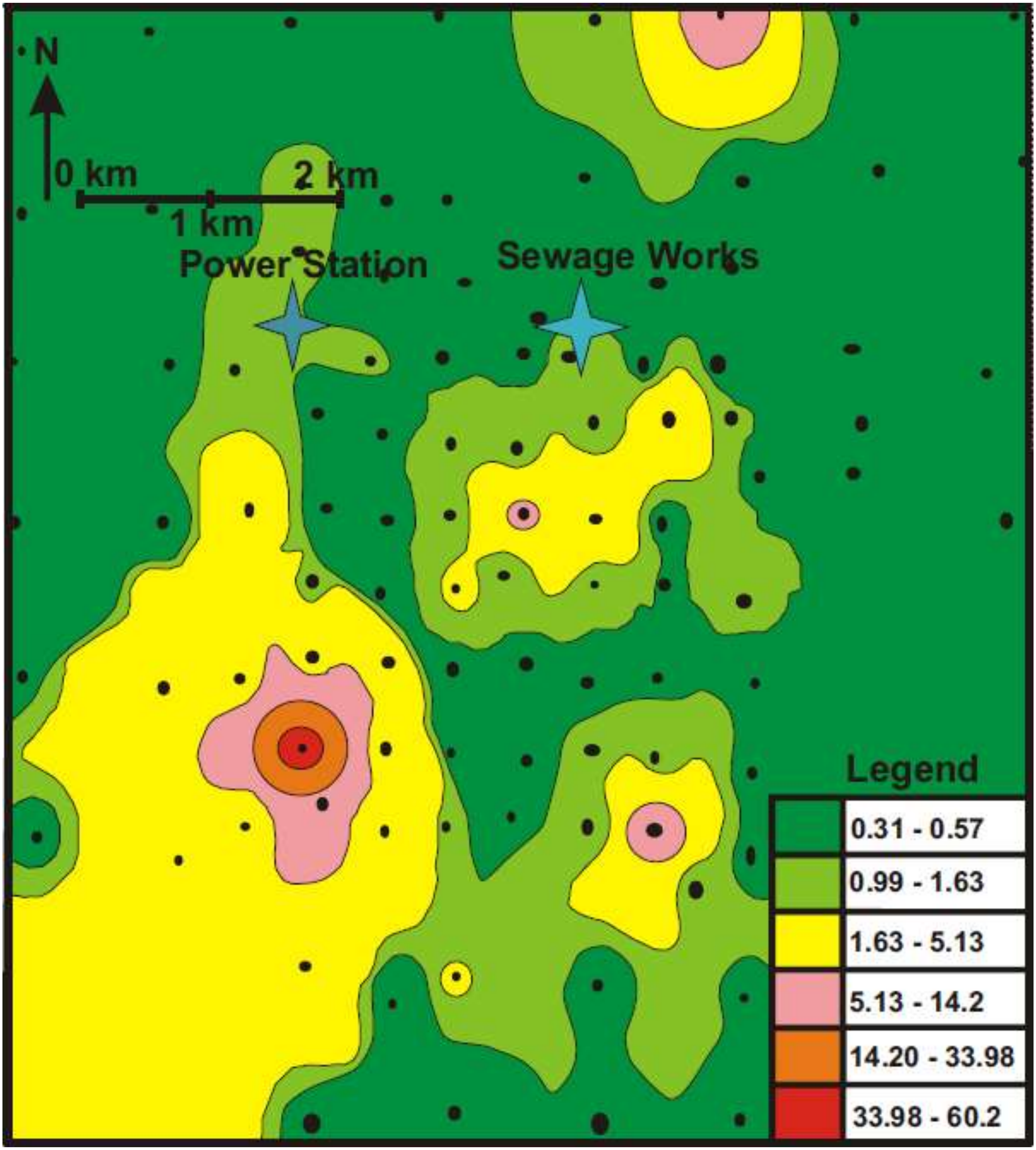


Figure 6.13 IDW detailed enrichment factor map of cadmium with red indicating areas with the highest enrichment factor values and dark green with the lowest enrichment factor values.

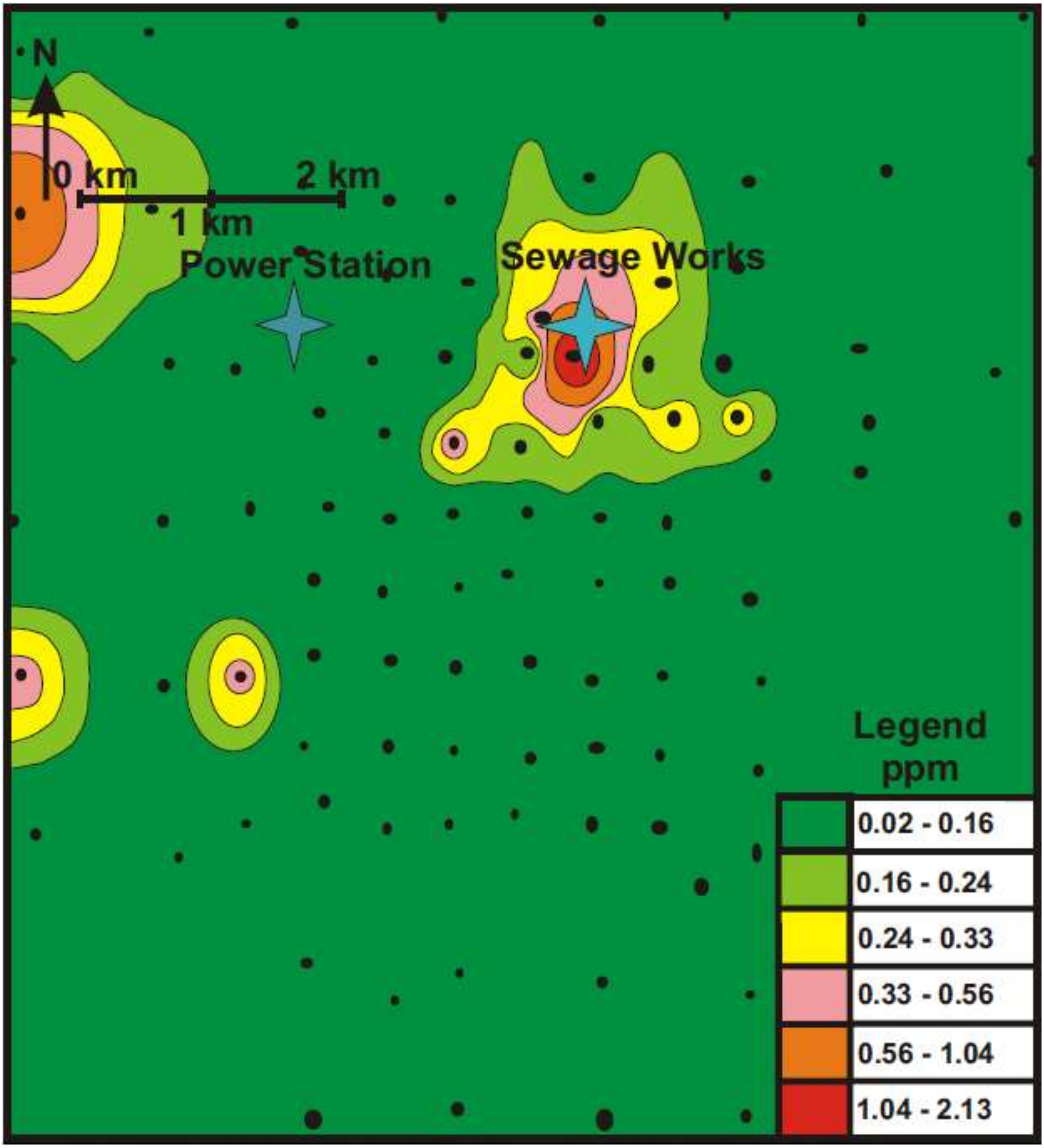


Figure 6.14 IDW concentration map of mercury with red indicating areas with the highest concentrations and dark green with the lowest concentrations.

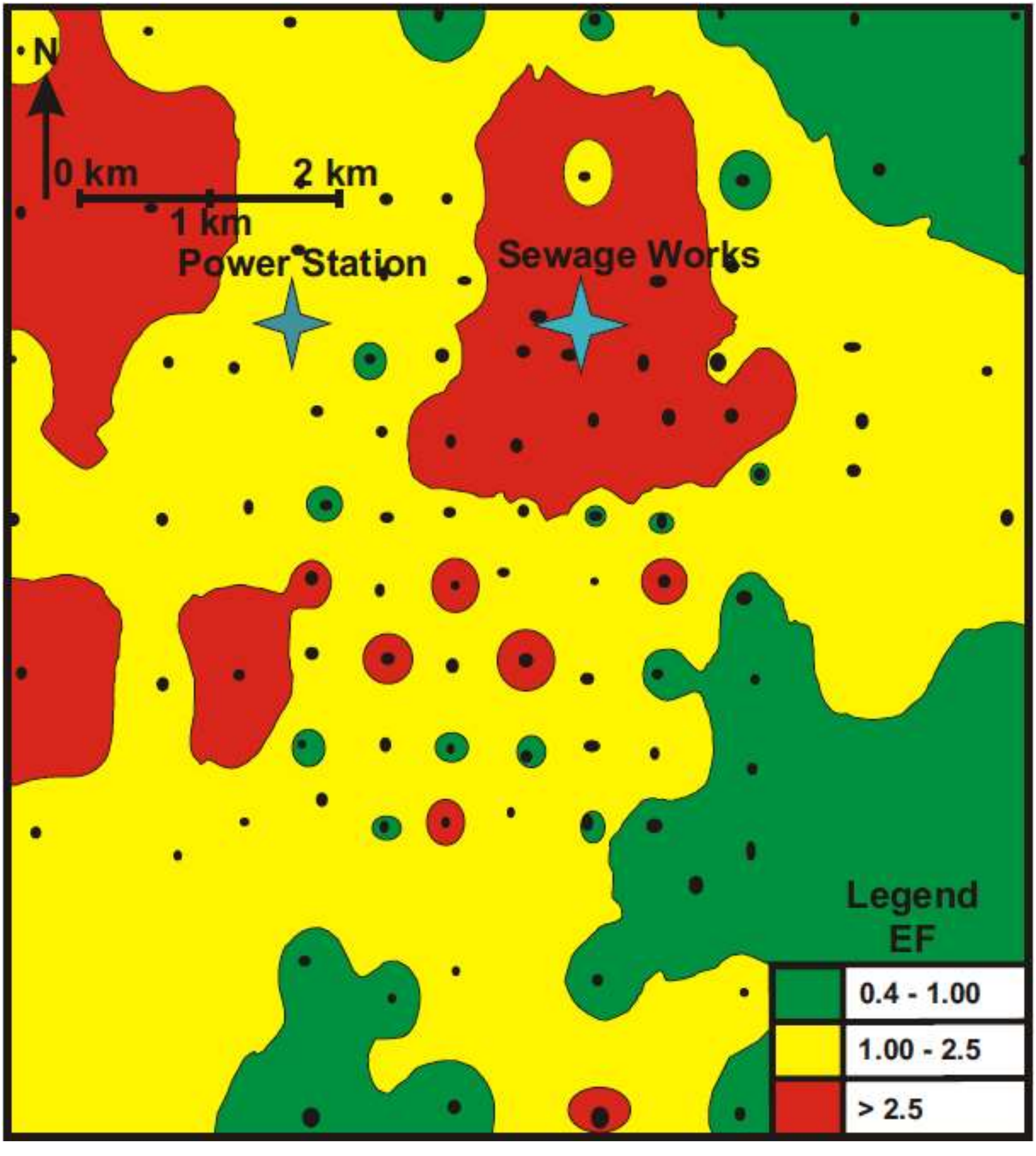


Figure 6.15 IDW enrichment factor map of mercury with red indicating possible contamination, yellow is moderate and green is below background values.

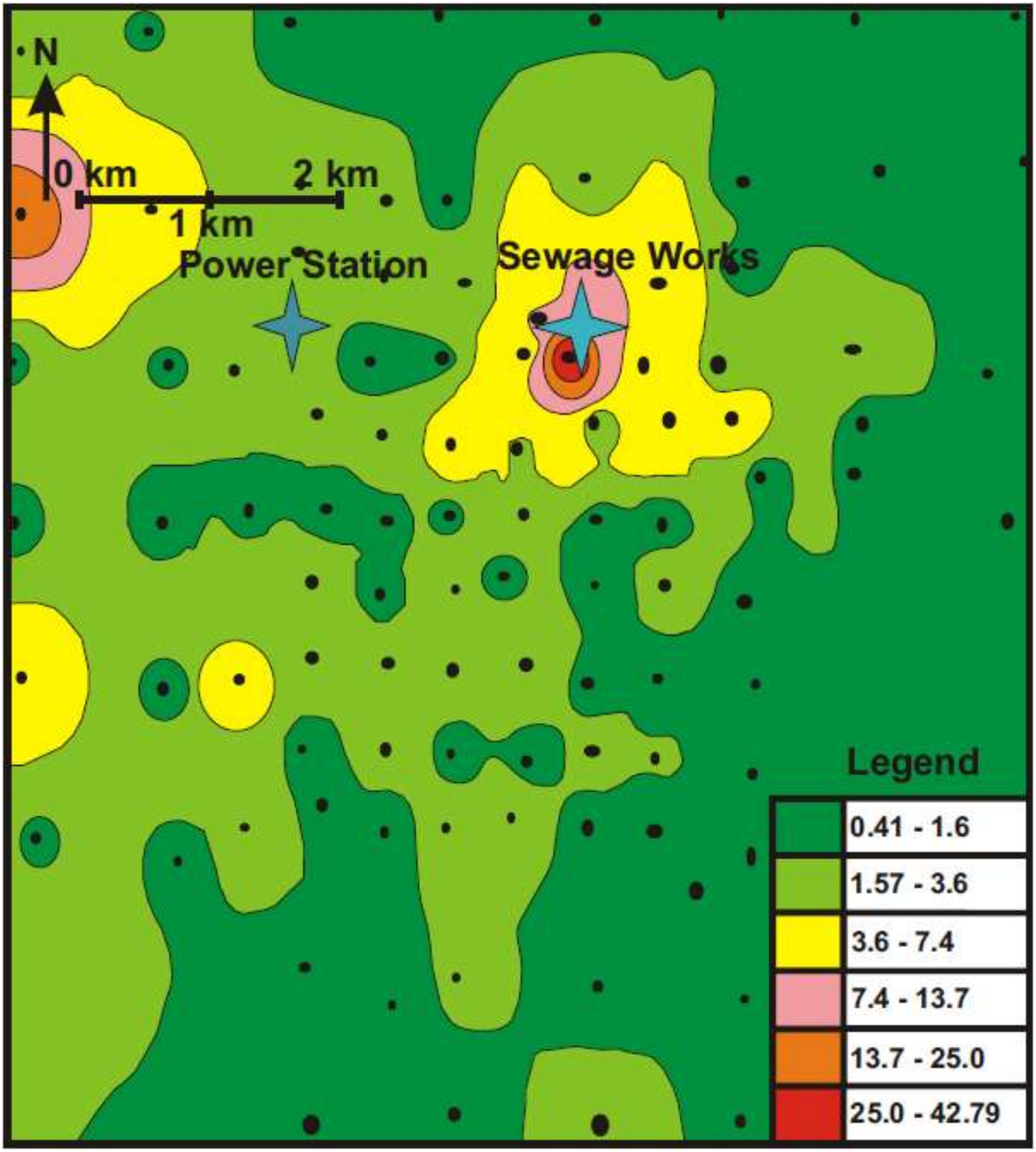


Figure 6.16 IDW detailed enrichment factor map of mercury with red indicating areas with the highest enrichment factor values and the dark green with the lowest enrichment factor values.

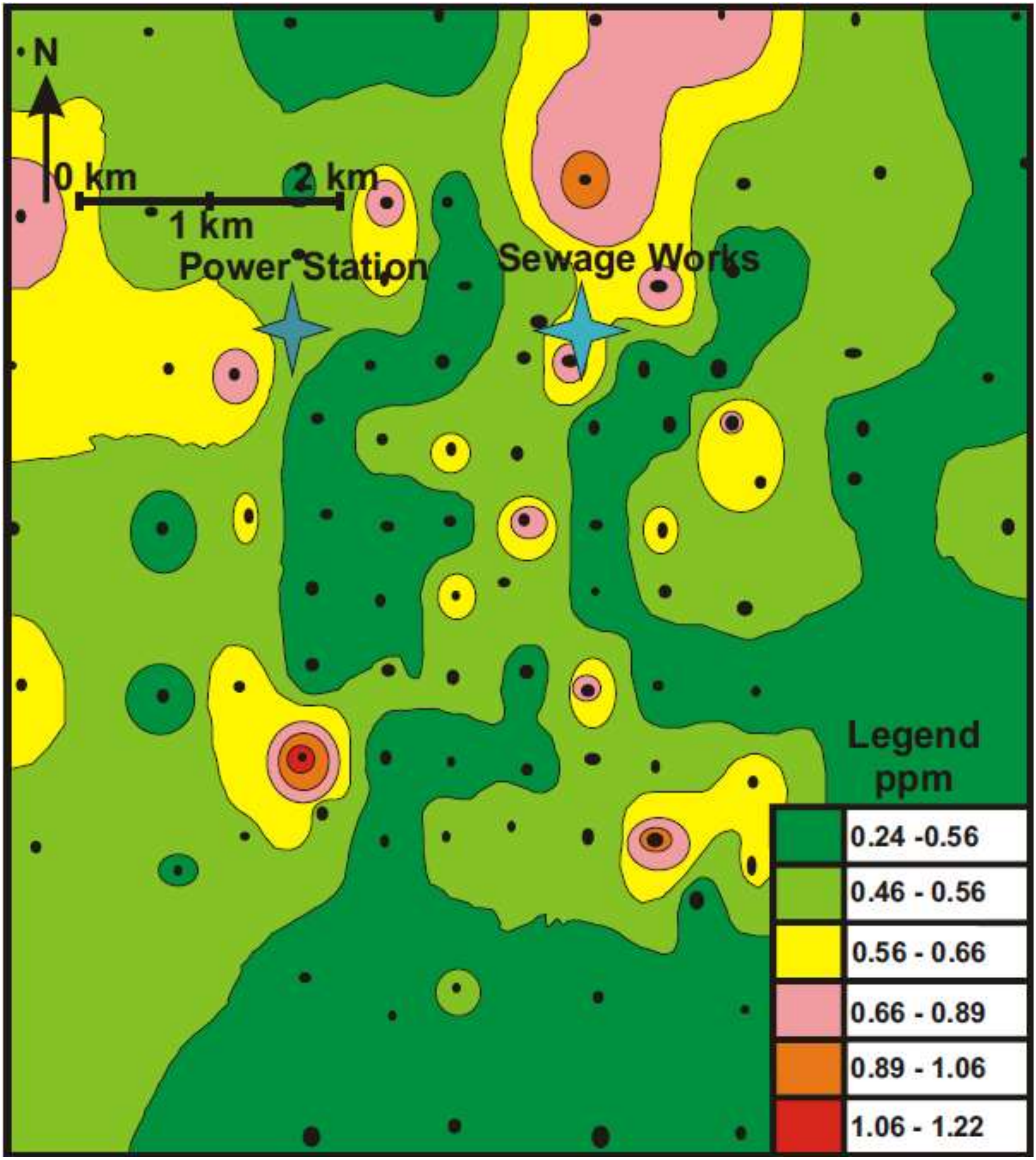


Figure 6.17 IDW concentration map of selenium with red indicating areas with the highest concentrations and dark green with the lowest concentrations.

