EVALUATION OF TRACE ELEMENTS IN THE ENVIRONMENT AROUND THE LEJWELEPUTSWA AREA OF THE FREE STATE, SOUTH AFRICA

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DECLARATION OF INDEPENDENT WORK

I PAUL NEBECHI EBENEBE, hereby declare that this research work submitted to the Central University of Technology, Bloemfontein, Free State, South Africa, for the degree of DOCTOR TECHNOLOGIAE: ENVIRONMENTAL HEALTH, is my own original and independent work and has not been submitted before to any institution by myself or any other person in fulfillment of the requirement for the attainment of any qualification.

……………………………………….. 02 September 2016 ...………………………………..

SIGNATURE OF STUDENT DATE

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SUMMARY

Trace elements were evaluated in the soil, leaves, water and sediments in six towns of Allenridge, Odendaalsrus, Welkom, Virginia, Theunissen and Brandfort in the Lejweleputswa Municipal District of the Free State, South Africa in light of the extensive mining activities taking place in the area. Samples of soil, leaves, water and sediments were collected on monthly basis over a period of 3 months (October, November and December, 2012 and April, May and June, 2013) to cover both the dry and wet seasons. The sampled environmental samples were analyzed for trace elements using an ICP-OES, model ICPS – 7510 (Shimadzu), sequential plasma spectrometer.

Soil samples were collected within 25 cm depth of soils and leaves collected from Acacia Karroo plants in the same vicinity at which the soil was collected. Water and sediment samples were also collected from streams in the same area from which the soil and leaves were collected. The reason for collecting all the different samples – soil, leaves, water and sediment samples from the same area for each location at a given sampling period, was to ensure proper comparison of trace elements content variation in the different media over the period of the study in a comparable environment.

Soil trace elements variations in the six studied towns over the paired 3 months period of the study, in the Lejweleputswa District Municipality (LMD) of the Free State, South Africa, suggested that the highly concentrated trace elements of the soil were calcium, followed by iron and magnesium. The excessive concentration of calcium and magnesium in the soil, other than their natural occurrence, is attributed to the regular liming exercise in which calcium hydroxide ($Ca(OH)_2$)and magnesium hydroxide (MgOH) are used to neutralize the excessive sulphuric acid (H_2SO_4) in the soil due to Acid Mine Drainage (AMD) caused by the dissolution of the sulphur occurring together with pyrite (FeS_2) in water. This often leads to the formation of low pH-value (high concentration) of sulphuric acid.

Calcium was the predominant trace element in leaves obtained from Lejweleputswa District Municipality. In Allenridge, the highest calcium concentration occurred in April, 2013 at above 100 ppm (2.12%). In Brandfort and Theunissen their highest calcium concentrations of above 100 ppm occurred in June 2013. The highest calcium concentration in Welkom above 100 ppm occurred in October, 2012 (2.10 %) and June, 2013 (2.08 %) respectively. For Virginia and

Odendaalsrus, their highest calcium concentrations occurred in November, 2012 at about 1.50 % (>10 ppm) and December, 2012 at about 1.95 % (> 10 ppm).

The highest mean concentration and distribution of calcium in the leaves was observed from Lejweleputswa District Municipality area of the Free State, South Africa. The calcium versus magnesium (Ca-Mg) ratio in leaves was statistically insignificant for all the towns. The second most abundant element in the leaves was magnesium, occurring at concentrations greater than 1.0 ppm. Sulphur and phosphorous also occurred mostly at concentrations greater than 1.0 ppm in the leaves.

In the water bodies in Lejweleputswa District Municipality, the most dominant trace element was calcium in the environment. Sulphur showed great prominence especially in Allenridge where they occurred above 100 ppm most of the time. The highest occurrence of calcium by far was in Allenridge at about 1262 with drastic decrease in April, 2013 culminating in a relatively low calcium concentration in May, 2013. For other towns, the calcium concentration remained generally low except for Odendaalsrus where calcium concentration elevated to approximately 123.33 and 126.32 for the months of May and June, 2013 respectively. Welkom had the third highest concentration of calcium in the water surpassing Odendaalsrus only in October, 2012 and April, 2013. Allenridge recorded the highest concentration of magnesium in the water during October, November and December, 2012 at 195, 278 and 249 % respectively and 142 % in June, 2013. For other towns, magnesium concentrations remained generally moderate except for Welkom where it remained in the region of 60 % for most of the time.

In the sediment, calcium and iron were the predominant trace elements in all the studied towns with sulphur, magnesium and aluminum showing significant prominence. The highest occurrence of calcium in sediment was in Welkom with least occurrences in Odendaalsrus and Virginia. However, in general, calcium occurrence in the sediment in all the studied towns appears relatively uniform. The highest occurrence of magnesium in sediment was recorded in Branfort, followed respectively by Theunissen and Welkom. Allenridge, Odendaalsrus and Virginia had even occurrence of magnesium in sediment.

TABLE OF CONTENTS

CHAPTER 1
GENERAL INTRODUCTION

CHAPTER 2
LITERATURE REVIEW

CHAPTER 3
PUBLIC AWARENESS OF THE ENVIRONMENTAL IMPACT OF MINING ACTIVITIES IN LEJWELEPUTSWA DISTRICT OF THE FREE STATE

CHAPTER 4
EVALUATION OF TRACE ELEMENTS AROUND THE ENVIRONMENT IN THE LEJWELEPUTSWA AREA OF THE FREE STATE, SOUTH AFRICA

CHAPTER 5
GENERAL DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

APPENDIX

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBREVIATION AND ACRONYMS

As - Arsenic

Sb - Antimony

Pb - Lead

Be - Berrylium

Cd - Cadmium

Hg - Mercury

Co - Cobalt

Cr - Chromium

Mn - Manganese

Ni - Nickel

V - Vanadium

Zn - Zinc

Sr – Strontium

Sn – Tin

Mo – Molybdenum

Se – Selenium

QC – Quality control

QA – Quality assurance

BIS – Bank of International Settlements

ICMR – Indian Council of Medical Research

US EPA – United States Environmental Protection Agency

EPE – Environmental Performance Evaluation

PTY – Public

Eh – Redox potential

pCO_2 – Partial pressure of carbondioxide (i.e. Carbondioxide partial pressure)

pH – Hydrogen ion concentration

AMP – Air quality monitoring program

TDS – Total dissolved solids

TSS – Total Suspended Solids

CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

Mining is a major driving force behind South African economy and development. Despite the declining production of gold and diamond, South Africa, still ranks fifth in gold production in the world (U.S. Geological Survey, 2013). South Africa, however, remains the world's largest producer of chrome, Manganese, Platinum, Vanadium and Vermiculite and second largest producer of ilmenite, palladium, rutile and zirconium (U.S. Geological Survey, 2013). On global stands, South Africa has the largest coal export terminal (Eberhard, 2011) and third largest coal exporter and a huge producer of iron ore (Wikipedia 2015).

The discovery of gold deposits in Pilgrim Rest and Berbarton preceded the biggest discovery of gold in South Africa – the Main Reef/Main Reef farm Langlaate, Portion C in 1886 dubbed the Witwatersrand Gold rush. The South African mining industry represents approximately 18% of South Africa's gross domestic product. Mining subsequently, contribute directly to the establishment of the Johannesburg stock exchange since the late 19th century and still accounts for a third of its market capitalization. Mining has subsequently had positive effect/impact in shaping South Africa politically, culturally, and economically. The main raw materials mined in South Africa are: gold, diamond, platinum, chromium, vanadium, magnesium, uranium, iron ore, coal and copper. Figure 1.1 presents the value of the South African mineral outputs in South African Rands.

South African mining accounts for over 10 % of global gold production and world's fourth largest producer of diamonds. About 40 % of the world's total gold reserves are found in the Witwatersrand area of South Africa. On the other hand; Koster, Lichtenburg, Bloemhof and Christiana areas are mainly mined for diamonds.

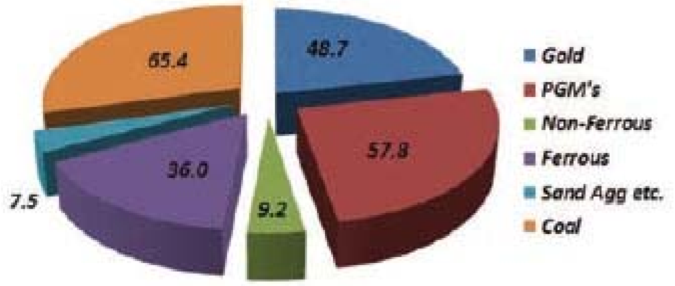


Figure 1.1 Value of South African mineral in South African Rands

South Africa is furthermore the world's fifth largest coal producer and produces on the average about 247 million tonnes of marketable coal every year (Eberhard, 2011). The Highveld and Low-veld regions are the areas mainly mined for coal. Witbank and Ermelo are the major towns in the area mainly mined for coal. The Bush-veld Complex north of Pretoria is mined for vanadiferous magnetite ore and is home to the world's largest reserve. In recent times, mining in South Africa:

- Contributes an average of 20 % to South Africa's GDP of which about 50 % is contributed directly
- Boasts total annual income exceeding R330 billion
- Is one of the country's major employers, with more than one million people in mining related employment
- Is the largest contributor by value to black economic empowerment in the economy

Figure 1.2 details the various mineral resources of South Africa and the locations where they occur in the country.

1.1.1. Provincial economics

Gauteng Province: Gauteng province is South Africa's economic centre and it is responsible for 34.8 % of South Africa's total gross domestic product (GDP). It is also the financial service capital of Africa. There are approximately 159 mines in Gauteng with 44 being gold mines accounting for a quarter of South Africa's total mineral production. Most of the mines in Gauteng are for gold, amounting to 80 % of Gauteng's output.

KwaZulu Natal Province: KwaZulu Natal is not known for mining but rather for its forestry, wood and wood products. Major businesses in the area are associated with forestry and wood and hence, furniture making is thriving in the area and forms a major part of the business in the area.

Limpopo Province: The province's natural reserves include more than 50 provincial reserves as well as several private game reserves. A large section of Kruger National Park is situated along the eastern boundary of Limpopo and Mozambique. Mining in the area include: platinum, chrome, nickel, cobalt, vanadium, tin, limestone and uranium clay.

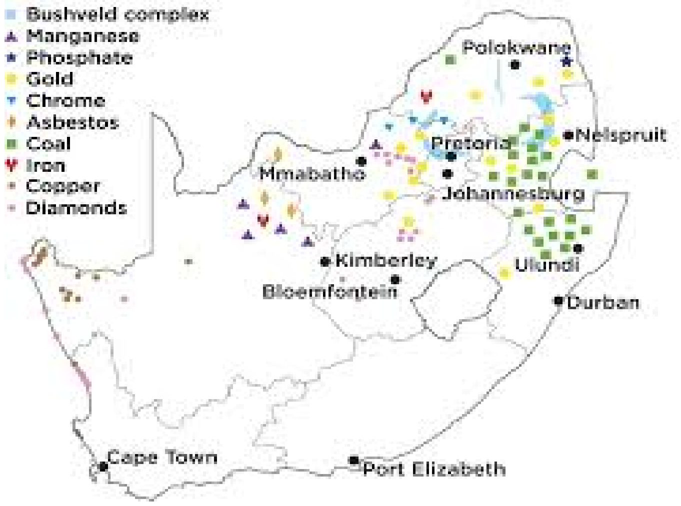


Figure 1.2 South African mineral resources and locations

Other reserves include: antimony, phosphates, fluorspar, gold, diamonds, copper, emeralds, magnetite, vermiculite, silicon, mica, black granite, corundum, feldspar and salt.

Northern Cape Province: Mining contributes approximately, 27.6 % to the gross regional domestic product of Northern Cape. Iron ore mining is thriving in the area with Sishen (subsidiary of Kumba Iron Ore), located in the area as the biggest iron ore mine in the country. New manganese projects have also been commissioned and the province is also known to be rich in other minerals such as copper, asbestos, fluorspar, semi-precious stones and marbles. Kimberly – the capital city - has rich deposits of diamond, hence, diamond and alluvial mining is actively taking place in Northern Cape Province. The discovery of a diamond on the bank of the Orange River in 1867 and subsequent discovery and exploitation of the Kimberly pipes a few years later led to large scale and profitable mining in South Africa. Iron ore is mined in Sishen and Thabazimbi accounting for over 80 % of South Africa’s output.

North West Province: Mining contributes 23.3 % to North West economy and makes up 22.5 % of South Africa’s mining industry. Approximately, 94 % of platinum is produced in Rustenburg and Brits towns in the North West province – more than any other single area in the world. About a quarter of South Africa’s gold is also produced in the province. The province is known for its production of minerals such as granite, marbles, fluorspar and diamond. The North Western also, boasts substantial reserves of platinum and diamond accounting for more than 90 % of South Africa’s platinum production with five of the largest platinum producing mines located in Rustenburg area of the province.

Western Cape Province: The economy of the Western Cape contributes roughly 14.5 % to South Africa’s Gross Domestic Product (GDP), growing at an average rate of 3.2 % a year. The manufacturing sector is the third largest in the country, coming only after Gauteng and KwaZulu Natal.