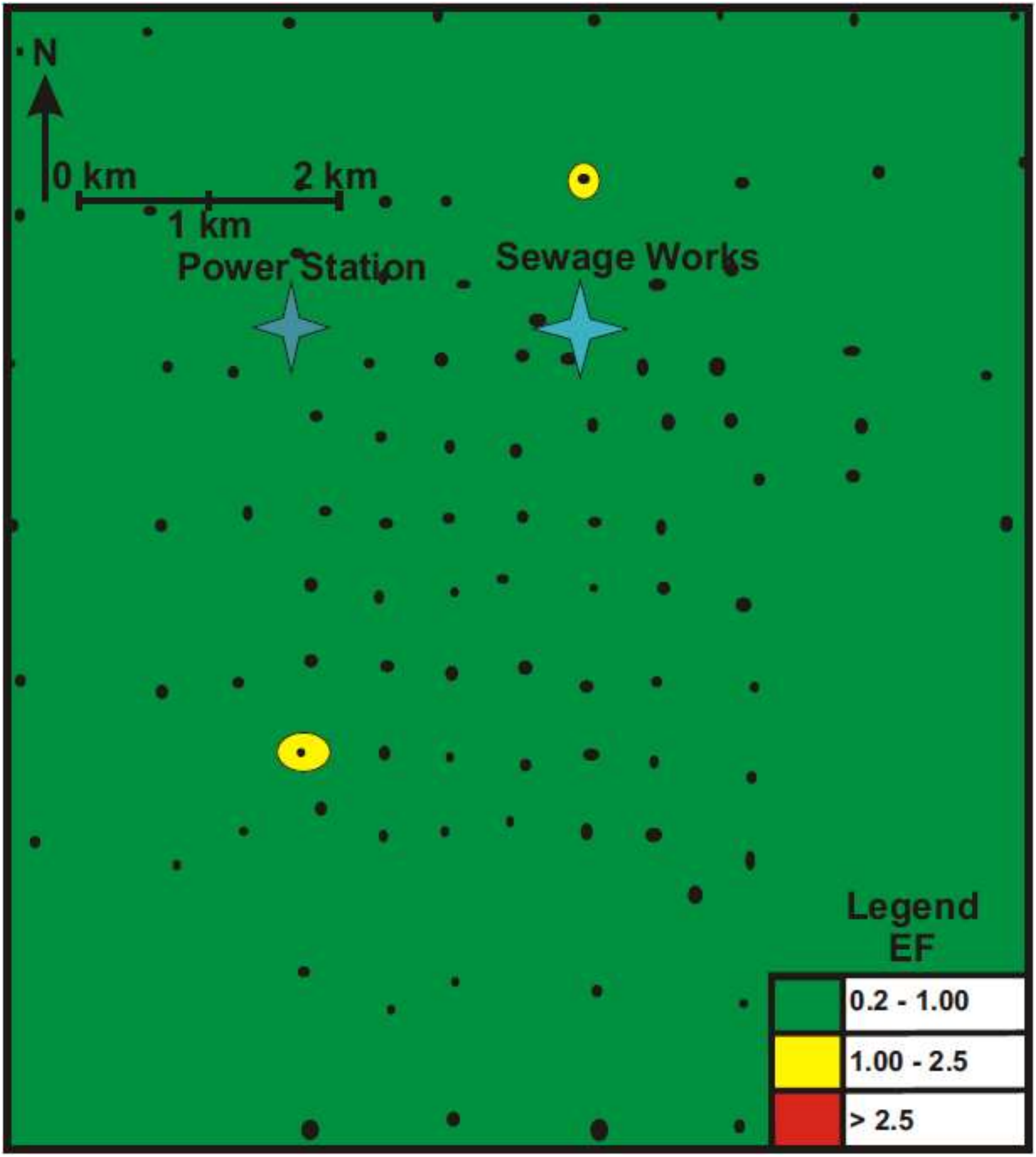


Figure 6.18 IDW enrichment factor map of selenium with yellow being moderate and green is below background values.

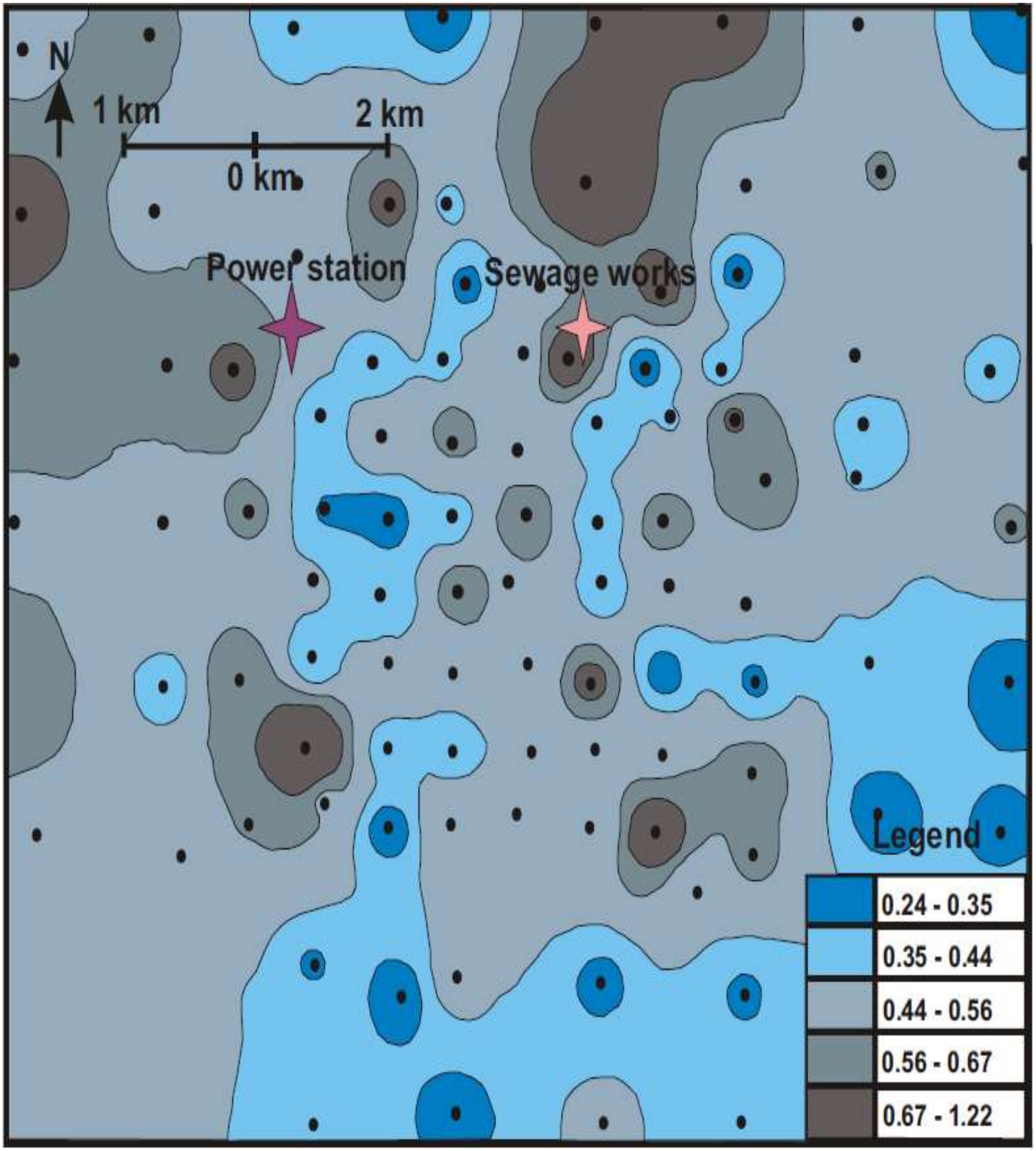


Figure 6.19 IDW detailed enrichment factor map of selenium with dark grey indicating areas with the highest enrichment factor values and the dark blue with the lowest enrichment factor values. The dark blue indicates areas with a possible deficiency in selenium.

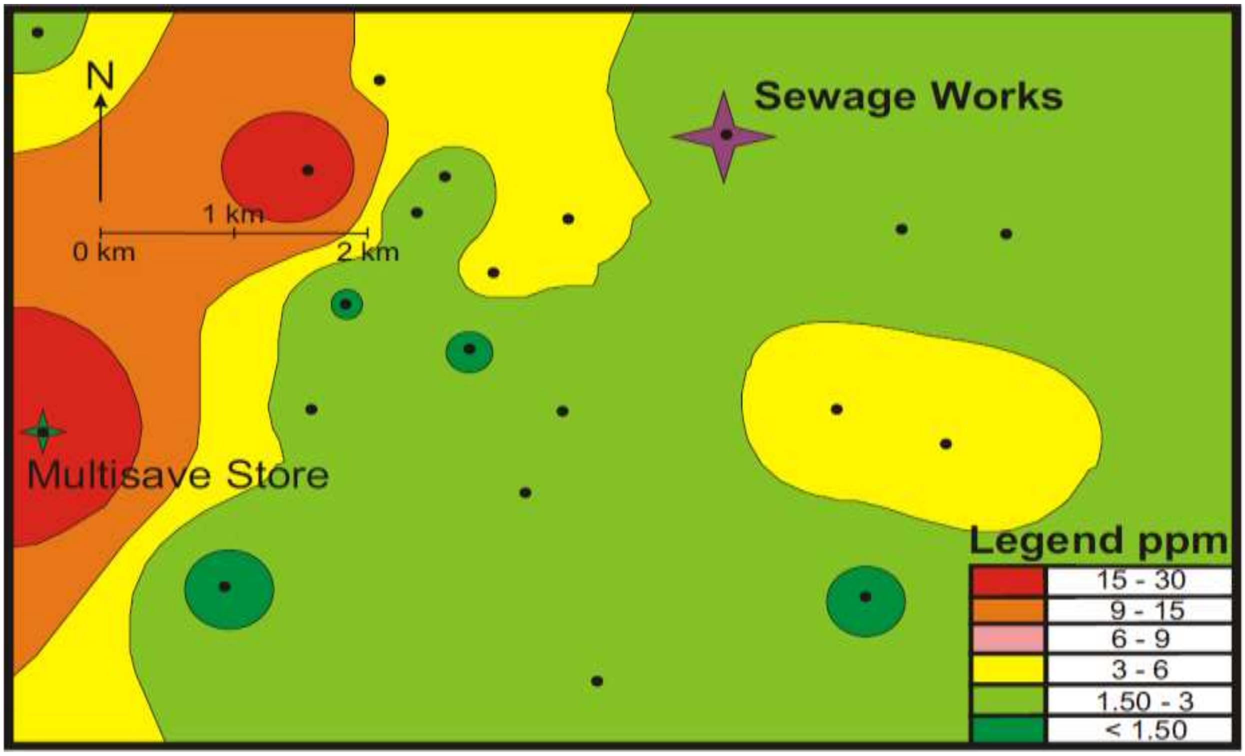


Figure 6.20 IDW dust sample concentration map of antimony with red indicating areas with the highest concentrations and dark green with the lowest concentrations.

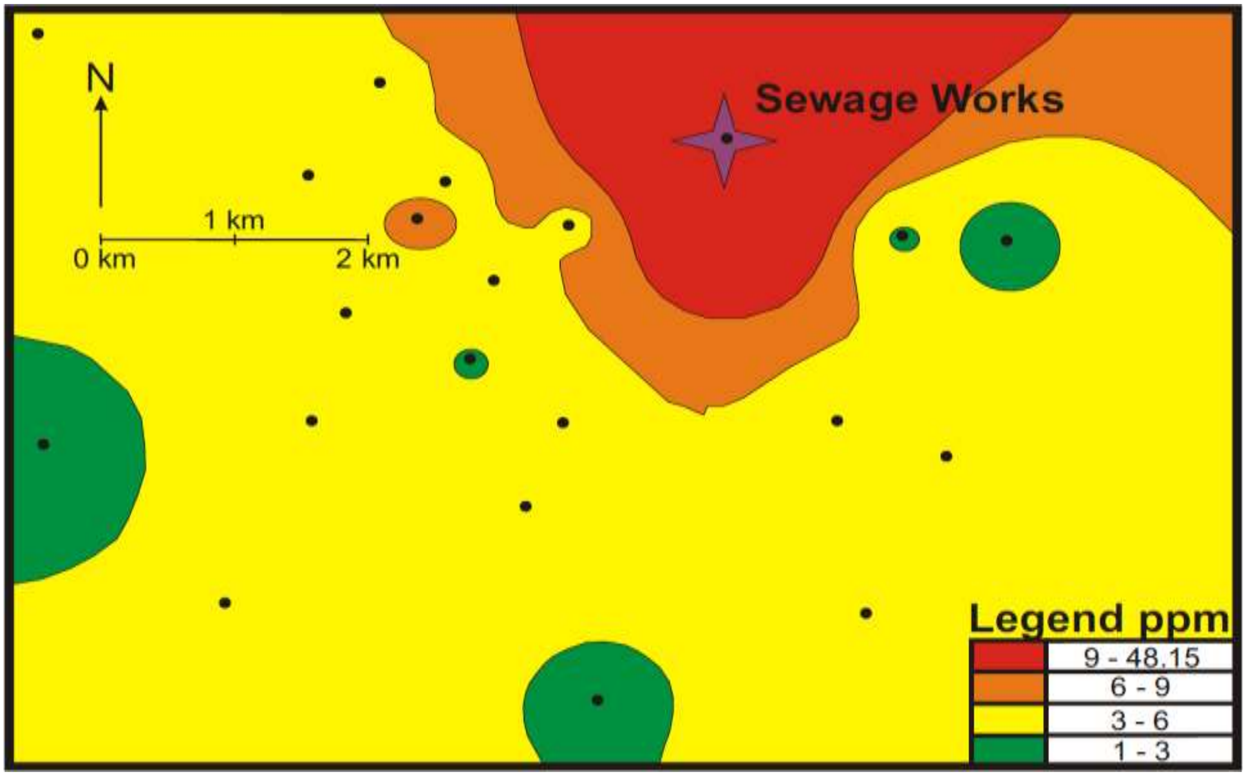


Figure 6.21 IDW dust sample concentration map of arsenic with red indicating areas with the highest concentrations and dark green with the lowest concentrations.

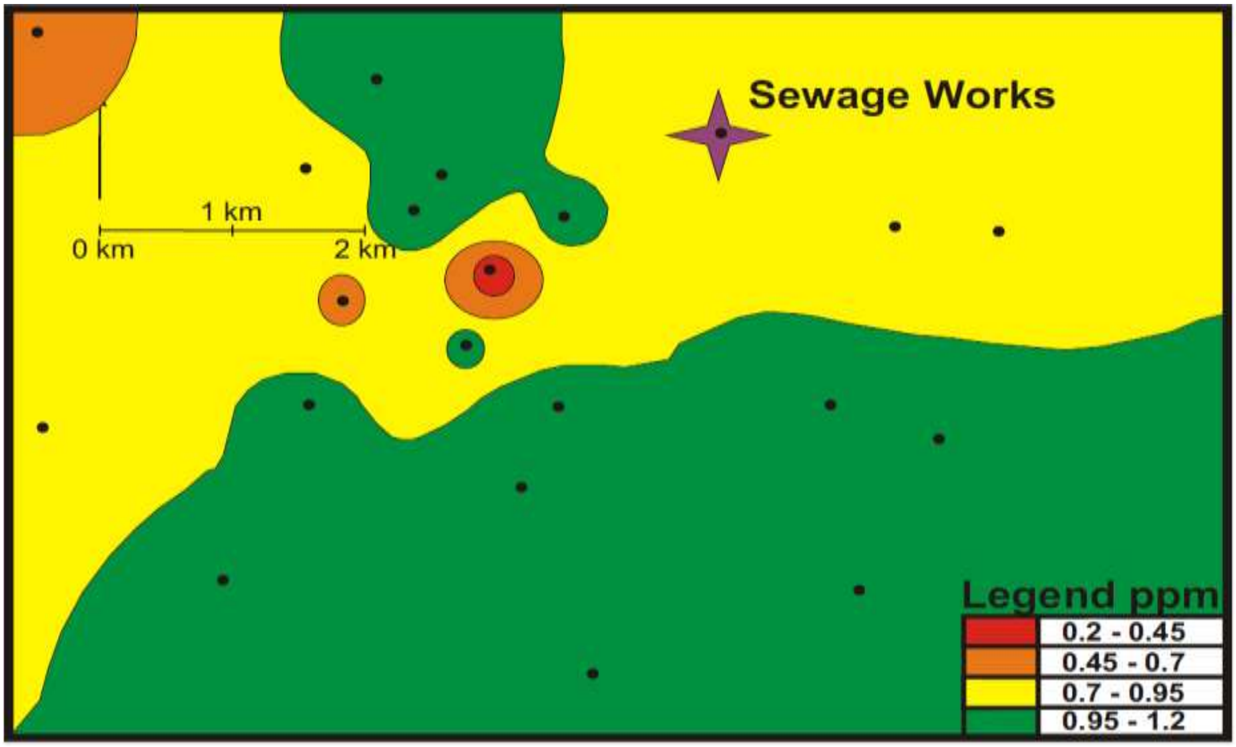


Figure 6.22 IDW dust sample concentration map of bismuth with red indicating areas with the highest concentrations and dark green with the lowest concentrations.

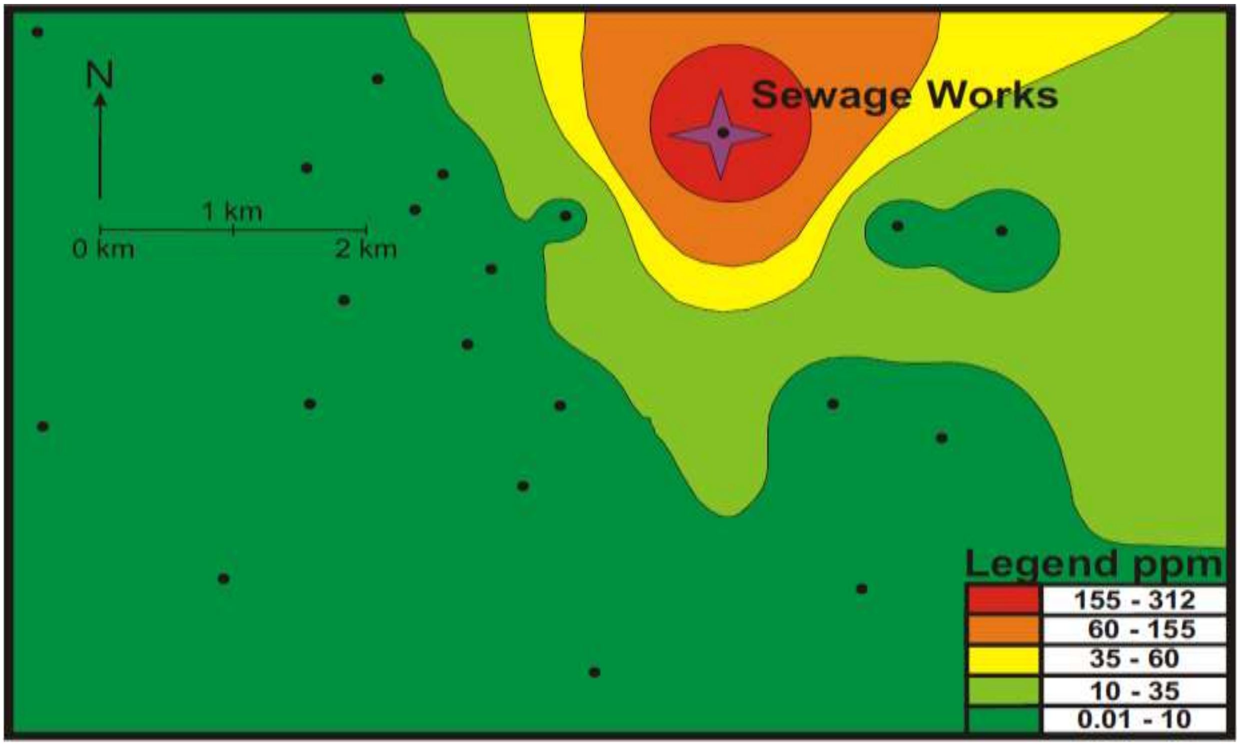


Figure 6.23 IDW dust sample concentration map of cadmium with red indicating areas with the highest concentrations and dark green with the lowest concentrations.

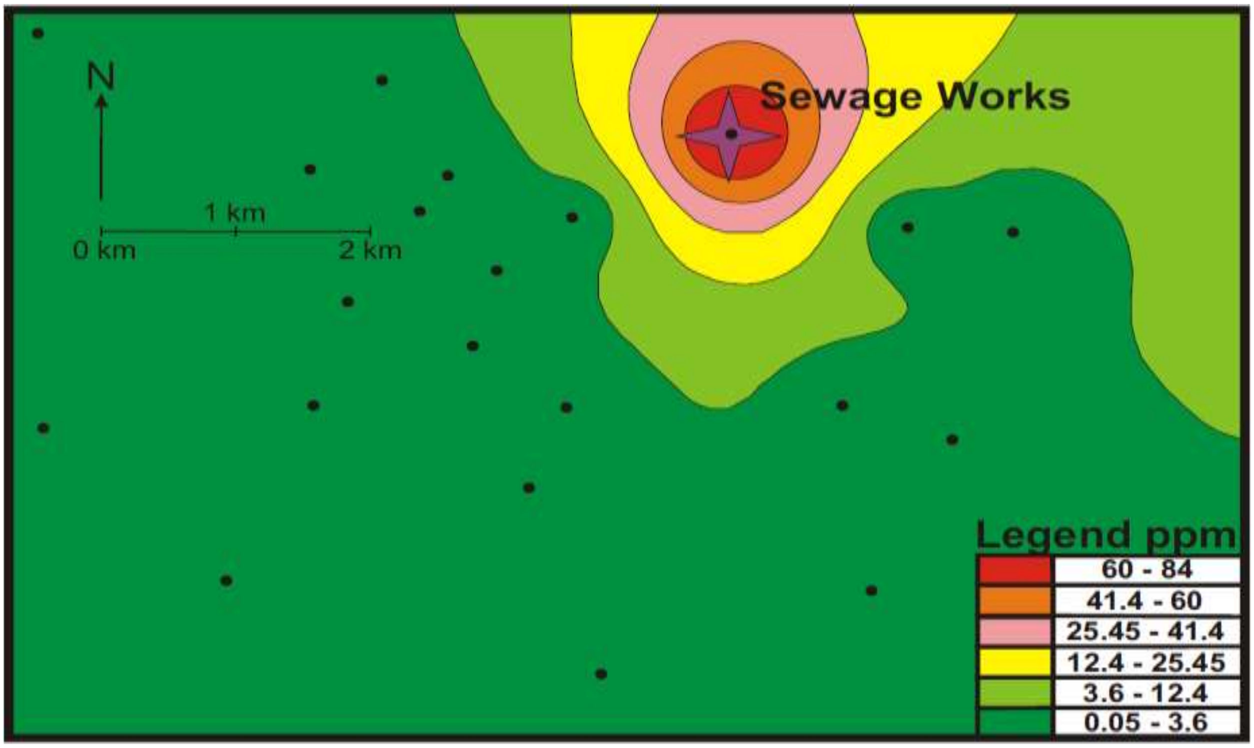


Figure 6.24 IDW dust sample concentration map of mercury with red indicating areas with the highest concentrations and dark green with the lowest concentrations.

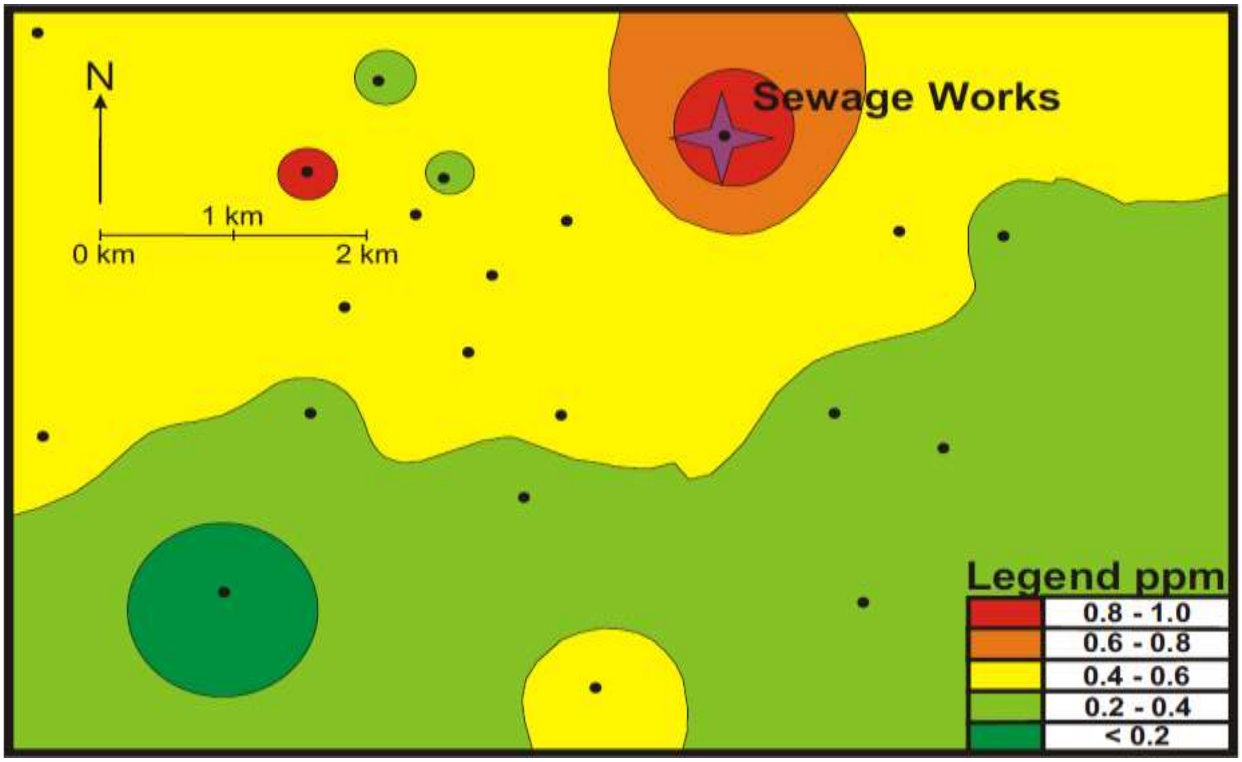


Figure 6.25 IDW dust sample concentration map of selenium with red indicating areas with the highest concentrations and dark green with the lowest concentrations.

Chapter 7: Conclusions

Results of the heavy metals that were analyzed showed interesting findings. On an overall basis contamination of the eastern side of Bloemfontein is not very harsh depending on the area of interest. Most of the analyses indicate that there is little contamination of the area except for antimony, cadmium, and mercury in certain local positions. Most locations that show strong anomalies for the elements are found in the industrial area of Bloemfontein. Antimony contains below background values and above background values. Anomalies are found south, east and north-east of the power station (Figure 6.4).Arsenic levels are comfortably below background values, except for position A80 that has an enrichment factor of 2 which can possibly be serious in the future (Figure 6.7). The strong anomaly (A85) for cadmium is south of the power station in the industrial area and the other strong anomaly (A77) is found north east of the power station (Figure 6.11). All anomalies (A85, A99, A27, and A28) are found in the industrial areas of Bloemfontein. Mercury has a high value east of the power station situated at the sewage works (Figure 6.14). The concentration value found at the sewage works can be considered contaminated. Selenium concentration values are comfortably below background values and are actually quite below the background values indicating a possible deficiency in the land in and around Bloemfontein (Figure 6.17).

Contamination of the area has occurred for 3 of the 6 studied elements. Antimony, cadmium and mercury are a cause for concern in the study area because certain areas show elevated concentration levels compared to background values. Compared to other places in the world that contain major contamination of these elements, the Bloemfontein area has low contamination. The contaminated areas of this study area have concentrations that are quite above the background values, but other areas across the world have extremely high values. Other places around the world with concentration values that reach over 100s of ppm such as antimony (Wilson et al., 2004a; Hammel et al., 2000) and cadmium (Limei et al., 2008) to 1000s of ppm such as antimony (Wilson et al., 2004a) can be seen. In this study area there are no areas with any concentrations as high as other studied areas of the world. The study area can be deemed contaminated for some elements, but not like other heavily contaminated areas around the world.

Arsenic and selenium are at similar to lower concentrations to background values. It can be concluded that there is very little to no contamination in this study area. Bismuth has elevated levels at the sewage works (Figure 6.8) but further research should be done to see if there is possible contamination.

Overall the main sources of contamination of the area possibly originate from the industrial area as all the main contaminated areas fall in the industrial area. While the power station was in operation it could have been a source for contamination because the coal contained trace amounts of the studied heavy metals (Wagner and Hlatshwayo, 2005; Bergh et al., 2011). The heavy metals could be released into the atmosphere from burning the coal at the power station for electricity generation and then could have been redistributed to soils in the study area causing the elevated concentrations in some elements. But at present time (2013) the power station is not in use therefore the primary sources of contamination of the study area is most probably from industrial activities in the industrial areas.

Further analysis should be done on areas considered contaminated with the heavy metals. More detailed research should be done in the contaminated areas to identify the sources of the contamination and possible solutions should be made to remediate the soils that are considered contaminated.

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Internet websites

http://www.ceva.com.au/Products/Products-list/JUROCYL-R-Injection (obtained 19 June 2013)

Appendix 1 Sampling Localities

A1.1 Soil sample localities

The sampling localities of the study area can be found in Figure 3.2.

Soil samples				
Sample	**Position**	**Elevation**	**Date sampled**	**Description**
A01	S29.12642 E26.23119	1383 m	2006/05/02	Next to Fort street, next to the progressive primary health care board.
A02	S29.12619 E26.23657	1374 m	2006/05/02	Taken next to the wall facing the main road, next to an Engen garage.
A03	S29.12595 E26.24259	1358 m	2006/05/03	Next to a quiet road. First removed grass. Took sample with scoop, top ~5cm
A04	S29.12621 E26.24588	1361 m	2005/05/03	In the sewerage plant grounds, next to a road. Took sample with scoop, top 5cm
A05	S29.12666 E26.25149	1362 m	2005/05/03	~50m from road into open field. Removed grass sampled with scoop, top ~5cm. Close to a stream, ~20m away.
A06	S29.12671 E26.25719	1364 m	2005/05/03	Next to a road in an open field. Removed grass with spade, sampled top 5cm with scoop.
A07	S29.12581 E26.26706	1363 m	2005/05/03	Next to the road, 5m into the field. No buildings around. Removed grass with spade, samples top 5cm with scoop.
A08	S29.12709 E26.27700	1363 m	2005/05/03	On a farm into the field close to a dam. Removed wild grass close to a tree sampled top 5cm with scoop.
A09	S29.13575 E26.27850	1365 m	2005/05/03	Next to a dirt road between plots and farms. Removed wild grass and sampled top 5 cm
A10	S29.14495 E26.27833	1376 m	2005/05/03	On a plot ~50m from the dirt road. Removed wild grass, sampled top 5cm
A11	S29.15362 E26.27778	1385 m	2005/05/03	In an informal settlement, 5m from dirt road on the side, close to a power line pole. Removed wild grass and sampled top 5cm
A12	S29.16254 E26.27793	1392 m	2005/05/03	In an informal settlement, 5m from dirt road.
A27	S29.13121 E26.23726	1380 m	2005/05/03	Closed to a paved road, ~20m from shopping centre (checkout). Power station ~1km away. Removed grass sampled top 5cm of soil.
A28	S29.13147 E26.24211	1379 m	2005/05/03	Close to tarred road~10m in an open field. Removed wild grass and bushes. ~100m from railway and power lines. Rubbish lying around, lots of worms in sample. Removed wild grass, sampled top 5cm.
A29	S29.13002 E26.24789	1366 m	2005/05/03	Next to a road, removed grass, samples top ~5cm with scoop
A30	S29.12982 E26.25336	1376 m	2005/05/03	Next to a tarred road. In industrial area, buildings around. Removed grass and sampled top 5cm
A31	S29.12968 E26.25805	1368 m	2005/05/03	Next to a road ~5m into a field in an industrial area. Removed grass with spade, samples top 5cm with scoop
A32	S29.13012 E26.26771	1368 m	2005/05/03	Next to the road, close to an intersection. Removed wild grass, samples top 5cm
A33	S29.13291 E26.26706	1371 m	2005/05/03	Next to the road on a bridge on the side - the gradient. Removed wild grass, samples top 5 cm
A34	S29.14373 E26.26798	1384 m	2005/05/03	Next to a dirt road in an open space close to a soccer field. Removed grass sampled top 5cm

A35	S29.15243 E26.26868	1389 m	2005/05/03	Next to a tarred road, close to houses on an open space. Removed wild grass and sampled top 5cm.
A47	S29.13534 E26.24261	1390 m	2005/05/03	~1m from tarred road. Close to walkway, might be disturbed. Removed grass and sampled top 5cm.
A48	S29.13558 E26.24804	1388 m	2005/05/03	~2m from tar road, ~10m from school fence. Lots of rubbish lying around. Removed grass and sampled top 5cm.
A49	S29.13577 E26.25285	1379 m	2005/05/03	~20m from tar road in vicinity of an illegal dumping site in the field.
A50	S29.13312 E26.26004	1373 m	2005/05/03	Close to a mechanical plant of some sort (e.g. crusher stone?). Looks like ash on the ground, dark grey colour, couldn't find other soil. Close to the railway line ~15m.
A51	S29.14034 E26.25902	1379 m	2005/05/03	~2m from tar road on sidewalk not used often. Removed wild grass sampled top 5cm.
A52	S29.14486 E26.25954	1385 m	2005/05/03	~3m from tar road at intersection, in residential area. Removed grass, sampled top 5cm of soil
A53	S29.15022 E26.25945	1393 m	2005/05/03	~20m from tarred road next to a sport stadium. Removed grass, sampled top 5cm
A64	S29.13949 E26.24822	1388 m	2005/05/03	~3m from tarred road on sidewalk. Sample might be disturbed. Removed grass next to fence
A65	S29.13941 E26.25326	1384 m	2005/05/03	~70m from tar road in open field. Removed grass sampled top 5cm
A66	S29.14443 E26.25287	1390 m	2005/05/03	~15m from road in open field in residential area. Close to a petrol station. Lots of people walking around and lots of rubbish lying around
A72	S29.12017 E26.22592	1382 m	2006/05/04	In town, lots of rubbish lying around, close to railway, not sure that the sample is undisturbed.
A73	S29.11619 E26.22606	1388 m	2006/05/04	In town, ~1m from tar road on sidewalk. Possibly disturbed, removed bushes and sampled top 5cm.
A74	S29.10675 E26.22541	1496 m	2006/05/04	Sample taken at viewpoint in naval hill nature reserve. View over the whole of Bloemfontein, power station ~3km to the south.
A75	S29.10623 E26.23628	1397 m	2006/05/04	Next to a busy road on the sidewalk ~ 5m from the road. There is a paved walkway for pedestrians. Sample was taken as close to the fence as possible.
A76	S29.10671 E26.24797	1382 m	2006/05/04	In Transnet/Spoornet grounds, very close to railways and buildings and containers. Not sure if soil is undisturbed.
A77	S29.10642 E26.25726	1373 m	2006/05/04	In transwerke grounds very close to railways and buildings, not sure if soil is undisturbed
A78	S29.10668 E26.26712	1370 m	2006/05/04	In an open field close to a concrete producer. Soil is black clay, turf.
A79	S29.10614 E26.27938	1363 m	2006/05/04	Next to a dirt road between residential plots. Removed wild grass from sidewalk close to the fence of the plot. ~10 m from electricity line pole. Cobbles of dolerite? In soil.
A80	S29.11487 E26.27961	1360 m	2006/05/04	On the grounds of Bloemfontein racing track next to a dirt road in an open field
A81	S29.11534 E26.26897	1367 m	2006/05/04	On the off ramp to the N8 Just next to the road ~2m from tar.
A82	S29.11606 E26.25892	1368 m	2006/05/04	Next to the N8 highway. ~10m from the road close to trees. Soil is harder and dryer than all the other samples taken. Next to the golf course ~50m.
A83	S29.11583 E26.24716	1377 m	2006/05/04	~10 m from tar road, road is between golf course and transwerke.
A84	S29.11721 E26.23693	1379 m	2006/05/04	At a shell filling station ~ 15m from road, ~20m from petrol tanks