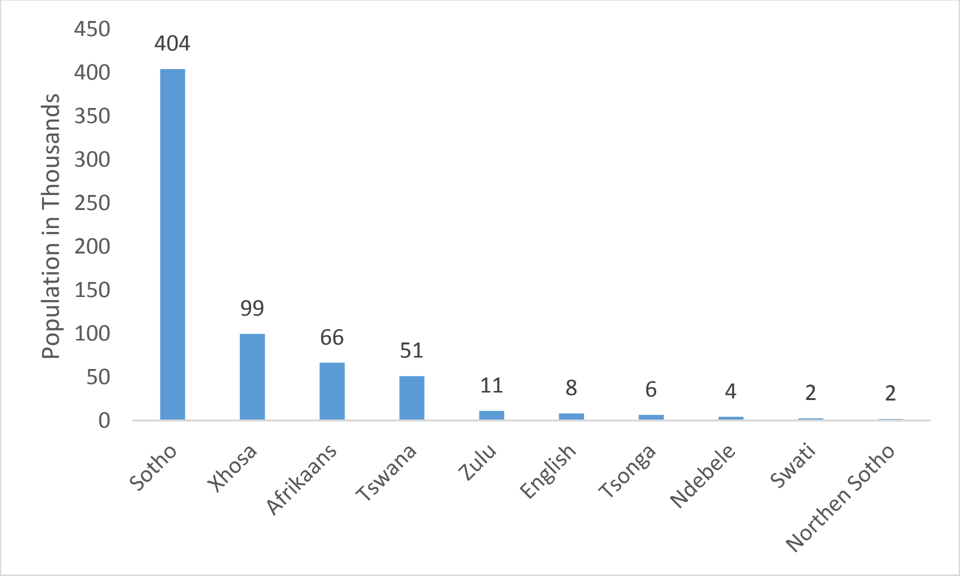
Free State Province: Mining, particularly gold is the biggest employer of labour in the Free State, followed by manufacturing. With about 12 gold mines in operation in the area, the province accounts for 30 % South Africa’s total gold production, and contributes a significant amount of silver, bituminous coal and diamonds. In the light of the extensive mechanized farming activities in the area, it is subsequently also known as the “bread basket" of South Africa with about 90 % of the province under cultivation for crops production.

Lejweleputswa (grey rock) is however, one of the five district municipalities of the Free State Province, South Africa, predominantly mined for gold and to a lesser extent diamond. It is also one of the most mined areas in South Africa and lies in the north western part of the Free State, bordering the North West province in the west and Northern Cape Province, in the north. The major mining companies operating in the area, are: Gold Fields Limited, Harmony Gold and Pedra Diamond. Lejweleputswa Municipal District lies in the heart of the country's agricultural belt, and is a home to some of the province's nature reserves - the Willem Pretorius Nature Reserve which encircles the Allemanskraal dam near the SandRiver, Soetdoring Nature Reserve in Dealesville, Tweefontein Nature Reserve in Theunissen and A.C. Van Wyk Game Park in Bultfontein (South African Venues, 2011).

The district comprises the local municipalities of Masilonyana, Matjhabeng, Nala and Tokologo, with most of the mining activities taking place at the Matjhabeng local municipality of the district. The district is home to towns such as Brandfort, Bothaville, Allanridge, Henneman, Welkom, Ventersburg, Virginia, Theunissen and Odendaalsrus (South African Venues, 2011). Welkom (the capital), Odendaalsrus and Virginia (Matjhabeng Local Municipality) have the largest portion of the population. The predominant languages spoken in the area are English, South Sotho, and Afrikaans with lesser part of the population speaking Xhosa, Tswana and the other ethnic languages (Table 1.1). South Sotho is the dominant language of the area constituting about 61.5 % of the overall population. Economically; gold mining, agriculture, small industries and diamond mining form the backbone of the area's economy. The mining sector contributes about 31.5 % of the District's GDP and about 23.8 % to the Free State total GDP making it the second largest contributor of the five District Municipalities constituting the Municipal District.

The Lejweleputswa District Municipality also has a population of approximately 500,000 people about 23.2 % of the population of the Free State Province. Table 1.1 illustrates the population dynamics of the Lejweleputswa Municipal District (LMD) area.

Table 1.1 Distribution of ethnic/language groups of Lejweleputswa District Municipality residents (Statistic SA, 2011).



1.1.2 Motivation for the study

Mining and industrial activities are among the main sources of trace elements contaminations in the environment (Adriano (1986); Dampare (2006) and Zhou (2007). The regular milling and grinding operations undertaken in both mining and industrial processes coupled with concentrating of ores and disposal of tailing serve as obvious sources of trace metal contamination in the environment (Antwi-Agyei, 2009). Furthermore, trace and radioactive elements also enter the environment through runoffs from mining activities, cleaning and storage operations. Combustion activities result in atmospheric emissions while runoffs and leachates infiltrate into the ground water from bottom ash, flash ash and scrubber sludge deposited in settling ponds and landfills leading to the release of trace elements into the environment (Van Hook, 2009).

Apart from few environmental projects commissioned by the Lejweleputswa local municipal authorities, such as The Environmental Impact Assessment Process, Draft Scoping Report, Grootkop Solar Energy Facility Project; there has not been any proper scientific study in the area aimed at extensively evaluating the impact of the numerous mining activities on the environment and residents. Mining operations are well known to be associated with chemical proliferation in the environment, hence, it is deemed necessary to establish the extent to which chemicals resulting from the mining activities in the area have infiltrated the environment in the Lejweleputswa Municipal District area of the Free State, South Africa particularly trace elements. If any project had been done previously with regard to establishing the extent of chemical pollution of the environment due to the mining activities in area, the findings/data obtained from such studies are often confidential and not disclosed to the public (Horizon Environmental Specialists, 2013; Savannah Environmental, 2013; Mortvedt, 1996).

The current study seeks to evaluate the extent of chemical (trace element) proliferation in the environment in light of the constant and numerous mining activities taking place in the Lejweleputswa area of the Free State, South Africa. The current study intended to shed light of food safety perspective, thus bringing a different view about the impact from trace elements.

1.1.3 Problem Statement

Mining activities lead to the release of trace elements such as uranium (U), sliver (Ag), gold (Au), mercury (Hg), iron (Fe) and arsenic (As) into the environment and may distribute the concentration levels of other trace elements important for the environment. The significant number of mining companies operating in the Lejweleputswa area implies that the sizable mining activities taking place in the area will result in the release of these trace elements into the environment (Koranteng-Addo *et al*., 2011; Van Hook, 2009). Some trace elements are known to lead to serious health hazard and are the contributing factor to high blood pressure (barium), kidney damage (cadmium and uranium), intestinal lesions (beryllium) and cancer (radium and uranium) to list a few (Brune and Dietz, 1996). It is subsequently important to evaluate the level of trace elements of surrounding areas near mining industries. This is important so as to keep track of the buildup of trace elements in the environment and observe its compliance with national norms and standards especially from a food safety perspective. It will be interesting to observe any link between the elemental levels and health situations in the region. Possible contamination of foods in the area with trace elements could be of particular interest when assessing the movement of trace elements from one phase to another (inclusive of soil, plants, water and sediment).

1.2 Main objectives of the study

The main objectives of this study were to establish the public awareness of possible impact of mining activities and secondly, to ascertain the levels of selected trace element for possible pollution due to the numerous mining activities taking place in the environment around the Lejweleputswa area of the Free State, South Africa. The drive of the project was however more from a food safety perspective.

1.2.1 Specific objectives of the study

To achieve the main objectives, the specific objectives of the study were to:

i) Assess the level of the public awareness of the possible impact of the mining activities in the area;

ii) Ascertain the prevalence of selected trace elements in the soil, leaves, water and sediment;

iii) Establish the levels of trace elements in the different media to observe seasonal variation and any relationship between trace elements concentrations in the soil, leave, water and sediment;

iv) Model the role of trace elements from one medium to another;

v) Compare and establish any food safety challenges due to the recorded concentrations.

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Trace elements are defined differently depending on the particular discipline. In analytical chemistry, trace elements are defined as elements in a sample with an average concentration of less than 100 parts per million (ppm) measured in atomic counts or less than 100 micrograms per gram. In geology, trace elements are defined as chemical elements whose concentration in the Earth's crust is less than 1000 ppm or 0.1 % by weight respectively or chemical elements occurring in very minute amounts, between 1 to 10 ppm in water, air, soil, rocks, sediments and animal tissues (Duffus, 2002; He *et al.*, 2005; Hodson, 2004; Navratil and Minarik, 2005).

Trace elements such as Co, Cu, Cr, F, Fe, I, Mn, Mo, Se and Zn are also classified as 'micronutrients' (He *et al.*, 2005). In addition, trace elements such as Ni, Sn, V, Si and Bo, have also been found to be important micronutrients although not mostly listed with others. On the other hand, Al, As, Ba, Bi, Br, Cd, Ge, Au, Pb, Li, Hg, Rb, Ag, Sr, Ti and Zr have been found in both plant and animal tissues but their importance/functions need to be further investigated (He *et al.*, 2005; Srinivas *et al.*, 2009). The presence of trace elements in the environment lead to environmental pollution and can ultimately cause serious health problems to humans and animals (Alloway, 1995; Sharma *et al.*, 2004; Vousta *et al.*, 1996).

Mining operations are known for contaminating the environment with trace-elements due to the various activities which are undertaken, such as milling and grinding, concentrating of ores and disposal of tailings, all of which act as sources of contamination in the environment (Antwi-Agyei *et al*, 2009). However, some of these mining activities are normally regulated. Trace and radio-active elements enter the environment through runoffs from mining activities, cleaning and storage operations, material combustion and leachates infiltration into underground water from landfills, bottom and flash ash and scrubber sludge deposited in settling ponds (Van Hook, 2009).

Trace elements in concentration can have negative effects on both plants and animals including aquatic life. Trace elements are also known to be capable of imposing a long term burden on biogeochemical cycling in the ecosystem (Nriagu, 1988; Nriagu, 1996). Trace elements toxicity has also been shown to lead to excessive accumulation or depletion of nutrient elements in plants resulting in different plant sicknesses and other primary damages to the plant (Brune and Dietz, 1996). With regard to humans, trace elements in certain amounts have been shown to be dangerous. For example, Cadmium in even trace amounts can be harmful to humans (Mortvedt, 1996).

2.2 Sources of trace elements contaminations

The main sources of trace elements can be classified into two main categories, namely, the man-made sources and the natural sources. The man-made sources can be classified into three sub-categories which include: the industrial emissions (mining, smelting, ore and metal processing, chemical industries and coal combustion), vehicular and domestic emissions. Natural sources or emissions on the other hand, include the volcanic eruptions and forest fires, entrainment of soil and dust, entrainment of sea and salt spray and crustal sources (Richardson, 2002; U.S. EPA, 1996a&b). Motor vehicles are responsible for emitting Pb and CO, while geological matters are sources of trace elements such as Mn and Fe. Oil burning emit elements such as V and Ni into the environment and industries often release elements such as Zn, Cu and SO_4^{2+} (secondary aerosols) into the surroundings. The various sources of trace elements to the environment such as industries, vehicles, domestic and coal combustion are briefly described for the purpose of this study.

2.2.1 Industrial sources

Industrial activities such as mining, smelting and processing of ores have escalated in the second half of the twentieth century due to the growing need and demand for their products. As a result, the production of metals such as Pb, Cu, Ni, Sn and Zn increased by up to eight folds. Increased production and use of chemicals both industrially and domestically, has increased the risk environmental pollution from the twentieth century. For example, a large quantity of cyanide escaped into the water bodies during gold mining and processing in the Ore district of Baia Mare in Romania, leading to enormous spread of chemicals and subsequently, trace elements in the environment. The enormous ecological destruction and catastrophe which resulted from this activity had impact comparable to the Chernobyl nuclear disaster in 1986 (Navratil and Minarik, 2005).

Sulphide mining waste is also known to have serious environmental implications because metal sulphides in mining wastes are known to oxidize to produce acidic leachates containing heavy metals. Even though, sulphide ore bodies remain practically unchanged in the bed rock for very long periods of time, the substantial amount of sulphur that occur with gold ores form concentrated sulphuric acid when in contact with water, leading to acid mine drainage. The rate of mobilization of heavy metals such as Cu, Pb, Zn and Cr from mining operations, are estimated to exceed by a factor of ten their rate of mobilization from natural cycling (Navratil and Minarik, 2005).

2.2.2 Chemical industry

Chemical products such as detergents, cleansers, softeners, catalysators etc. have become an integral part of daily human requirements and used extensively in industries and machineries. Chemical industries have become a major source of revenue for many countries due to their production of household and industrial chemicals. However, the major problem arising from the use of chemical products is that they are made from a mixture of chemicals whose ecological and/or toxicological safety cannot be guaranteed (Navratil and Minarik, 2005). With increases in the demand and subsequent production of the various chemicals, the greater the likelihood of environmental pollution with these chemicals. Economic and chemical industrial growth have led to increases in chemical production hence have a direct link to chemical pollution of the environment. A sharp increase in the production of fertilizers and pesticides observed and the estimated 80 000 different chemicals produced worldwide have led to increased chemical pollution of the environment in areas in which chemical industries are situated worldwide (Navratil and Minarik, 2005). Figure 2.1 illustrates the global production and consumption of some toxic trace elements from 1895 to 1990, while tables 2.1 and 2.2 illustrate the world reserves and production of metals and estimates of trace elements' inputs and outputs of agricultural soils in California in gram per hectare per year (gha^{-1}yr) respectively.