A85	S29.11716 E26.23251	1383 m	2006/05/04	In transwerke grounds, very close to tarred road and railway line. Soil= gray-black?
A86	S29.12141 E26.23211	1379 m	2006/05/04	~15m from tar road in semi-industrial area. 1m from an old small railway lane/track. 1m from the fence of private property. Removed wild grass and sampled top 5cm.
A87	S29.12190 E26.23831	1376 m	2006/05/04	~5m from tar road on sidewalk 5m from the fence of the SPCA. Removed wild grass and sampled top 5cm
A88	S29.12199 E26.24365	1371 m	2006/05/04	Close to a stream between the sewerage plant and the golf course.
A90	S29.12206 E26.25269	1368 m	2006/05/04	Within the golf course in the rough.
A91	S29.12114 E26.25828	1363 m	2006/05/04	Within the golf course in the rough, very close to a stream.
A97	S29.10740 E26.21489	1441 m	2006/05/04	On a hill close to a construction site. Quartzite hill? Removed wild grass and sampled top 5cm. Took rock sample.
A13	S29.17031 E26.27909	1385 m	2006/05/04	Red loam-sandy soil, collected 1.8m from the gravel unpaved road, 0.5m from the sidewalk, 5m from the house fence. NB: sample was not collected at its co-ordinate, absence of road to its co-ordinate.
A14	S29.12954 E26.22741	1391 m	2006/05/03	Soil sample was collected about 500m from the power station (PW) under the little bushes, underneath the grass, about 2m from the home yard fence, between XABA & THOKO street according to the Global Positioning System (GPS)
A15	S29.13491 E26.22789	1382 m	2006/05/03	Red soil sample was collected 4.5m from the school fence, underneath the grass, about 10m from the main road, about 20m from the kids playing ground
A16	S29.13912 E26.22689	1390 m	2006/05/03	Soil sample collected under the grass in a vegetation cover; about 2m from a house fence, 2m from Magato road.
A17	S29.14353 E26.22694	1386 m	2006/05/03	Soil sample was collected under the bushes, in a vegetation cover, 3m from the tar road, in a residential area, in an area with bedrock of shales.
A18	S29.14866 E26.22646	1390 m	2006/05/03	Soil sample was collected in a residential area in a disturbed area; 2m from the house.
A19	S29.15184 E26.22781	1394 m	2006/05/04	Black loam soil, was collected underneath the grass and naturally grown plants, 2m from the tree trunk, 3m from the stream, 1.5m from the dam.
A20	S29.16126 E26.22692	1397 m	2006/05/04	Black loam soil, collected in an open space, covered by ~10cm tall grass, about 30m from the industrial shops.
A21	S29.17058 E26.22689	1417 m	2006/05/04	Brown loam soil, collected underneath the grass, 1.2m from the industrial fence, 20m from VOLVO garage, 15m from CROSS CAPE EXPRESS shop, few industries around, approximately 30-50m away from the co-ordinate, 5m from the tar road
A22	S29.16989 E26.23746	1419 m	2006/05/04	Loam brown soil, collected 3m from the tar road, 2m from the dumping site, underneath 10cm tall grass, 7m from the house fence, 5m from the electric pole.
A23	S29.17044 E26.24829	1430 m	2006/05/04	Loamy clay black soil, collected underneath the grass, 3m from the gravel road, 7m from the houses, 4m from school fence, 6m from the dumping site.
A24	S29.17028 E26.25857	1413 m	2006/05/04	Brown-black loam soil, 0.5m from the sidewalk, 3m from the tar road, 4m from the house fence, 8m from the house, 6m from the electric pole.
A25	S29.17113 E26.26900	1401 m	2006/05/04	Red loam-sandy soil, collected underneath the grass, 1.7m from the gravel road, 2m from the church fence.

A26	S29.13059 E26.23207	1381 m	2006/05/04	Red loam soil, collected2m from the wire fence, 1.8m from the gravel road, underneath the grass.
A36	S29.16148 E26.26758	1387 m	2006/05/04	loam soil, collected underneath the grassy bushes surrounded by flowers, 1.8m from the muddy unpaved gravel road, 3.2m from the block brick houses, 2.5 m from the small dumping site
A37	S29.13562 E26.23257	1376 m	2006/05/03	Reddish brown loam soil, collected underneath the grass, 4m from the house fence, 2m from the road.
A38	S29.13986 E26.23192	1381 m	2006/05/03	Clay loamy soil, collected 2m from the road, not covered by grass, 2.5m from the house fence.
A39	S29.14382 E26.23255	1384 m	2006/05/03	Loamy clay soil, collected 2.5m from the road, under the grassy bushes, 4m from the house
A40	S29.14875 E26.23245	1397 m	2006/05/03	Reddish brown loam soil, collected under the grass, 3m from the road, 2m from the house fence.
A41	S29.15345 E26.23253	1401 m	2006/05/03	Reddish-yellow soil sample was collected in an unpaved road, under the grass, about 2m from the residential house
A42	S29.16314 E26.23339	1404 m	2006/05/04	Loam, a bit clay, red brown soil, collected 1m from the graveyard, underneath blackjack plant, underneath the grass, 1m from the sidewalk, no houses nearby.
A43	S29.16199 E26.23754	1414 m	2006/05/04	Loam soil, collected underneath the grass, 2.2m from the school fence, 3m from the gravel road, 2.3m from the tree.
A44	S29.16235 E26.24826	1422 m	2006/05/04	Loamy sandy soil, collected in a sidewalk, 1m from the house fence, 1.0m from the electric pole, 2m from the gravel road
A45	S29.16300 E26.25882	1400 m	2006/05/04	Sandy loamy soil, collected underneath the grass, 1.8m from the gravel road, 7m from the house fence, 8m from the dumping site
A46	S29.13531 E26.23714	1380 m	2006/05/04	Loose red loam soil with rocks was collected 1.2m from the gravel road, underneath the grass, in a rocky surface, 2m from the naturally grown plants, 4m from the smelly dumping site.
A54	S29.15491 E26.25944	1402 m	2006/05/03	Reddish loam, clay-sandy soil collected in a residential area, 2m from the house fence, underneath the grass, about 1.2m from the road.
A55	S29.13972 E26.23786	1385 m	2006/05/03	Grayish loam soil, collected 2m from a house fence, under the grassy bush, about 2m from the road
A56	S29.14424 E26.23729	1387 m	2006/05/03	Damp black clay soil, collected under the tall grass, 2.5m from the house, 2m from the road
A57	S29.14893 E26.23741	1392 m	2006/05/03	Brownish sandy soil, collected under bushy grass 5m from the house, 2m from the road.
A58	S29.15313 E26.23708	1405 m	2006/05/03	Brown-black damp soil sample was collected 1.2m from the school fence, underneath the grass, in an undisturbed area, about 2m from the road.
A59	S29.15245 E26.24189	1406 m	2006/05/03	Damp brown-black loam soil sample collected under a tree, underneath the grass, about 2.5m from the road, about 4m from the houses
A60	S29.15332 E26.24745	1406 m	2006/05/03	Damp loam soil collected 2.5m from the tar road, underneath the grass, 5m from the spaza shop and a hotel.
A61	S29.15363 E26.25227	1407 m	2006/05/03	Damp loamy-sandy brown-reddish soil collected 1m from the fence, underneath the grass
A62	S29.15696 E26.25537	1407 m	2006/05/03	Damp loam sandy soil, collected 1m from the fence, collected underneath the grass.
A63	S29.13888 E26.24129	1385 m	2006/05/03	Dark brown loam soil, collected 2m from the hospital fence, 2m from the tar road.
A67	S29.14921 E26.25267	1391 m	2006/05/04	Black loam soil, was collected 4m from the tar road, 3m from a cement sidewalk.

A68	S29.14887 E26.24772	1395 m	2006/05/03	Loose sandy-loamy soil, collected under the little bushes, underneath the grass, 4m from the house fence.
A69	S29.14908 E26.24308	1396 m	2006/05/03	Yellowish-red loamy clay soil, collected 2m from a house, inside the yard.
A70	S29.14392 E26.24281	1388 m	2006/05/03	Reddish-brown sandy soil, collected under a tree trunk, 3m from the house, 2m from the road.
A71	S29.14494 E26.24744	1390 m	2006/05/03	Reddish-brown loam soil, collected 2.5m from the house fence, 3m from the road.
A92	S29.12697 E26.22117	1398 m	2006/05/04	Dark loam soil, collected under a tree, 0.5m from a tar road, 1m from the sidewalk
A93	S29.12663 E26.21623	1390 m	2006/05/04	Red-brown loam soil, collected under a tree, inside the hospital yard, 7m from the tar road, 1m from a brick sidewalk.
A94	S29.12638 E26.20466	1409 m	2006/05/04	Clay loam soil, collected underneath the grass, 4m from the tar road, 3m from the sidewalk.
A95	S29.11789 E26.20540	1397 m	2006/05/04	Black loam-sandy soil, collected underneath man-grown plants, 0.2m from the fence of the industrial building (selling tyres), 1.5m from the tar road.
A96	S29.10851 E26.20538	1403 m	2006/05/04	Black loam soil, 0.1m from the brick-wire wall of an apartment, 1.5m from the sidewalk, 2.3m from the tar road, collected underneath the lawn grass.
A98	S29.11772 E26.21509	1391 m	2006/05/04	Red loam soil, collected under a tree, 1.5m from the tree-trunk, 2m from wire fence, 2.5m from the sidewalk, 3m from the tar road.
A99	S29.13507 E26.22221	1389 m	2006/05/04	Black loam soil, 3m from a house, not covered by grass, 2m from the gravel road.
A100	S29.14471 E26.22146	1391 m	2006/05/04	Brown damp loam soil, collected under the grass1.5m from the wall yard of INCLEDON DPI shop, 5m from the road.
A101	S29.15321 E26.22215	1393 m	2006/05/03	Red loam soil, collected underneath the grass5m from the tree, 7m from the road.
A102	S29.15506 E26.21723	1398 m	2006/05/03	Red loam soil, collected under the grass, 3m from the tree, 2m from the road, in an undisturbed area
A103	S29.14537 E26.21598	1396 m	2006/05/03	Red loam soil, collected under the grass, 2m away from the busy highway road, 5m away from the houses.
A104	S29.13566 E26.21582	1397 m	2006/05/04	Red loam soil, 1m from the tar road, 1.2m from the tree trunk, 3m from the brick wall, under the grass.
A105	S29.13576 E26.20483	1413 m	2006/05/04	Loam sandy soil, collected 1m from the stone wall/yard of the building, 1.5m from the fence, not covered by grass. NB: sample not taken its co-ordinate, the actual co-ordinate was inside the building.
A106	S29.14470 E26.20541	1414 m	2006/05/04	Red loam soil, collected underneath the grass, under a tree, 20m from the petrol station, 8m from the tar road
A107	S29.15384 E26.20653	1417 m	2006/05/04	Reddish brown sandy loam soil, collected underneath the grass, 0.5m from the wall of the residential apartment, 7m from the electric pole, 4m from the tar road.
A108	S29.12353 E26.32818	1335 m	2006/05/05	Black sandy-loam soil, collected in a farm, about 350m from the exact co-ordinate, because the route was obstructed by the stream, so it’s about 7km from the power station, collected underneath a long (~15cm tall grass), about 7m from a ploughed field
A109	S29.03657 E26.22810	1363 m	2006/05/05	Black clay loam soil, collected 0.5m from the fence, underneath the grass, 7m from the tar road in an open space, surrounded by trees.

A110	S29.11851 E26.13235	1404 m	2006/05/05	Loamy clay red soil, was collected underneath the grass in an open space, 1.2m from the gravel road, 10m from the dam, no houses around.
A111	S29.21743 E26.22645	1426 m	2006/05/05	Black loam soil, collected underneath ~40cm tall grass, 8m from the tar road, in an abandoned area.

A1.2 Dust sample localities

Second Batch of Bloemfontein Samples (for Hg, Se, Sb, Bi, As, Cd)				
D004	S29.12431 E26.24661	2006/09/19	Inside the sewage water purifying lab, on the shelves	Bloemspruit Purification Plant
D010	S29.07379 E026.13450	2006/09/20	On top of chipboards used to build wall units and cupboards	Shatima Furniture Manufactures, SechabeloCentre,Batho
D014	S29.07463 E026.13399	2006/09/19	Windowsills and top of cupboards inside a house	Batho township, Cape stands, 2min walk to power station
D027	S29.07480 E026.14127	2006/09/20	Top of inside walls, House of Hope, Safe house	Heidedal suburb
D033	S29.07424 E026.15487	2006/09/20	Top of inside walls, Free state coffin & caskets distributors	Industrial area, no houses nearby
D038	S29.08234 E026.13559	2006/09/19	Inside the home garage, on top of an old stove	Batho township
D040	S29.08566 E026.14035	2006/09/19	On top of geyser attached to the outside wall of the house	Butshabela township
D042	S29.09444 E026.14198	2006/09/19	Inside a bottle store, on top of the board	Phame township, school across the road
D052	S29.08441 E026.15360	2006/09/20	Top of windowsills, inside classrooms	Heatherdale Sec School in Heidedal
D056	S29.08366 E026.14117	2006/09/20	windowsills inside the house	Butshabela township
D062	S29.09225 E026.15188	2006/09/19	Inside the home garage, on top of the inside door	Heidedal suburb
D092	S29.07370 E026.13153	2006/09/20	House veranda, top of inside wall & bedroom windowsills	Bloem town, in an industrial area
D095	S29.07020 E026.12157	2006/09/19	Inside Good Year Cricket Stadium, storeroom windowsills	Bloemfontein town
D099	S29.08095 E026.13237	2006/09/19	On top of a fridge and cupboard inside a house	Batho township
D100	S29.08353 E026.13156	2006/09/20	On top of fridge inside Continental tuckshop	Hamalton, industrial area
D106	S29.08414 E026.12168	2006/09/20	On top of fridges in Multisave supermarket	Market area, surrounded by high income houses
DD01	S29.12067 E26.22530	2006/05/04	On top of fridge in Jack's meat market. Area samples = 135cmx70cm	
DD02	S29.13391 E26.23235	2006/05/04	On top of cupboard in Tony's Restaurant, fresh fruit and vegetables. Situated ~ 1km SE of Power station. Sample area = 60cmx27cm	
DD03	S29.14334 E26.25357	2006/05/04	On top of fridge in foyer of 4 ways hotel. Area = 81cmx63cm	
DD04	S29.16469 E26.27639	2006/05/05	Approximately 1g dust sample was taken on top of the refrigerator inside Khulula cash store (tuckshop) store room.Area of the top of the refrigerator = 64cm X 59cm	
DD05	S29.13085 E26.25730	2006/05/05	Approximately 1g dust sample was collected on top of the cutting table inside the Garment Rental shop, in Corner Fritz Stockenstrom street and WilhemKotze street. Area of the top of the table = 48cm X171cm	
DD06	S29.15550 E26.21590	2006/05/05	~ 1g dust sample was collected on top of the refrigerator in a fast-food shop (IETS VAN ALS TUCKSHOP). Area on top of the refrigerator = 66cmX64cm	

A1.3 Soil profile localities

P004-20	S29.07350 E026.14471	2006/09/19	Collected,20,40,60 cm respectively, 500m from humer sedimentation dam, In Bloemspruit Purification Plant
P004-40			
P004-60			
P095-20	S29.07025 E02612143	2006/09/19	Profile sample - collected 20,40,60cm deep respectively, 100m from the brick wall, in a lawn, undisturbed soil Inside GoodYear Park Cricket Stadium
P095-40			
P095-60			
P099-20	S29.08097 E026.13239	2006/09/19	Profile sample - collected 20,40,60 cm deep respectively, inside a home yard, undisturbed land Batho township
P099-40			
P099-60			
P107-20	S29.10096 E026.11531	2006/09/19	Profile sample - collected 20,40,60cm deep respectively, 500m from railway Open space, no houses nearby line, no houses nearby,
P107-40			
P107-60			

A1.4 Background sample localities

212	S29.04292 E026.18220	2006/09/21	Background sample - collected in grazing camps 10km NE of the Power Station
216	S29.10091 E026.12372	2006/09/21	Background sample - collected in an open grassland field, 300m from industrial area from the north, and 1km from residential area
214	S29.11209 E026.09125	2006/09/21	Background sample - collected under a grass, in an open grassland field/grazing camp in a farming area, 40m from the road.
213	S29.03123 E026.09488	2006/09/21	Background sample - collected at Froenvlei at the fence wild farm 4441596 Mr Venter
215	S29.09597 E026.18569	2006/09/21	Background sample - grazing land in a farm, no crops grown in a farm
R01	S29.08134 E026.15349	2006/09/21	Sample of brown shale interlayered with beige sandstone (not included), collected at the entrance of the big quarry.Outcrop show some layering
R02	S29.17625 E26.20005	2006/09/21	A dolerite rock collected at the south western side of the sampling area on top of the hill of Ehrlichpark reservoir.
R03	S29.08134 E026.15349	2006/09/21	Sample of beige sandstone interlayered with brown shale (not included), collected at the entrance of the big quarry.Outcrop show some layering
A	S29.07336 E026.13297	2006/09/21	Three samples were collected within a 1m2 box at the inloading section, from a single carriage from Witbank
B	S29.07336 E026.13297	2006/09/21	Three samples were collected within a 1m2 box at the inloading section, from a single carriage from Witbank
C	S29.07336 E026.13297	2006/09/21	Three samples were collected within a 1m2 box at the inloading section, from a single carriage from Witbank

Appendix 2: Results

A2.1 Trace element distribution in soils

Soil Samples	Se (ppm)	Cd (ppm)	As (ppm)	Sb (ppm)	Bi (ppm)	Hg (ppb)
A01	0.14	0.39	2.37	1.64	0.17	36.68
A02	0.17	0.27	4.10	3.33	0.28	56.68
A03	0.19	0.13	3.77	0.72	0.39	95.96
A04	0.37	0.49	3.89	1.65	5.70	2149.67
A05	0.11	0.17	4.04	0.45	0.35	51.63
A06	0.15	0.17	5.18	0.70	0.44	80.38
A07	0.20	0.18	5.28	0.83	0.75	124.42
A08	0.17	0.13	4.82	0.35	0.28	67.56
A09	0.23	0.14	5.21	0.46	0.29	82.00
A10	0.12	0.16	3.27	0.54	0.32	35.77
A11	0.13	0.17	3.74	0.58	0.35	39.40
A12	0.19	0.13	3.23	0.28	0.20	29.17
A13	0.29	0.11	3.44	0.34	0.35	63.38
A14	0.15	0.25	5.40	1.32	0.33	110.17
A15	0.13	0.13	2.52	0.47	0.18	29.73
A16	0.18	0.28	4.15	1.44	0.27	145.92
A17	0.13	0.48	7.18	1.60	0.36	82.45
A18	0.49	21.15	6.67	1.22	0.18	30.16
A19	0.22	0.78	6.11	3.11	0.68	53.55
A20	0.14	0.15	3.59	0.59	0.28	41.15
A21	0.17	0.15	2.81	0.43	0.22	32.07
A22	0.12	0.22	2.40	0.85	0.17	24.68
A23	0.19	0.23	3.14	0.82	1.35	191.50
A24	0.14	0.21	2.40	0.75	0.27	41.45
A25	0.13	0.14	1.87	0.34	0.18	21.64
A26	0.22	0.22	5.05	1.04	0.30	88.41
A27	0.26	0.49	9.00	7.49	0.88	400.71
A28	0.18	0.22	6.00	6.46	0.38	142.03
A29	0.13	0.14	8.70	0.61	0.32	52.84
A30	0.17	1.87	10.50	2.53	1.50	293.73
A31	0.29	0.34	7.10	5.98	1.50	316.86
A32	0.15	0.14	3.58	0.42	0.25	50.02
A33	0.18	0.25	5.50	1.12	0.40	68.27
A34	0.17	0.14	3.02	0.42	0.26	74.04
A35	0.12	0.17	2.52	0.31	0.15	23.37
A36	0.17	0.53	2.66	0.65	0.18	32.51
A37	0.11	0.18	2.83	0.69	0.20	50.49
A38	0.13	0.23	5.67	1.24	0.30	47.38
A39	0.19	0.32	7.93	2.90	0.42	160.66
A40	0.15	0.28	4.69	1.13	0.26	110.46
A41	0.10	0.18	1.65	0.27	0.14	44.23
A42	0.11	0.13	3.08	0.43	0.30	34.60
A43	0.21	0.71	3.23	1.50	0.46	111.16

A44	0.12	0.15	3.64	0.35	0.15	25.76
A45	0.13	0.28	2.87	0.66	0.20	58.36
A46	0.14	0.46	2.34	0.75	0.19	46.48
A47	0.28	2.51	3.09	1.90	0.70	99.67
A48	0.14	1.86	2.42	0.96	0.25	40.87
A49	0.27	0.12	3.26	0.38	0.26	40.55
A50	0.27	0.22	11.55	0.85	0.80	38.75
A51	0.19	0.54	3.89	0.47	0.20	28.34
A52	0.12	0.16	2.66	0.52	0.16	21.97
A53	0.27	0.13	3.34	0.43	0.26	38.11
A54	0.24	0.11	3.63	0.28	0.20	25.03
A55	0.27	0.69	4.68	2.41	0.51	159.06
A56	0.21	0.27	4.33	1.20	0.32	110.38
A57	0.15	0.15	2.53	0.57	0.17	38.94
A58	0.24	0.47	2.94	0.88	0.26	149.68
A59	0.23	0.22	4.62	2.01	0.37	124.42
A60	0.15	0.18	4.40	0.38	0.27	44.97
A61	0.38	4.03	3.12	5.71	0.22	28.48
A62	0.15	0.17	3.53	0.41	0.20	26.02
A63	0.22	0.16	4.44	0.65	0.25	55.21
A64	0.15	0.22	2.23	0.79	0.29	48.45
A65	0.19	0.30	6.34	2.56	0.43	168.76
A66	0.11	0.21	2.47	0.68	0.20	28.94
A67	0.21	0.19	4.24	1.23	0.34	89.14
A68	0.19	0.47	3.42	0.99	0.24	136.07
A69	0.16	0.18	4.07	0.53	0.27	31.51
A70	0.16	0.19	2.90	0.80	0.40	177.73
A71	0.32	0.12	4.12	0.45	0.25	42.79
A72	0.20	0.37	3.83	2.10	0.32	107.14
A73	0.18	0.40	4.59	2.67	0.26	82.67
A74	0.15	0.18	1.62	0.59	0.22	55.71
A75	0.11	0.18	1.46	0.93	0.13	33.12
A76	0.27	0.34	4.61	3.39	0.25	48.05
A77	0.32	3.07	8.88	4.54	0.30	46.35
A78	0.19	0.11	2.65	0.26	0.18	26.13
A79	0.10	0.15	1.92	0.34	0.15	25.44
A80	0.18	0.15	14.61	0.34	0.17	20.54
A81	0.23	0.11	4.60	0.60	0.19	31.56
A82	0.20	0.13	4.15	0.55	0.19	35.91
A83	0.41	0.27	4.91	6.33	0.32	65.23
A84	0.17	0.14	3.87	1.00	0.19	36.02
A85	0.30	0.32	10.45	21.31	0.53	107.68
A86	0.25	0.34	5.64	4.12	0.32	95.72
A87	0.12	0.16	1.31	0.69	0.16	32.21
A88	0.19	0.19	4.22	1.40	0.41	280.35
A90	0.32	0.12	4.59	0.58	0.90	249.51
A91	0.12	0.13	2.40	0.33	0.21	35.05
A92	0.30	0.52	4.10	8.38	0.37	116.43

A93	0.26	0.13	4.07	0.53	0.26	67.80
A94	0.25	0.12	3.57	0.48	0.25	51.84
A95	0.32	0.30	2.64	1.18	1.44	1004.92
A96	0.21	0.22	2.99	1.31	0.20	73.45
A97	0.23	0.12	2.08	0.34	1.03	67.07
A98	0.20	0.18	2.58	0.76	0.64	238.25
A99	0.24	1.64	3.19	12.23	0.31	64.52
A100	0.26	0.32	3.93	2.20	1.17	401.66
A101	0.22	0.18	3.84	0.76	0.52	119.67
A102	0.18	0.12	3.66	0.39	0.23	51.40
A103	0.15	0.15	2.99	0.83	0.23	41.81
A104	0.17	0.13	2.85	0.68	0.18	52.42
A105	0.21	0.13	3.11	0.74	0.22	43.29
A106	0.25	0.20	3.86	0.75	1.16	376.07
A107	0.22	0.15	6.16	0.60	0.33	64.38

A2.2 Enrichment factors

Soil samples	Sb	As	Cd	Hg	Se
1	1.64	0.3	1.1	0.73	0.4
2	3.33	0.6	0.8	1.13	0.4
3	0.72	0.5	0.4	1.92	0.5
4	1.65	0.5	1.4	42.99	0.9
5	0.45	0.6	0.5	1.03	0.3
6	0.70	0.7	0.5	1.61	0.4
7	0.83	0.7	0.5	2.49	0.5
8	0.35	0.7	0.4	1.35	0.4
9	0.46	0.7	0.4	1.64	0.6
10	0.54	0.5	0.4	0.72	0.3
11	0.58	0.5	0.5	0.79	0.3
12	0.28	0.4	0.4	0.58	0.5
13	0.34	0.4	0.3	1.27	0.7
14	1.32	0.4	0.7	2.2	0.4
15	0.47	0.3	0.4	0.59	0.3
16	1.44	0.6	0.8	2.92	0.5
17	1.60	1	1.4	1.65	0.3
18	1.22	0.9	60.1	0.6	1.2
19	3.11	0.8	2.2	1.07	0.5
20	0.59	0.5	0.4	0.82	0.3
21	0.43	0.4	0.4	0.64	0.4
22	0.85	0.3	0.6	0.49	0.3
23	0.82	0.4	0.6	3.83	0.5
24	0.75	0.3	0.6	0.83	0.4
25	0.34	0.3	0.4	0.43	0.3

26	1.04	0.7	0.6	1.77	0.6
27	7.49	1.3	1.4	8.01	0.6
28	6.46	0.8	0.6	2.84	0.4
29	0.61	1.2	0.4	1.06	0.3
30	2.53	1.5	5.3	5.87	0.4
31	5.98	1	1	6.33	0.7
32	0.42	0.5	0.4	1	0.4
33	1.12	0.8	0.7	1.37	0.4
34	0.42	0.4	0.4	1.49	0.4
35	0.31	0.4	0.5	0.47	0.3
36	0.65	0.4	1.5	0.65	0.4
37	0.69	0.4	0.5	1.01	0.3
38	1.24	0.8	0.7	0.95	0.3
39	2.90	1.1	0.9	3.21	0.5
40	1.13	0.7	0.8	2.21	0.4
41	0.27	0.2	0.5	0.88	0.3
42	0.43	0.4	0.4	0.69	0.3
43	1.50	0.4	2	2.22	0.5
44	0.35	0.5	0.4	0.52	0.3
45	0.66	0.4	0.8	1.17	0.3
46	0.75	0.3	1.3	0.93	0.3
47	1.90	0.4	7.2	1.99	0.7
48	0.96	0.3	5.3	0.82	0.4
49	0.38	0.5	0.3	0.81	0.7
50	0.85	1.6	0.6	0.78	0.7
51	0.47	0.5	1.6	0.57	0.5
52	0.52	0.4	0.5	0.44	0.3
53	0.43	0.5	0.4	0.76	0.7
54	0.28	0.5	0.3	0.5	0.6
55	2.41	0.6	2	3.18	0.7
56	1.20	0.6	0.8	2.21	0.5
57	0.57	0.4	0.4	0.78	0.4
58	0.88	0.4	1.3	2.99	0.6
59	2.01	0.6	0.6	2.49	0.6
60	0.38	0.6	0.5	0.9	0.4
61	5.71	0.4	11.5	0.57	1
62	0.41	0.5	0.5	0.52	0.4
63	0.65	0.6	0.5	1.1	0.5
64	0.79	0.3	0.6	0.97	0.4
65	2.56	0.8	0.9	3.38	0.5
66	0.68	0.3	0.6	0.58	0.3

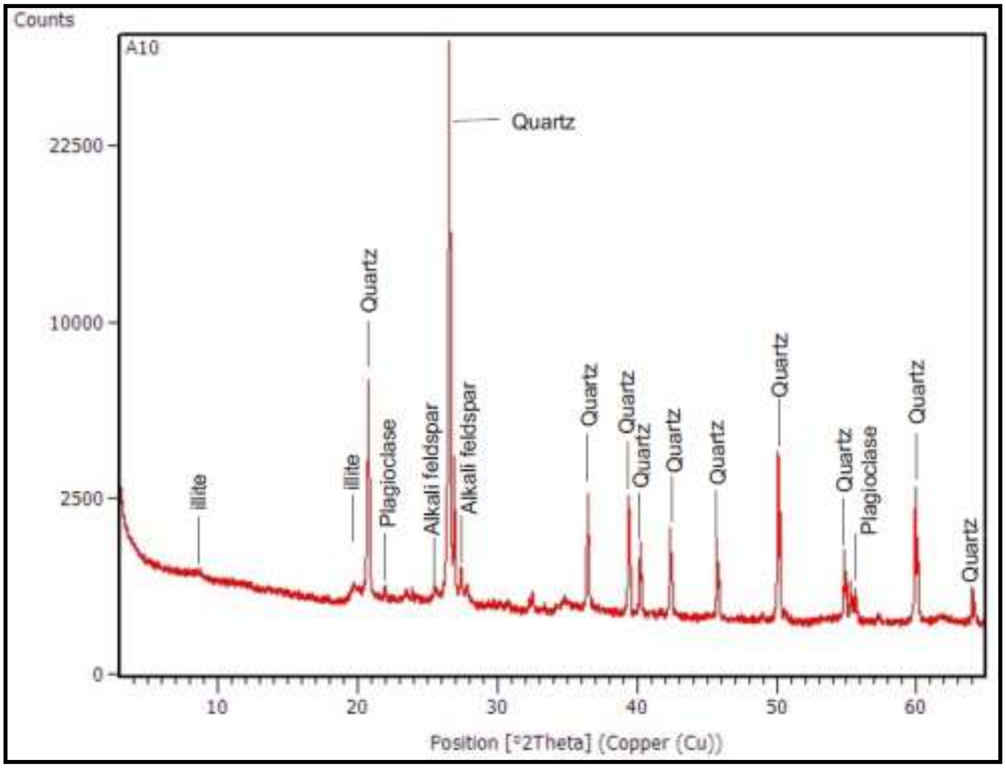
67	1.23	0.6	0.5	1.78	0.5
68	0.99	0.5	1.4	2.72	0.5
69	0.53	0.6	0.5	0.63	0.4
70	0.80	0.4	0.53	3.55	0.4
71	0.45	0.6	0.35	0.86	0.8
72	2.10	0.5	1.1	2.14	0.5
73	2.67	0.6	1.1	1.65	0.4
74	0.59	0.2	0.5	1.11	0.4
75	0.93	0.2	0.5	0.66	0.3
76	3.39	0.6	1	0.96	0.7
77	4.54	1.2	8.8	0.93	0.8
78	0.26	0.4	0.3	0.52	0.5
79	0.34	0.3	0.4	0.51	0.2
80	0.34	2	0.4	0.41	0.5
81	0.60	0.6	0.3	0.63	0.6
82	0.55	0.6	0.4	0.72	0.5
83	6.33	0.7	0.8	1.3	1
84	1.00	0.5	0.4	0.72	0.4
85	21.31	1.5	0.9	2.15	0.8
86	4.12	0.8	1	1.91	0.6
87	0.69	0.2	0.5	0.64	0.3
88	1.40	0.6	0.5	5.61	0.5
90	0.58	0.6	0.4	4.99	0.8
91	0.33	0.3	0.4	0.7	0.3
92	8.38	0.6	1.5	2.33	0.7
93	0.53	0.6	0.4	1.36	0.7
94	0.48	0.5	0.3	1.04	0.6
95	1.18	0.4	0.9	20.1	0.8
96	1.31	0.4	0.6	1.47	0.5
97	0.34	0.3	0.3	1.34	0.6
98	0.76	0.4	0.5	4.77	0.5
99	12.23	0.4	4.7	1.29	0.6
100	2.20	0.5	0.9	8.03	0.7
101	0.76	0.5	0.5	2.39	0.6
102	0.39	0.5	0.4	1.03	0.5
103	0.83	0.4	0.4	0.84	0.4
104	0.68	0.4	0.4	1.05	0.4
105	0.74	0.4	0.4	0.87	0.5
106	0.75	0.5	0.6	7.52	0.6
107	0.60	0.9	0.4	1.29	0.5

A2.3 Statistical data

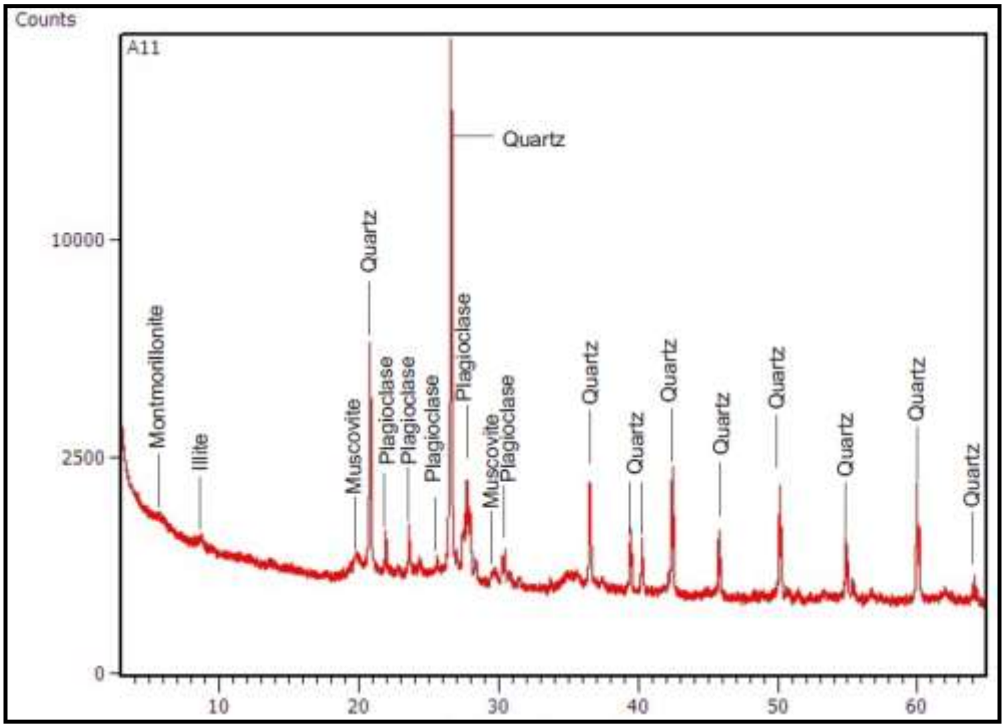
All soil data statistics						
	Se	Cd	As	Sb	Bi	Hg
Number of values	112	112	112	112	112	112
Minimum	0.10	0.08	1.31	0.26	0.13	20.54
Maximum	0.58	21.15	14.61	21.31	5.70	2149.67
Range	0.48	21.07	13.29	21.05	5.57	2129.13
Mean	0.21	0.56	4.21	1.61	0.47	131.78
Median	0.19	0.19	3.75	0.75	0.27	54.84
95% confidence interval	0.02	0.38	0.40	0.49	0.14	55.51
Standard deviation	0.08	2.04	2.14	2.64	0.77	296.30
Background Soil Statistics						
	Se	Cd	As	Sb	Bi	Hg
Number of values	9	9	9	9	9	9
Minimum	0.12	0.05	1.50	0.15	0.08	16.23
Maximum	0.27	0.18	4.36	0.39	0.20	46.12
Range	0.15	0.13	2.86	0.24	0.12	29.89
Mean	0.19	0.10	2.58	0.27	0.14	31.76
Median	0.18	0.09	2.36	0.26	0.14	31.96
95% confidence interval	0.04	0.03	0.65	0.06	0.03	8.55
Standard deviation	0.05	0.04	0.84	0.08	0.04	11.13
Stats of all dust Hg values						
	Se	Cd	As	Sb	Bi	Hg
Number of values	20	20	22	22	22	22
Minimum	0.20	0.59	1.65	1.64	0.20	52
Maximum	1.00	312.00	48.15	27.13	1.10	83115.6
Range	0.80	311.41	46.49	25.49	0.89	83064.1
Mean	0.47	18.05	6.04	6.53	0.46	3980.2
Median	0.45	2.24	4.03	3.87	0.36	183.4
95% confidence interval	0.09	32.39	4.21	3.07	0.11	7838.5
Standard deviation	0.20	69.20	9.50	6.92	0.24	17676.0
Dust Stats less highest Hg	Se	Cd	As	Sb	Bi	Hg
Number of values	19	19	21	21	21	21
Minimum	0.20	0.59	1.65	1.64	0.20	51.55
Maximum	0.89	6.40	6.73	27.13	1.10	818.68
Range	0.69	5.81	5.08	25.49	0.89	767.13
Mean	0.44	2.57	4.03	6.68	0.45	211.86
Median	0.44	2.22	3.89	4.10	0.35	171.29
95% confidence interval	0.07	0.69	0.62	3.21	0.11	79.69
Standard deviation	0.15	1.42	1.37	7.05	0.24	175.06

Appendix 3 XRD angular spectra

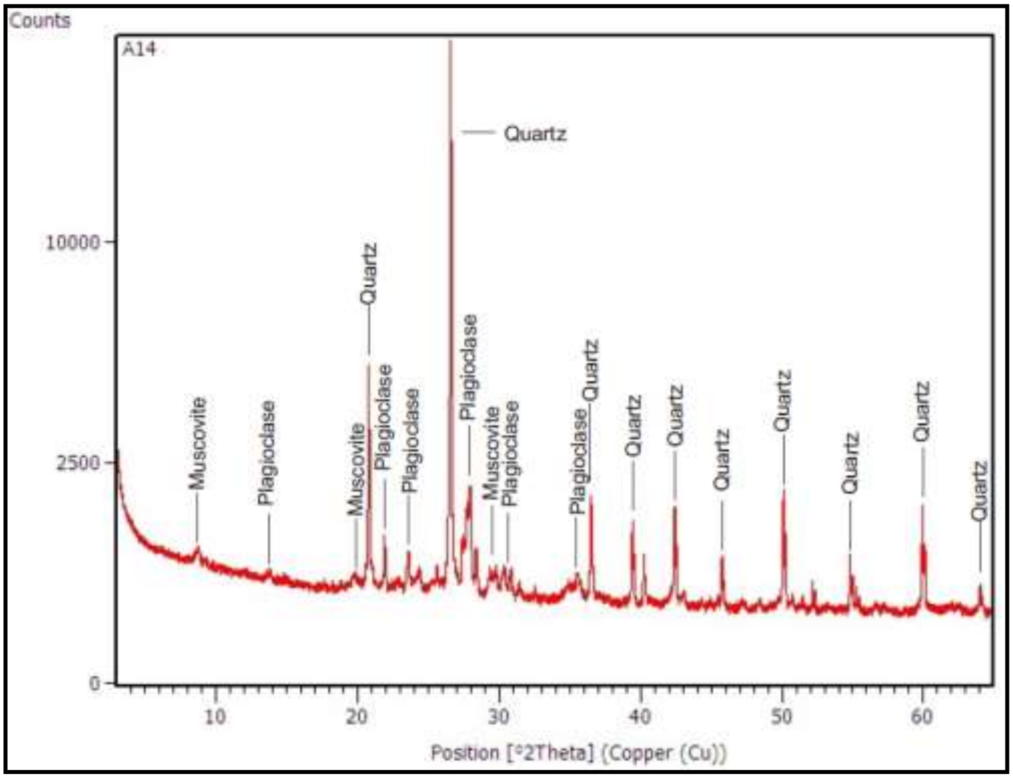
Sample A10: Quartz, plagioclase, alkali feldspar, illite.