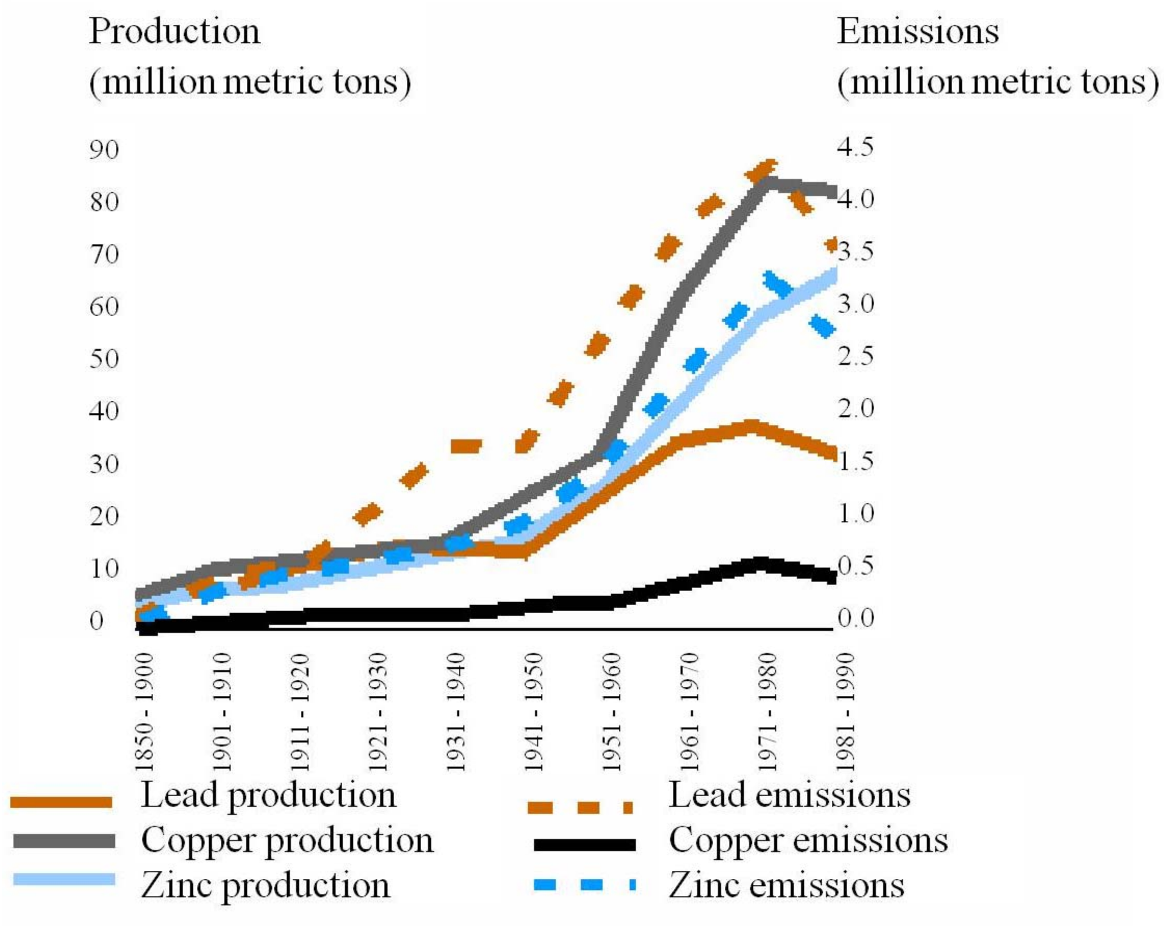


Figure 2.1 Global production and consumption of some toxic metals from 1895-1990 (Nriagu, 1996)

Table 2.1 World reserves and production of metals (Jung *et al*., 2004).

Elements	**Reserves(R) (1000t)**	**Production(P) (1000.t/year)**	**Reserves per Production (R/P)(year)**
Aluminium	28 000 000	111 024	252
Antimony	4700	36	130
Arsenic	11000	35	314
Bismuth	250	3	83
Cadmium	970	18	53
Chromium	6700 000	10 000	670
Copper	590 000	9523	62
Iron	230 000 000	988 797	233
Lead	130 000	2765	47
Selenim	130	2	75
Tin	10 000	206	49
Zinc	330 000	6895	48

Table 2.2 Estimated trace elements inputs and outputs of agricultural soils in California (Chang and Page, 2000)

	Input							Output		
Elements	**Irrigation**	**Wastewater**	**Biosolids**	**Fertilizer**	**Manure**	**Weathering**	**Fallout**	**Drainage**	**Runoff**	**Harvest**
Arsenic	25	30	120	4	8	0.4	5	1	-	6
Boron	4200	6000	500	30	250	20	40	1	-	30
Cadmium	2	30	64	6	4	0.03	5	3	2	6
Chromium	144	12	1030	20	150	3	100	15	4	10
Copper	22	240	5080	4	130	13	50	25	-	100
Lead	56	60	1100	125	40	4	100	6	3	1
Mercury	-	24	21	-	-	0.1	2	1	0.1	0.2
Molybdenum	38	60	15	90	300	5	5	1	-	12
Nickel	28	120	570	5	200	22	50	12	4	4
Selenium	18	20	87	1	5	1	0.5	1	-	2
Zinc	89	400	8300	40	200	20	200	30	5	100

2.2.3 Coal combustion

Coal burning is one of the major contributors of trace elements to the environment and ranked second most serious source of trace elements contamination of the environment. Most trace elements in coal are associated with the fly ash removed from gases and slags. Small amounts of trace elements escape into the atmosphere in fine fly ash particles. Fine particles of fly ash that escape with the stack gases to the atmosphere may have higher trace elements content – especially volatile elements such as As, Sb, Su, Pb, etc., than large particles. It has been observed that metals such as Be, Cd and Hg tend to be concentrated in light density fractions of fly ash, whereas Co, Cr, Mn, Ni, V and Zn tend to concentrate in higher density fractions (Navratil and Minarik, 2005).

2.2.4 Vehicular (Traffic)

Traffic is a major source of pollution in urban areas and soils adjacent to highways. Pb concentrations in soils near highways have been shown to be high and decrease exponentially as a function of distance from the highways (Navratil and Minarik, 2005). Other factors that influence Pb concentration in roadside soil include: meteorological situation, vegetation, and topography and traffic intensity. Modes of transportation such as trains and aircraft also contribute to the contamination of the environment by heavy/trace metals such as Cd, Ni, Pb, V, Pt and Zn. However, Pb emission into the environment has been considerably reduced since the advent of the use of unleaded fuel in vehicles since the 1980s (Navratil and Minarik, 2005).

2.2.5 Domestic

Domestically, coal, wood and other combustible sources of energy are burnt to generate energy for cooking purposes and to generate heat during the winter to warm-up the homes. Numerous domestic activities require the combustion of various materials such as woods, coal for heat and other materials such as candle and kerosene (paraffin) for the purpose of generating light for the home. These combustible materials are very good sources of trace elements in the environment.

The domestic sources of potentially toxic elements in wastewater include the potentially toxic elements (PTE) discharged from the household to Urban Waste Water (UWW) collecting system, corrosion from materials used in distribution and plumbing networks, tap water and detergents. Waterborne emissions of potentially toxic elements (PTE) from household sources, dentistry and utility buildings in the urban environment quantified by the Dutch Institute of Public Health and the Environment (RIVM) in Netherlands indicated households, followed by utility buildings and then dentistry as major sources of waterborne trace elements such as copper, zinc, lead, cadmium, nickel, chromium and mercury in the environment (Speed, 1993). Table 2.3 summarizes the Statistical description of element content in household dusts ($\mu g g^{-1}$) of the city of Warsaw (Lisieqicz *et al.*, 2000).

A review of domestic products containing potentially toxic elements used on a regular basis in homes outlined the principal potentially toxic elements (PTE) and products containing them that may enter urban wastewater. Table 2.4 outlines some potentially toxic elements and their main domestic source.

2.3 Pathways of trace elements spread in the environment

The various pathways of trace elements migration in the environments are through ground deposition, surface runoff, dry deposition, air/water gas exchange, surface water runoff, wet deposition and groundwater. The reservoirs for trace elements include: the soil, bedrocks, water and atmosphere (gases particles). Figure 2.2 illustrates the different pathways through which trace elements migrate in the environment (Navratil and Minarik, 2005).

2.4 Dispersion mode of trace elements

For proper understanding of the role of trace elements in the environment, it is imperative to investigate the three main dispersal mechanisms of trace elements, which have been identified as: primary dispersion, secondary dispersion and tertiary dispersion.

Table 2.3 Statistical description of element content in household dusts (μgg^{-1}) (Lisieqicz et al., 2000)

Fraction	Cr	Ni	Cu	Zn	Pb	Br
63–125 μm						
Geometric mean	81	33	121	1250	131	26
Median	90	30	109	1070	124	19
Range	17–268	14–107	48–336	534–4080	64–318	7–558
Arithmetic mean	93	39	141	1430	144	54
S.D.	49	24	82	813	66	109
32–63 μm						
Geometric mean	95	42	129	1150	158	29
Median	101	37	132	1020	169	23
Range	32–168	20–400	56–294	592–2450	80–318	13–869
Arithmetic mean	102	54	136	1230	169	59
S.D.	37	68	48	487	66	155
0–32 μm						
Geometric mean	100	58	162	1150	194	26
Median	100	52	149	1070	206	25
Range	36–202	23–357	76–609	609–2100	91–334	10–100
Arithmetic mean	106	74	186	1200	209	31
S.D.	37	74	121	376	80	24

Table 2.4 Potentially toxic elements and their main domestic sources (Lewis, 1999)

Potentially toxic elements	**Main sources**
Cadmium	Rechargeable batteries (Ni-Cd batteries), paints, photography, food products, detergents, body care products and storm water (Ulmgren, 2000a and Ulmgren, 2000b)
Copper	Corrosion and leaching of plumbing, fungicides (cuprous chloride), pigments, wood preservatives, larvicides (copper aceto arsenite) and antifouling paints. Sources in urban wastewater include: food products, detergents, body care products and storm water.
Mercury	Thermometers, dental amalgams, paints (mercuric arsenate), pesticides (mercuric chloride in fungicides, insecticides), wood preservatives (mercuric chloride), embalming fluids (mercuric chloride), germicidal soaps and antibacterial products (mercuric chloride and mercuric cyanide), Mercury – silver – tin alloys and silver mirrors.
Nickel	Alloys for food processing, sanitary installations, rechargeable batteries and protective coatings.
Lead	Lead piping, old paint pigments, solder, pool cue chalk, cosmetics, ceramic dishes, porcelain and in wine processing.
Zinc	Corrosion and leaching of plumbing, water-proofing products(zinc formate, zinc oxide), anti-pest products (zinc arsenate – in insecticides), zinc sithioamine as fungicides, rat poison, rabbit and deer repellent, zinc fluorosilicate and anti-moth agent, wood preservatives (as zinc arsenate), deodorants and cosmetics (as zinc chloride and zinc oxide), medicines and ointments (zinc chloride and oxide as astringent and antiseptic, zinc formate as antiseptic), Paints and pigments (zinc oxide, zinc carbonate, zinc sulphide), printing inks and artists paints (zinc oxide and carbonate), colouring agent in various formulations (zinc oxide), a UV absorbent agent in various formulations (zinc oxide) and in health supplements (as zinc ascorbate or zinc oxide).
Silver	Photography, household products such as polish, domestic water treatment devices etc. (Shafer, *et al*., 1998, Adams and Kramer, 1999)
Arsenic	Natural background source, and household products such as: Washing products, medicines, garden products and food supplements, shampoos, cosmetics, old paint and pigment. Arsenic is present mainly as dimethylarsenic acid (DMAA) and as arsenite – As (III) in urban effluents and sewage sludge (Carbonell-Barrachina *et al., 2000).*
Selenium	Food products, food supplements, shampoos, cosmetics, old paint and pigments.

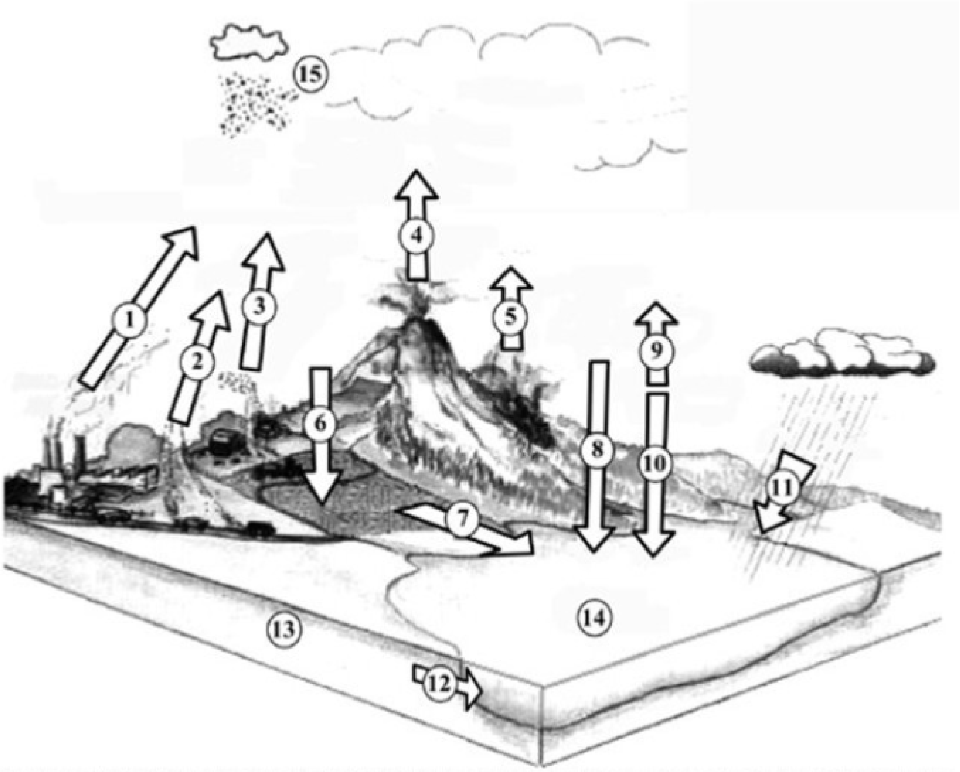


Figure 2.2 Sources, reservoirs and pathways of trace elements and other chemical substances in the environment (Navratil and Minarik, 2005). **Man-made source** (1) Industrial emissions; (2) Vehicular emissions; (3) Domestic emissions; **Natural sources** (4) Volcanic eruptions emissions; (5) Forest fires; **Pathways (**6) Ground deposition; (7) Surface runoff; (8) Dry deposition; (9, 10) Air/water gas exchange; (11) Wet deposition; (12) Groundwater and surface water runoffs; **Reservoirs (**13) Soils and bedrocks; (14) Water; and (15) Atmosphere (gases, particles, etc).

2.4.1 Primary dispersion

In primary dispersion, trace and major elements are concentrated in certain types of geological formations. During the crystallization of rocks via cooling and solidification of magma, the major constituents form a sequence of minerals dependent on the prevailing temperature and pressure. The microelements usually occupy spaces in the lattices of these minerals according to the rules of diadochic substitution. The elements' valence, ionic radius and electronegativity, play a major role in the control of minerals and occupation of spaces by microelements in the lattices of these minerals. The crystal field stabilization energies are also important in the case of first row transition elements. The concentrations of major elements rarely vary by more than a factor of two over a wide range of geological formations while the concentrations of trace elements vary considerably from material to material (Navratil and Minarik, 2005).