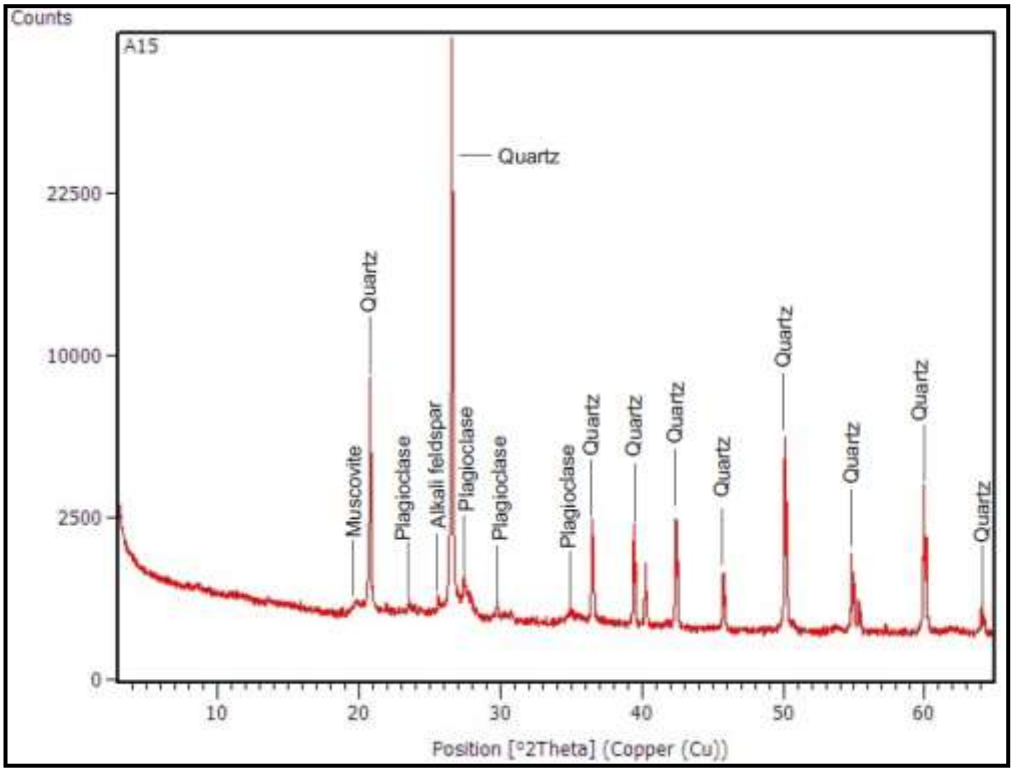
Sample A11: Quartz, plagioclase, muscovite, illite, montmorillonite.



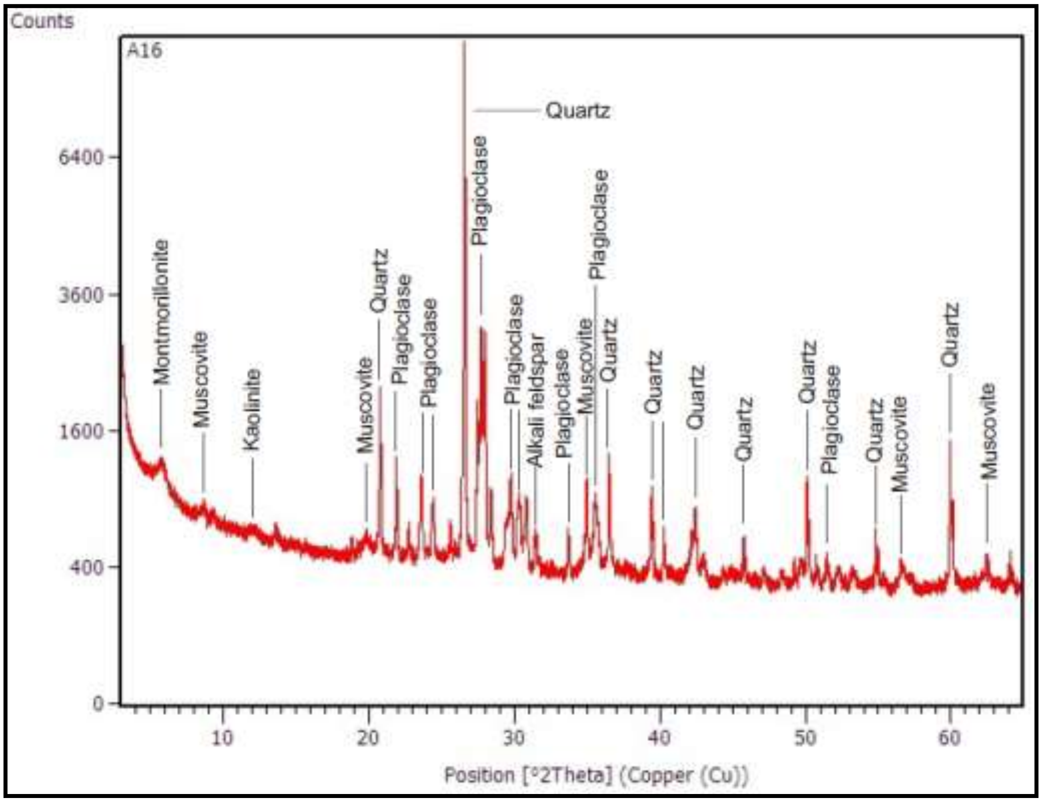
Sample A14: Quartz, plagioclase, muscovite.



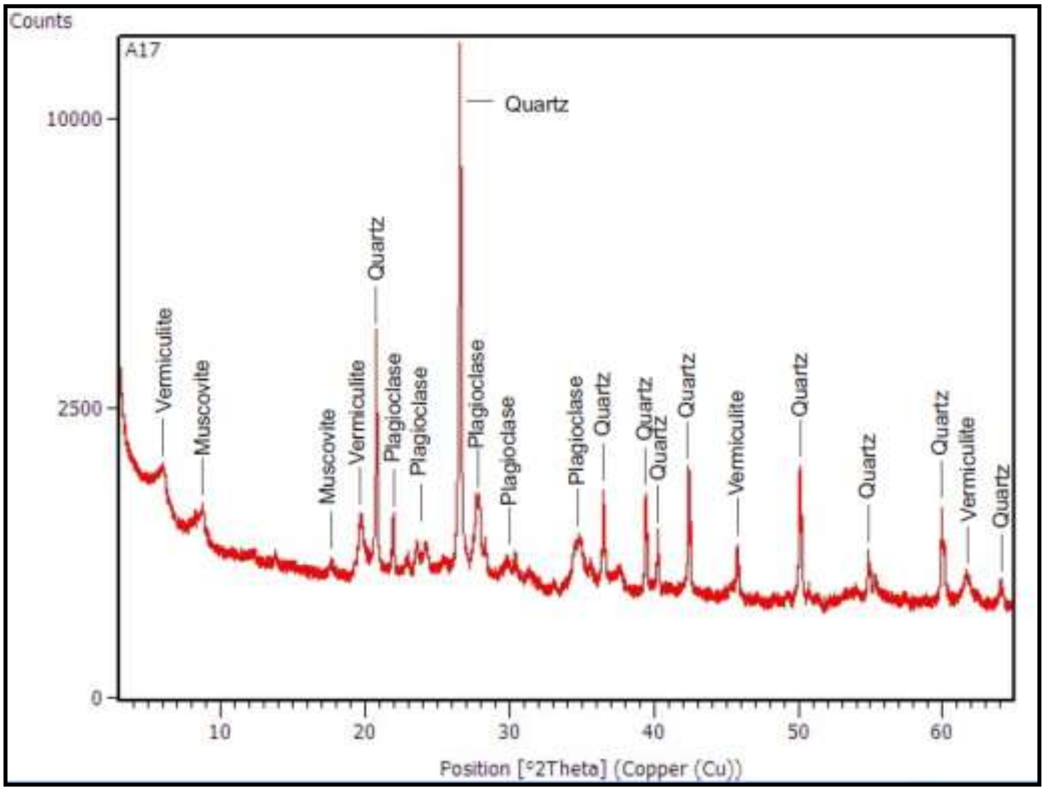
Sample A15: Quartz, plagioclase, alkali feldspar, muscovite.



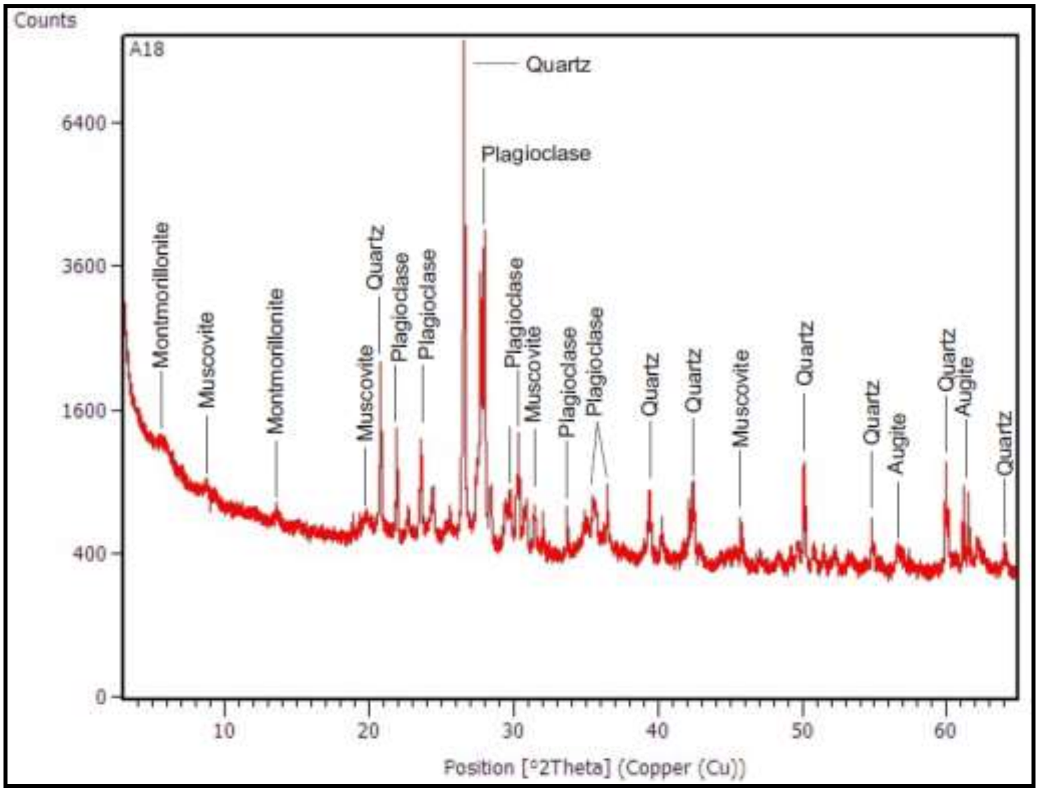
Sample A16: Quartz, plagioclase, alkali feldspar, muscovite, montmorillonite, kaolinite.



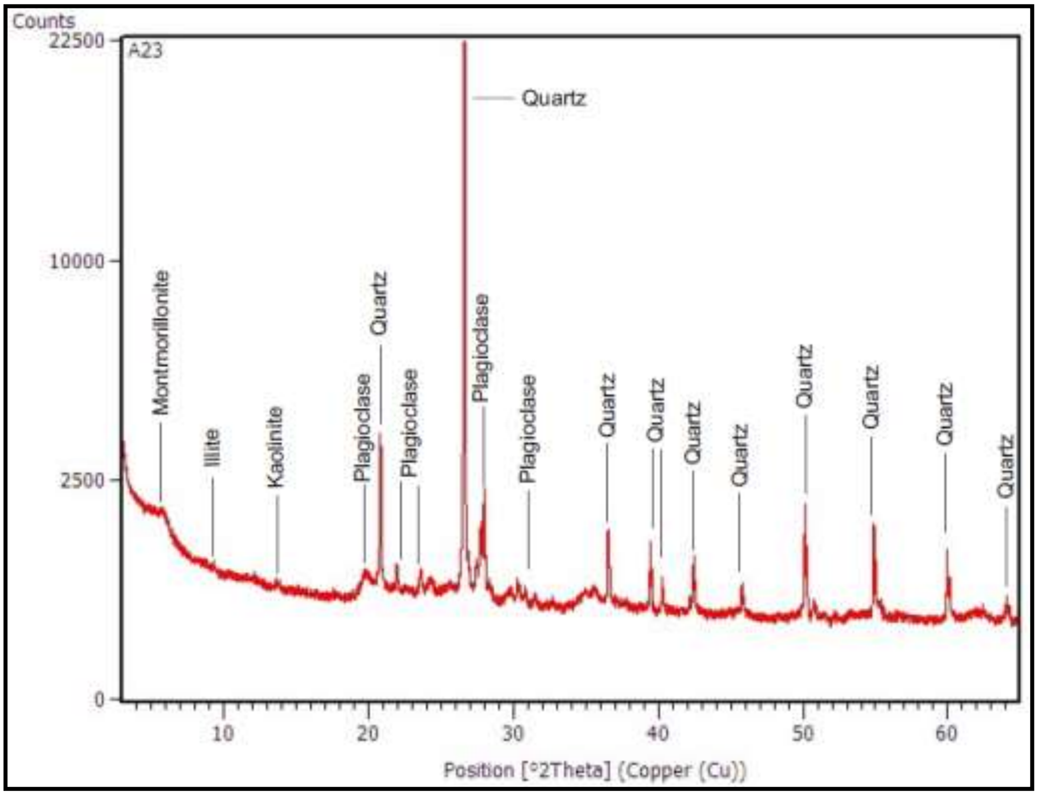
Sample A17: Quartz, plagioclase, muscovite, vermiculite.



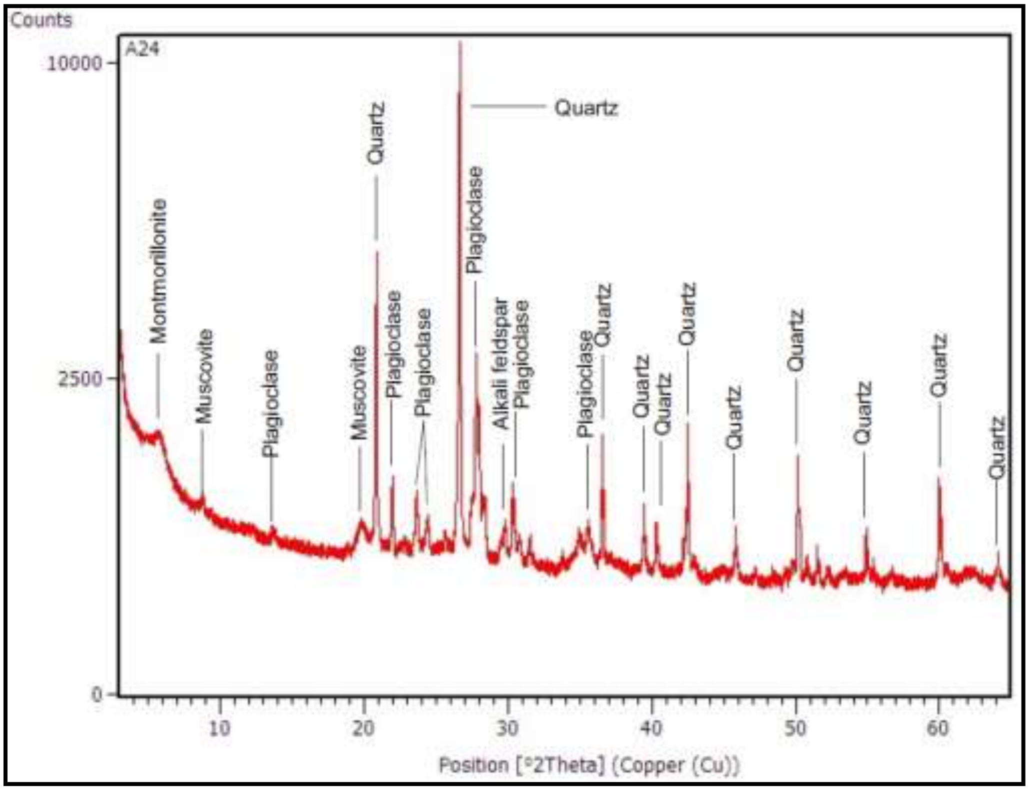
Sample A18: Quartz, plagioclase, muscovite, montmorillonite.