2.4.2 Secondary dispersion

Secondary dispersion occurs as a result of physical and chemical weathering which transforms fresh rock, which is frequently non porous, into soft and porous soil resulting in secondary dispersion of elements from the bedrock into the surface environment. Physical weathering breaks the rock into smaller particles, thereby increasing the surface area of the materials which is exposed to air and water. Atmospheric oxygen and water are the main agents of chemical weathering. Primary minerals, which have been formed at high temperatures and pressures mostly in the absence of air and water, are changed into phases that are stable under surface conditions. Surface conditions are characterized by low temperatures and pressures and also by the presence of air and water. The redistribution of chemical elements involves interactions between bedrocks and water from atmospheric precipitations containing dissolved gases. The physical properties of the newly formed phases – the particulate and colloidal materials – are intermediate between bedrock, water and fragments of minerals which are resistant to weathering. The fate of a trace element in solution then depends on the behaviour of its aqueous species. The ionic potential and the effective hydrated ionic diameter are the parameters responsible for the behaviour of the aqueous species. The trace elements may be either leached from weathered material into surface and subsurface water or precipitated from solution as hydroxide, oxyhydroxide, carbonate, sulphate, phosphate etc. Trace elements can also be incorporated into a newly formed phase and on less frequent occasion, it may be adsorbed onto the charged surfaces of clay particles or organic matter. The secondary dispersion of trace elements is strongly affected by Eh, pCO_2 and pH and the stability of host minerals are subject to decomposition in particular weathering environment (Navratil and Minarik, 2005).

Both primary and secondary dispersions take place spontaneously, independent of human activities. Some exceptions however, include: that acidic atmospheric precipitations which accelerate rock weathering by the addition of H^+ (hydrogen ions). Subsequently, hydrogen ions release some cations from the structure of primary phases and thus nutrients are also leached away out of the soil formed on the bedrock, while toxic metals become more mobile and more readily available (Navratil and Minarik, 2005).

2.4.3 Tertiary dispersion

Modern industrial development has led to the enrichment of the basic environmental media such as soil, vegetation, water and air with trace elements. Geochemical neo-anomalies results in the situation in which the environmental media (soil, vegetation, water, air, and sediment) may contain up to 1000 times the normal crustal trace element content. The normal crustal trace element concentration is usually described as the 'background concentration'. Heavy metals (density>6 g.cm-3) are the predominant trace elements concentration in neo-anomalies. Some of the trace elements are essential for life processes in trace quantities but in higher concentrations are all toxic to organisms. Heavy and trace metals pollute the environment due to their pulverization as well as their heating and dissolution during industrial usage. Mines, smelters and industrial complexes along roads and most urban areas constitute the major sources (neo-anomalies) of many trace elements. Human activities constitute a number of pathways for tertiary dispersion or pollution however, it has subsequently been well established that the natural geochemical cycles of some trace elements are considerably disrupted by human activities (Navratil and Minarik, 2005). Table 2.5 illustrates the annual atmospheric emission of trace elements by various industrial processes.

Table 2.5 Atmospheric Emissions of Trace Metals Worldwide (Pacyna and Pacyna 2001)

Elements	Energy Production	Smelting and Refining	Manufacturing Processes	Commercial, Waste Tmt., Transport	Total Anthropogenic Flux	Total Natural Flux
Antimony	1.3	1.5	-	0.7	3.5	2.6
Arsenic	2.2	12.4	2.0	2.3	19.0	12.0
Cadmium	0.8	5.4	0.6	0.8	7.6	1.4
Chromium	12.7	-	17.0	0.8	31.0	43.0
Copper	8.0	23.6	2.0	1.6	35.0	6.1
Lead	12.7	49.1	15.7	254.9	332.0	28.0
Manganese	12.1	3.2	14.7	8.3	38.0	12.0
Mercury	2.3	0.1	-	1.2	3.6	317.0
Nickel	42.0	4.8	4.5	0.4	52.0	2.5
Selenium	3.9	2.3	-	0.1	6.3	3.0
Thallium	1.1	-	4.0	-	5.1	29.0
Tin	3.3	1.1	-	0.8	5.1	10.0
Vanadium	84.0	0.1	0.7	1.2	86.0	28.0
Zinc	16.8	72.5	33.4	9.2	132.0	45

2.5 Occurrence of trace elements in different media

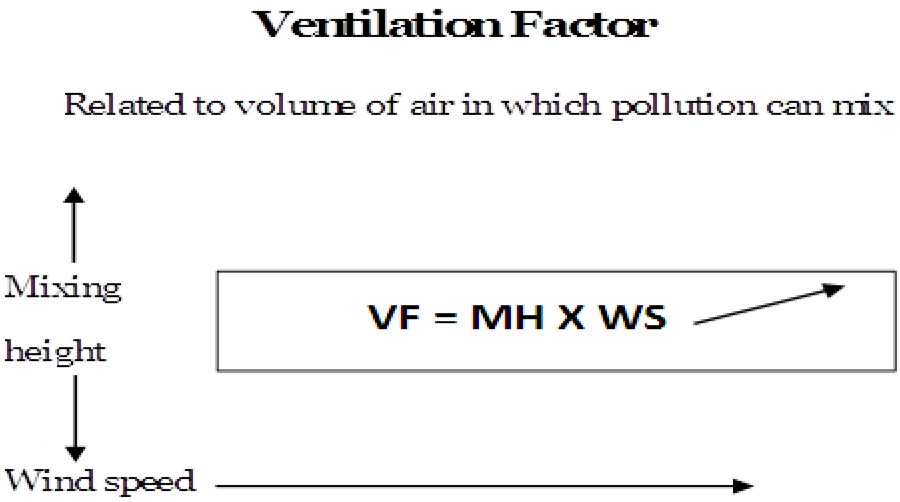
2.5.1 Prevalence of trace elements in ambient air

Air pollution is defined as the presence of contaminants such as dust, smoke, chemical (trace elements), gases, in the atmosphere. Atmospheric trace element pollution is as a result of wind action transporting materials from the ground, water mass into the atmosphere. Air pollution dispersion is often studied with box models where, the ventilation factor relates the pollution concentration to the parameters that control dispersion of the pollution in the local environment. Basically, increasing either the mixing height or the wind speed increases the effective volume in which pollutants are allowed to mix. The larger the volume of space of spread of the air, the lower the pollution concentration in the area (Krzeminska-Flowers *et al*., 2006). The ventilation factor is related to the volume of air in which pollution can mix as shown in the equation 2.1.

Ventilation factor (VF) = (Mixing height (MH)) X (Wind speed (WS))

$$VF = MH \times WS \tag{2.1}$$

Scheme 2.1 illustrates diagrammatically the ventilation factor with respect to its determining factors.



Scheme 2.1 Schematic representation of the ventilation factor (Krzeminska-Flowers *et al*., 2006)

With scheme 2.1 reflecting the ventilation factor, long term air sampling period of one year allows for the integration of diurnal and weather influenced fluctuations of the trace-element concentrations in the urban atmosphere (Krzeminska-Flowers *et al*., 2006). Furthermore, air particulate matter in the fine particles region (<2 µm) was reported to be higher during winter period suggesting this is an indication of higher contribution of the fuel combustion sources. The increased input of the coarse fraction during the summer months can be explained to be due to higher contribution of surface soil re-suspension to total AMP concentration. Three types of concentration size distribution tendencies were observed for particulate elements in all locations and for both sampling periods by Krzeminska-Flowers *et al*., (2006). Predominant part of the trace-elements from both high level emission and traffic sources was concentrated in a fine fraction of aerosols with particulate diameter below 1 µm, which are the most dangerous from an epidemiological point of view (Krzeminska-Flowers *et al*., 2006).

Another study by Clyde *et al*., (1990), on airborne cadmium, lead, zinc, and copper, showed that they come from emissions from wind-blown dust, material handling, and vehicle traffic. These sources were identified as the important sources of airborne toxic trace elements in all the studied areas. It was concluded that the existing standards for airborne inhalable particle do not adequately control the levels of many toxic trace-elements. The first step in the control of the pollutants is to identify the sources of individual elements rather than sources of particulate matter in general. Cadmium concentrations in East St. Louis have been reported to be more than ten times higher than normal 'urban level'. Airborne chromium being an important carcinogen at typical urban levels needs to be reduced by better control of the pollutants (Clyde *et al*., 1990).

2.5.2 Trace elements occurrence in water

The occurrence of trace elements in natural water is affected mainly by both hydro-chemical factors like mineral composition of the rocks and soil characteristics as well as by anthropogenic activities amongst others. While it is likely to show both temporal and spatial variation (Jinwal *et al*., 2009; Durand, 2012), trace elements have many of the same mechanisms that control their distribution in the oceans which are also important in lakes. Specifically, these include: biological recycling, sediment fluxes, oxidation-reduction cycling, and scavenging by particles. The influence of each of these mechanisms can be seen in the trace elements profiles of lakes despite the fact that lakes are intrinsically much more difficult to study than oceans. This difficulty in the study of lakes arises due to the fact that lakes are not at steady state, and the magnitude of the controlling mechanisms varies with time. The large sediment-to-water-volume (sediment-volume) ratios in lakes, together with the rapid horizontal mixing, result in sediment fluxes that tend to mask the other processes. Nevertheless, lakes are more accessible and in most cases easier to sample than the ocean. Because of the wide variety in types of lakes, isolating variables is possible by choosing the lake with the right properties (Jinwal *et al*., 2009).

The fate of trace metals (elements) in the environment is determined by considering the current source and sink sizes of the elements and their changes over a particular period of time. The emission of colouring pigments into the waterway in the period between 1880 and 1930 was the primary source of trace metals in the environment (Graedel and Crutzen, 1993). Lead concentration in water bodies as an example; increased globally and subsequently, the total emission of Lead into water bodies with increasing concentrations occurred globally. Also, the emission from Lead additions as a result of the combustion of automotives fuel became prominent (or come to the fore) with subsequent transfer of Lead materials into the atmosphere. The prohibition by industrialized nations of the use of Lead in gasoline (petrol) in mid 1970s, led to the reduction of air emission of Lead considerably and is reflected in the amount discharged in the surface water and riverbeds (Graedel and Crutzen., 1993).

Metals in the environment tend to persist in their localities because they cannot be biologically or chemically degraded like organic substances. Metal ions, however, can be converted into other compounds or metal species (as physicochemical states) through adsorption, precipitation and complexation processes. Biochemical processes such as assimilation and biomethylation of Lead to new bond types and the conversion of mercury to the methyl mercury are both processes that result in the conversion to more toxic metal species. Metals are transferred from water bodies to the food chain via assimilation and processes of bioaccumulation and biomethylation. A cycle of trace metal migration is established in which the geochemical processes in water occur via interfaces into the atmosphere and into the sediment. Trace metals are distributed by the atmosphere as solids (dry deposition) and in dissolved form (precipitation) as wet deposition in water bodies (Graedel and Crutzen, 1993; Durand, 2012).

Metals are deposited by means of inflow in dissolved form or as solids (suspended matter). The cycle is completed by the process of sedimentation at the sediment stage which returns back to bodies of water via desorption, dissociation, dissolution and redox processes as a result of mobilization or remobilization. The physical and chemical states of metals in water bodies influence significantly the metal levels in water bodies, the effect on organisms and the behaviour with respect to the neighbouring compartments such as evaporation into the atmosphere or precipitation in sediment. Table 2.6 illustrates the impact of mining and mineral processing activities on the water resources of the Limpopo River basin in South Africa.

2.5.2.1 Chemical factors affecting metal distribution in interstitial water

Interstitial water is the water occurring in the small openings, spaces, and voids between particles of unconsolidated materials in the portion of the vadose water zone between the roof zone and the water table. The water is held in place by entrapment, ionic attraction, and capillary or adhesive forces rather than from upward pressure components of saturation. Sediment interstitial water or pore water is subsequently defined as the water occupying the spaces between sediment particles. Contaminants in the interstitial water and in the solid phase are expected to be at thermodynamic equilibrium. This makes interstitial water useful for assessing contaminant levels and associated toxicity (U.S. EPA, 2001ab).

Metals can exist either in interstitial water in dissolved form or bind to sediment particles and the percentage of metal in interstitial water can be calculated by using equation 2.2 (Tabata *et al*., 2007):

$$M_{int.Water} = 100 - M_{sed} \qquad \text{where, } M_{sed} = (Cs/Ct) \times 10 \qquad (2.2)$$

M_{sed} = Metals (%) in sediment, $M_{int.\ water}$ = Metals (%) in interstitial water, Cs = Metals in sediments and Ct = Total concentration of metals (sediment and interstitial water).

The reasonable concentrations of Cr, Sr, Ni and Sn in interstitial water suggest a high potential flux of these metals from sediment into the surface waters (Tabata *et al*., 2007).

Table 2.6 Impact of mining and mineral processing activities on the water resources of the Limpopo River basin (Ashton et al., 2001)

Sub-basin	**Type of Mining**	**Water Quality Issues**
Ngotwane/Bonwapitse	Other	Localized Acid Mine Drainage (AMD)
Lotsane	Other	Localized AMD, pH, Total Dissolved Solids (TDS)
Motloutse	Base metals, smelters	Copper, nickel, sulphate (SO_4), TDS
Shashe [1]	Gold, base metals, smelters, alluvial gold	Arsenic, AMD, bismuth, copper-nicium, copper, nickel, mercury pH, TDS, Total Suspended Solids (TSS)
Mzingwane [1]	Gold, base metals, small-scale	AMD, arsenic, cobalt, mercury, nickel, pH, TDS, TSS
Dati [1]	Other	Minor TSS
Bubye	---	---
Mwenezi	Small-scale, other (emerald)	Chromium, TSS
Lower Limpopo and Chagane [1]	Other	Very minor localized TSS
Marico	Base metals, smelters, other	AMD, chromium, fluorine, lead, pH, TDS, TSS, zinc
Crocodile [1]	Gold, base metals, smelters, other	AMD, alkalinity, copper, chromium, copper-nicium, fluorine, iron, lead, manganese, pH, TDS, silver, TDS, TSS, zinc
Matlabas-Mokolo	Smelters, other	AMD, pH, TDS
Lephalala [1]	Base metals, other	Lead, tin, TSS
Theuniskloof [1]	Base metals, other	Iron, manganese, TSS
Mogalakwena	Gold, base metals, smelters, other	AMD, antimony, copper-nicium, pH, TDS, TSS, tin
Setoka-Soutsloot [1]	Other	TSS
Sand	Small-scale	Copper, mercury, nickel, TSS, TDS, zinc
Nzhelele	Other	Lead, nickel
Levuvhu	Other	AMD, pH, TDS, TSS
Wilge [1]	Gold, other	Localized AMD, fluorine, TSS
Riet & Little Olifants [1]	Base metals, smelters	AMD, copper, iron, manganese, pH, sulphate, TDS
Middle Olifants	Gold, base metals, other	AMD, chromium, copper-nicium, copper, iron, manganese, pH, tin, TDS, TSS, zinc
Steelpoort	Base metals, smelters	AMD, chromium, copper, iron, manganese, molybdenum, pH, sulphate, TDS, TSS, vanadium
Blyde [1]	Gold, small-scale	AMD, copper-nicium, TDS, TSS
Selati [1]	Gold, base metals, smelters, other	AMD, antimony, arsenic, cadmium, copper, iron, manganese, mercury, copper-nicium,

		pH, phosphorus, sulphate, TDS, TSS, zinc
Middle Letaba and Great Letaba [1]	Gold, base metals, small-scale, other	AMD, antimony, arsenic, copper-nicium, iron, mercury, pH, TDS, TSS, tin
Shingwedzi	Gold, small-scale	Arsenic, mercury, TDS, TSS

[1] Sub-catchment

2.5.2.2 Physical processes affecting metal release from pore water

Pure water or sediment interstitial water is the water occupying the spaces between sediment particles (U.S. EPA, 2001a & b).

The physical processes favourable for the transfer of trace metals from pore solutions onto the open water fall under three mechanisms, namely:

i) The whirling up of settled sediments as a result of hydraulic phenomena particularly effective in high energy environment such as rivers and marine tidal areas, but which can also be caused by episodic storm events in the shallow parts of lakes and seas.

ii) The distribution of surface sediments by burrowing benthic organisms (bioturbation) and by gas bubbles from the decay of organic matter.

iii) The dredging and associated activities in river, lakes and coastal marine areas.

2.5.2.3 Metal release by acidic water

The level of acidity of water, soil and (environmental media) is very crucial in determining the extent of metal enrichment, ranging from the toxification of drinking water to problems concerning the growth and reproduction of aquatic organisms (Hooda, 2010). The pH is the single most important variable influencing the behaviour of metals in the environment. Metal complexes with sulphates, fluorides, chlorides, and phosphates, are most stable and important below pH 7. Metal complexes with carbonates and hydroxides become increasing more important above, pH 6-8. Hydrogen ions compete with metal cation for adsorption sites; hence, the adsorption of metal cations by hydrous ferric oxide (HFeO), for example, is low in acid system but increasing with increasing pH. Contrarily, oxyanions of As, Mo, Se and Cr tend to be desorbed from HFeO with increasing pH because of competition between the oxyanions and OH^- ions for sorption sites. Also, the solubility of most metal-containing minerals is greatest under acidic conditions, decreasing with increasing pH (Hooda, 2010).

2.5.2.4 Impact of heavy metals on groundwater quality

The serious problem with regard to sewage disposal and landfills is percolation of enriched metal solution into the soil and ground water. There are six mechanisms controlling the development of chemical concentrations in the groundwater in areas that are polluted from the domestic and industrial sectors (Singh *et al*., 2007; Akhilesh *et al*., 2009). These include:

i) Contacts of the geologic sediment with the interstitial water

ii) Interface and mixed water along freshwater/saltwater boundaries

iii) Permanent periodic and episodic admixture processes caused by leakage factors i) and ii) occur mainly in coastal marine areas.

iv) Admixture of deep groundwater along tectonic structures

v) Solution processes in confined groundwater with a different solubility behaviour

vi) Anthropogenic influences such as fertilizing, sewage and industrial effects.

A study of groundwater pollution from sanitary landfill leachate, simulated landfills and areas treated with sewage sludge showed that deeper fills pose less of a pollution problem than shallow fills, which may leach the bulk of the pollution in a shorter time period, and hence, exceeding the dilution capacity of moving groundwater. The study also suggests the existence of an empirical relationship between some specific indicator parameters such as heavy metals of the solid waste, leachate and groundwater (Singh *et al*., 2007).

Landfill was indicated to impact on groundwater quality especially along the hydraulic gradient. Metals infiltrate into the groundwater in areas/sites:

i) Where activities associated with plating shops, where a variety of metals are present at high concentrations in forms that are soluble.

ii) With releases of radionuclides that, due to unique health risks, can have significant impact at very low concentrations. In addition, the use of chelating agents, making these contaminants mobile in the environment, is common during processing of these materials.

iii) In which metals and high levels of inorganic Total Dissolved Solids (TDS) are associated with leaks from sanitary solid waste and hazardous waste landfills.

iv) In which high TDS impacts are also associated with salt storage areas and petroleum production activities.

The trace element content of the surface drainage water is mainly influenced by the adsorption capacities of the specific soil. The ion exchange capacity increases as the type of soil becomes finer grained (sand – loam – clays). The potential usefulness of clay materials as liners for waste disposal sites depends to a large extent on the pH of the leachate solution. The precipitation of heavy metal cations in leachate was an important mechanism at pH (values) of 5 and above (Vance, 1993).

Metals in groundwater interact with and adsorb to components of the soil matrix. One of the most common problematic metals found to contaminate groundwater is the chromium (Cr^{+6}) which is soluble over a wide range of pH. The high degree of mobility in conjunction with its common use, and the fact that it is a known carcinogen, makes the chromate molecule one of the most common problematic metals found to contaminate the ground water. Metals in groundwater interact and adsorb to compounds of the soil matrix. The dominant adsorptive component of the soil matrix is iron (Fe), particularly, the ferric (Fe^{+3}) iron which has a very high adsorptive affinity and total capacity for metal ions and oxyanionic metal complex. This property of the ferric ion enables the use of ferric hydroxide in wastewater treatment and the knowledge of the total iron content in the soil matrix is paramount in understanding the fate and transport of metals in groundwater (Vance, 1993).

The suggested most suitable form of groundwater protection is the establishment of the ‘central sanitary landfills’ where waste materials of different origin and composition are deposited principally above the groundwater table. The removal of radioactive substances and other dangerous materials is fixed in special laws or government decrees. Suitable deposition/dumping sites are areas with relatively little precipitation, large distance between the ground surface and the groundwater table, aquifers of good self-purification capacity, poor groundwater quality and low groundwater velocity (Vance, 1993; Akhilesh *et al*., 2009).

2.6 Occurrence of trace elements in sediment

In geological term sediment is defined as a naturally occurring material that is broken down by the processes of weathering and erosion, and is transported and deposited by the action of wind, water and ice, and/or by the force of gravity or that accumulated through chemical precipitation or secretion by organisms. Sediments are also defined as fragmented materials that originate from weathering and erosion of rocks or unconsolidated deposits and are transported by, suspended in, or deposited by water (EPA, 2014).

Sediments have the capacity to hold up to a million times more metals than the equivalent volume of water. The distribution between the proportion of metal held by the sediment relative to water is dynamic (Diamond and Mudroch, 1990). Due to their large capacity to hold metals, sediments have been characterized as 'sinks'. Sediment can serve as temporary sinks from which some of the metals can enter the ecological and human food web through several routes (Diamond, 1993a), primarily through accumulation by benthic organisms (i.e. organisms that fully or partially live in the sediment, e.g. tubificids, chironomids, trichopteran) or those that feed from the sediment bed such as suckers and carps. Due to high chemical concentration in sediments, the benthic route is the dominant route for the uptake of chemicals to the pelagic route by some organisms (Morrison and Brand, 1986 & 2000). The major route of entry of metals from the sediments to humans is through water used for drinking, cooking, bathing, and swimming. In light of the ability of mercury to bio-accumulate in its monomethyl form, fish consumption is the critical route of exposure of mercury to humans.

The availability of metals in sediments is determined by the sediment water exchange processes that can result in the release or remobilization of chemical from the sediment bed. The metal chemistry in sediments is controlled by the redox potential and pH (Forstener, 1998; Diamond, 1993b).

The percentage of metal in sediment can be determined as shown in equation 2.3:

$$M_{sed} = (Cs/Ct) \times 100 \qquad (2.3)$$

Where, M_{sed} = metal percentage (%) in sediment, Cs = metals in sediment, Ct = total concentration of metals (sediment + interstitial water).

Many important chemical reactions involving the metals occur in the fine-grained materials that accumulate in the deep part of water bodies (Diamond, 1993b). A depth profile of the sediment revealed a decreasing sediment porosity and concentration of dissolved oxygen because oxygen is consumed as organic matter decomposes. The pH is often relatively constant or may decrease with depth, but alkalinity may increase due to mineralization of organic matter (Stumm and Morgan, 1996).

2.6.1 Mobilization of heavy metals from sediments

Remobilization of trace metals from sediments and suspended materials is due to four types of chemical changes in waters and include:

i) Elevated salt concentration
ii) Changes in redox conditions
iii) Lowering of pH
iv) Increased use of natural and synthetic complexing agent (Stumm and Morgan, 1996; Forstener, 1998).

i) Elevated salt concentration Increased salt concentration furnishes alkali and alkaline cations from the salts to the medium. This leads to competition between the metal ions sorbed onto solid particles (sediments) and the alkali and alkaline earth cations. Subsequently, metals originally attached to the sediments are displaced by metals of the alkali and alkaline earth cations (Stumm and Morgan, 1996).

ii) Changes in redox conditions Due to advanced eutrophication, redox conditions are altered in conjunction with a decrease in oxygen potential. Part or complete dissolution of iron and manganese hydroxide occurs with some of the incorporated or sorbed heavy metal load released into the medium (Stumm and Morgan, 1996).

iii) Lowering of pH Lowering of pH leads to dissolution of carbonates and hydroxides as well as increase desorption of metal cations due to competition with H^+ (Stumm and Morgan, 1996).

iv) Increased use of natural and synthetic complexing agent This occurs on occasions in which natural and synthetic complexing agents applied to the soil may form a more stable and soluble metal complexes with heavy metals that are otherwise adsorbed to solid particles of the sediments (Stumm and Morgan, 1996).

Some biochemical transformation processes lead to either the transfer of heavy metals from sediments to animals or plant organisms. This could possibly lead to the enrichment of trace metals along the food chain or the discharge directly or via decomposition products into the water (Stumm and Morgan, 1996).

2.6.2 Saltwater/sediment interactions

Most important interaction between saltwater and sediment (saltwater/sediment interaction) occurs in the mixing zone between river and the sea (i.e. the estuarine environment). Suggestions are that the distribution of heavy metals in particulate matter and in sediments is dominated by mixing processes between river induced materials (more or less polluted) and sea derived (fairly uncontaminated) particulates (Salomons and Forstner, 1988 and Salomonses, 1995). It is expected that other processes are responsible for the remobilization of metals from particulates by desorption or dissolution. The distribution of dissolved metals in water/sediment is controlled by the processes of sorption/desorption, precipitation/solubilization, coagulation, flocculation and complexation.

Other processes not involving elevated salt concentrations but also, and often preferentially, those involving effects of oxidation and reduction, particularly of iron and manganese compounds, and reactions with organic matter since estuaries display high levels of biological activities are yet to be scientifically understood (Vance, 1993).

2.6.3 Redox changes and metal release

Oxygen depletion usually as a result of the process of eutrophication (the acquisition of high concentration of nutrients especially phosphates and nitrates by a water body. This leads to excessive growth of algae observed in a great number of water bodies such as lakes and dams (Forstener, 1998).

The degradation of often rapid spreading organic substances such as algae resulting from increased nutritious substances such as nitrogen and phosphorous compounds from fertilizers, detergents and faeces in water bodies need oxygen. The sediment acts, therefore, as a sink for the oxygen supplied through the sediment surfaces at a rate controlled by:

i) A biologic oxygen demand arising from respiration and metabolic activities in the sediment.
ii) A chemical oxygen demand arising from the fact that inorganic elements such as Fe^{2+} released to the sediment from decomposing biologic matter accumulate in reduced form.
iii) Diffusion, which regulates transport (Kersten, 1988).

The medium of metal transport is the interstitial water with major components affecting the rate of transportation of metals being organic matter, iron and manganese which are available for redox processes. Manganese oxides of higher valence precipitate in the oxidized superficial sediment and are reduced and mobilized in the sediments at higher oxygen potential than are the ferric complexes. Consequently, manganese is mobilized before iron when a lake (water body) enters a reducing phase in its history or undergoes the seasonal onset of hypolimnic reduction. Conversely, manganese will persist in the water longer than iron after oxygen is reintroduced at the turnover (Kersten, 1988).

2.7 Soil (terrestrial)

The soil or pedosphere is the uppermost layer of the earth's crust and consists of lithogenic, biogenic, atmogenic and hydrogenic compounds. The soil structure directly determines the amount of water, air and heat enabling that the earth is inhabited by living organisms. All soils naturally contain trace levels of metals. The concentration of metals in uncontaminated soil is primarily related to the geology of the parent material from which the soil was formed. Metals associated with the aqueous phase of the soil are subject to movement with soil water and may be transported through the vadose zone to the groundwater. Metals cannot be degraded and some metal, such as Cr, As, Se, and Hg, can be transformed to other oxidation states in soil, reducing their mobility and toxicity (Wuana and Okieimen, 2011).

In the soil, metals can exist in different forms, such as: dissolved in the soil solution, occupying exchange sites on inorganic soil constituents; specifically adsorbed on inorganic soil constituents; associated with insoluble soil organic matter; precipitated as pure or mixed solids; present in the structure of secondary minerals; and/or, present in the structure of primary minerals. The aqueous fraction and those fractions in equilibrium with this fraction (the exchange fraction) are of primary importance when considering the migration potential of metals associated with soils. Multiphase equilibria must be considered when defining metal behaviour in soils. Metals in the soil solution are subject to mass transfer out of the system by leaching to ground water, plant uptake, or volatilization, a potentially important mechanism for Hg, Se, and As (Wuana and Okieimen, 2011).