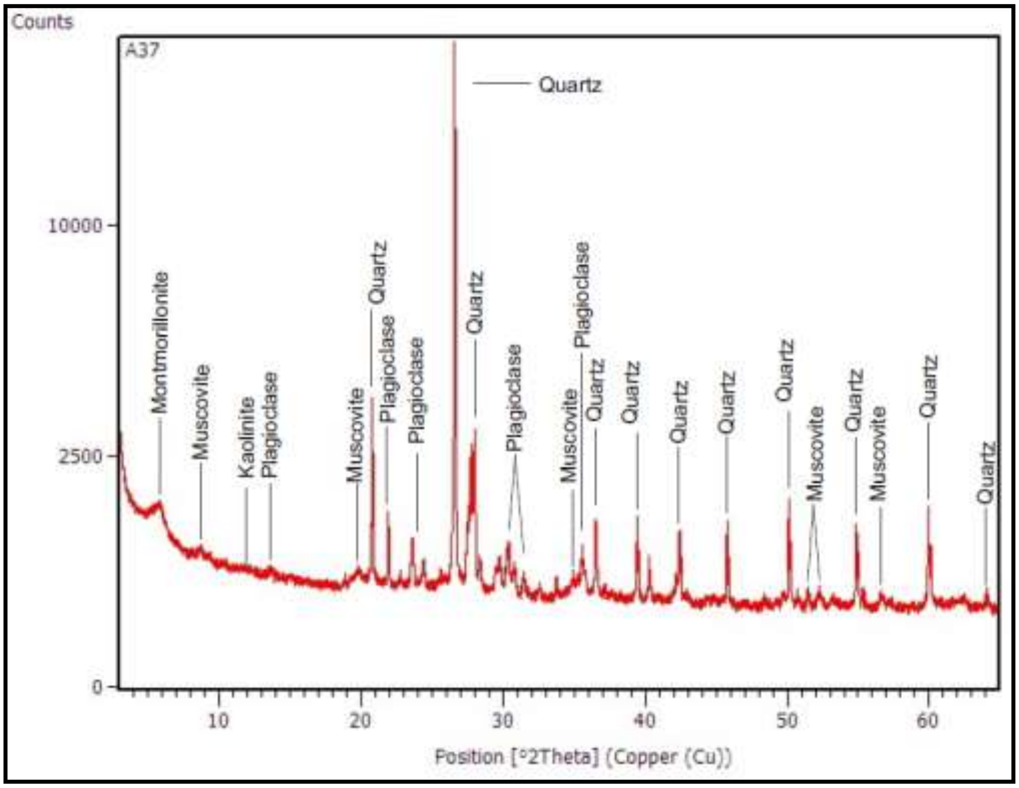
Sample A23: Quartz, plagioclase, illite, montmorillonite, kaolinite.



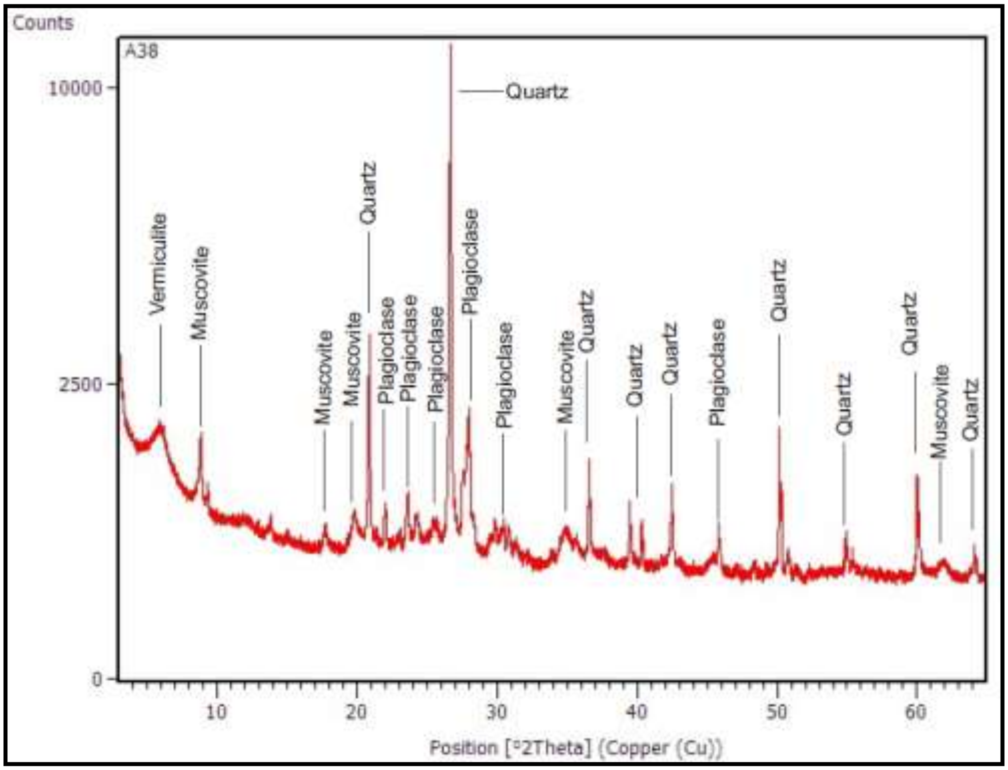
Sample A24: Quartz, plagioclase, muscovite, montmorillonite.



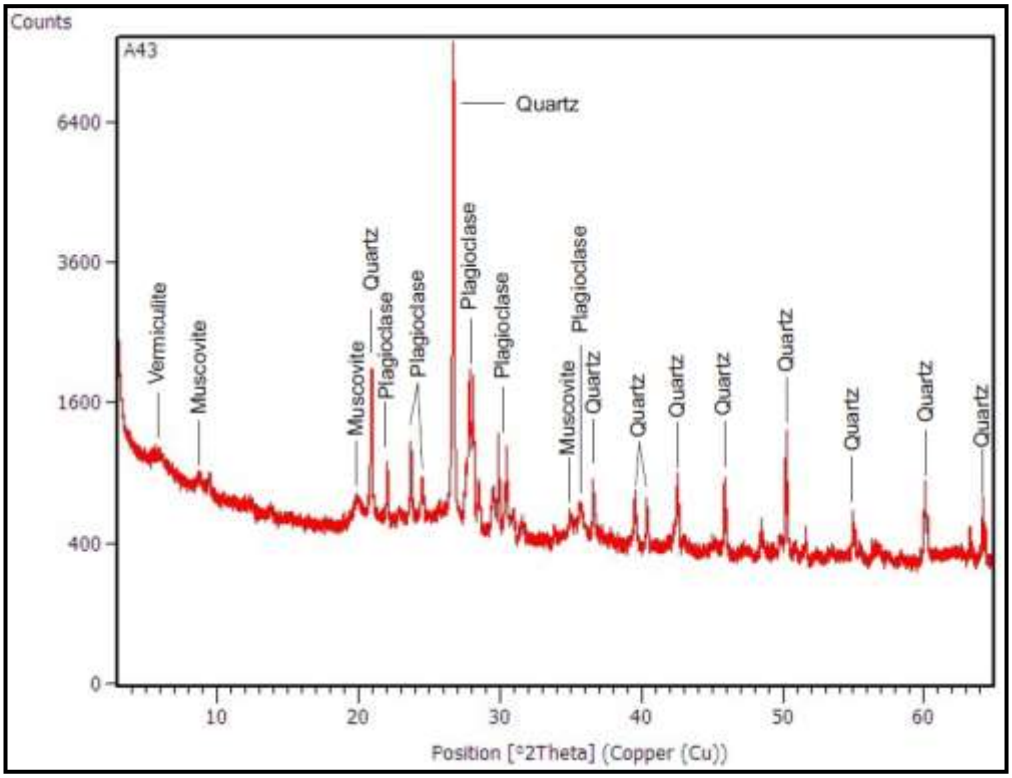
Sample A37: Quartz, plagioclase, muscovite, montmorillonite, kaolinite.



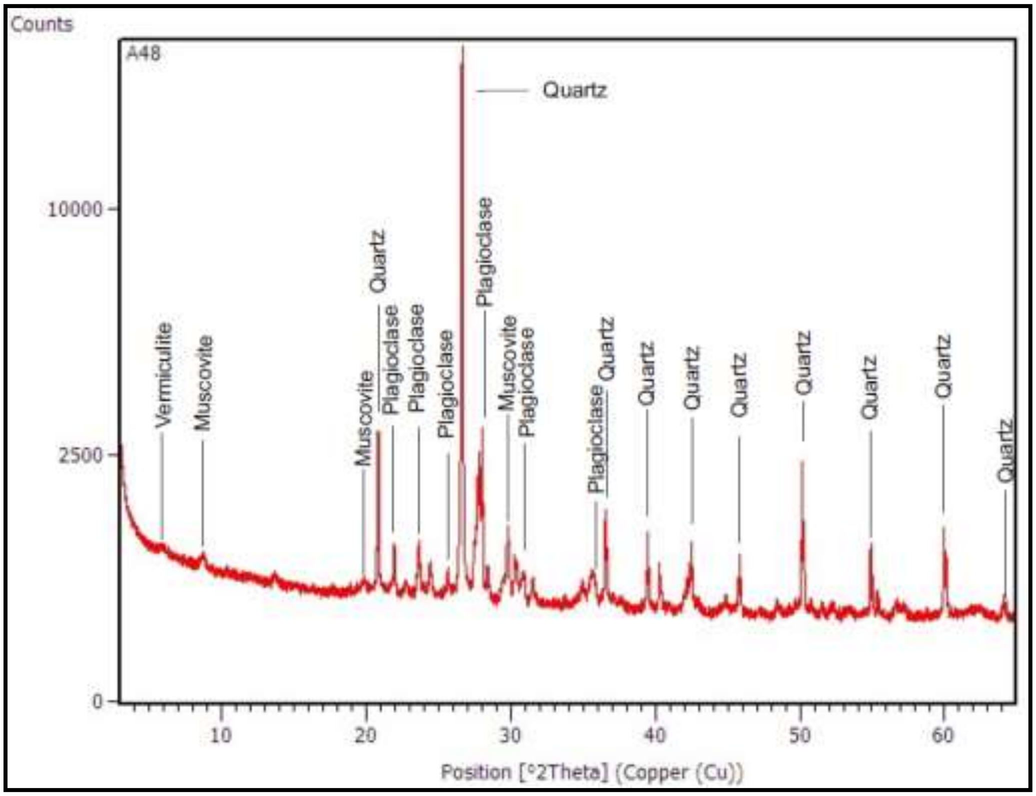
Sample A38: Quartz, plagioclase, muscovite, vermiculite.



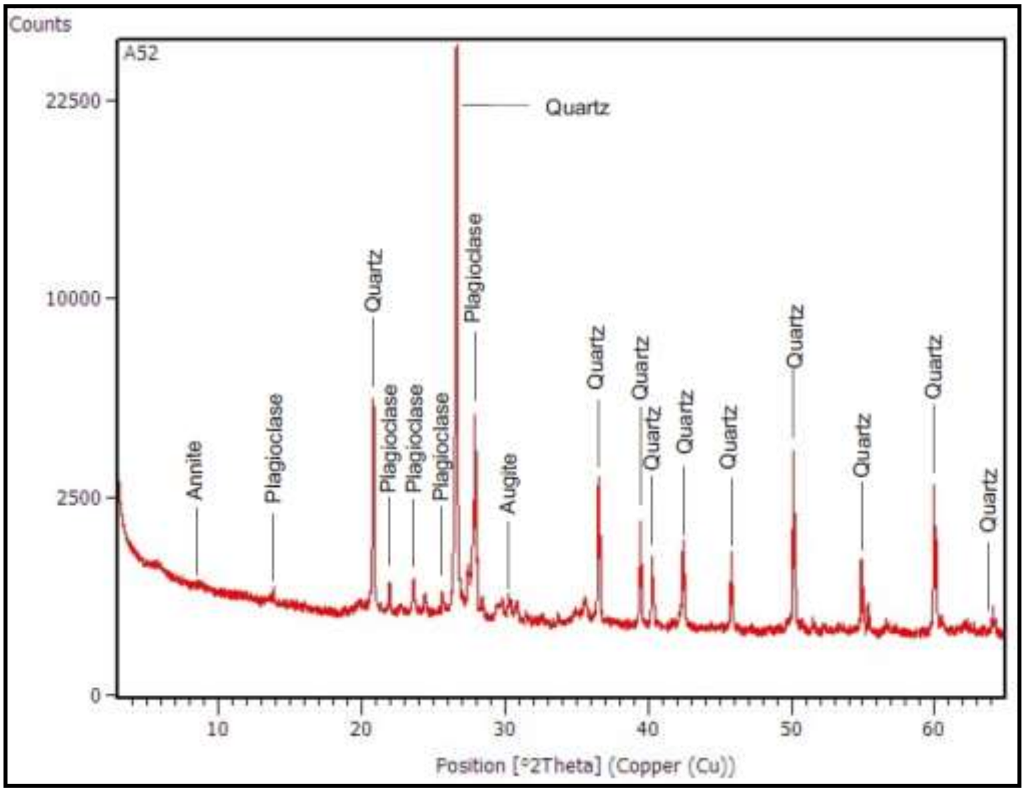
Sample A43: Quartz, plagioclase, muscovite, vermiculite.



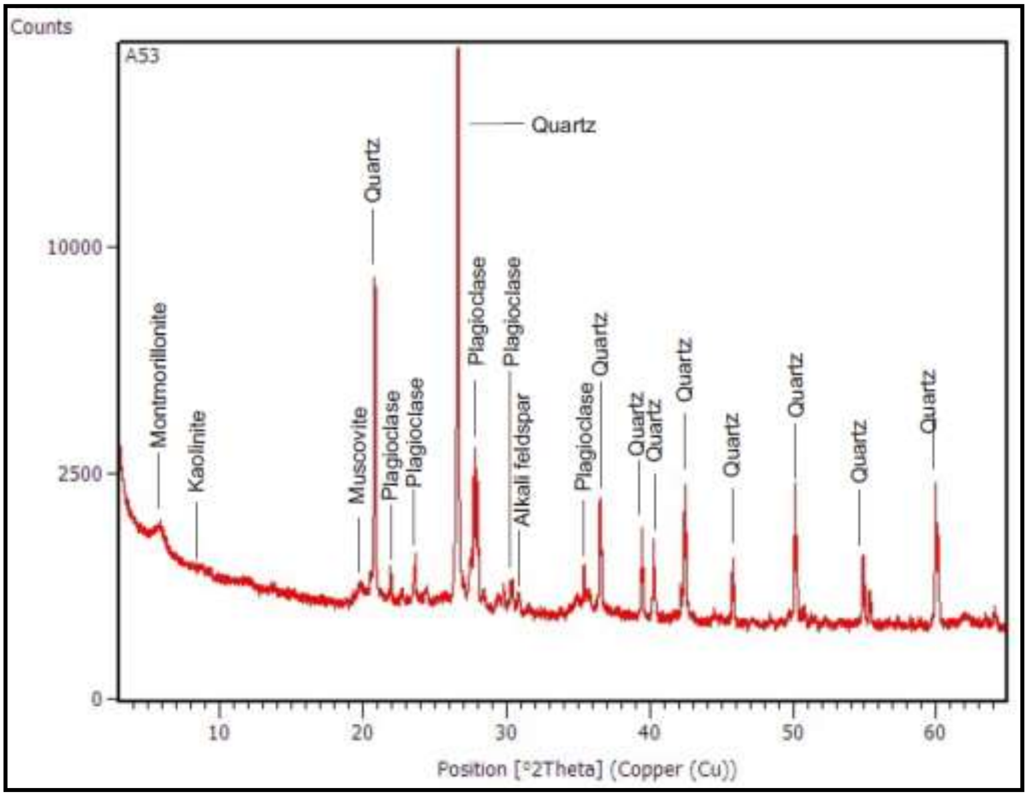
Sample A48: Quartz, plagioclase, muscovite, muscovite, vermiculite.



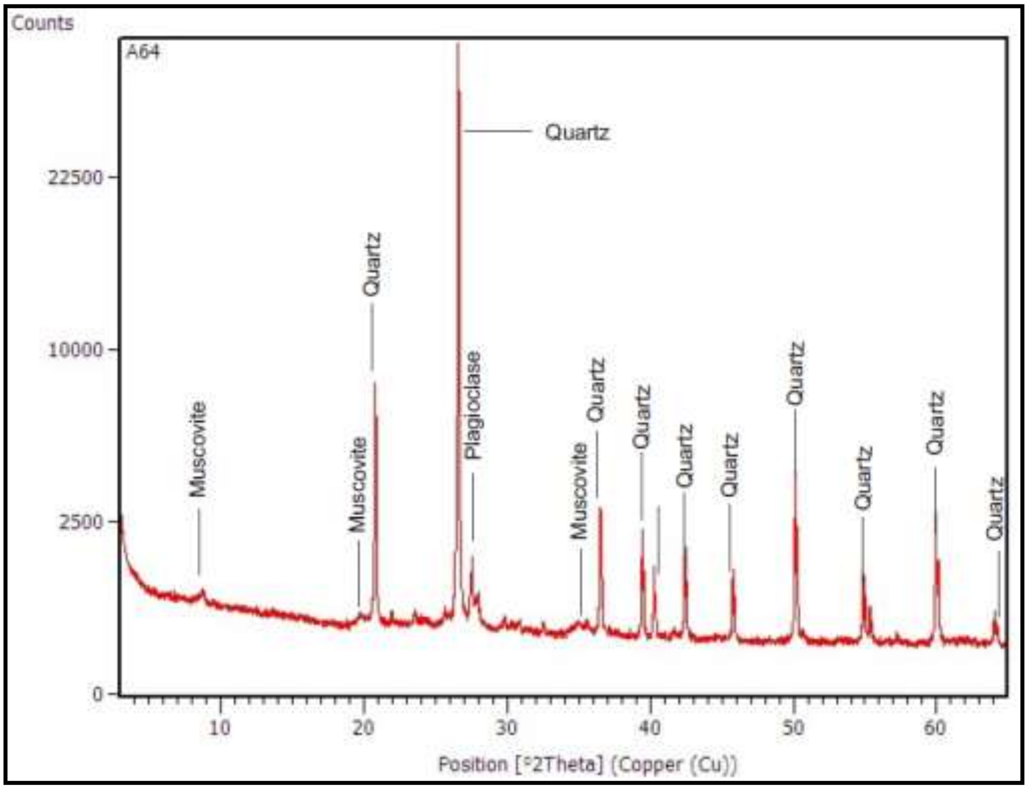
Sample A52: Quartz, plagioclase, annite, augite.