Concurrently, metals participate in chemical reactions with the soil solid phase. The concentration of metals in the soil solution, at any given time, is governed by a number of interrelated processes, including inorganic and organic complexation, oxidation-reduction reactions, precipitation/dissolution reactions, and adsorption/desorption reactions. The ability to predict the concentration of a given metal in the soil solution depends on the accuracy with which the multiphase equilibria can be determined or calculated. Equilibrium thermodynamics data can then be applied not only to predict which precipitation/dissolution, adsorption/desorption, and /or oxidation/reduction reactions are likely to occur under a given set of conditions, but also to estimate the solution composition, i.e., metal concentration in solution, at equilibrium. The potassium dynamics in the soil is well understood and serves as a good example for the behaviour of metals or cations in the soil. Potassium is bound largely to clay minerals, both inside and on the outside. The most loosely adsorbed potassium (trace elements) to the outer surfaces is readily available to the plants (Wuana and Okieimen, 2011).

The pH and redox conditions are two factors influencing the mobility of elements in the soil. At pH > 7, V, U, Se, As and Cr capable of forming anions, have a high mobility at pH > 7. The redox potential (E_h) also plays a significant role. Cr is more mobile in basic conditions with increasing redox potential due to the oxidation of Cr (III) to Cr (VI) as in CrO_4^{2-}. The solubility of elements as a function of pH has been well investigated (Wuana and Okieimen, 2011). Solubility of Zn, Cd and Pb increased greatly in the acidic region. Subsequently, the soil pH determines extensively the distribution rates of heavy metals and hence, heavy metal transfer into deeper soil layers and the distribution rates by plants are dependent on the soil pH (Wuana and Okieimen, 2011).

Immobilization of metals, by mechanisms of adsorption and precipitation, will prevent movement of the metals to ground water. Metals-soil interaction is such that when metals are introduced at the soil surface, downward transportation does not occur to any great extent unless the metal retention capacity of the soil is overloaded, or metal interaction with the associated waste matrix enhances mobility. Changes in soil environmental condition over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes, also may enhance metal mobility. The extent of vertical contamination is intimately related to the soil solution and surface chemistry of the soil matrix with reference to the metal and waste matrix in question (Wuana and Okieimen, 2011).

Clay minerals, oxides and organic matter exert a strong preference for some anions in comparison to other anions, indicating the existence of chemical bonds between the surface and the specific anion. Adsorption of metal cations has been correlated with such soil properties as pH, redox potential, clay, soil organic matter, Fe and Mn oxides, and calcium carbonate content. Anion adsorption has been correlated with Fe and Mn oxide content, pH, and redox potential. Adsorption processes are affected by these various soil factors, by the form of metal added to the soil, and by the solvent introduced along with the metal. The results of these interactions may increase or decrease the movement of metals in the soil water. The grain-size and chronological variation are important in the determination of metal content in single fractions of the grain-size spectrum of soil. It is advantageous to compare samples treated according to the same extraction procedures and analytical methods. The calculation of the phase concentration factor (PCF) values as the percentages of a specific metal association versus the percentage content of the respective carrier material makes the accumulation of metals in a specific phase more evident (Wuana and Okieimen, 2011).

Metals exist in the soil solution as either free (uncomplexed) metal ions (e.g., Cd^{2+}, Zn^{2+}, Cr^{3+}), in various soluble complexes with inorganic or organic ligands (e.g., $CdSO_4^{\circ}$, $ZnCl^{+}$, $CdCl_3^{-}$), or associated with mobile inorganic and organic colloidal material. The total concentration of a metal in the soil solution is the sum of the free ions concentration, the concentration of soluble organic and inorganic metal complexes, and the concentration of metals associated with mobile colloidal material. Metals will form soluble complexes with inorganic and organic ligands. Common inorganic ligands are SO_4^{2-}, Cl^{-}, OH^{-}, PO_4^{3-}, NO_3^{-}, and CO_3^{2-}. Soil organic ligands include low molecular weight aliphatic, aromatic, amino acids and soluble constituents of fulvic acids. Organic complexation of metals in soil is not well defined as inorganic complexation because of the difficulty of identifying the large number of organic ligands that may be present in soils (Wuana and Okieimen, 2011).

The presence of complex species in the soil solution can significantly affect the transport of metals through the soil matrix relative to the free metal ion. The metal complex may be only weakly adsorbed or more strongly adsorbed to soil surfaces relative to the free metal ion. Speciation not only affects mobility of metals but also the bioavailability and toxicity of the metal. The free metal ion is, in general, the most bio-available and toxic form of the metal. Several metals in the environment of concern can subsequently exist in soils in more than one oxidation state, such as: arsenic, As(V) and As(III), selenium, Se(VI) and Se(IV), chromium, Cr(VI) and Cr(III), and mercury, Hg(II), and Hg(I). The oxidation state of these metals determines their relative mobility, bioavailability, and toxicity. Hexavalent Cr is relatively mobile in soils, being only weakly sorbed by soils. Hexavalent Cr is also extremely toxic and a known carcinogen. Trivalent Cr, on the other hand, is relatively immobile in soil, being strongly sorbed by soils and readily forming insoluble precipitates, and is of low toxicity. Metals may precipitate to form a three dimensional solid phase in soils. These precipitates may be pure solids (e.g. $CdCO_3$, $Pb(OH)_2$, ZnS_2) or mixed solids (e.g., $(Fe_xCr_{1-x})(OH)_3$, $Ba(CrO_4, SO_4)$). Mixed solids are formed when various elements co-precipitate. There are several types of co precipitation, inclusion, adsorption and solid solution formation, distinguished by the type of association between the trace elements and the host mineral (Wuana and Okieimen, 2011).

Stability diagrams are used as a convenient technique for illustrating how the solubility of metal compounds varies with soil pH and with metal concentration (or activity). The diagram also allows some prediction of which solid phase regulates metal activity in the soil solution. The formation of a solid phase may not be an important mechanism compared to adsorption in native soils because of the low concentration of trace metals in these systems (Wuana and Okieimen, 2011). The biochemicals and humic substances provide sites (acid functional groups, such as carboxylic, phenolic, alcoholic, enolic-OH and amino groups) for metal sorption. The biochemicals form water soluble complexes with metals, increasing metal mobility. Binding of metals to organic matter involves a continuum of reactive sites, ranging from weak forces of attraction to formation of strong chemical bonds. Soil organic matter can be the main source of soil cation exchange capacity, contributing >200 meg/100 g of organic matter in surface mineral soils (Wuana and Okieimen, 2011).

Soil surfaces carry either a net negative or positive change depending on the nature of the surface and the soil pH. The charge arises from the association and dissociation of protons from the surface functional group. The permanent net negative charge on the surface is due to charge imbalance resulting from the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layers and/or substitution of Mg^{2+}, Fe^{2+}, etc. for Al^{3+} in the octahedral layers of aluminosilicate clays. The charge on the surface is not affected by changes in soil pH and hence, it is termed a permanent charged surface. Hydrogen ion concentration (pH) dependent charged surfaces are associated with the edge of clay minerals, with the surfaces of oxides, hydroxides and carbonates, and with organic matter (acid functional groups). With inner sphere complexation, metals are bound directly to the soil surface with no waters of hydration involved. This is distinguished from the exchangeable state by having ionic and/or covalent character in the binding between the metal and the surface. At low concentrations, metals are adsorbed at specific adsorption sites. These adsorbed metals are not removed by the input of major cations. With increasing concentrations, of metals, the specific sites become saturated and the exchange sites become filled (Wuana and Okieimen, 2011). Metals associated with these nonspecific sites are exchangeable with other metal cations and are thus potentially mobile. The affinity of a metal for soil surfaces is concentration dependent. The relative affinity of a soil surface for a free metal cation increases with the tendency of the cation to form strong bonds, i.e., inner sphere complexes, with the surface (Wuana and Okieimen, 2011).

Un-impacted soils from pre-industrial times have cadmium levels from 0.01 to 0.1$mgkg^{-1}$ and Lead levels from 0.1 to 1$mgkg^{-1}$. Current cadmium level stands at an average of 0.5 $mgkg^{-1}$ and lead at 30$mgkg^{-1}$. A simple mass balance of the heavy metal in the soil can be expressed as shown in equation 2.4 (Lombi and Gerzabek, 1998; Alloway, 1995):

$$M_{total} = [(M_p + M_a + M_f + M_{ag} + M_{ow} + M_{ip}) - (M_{cr} + M_l)] \qquad (2.4)$$

Where ‘M’ is the heavy metal, ‘p’ is the parent material, ‘a’ is the atmospheric deposition, ‘f’ is the fertilizer sources, ‘ag’ are the agrochemical sources, ‘ow’ are the organic waste source, ‘ip’ are other inorganic pollutants, ‘cr’ is crop removal, and ‘l’ is the losses by leaching, volatilization, and so forth (Alloway, 1995; Lombi and Gerzabek, 1998).

Metals tend to persist in the environment because they cannot be broken down but can merely be converted into other compound (metal species). The soil composition and reaction (dependent on soil pH and redox) determine the basic reaction possible in the soil. Metals occur in solution in the form of metal ions or of inorganic or organic complexes which are also adsorbed to the surface of clay minerals or clay – humus complexes. Some important bond types occurring in the soil occur in the sediment stage and include the – ionogenic, interchangeable bond to clay minerals, bound adsorptively, for example, to the surface of iron oxide and manganous oxides, as slightly soluble organic complex compound and bound for example to humic acids. Trace metals migrate from soil due to transition from solid phase to fluid phase to the water bodies and subsequently into the underground water. Critical importance in trace metal transformation is the accumulation in the food chain, from microorganisms and plants to animals especially humans.

2.8 Trace elements occurrence in plants

Plant analysis serves as useful sources of information on the elemental composition of plants matrices and on fluxes of elements between the biota, lithosphere and atmosphere. Generally, the elemental composition of plants, reflect the chemical composition of their growth media (i.e. soil, air, water, and nutrient solution). Several factors however, also, play vital roles in the determination of the elemental composition of a plant. Subsequently, even normal concentrations of trace elements in plants growing in various unpolluted environment show quite large variations (Markert, 1992). Metal accumulation in plants depends not only on environmental availability of elements but also on plant characteristics (species, age, state of health, temperature, moisture availability, substrate characteristics (Baker, 1983).

Toxic heavy metals entering the ecosystem may lead to geo-accumulation, bioaccumulation and bio-magnification. The trace or heavy metals accumulation in time in plants over time can affect negatively the physiological activities of plants (e.g. photosynthesis, gaseous exchange and nutrient absorption) which could result in reduction in plant growth, dry matter accumulation and yield (Suciu *et al*., 2008). Heavy metals get into plants via adsorption, binding onto the plant body and by absorption, penetrating into the inner matrix of the plant or through both processes concurrently (Lokeshwary and Chandrappa, 2006). Some trace elements are not toxic to plants and animals in small concentration (De Vries *et al*., 2007). However, lead, cadmium and mercury are quite toxic at low concentrations (Galas-Gorcher, 1991).

Plants are good environmental quality indicators and respond directly to air, soil and water (Diaz and Massol-Deya; 2003 Kabata-Pendias, 2000). In light of the fact that plants can naturally draw pollutants from their local environment, their chemical composition can indicate the degree of disturbances when assessed against the background values obtained from unpolluted vegetation (Masol-Deya *et al*., 2005).

Table 2.7, illustrates that the introduction of excessive trace elements to plants can result in the toxicity of plants and hence, lead to change of colour of leaves, inhibition to the germination of seeds and growth of plants or even death of the plant (Abbasi *et al*., 1992).

Inhibitory effects of excessive presence of certain trace elements in plants can result in among others, the blocking of the uptake of essential elements from the soil and hence, lead to the deprivation of plants of crucial nutritional substances (Altaf, 1997).

2.9 Environmental impact of mining activities

2.9.1 Acid mine drainage

The very low pH level of water seeping from mine refuse is due to the formation of concentrated sulphuric acid when FeS_2, pyrite and marcasite often associated with ores come in contact with water to form concentrated sulphuric acid. The oxidation of ferrous iron, sulphates and hydrogen ions is becoming a serious global problem.

Methods of controlling the problem of acid mine drainage include the thermodynamic measures which is the elimination of oxygen and the maintenance of reducing conditions and the kinetic effects (McCarthy and Durand, 2012).

The pathways for the release of heavy metals from tailings include:

- Structural failure from improper operational technique and design in regard to possible stimulus of catastrophic events such as earthquakes and flood.
- Direct discharge of mill waste water or total tailing to surface water.
- Dust from unstable and desiccated, wind-blown surfaces.

Table 2.7 Toxicity levels of trace elements and symptoms in plants (Brune and Dietz, 1996)

Elements	**Toxic MO Levels in Plants, Ranges, , µgg^{-1}**	**Toxicity symptoms in Plants**
Boron	10 – 50 >200 for tolerant crops	Marginal and tip chlorosis of older leaves
Copper	10 – 70	Chlorotic leaves and reduced branching, thickening and dark coloration in the rootlets.
Manganese	400 – 7000	Stunting, general chlorosis and nerotic leaf spots and brown spotting of older leaves.
Molybdenum	100 – 1000	Yellow or orange-yellow chlorosis, seedling injury and delayed maturity.
Nickel	8 – 147	Chlorosis, stunted root growth.
Zinc	95 – 340	Severe leaf scorching, reduced yield, and decreased net assimilation rate.

- Biologic concentration in plants and ultimately in animals
- Erosion of embankment surfaces.
- Leaching to the surface via capillary action due to high ground water leaching to subsurface waters by permeation.

2.9.2 Impacts of trace elements from mining on animals

Irrespective of the harmful effect of trace elements when consumed beyond certain optimal concentration, trace elements can generally pose serious health risk even at undetermined low concentration. Microgramal (μg) concentrations of the trace elements comprise part of the natural environmental of living organisms (human, animals, and plants) in the air, water and soil. Trace element speciation plays an important role in estimating mobility, biological activities and toxicity. For instance, methyl mercury is more toxic to animals than elemental mercury because it can easily pass through the blood brain barrier causing injury to the cerebellum and cortex.

Haxavalent chromium (Cr^{6+}) is much more toxic than trivalent chromium Cr^{3+}. At low concentrations, however, some of the elements are nutrients for plants and / or animal life and toxic at high concentrations. Metals of the 6th row (period) are potentially the most toxic elements of the periodic table i.e. Os, Ir, Pt, Au, Hg, Tl, and Pb. The relatively poor water solubility of the salts of these elements curtails their high toxicity.

Arsenic (As) is a metalloid that occurs in an elemental state to a small extent. Arsenic is a cumulative poison which inhibits thio (SH) group in enzymes. Chronic poisoning with arsenic, leads to weight and appetite loss, accompanied with gastrointestinal disorders.

Cadmium (Cd) is highly toxic to animals and mostly ingested by living organisms through the air, water and food. Inhalation of cadmium fumes or dust or from ingestion of heavily contaminated food and water leads to severe cadmium poisoning. Cadmium accumulates mainly in the soft tissues and more than half the body's burden of cadmium is found in the kidney and liver (Hunter *et al*., 1987).

Mercury (Hg) binds to the sulphydryl groups in many proteins in the body, while methylated mercury (Hg) is found mainly in the erythrocytes and brain. Mercury poisoning is associated with nausea, vomiting and diarrhea with bleeding, followed by death from gastro-intestinal and /or kidney lesions.

Lead (Pb) is moderately toxic to plants and animals. Lead poisoning leads to loss of appetite, weakness, anemia and colic. The excessive intake of Lead can also result in hypertension, renal dysfunction, and damage to the peripheral nervous system. The tetraethyl Lead is more toxic than either the methylated derivates or inorganic compounds.

The general effects of trace elements in humans and animals are summarized in tables 2.8, 2.9 and 2.10. Table 2.10 below summarizes the health effects of some trace elements when consumed, inhaled or in contact with the skin.

2.10 Special conditions for environmental sampling of trace elements

Some of the necessary considerations for environmental sampling for trace elements analysis have been described by Wong *et al*. (2003**)** as include:

- That sampling locations should be comparable (i.e. similar types of location).
- That records of climatic conditions (i.e. rainfall, wind-speed, temperature, etc.) be kept
- Consideration of seasonal variation

The use of silica based filter papers - do not use cellulose based filter papers. Silica based filters papers tend to be inert and much easier to handle. Use filter papers with greater diameter (i.e. one with diameters greater than fifteen centimeters (i.e. >15 cm) for greater sample size or collection area.

- The use of high purity acids for sample preparation so as to improve the QC/QA data. It also allows a low blank background and conveys a stronger statement to the formulated hypothesis.

2.11 Main sources of error in trace elements analysis

The predominant sources of errors in trace element analysis are changes in the composition of the samples under study brought about by: i) Loss of analyte ii) Occurrence of additional components in sample (interference) iii) Delivery of additional quantities of analyte to sample.

Table 2.8 Toxicity levels of trace element and their symptoms in livestock and body organs (Brune and Dietz, 1996)

Elements	**Toxic Mo level in body organs, µgg^{-1}**	**Toxicity symptoms in livestock**
Arsenic	>3 in liver, kidney	Reduced weight gain, blindness, dehydration and depression
Cobalt	58 – 69 in liver	Reduced feed intake, emaciation, and anermia and lack muscular coordination.
Copper	>15 in kidney 5 – 20 in blood > 150 in liver	Gastroenteritis, swollen gums, reduced hemoglobin levels, jaundice, metal – coloured kidney and splenic enlargement.
Fluoride	>5500 in compact bone >7000 in cancerous bone	Bones chalky white, soft and thickened and degenerative changes occur in liver and kidney.
Iron	>2000 in pigs blood	Reduced growth rate and feed intake, anorexia, diarrhea metabolic acidosis and death.
Lead	0.4 in kidney cortex and liver >0.2 in whole blood	Loss of appetite, weight has depressed stiffness of joint and anermia.
Molybdenum	Variable	Diarrhea, anorexia, depigmentation of hair and wool, neurological disturbance.
Selenium	0.3 in hair 2.2 – 3.3 in blood 21.2 – 39.3 in hoofs	Atrophy of heart, cirrhosis, of liver, cracking of hoof, lameness, loss of hair, stiffness of join and diarrhea.
Zinc	Variable	Gastrointestinal distress, anorexia, anemia and arthritis.

Table 2.9 Trace element toxicity in humans: Dosage and Symptoms (Brune and Dietz, 1996)

Element	Toxic dose	Symptoms of toxicity
Cadmium	10 µgd^{-1}continuous exposure for 50 years.	Acute: gastric cramps, vomiting, diarrhea, cough, headache, brown urine. Chronic: hypertension, malignancy, immune disorder, renal failure.
Copper	0.1 – 0.2 mgkg^{-1} body weight.	Wilson's disease and cirrhosis, haemolysis, hepatic necrosis, renal damage and salivary gland swelling.
Iron	20 -30 mgkg^{-1} body weight (> 60 mgkg^{-1} is lethal).	Mild – moderate: Vomiting, upper abdominal pain, pallor, diarrhea, drowsiness, Severe: Metabolic acidosis and shock (disruption of cellular electron transport).
Lead	80 – 100µgdL^{-1} (blood) >120µg 24 h^{-1} (urine).	Pallor, gingival lead line, anemia, multiple neurological symptoms (cognitive).
Manganese	Variable in different organs.	Psychiatric disorder followed by neurological disorder resembling Parkinson's diseases.
Mercury	Highly variable for both elemental and organic forms.	Acute: gastrointestinal track inflammation (oral, gastric, and colonic), abdominal pain, neurological deficit. Chronic: depression, irritability, confusion, tremor. Central Nervous System (CNS) damage: Visual and auditory defects, a taxa and cognitive disturbances.
Molybdenum	Unknown.	Epidemiological evidence of increased blood xanthine oxidase and incidence of gout.

Selenium	Average of 3180μgL^{-1} (blood) Average of 4990 μgd^{-1} (diet).	Hair loss. Nail deformities.
Zinc	Several grams required for acute toxicity 160 mgl^{-1} for Cu deficiency.	Acute: Vomiting, diarrhea, neurological damage (Zn shakes). Chronic: depression of copper utilization, Fe deficiency, lowered level of HDL cholesterol.

Table 2.10 Trace element and their potential effects on human health (Brune, and Dietz 1996; Mortvedt, 1996)

Trace Elements	Source	Potential Health Effect
Antimony	Discharge from petroleum, refineries, fire retardants, ceramics, electronics solders.	Increase in blood cholesterol, decrease in blood sugar.
Arsenic	Erosion of natural deposits, runoff from orchards and run-off from glass and electronics production wastes.	Skin damage or problems with circulatory systems, carcinogen.
Barium	Refineries, erosion of natural deposits, discharge from metal refineries and coal burning.	Increase in blood pressure.
Beryllium	Factories, discharge from electrical, aerospace, and defense industries.	Intestinal lesions.
Cadmium	Discharge from metal refineries; runoff from waste batteries and paints.	Kidney damage.
Copper	Corrosion of household plumbing systems; erosion of natural deposits.	Could exacerbate Wilson’s disease.
Lead	Corrosion of household plumbing systems; erosion of natural deposits.	Delays in physical and mental development in infants and children, deficits in attention span and learning abilities in children; Kidney problems and high blood pressure in adults.
Mercury	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands.	Kidney damage.
Selenium	Discharge from petroleum refineries, erosion of natural deposits; discharge from mines.	Hair or fingernail loss; numbness in fingers or toes; circulatory problems.
Thallium	Leaching from ore-processing sites; discharge from electronics, glass, and drug factories.	Hair loss, changes in blood, kidney, intestine, or liver problems.
Radium 228	Erosion of natural deposits	Increased risk of cancer.
Uranium	Erosion of natural deposits.	Increased risk of cancer, kidney toxicity.

The temperature of the sample and its changes, presence and intensity of solar radiation and the presence of living organisms in the sample may affect the intensity of the process and phenomena.

According to Namiesnik (2002) the sources of error that can distort the result of the determination of a trace component in a liquid sample are

- Contact of sample with laboratory air quality
- Residues of components of dishwashing mixtures
- Distilled water
- Reagents and solvents employed
- Contact with analyte
- Vaporization of the most volatile components
- Processes of adsorption – desorption (wall memory effect)
- Adsorption of analytes on a suspension
- Permeation of solution components through vessel walls
- Reaction of the analyte with vessel materials
- Chemical reactions among solution components.

Contact of analytes in gaseous and liquid mixtures with the walls of the vessels, tubings and appliances affect the concentration levels of trace and ultra-trace components enormously due to the adsorption and desorption of analyte on the surface of a solid, a process known as the wall memory effect and cross contamination.

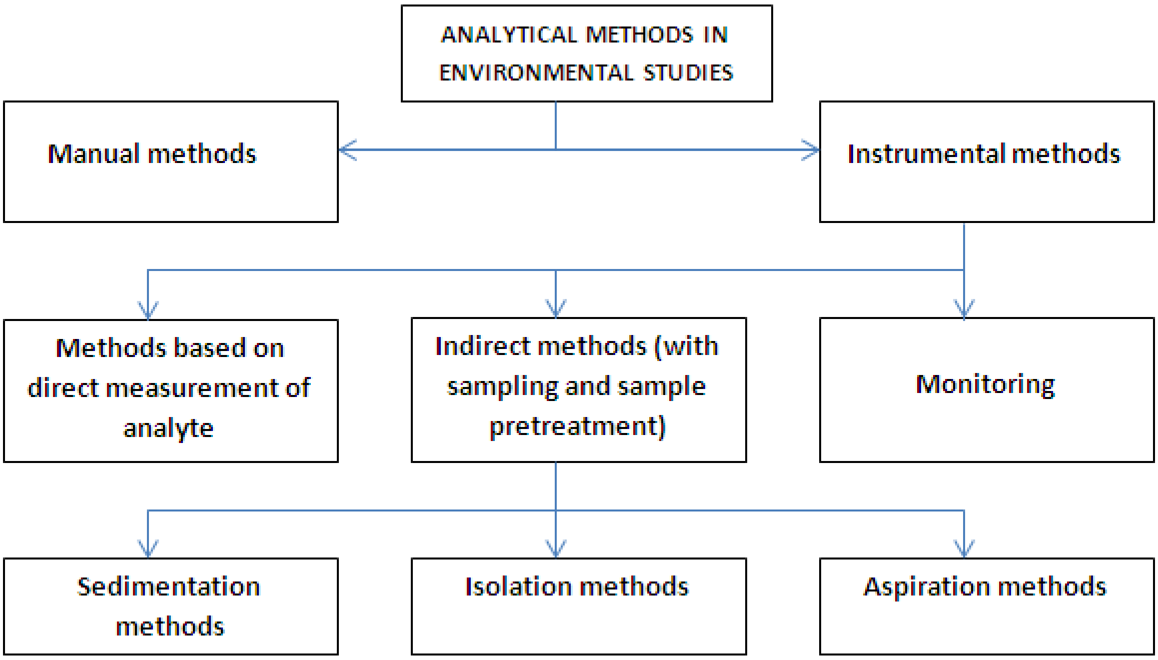
2.12 Analytical methods and techniques for environmental monitoring

All analytical methods and techniques used in environmental monitoring can be divided into two groups with respect to the method of analyte determination (Namiesnik, 1998), namely, the direct and indirect methods.

2.12.1 Direct methods In the direct method, analytes are determined directly in the sample without prior sample preparation. This approach is applicable only when the matrix is relatively simple (no interfering substance), and analyte concentration is higher than the detection limit of the method or instrument. Direct methods find only limited applications in environmental analysis and monitoring. Examples of methods which do not require sample preparation include:

- i) Potentiometric technique (ion selective electrode used in the analysis of surface waters), etc.
- ii) Graphite furnace atomic absorption spectrophotometry (GFAAS)
- iii) Atomic emission using inductively coupled plasma (ICP)
- iv) Proton-induced X-ray fluorescence (PIXE)g
- v) Neutron activation analysis
- vi) Surface analysis techniques (SEM, AES, XPS, SIMS, ISS, ESCA)

2.12.2 Indirect methods In the indirect methods, analytes present in trace and ultra-trace levels are detected not directly in the original matrix, but in a matrix resulting from sample preparation, analyte isolation and/or pre-concentration. Scheme 2.2 illustrates the main analytical methods used in environmental studies.



Scheme 2.2 Analytical methods in environmental studies (Namiesnik and Gorecki, 2001).

2.13 Sample preparation for trace elements analysis

The additional preparations included in the vast majority of analytical methods used in environmental analysis, make it possible to:

i) Increase analyte concentration in the final sample to a level higher than the detection limit of the instrument used
ii) Simplify the matrix and remove interference by replacing the original matrix with a recipient matrix (a substance solvent or gas).
iii) Average the sample composition
iv) Store the sample for prolonged periods of time (the concentrate is usually much more stable than the original sample) (Namiesnik and Gorecki, 2001).

The different sample preparation methods for trace elements analysis include: the precipitation, isolation and aspiration methods and are briefly discussed below.

2.13.1 Precipitation methods In the precipitation method, the analytes are separated from the original matrices by precipitation on the surfaces of suitable devices. Examples are the contact method of SO_2 determination in air and the determination of dust precipitation (Namiesnik and Gorecki, 2001).

2.13.2 Isolation methods In the isolation method, the environmental samples such as air, water, soil, etc are isolated in a vessel of known volume. Analyte amount or concentration in a particular sample is determined either directly by analyzing a liquot of the sample, or following additional stages of isolation and/or pre-concentration (Namiesnik and Gorecki, 2001).

Examples:

i) Collecting gas (air) samples in gas pipettes bags or other similar containers.
ii) Collecting water samples in suitable vessels

In both cases, the processes can be carried out manually or automatically using an auto sampler.