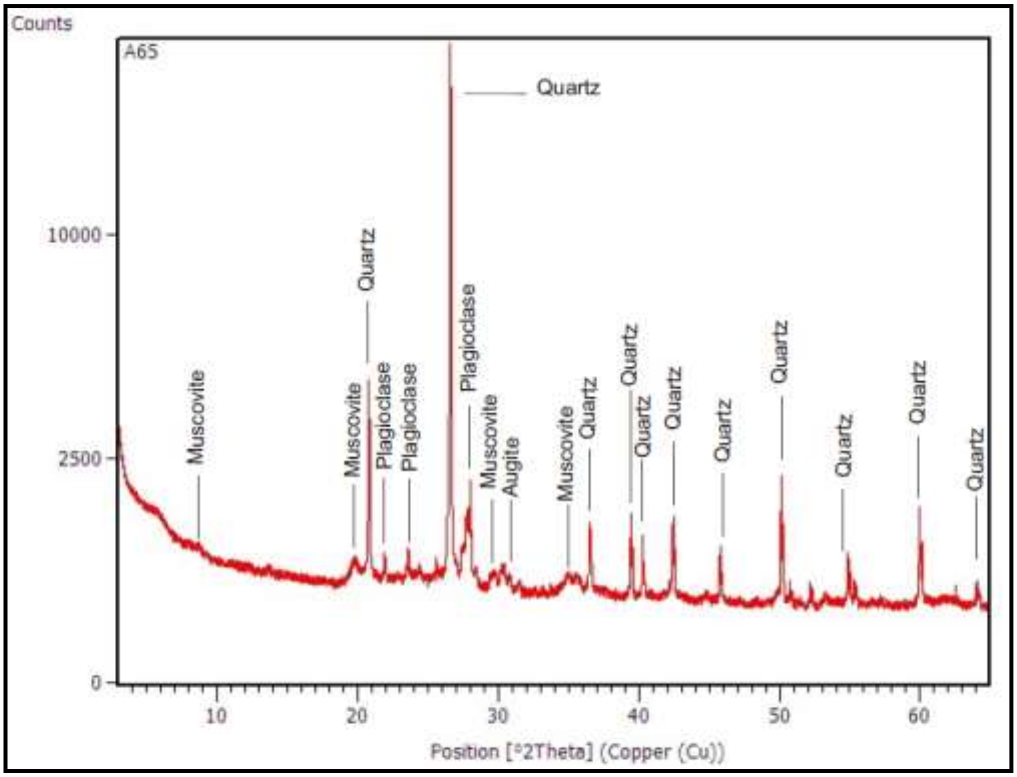
Sample A53: Quartz, plagioclase, muscovite, montmorillonite, kaolinite.



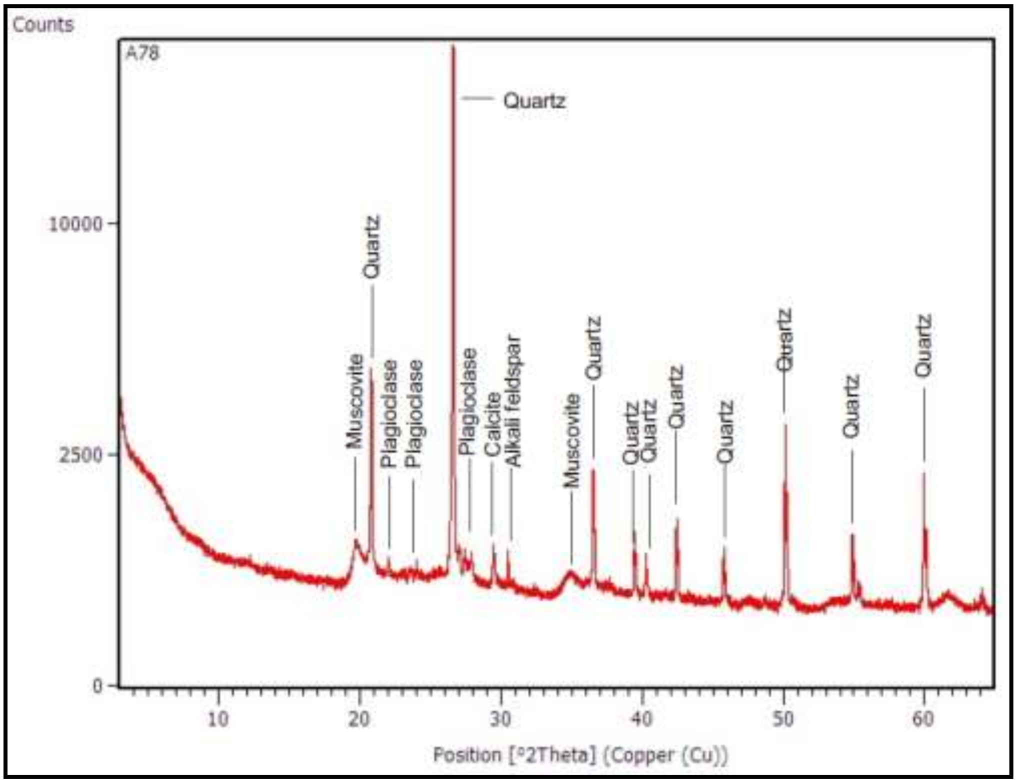
Sample A64: Quartz, plagioclase, muscovite.



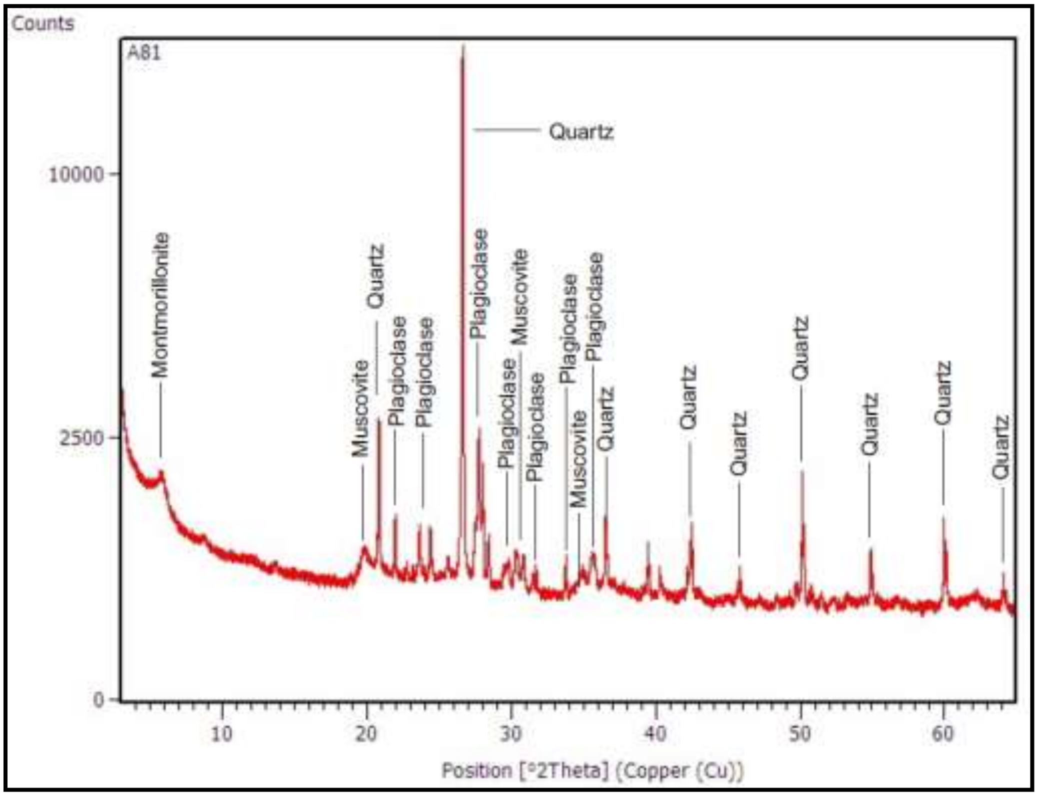
Sample A65: Quartz, plagioclase, augite, muscovite.



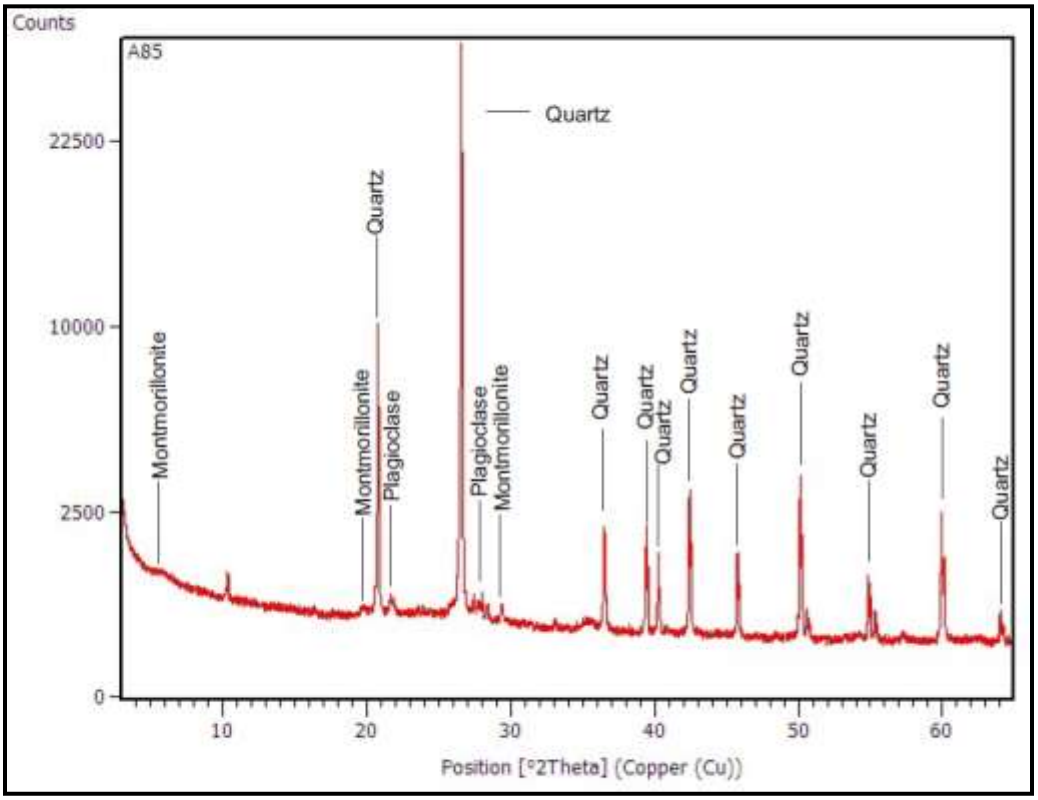
Sample A78: Quartz, plagioclase, muscovite, calcite.



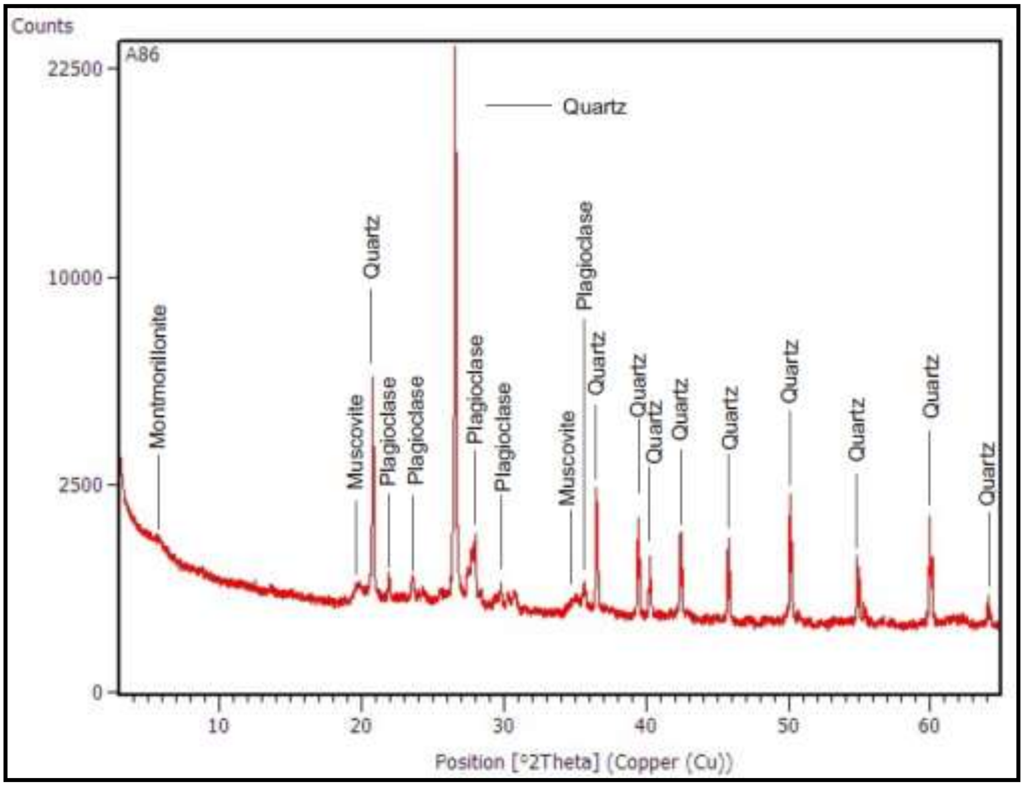
Sample A81: Quartz, plagioclase, muscovite, montmorillonite.



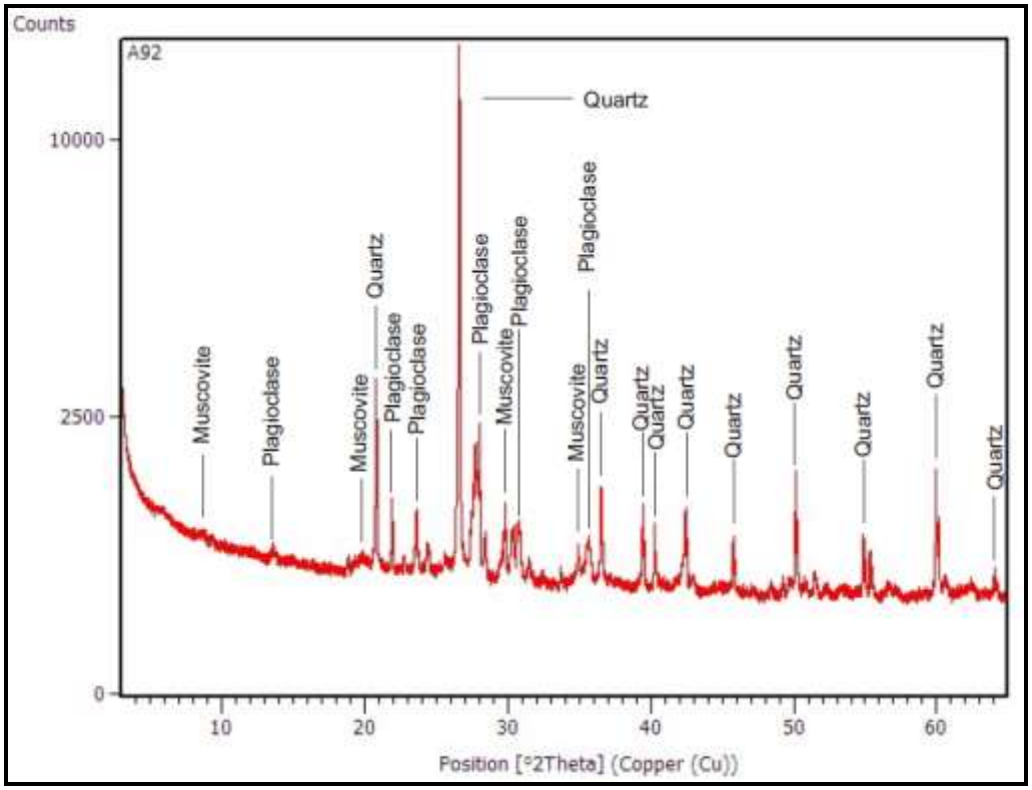
Sample A85: Quartz, plagioclase, montmorillonite.



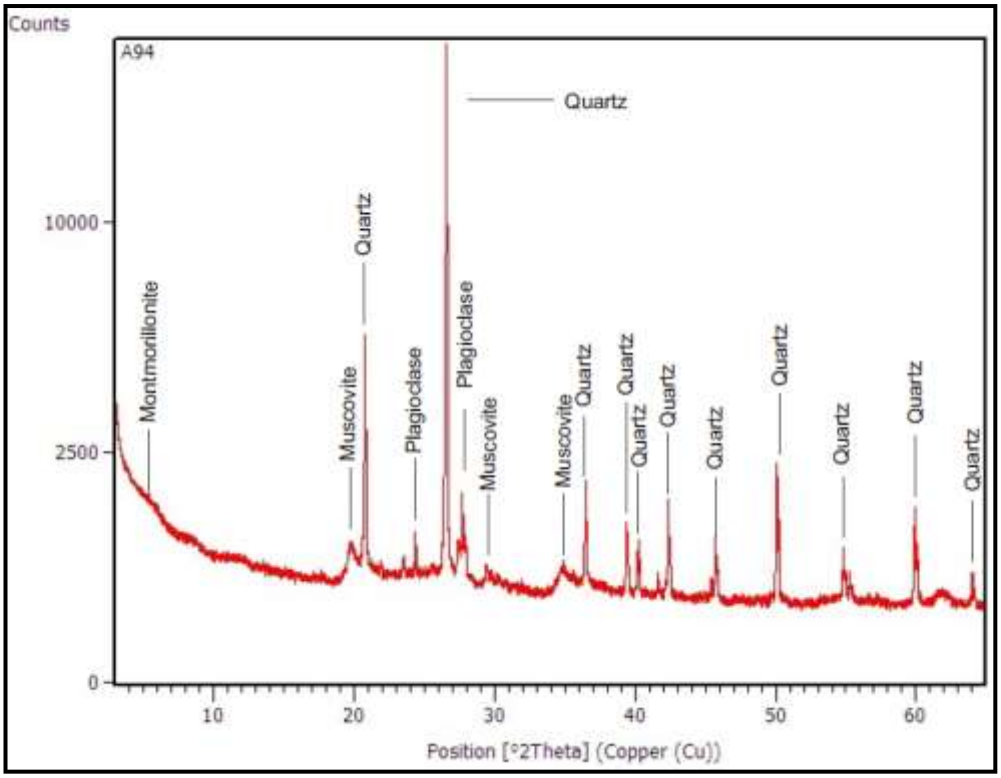
Sample A86: Quartz, plagioclase, muscovite, montmorillonite.



Sample A92: Quartz, plagioclase, muscovite.



Sample A94: Quartz, plagioclase, muscovite, montmorillonite.



Sample A102: Quartz, plagioclase, muscovite, montmorillonite, kaolinite.