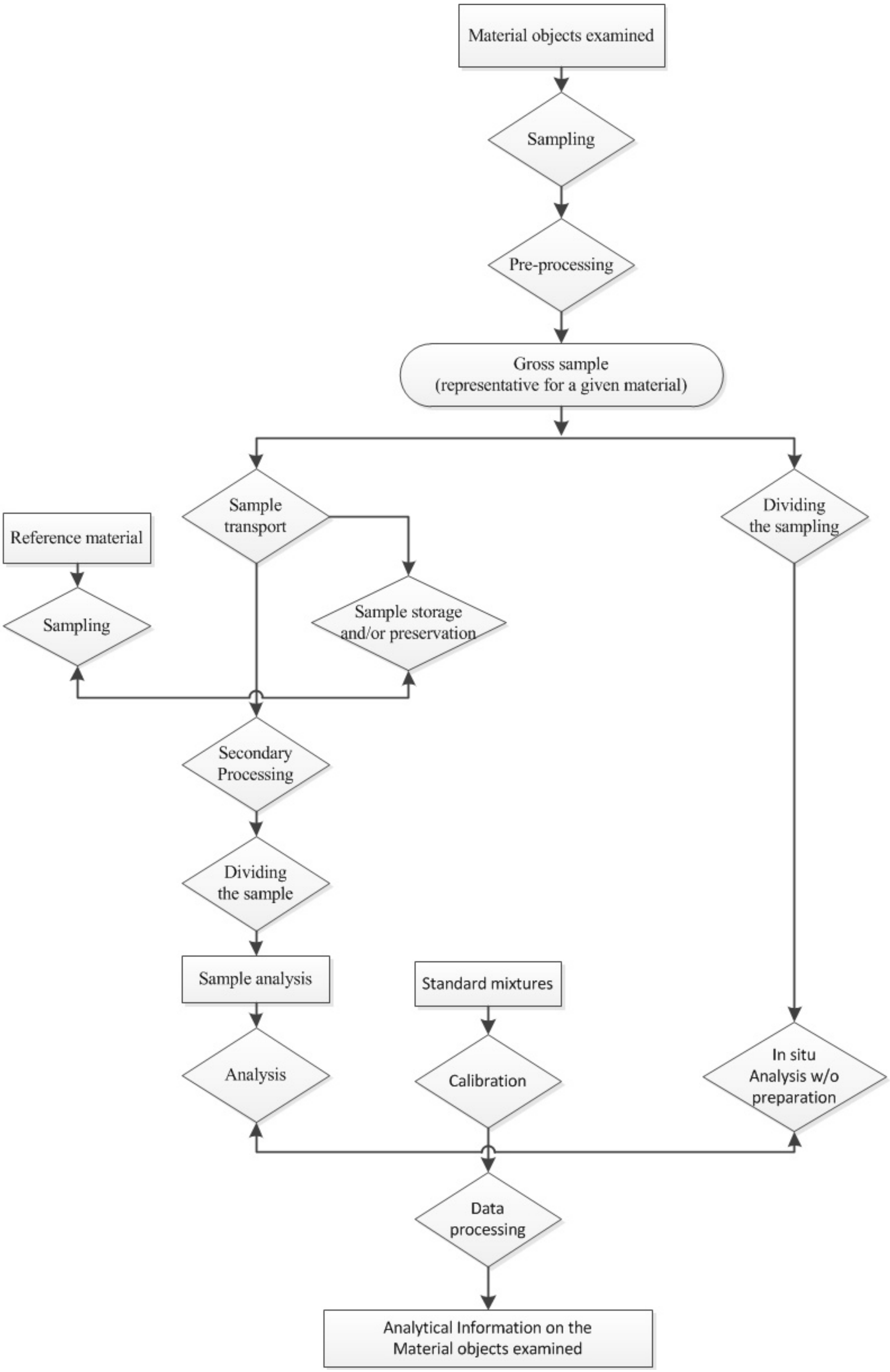
2.13.3 Aspiration method In the aspiration method, the sample or analyte isolation is carried out by forcing the flow of the sample through a suitable trap. When trap is equipped with a suitable (selective) filter, analyte are pre-concentrated during sampling. Examples include the:

i) Determination of dust concentration in atmospheric air.
ii) Determination of suspended particulate matter in water.
iii) Trapping of analytes from liquid or gaseous streams on a solid sorbent, in an absorbing solution, on the surface of a chemical reagent or in a cryogenic trap (Namiesnik and Gorecki, 2001).

Table 2.11 illustrates the different stages of sample preparation for final elemental determination, while scheme 2.3 details the main types of analytical tools used in trace elements analysis.

Table 2.11 Different stages of sample preparations for final elemental determination (Brune and Dietz, 1996)

Task	**Way of implementation**
Ensuring sample stability during transportation and storage.	Chemical conservation, Thermal conservation and lyophilization**.**
Sample homogenization.	Grounding, mixing and screening.
Removal of interfering components.	Dust removal (gaseous samples), suspension removal (liquid samples), Sample drying, Sample deoxidation removal of reactive components
Chemical conversion of analytes (derivatization) into forms easy to: Isolate, separate mixture components and Detect and quantitate	In situ derivatization (while sampling Analytes), Derivatization in column and derivatization
Exchange of sample matrix for one friendly to measuring device used.	Extraction of analytes from sample used: stream of washing gas suitable solvents (including supercritical fluids), membrane devices thermal desorber.
Increasing analyte concentration in examined sample to level enabling quantitative analysis.	Use of wide variety of analyte enrichment techniques (in many cases, this is connected with matrix exchange).



Scheme 2.3 Classification of the main types of analytical tools used in trace elements analysis (Namiesnik and Gorecki, 2001)

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CHAPTER 3

PUBLIC AWARENESS OF THE ENVIRONMENTAL IMPACT OF MINING ACTIVITIES IN LEJWELEPUTSWA DISTRICT OF THE FREE STATE, SOUTH AFRICA

3.1 Abstract

A survey was conducted to assess the public's awareness of mining activities. A validated structured questionnaire was administered to 94 randomly selected respondents in Lejweleputswa district. The questionnaire focused on evaluating the awareness of the members of the public about the impact of gold mining activities on the environment. Approximately 60 % of the respondents admitted to being concerned about the environmental pollution in the area with 57 % attributing the pollution to the gold mining activities. The mining activities were blamed for the high prevalence of tuberculosis and other sicknesses in the area. The wind condition (69 % of respondents) was indicated as a major factor influencing the level of pollution. The questionnaire revealed that there were reports made by the members of the authorities concerned with environmental pollution in the area without positive responses regarding their concerns. . There is subsequent disillusionment on the part of residents in light of negligence by the authorities towards addressing the environmental concerns in these mining areas of the Free State, South Africa.

3.2 Introduction

Mining is an important economic activity upon which many countries derive a substantial part of their revenues. In Africa, mining is responsible for about 10 % of South-Africa's GDP (Mining IQ, 2011), Angola (69.1 %), Algeria (33.5 %), Botswana (29.1 %), Guinea (21.0 %), Mauritania (20.0 %), Namibia (10.8 %) (African Mining Investment Environment Survey, 2011). South Africa remains the world's largest gold producer, although, the industry faces long-term decline because of its high production costs and falling gold prices (Mining IQ, 2011). The high gold costs are primarily due to the great depths of the South African mines. Other major minerals, in order of the value of total output, are coal, platinum-group metals, iron ore, copper, nickel, and manganese (Mining IQ, 2011).

Mining operations however, bring about debilitating effect on the environment through environmental destruction and the release of dangerous chemicals and heavy metals in quantities dangerous to plants and animals (Boamponsem, *et al*., 2010). Mining activities, through milling operations coupled with grinding, concentrating of ores and disposal of tailings, run-offs and leachates infiltration into ground water from bottom ash, flash ash and scrubber sludge deposited in settling ponds and landfills, provide obvious sources of metal contamination in the environment (Antwi-Agyei *et al*., 2009; Van Hook, 2009). Uranium and silver are two notable by-products of the gold mining activities and contribute largely to trace-element pollution in the mining areas. As, Cu, Pb, Zn, Hg and Ag trace-elements in the environment, have subsequently been associated with gold mining at Obuasi, Ghana (Antwi-Agyei *et al*., 2009).

Lejweleputswa – meaning ‘grey rock’ is the District Municipality area of the Free State, South Africa predominantly mined for gold and to a lesser extent diamond. This area is and lies in the North western part of the Free State, bordering on the North West province in the north and Northern Cape to the west – an area that also constitute the heart of the country’s agricultural belt, and includes two of the province’s nature reserves. The district comprises the local municipalities of Masilonyana, Matjhabeng, Nala, Tokologo, with the mining activities taking place mainly at the Matjabeng Local Municipality of the district. The district is home to towns; Brandfort, Bothaville, Hennenman, Welkom, Ventersburg, Virginia, Winburg, Theunissen, and Odendaalsrus. It is also one of the most mined areas in South Africa.

Current study used questionnaires to evaluate the level of public awareness about the impact of mining activities in the Lejweleputswa area of the Free State, South Africa. It was intended to ascertain the awareness level of the residents of this area about the actual environmental, health and social impact of the mining activities in the area. Focus was also placed on government’s effort to regulate and monitor mining activities and to address complaints from the public with regard to environmental pollution/damage resulting from the mining activities taking place in the area.

3.3 Materials and Methods

3.3.1 Study location

Figures 3.1 and 3.2 are map illustrations of the Free State Province depicting the Lejweleputswa District Municipality (LDM) and the Lejweleputswa District Municipality with the Local Municipalities of the district respectively. The study was restricted to the Matjabeng local municipality in the Lejweleputswa District Municipality of the Free State where most of the mining activities are taking place. Questionnaires were administered to randomly selected people on voluntary basis in Welkom town centre where most commercial activities take place.

The choice of the locations was to be able to meet people of diverse walks of life residing in the area of study to primarily determine their awareness about mining in the area and the impacts thereof on the environment.

3.3.2 Questionnaire design

Questionnaires (Appendix A) were prepared covering all necessary questions expected to give insight into the level of awareness of the members of the public residing in the area where active mining activities are taking place with regard to health, environmental and social impact of mining activities in the area. The questionnaires comprising open and closed-ended questions were administered to the members of the public in Welkom town to self-complete the questionnaires immediately and be collected for analysis. The town of Welkom was preferred because it is the biggest town in the study area and the town in which most of the miners resided.

3.3.3 Data collection

Simple random sampling method w. For data collection, surveys in the form of questionnaire was used to collect data. Surveys are recommended by William and Mohamed (2012), given their suitability in studies that have a not less than 30 participants. As a result, questionnaires were be used to collect data from sampled respondents. The use of questionnaires in the study

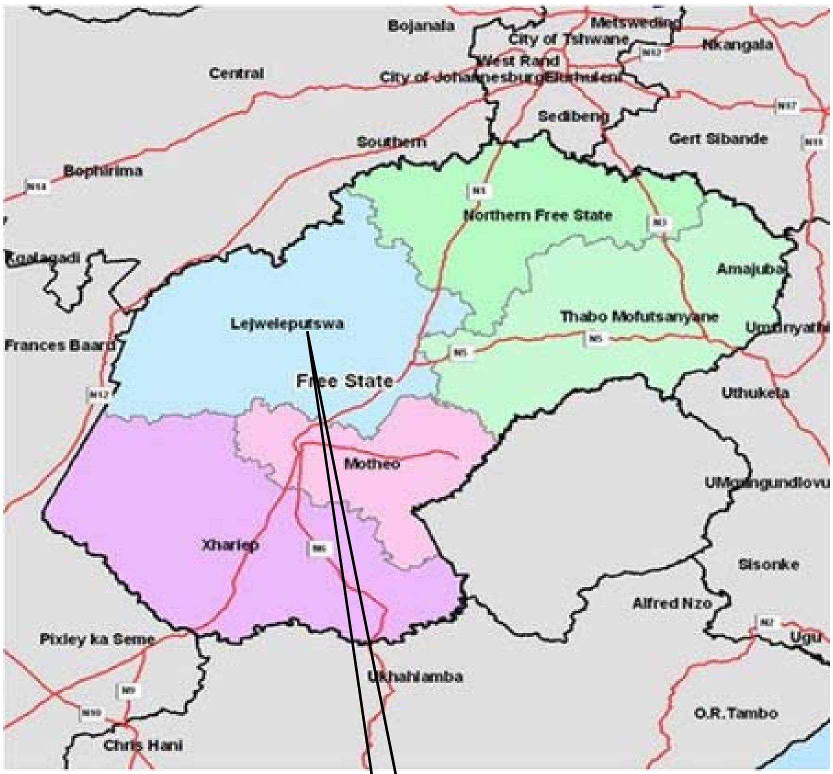

Figure 3.1 Map of Free State depicting the location of the Lejweleputswa District Municipality (LDM)

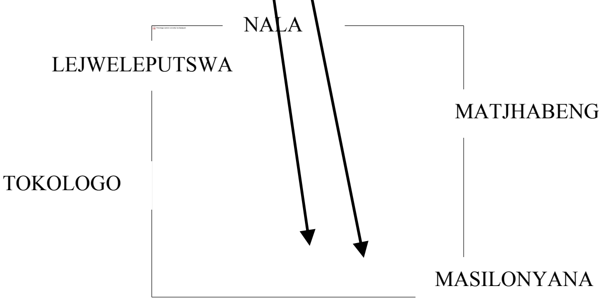

Figure 3.2 Map of Lejweleputswa District Municipality depicting the Local municipalities of the district

made the study cost-effective and helped this study to get perceptions and level of knowledge of respondents about food safety, hygiene and handling. The collected data was both qualitative and quantitative in the form of nominal, ordinal and some interval data types (Keller, 2014). Randomly selected members of the public were served with the questionnaires and requested to complete them and submit immediately. Interviewees were randomly selected at the Central Business District (CBD) of the town (Welkom) - close to the town's main library - and the questionnaires administered to them. Interviewers previously groomed on the questionnaire format and purpose described the essence of the study to the interviewees before allowing them to complete the questionnaires.

3.3.4 Data analysis

The various questions in the demographic section and the main body of the questionnaire were assessed by physically enumerating the nature of responses by respondents with regard to the question. Total number and percentage of respondents replying in affirmative or non - affirmative were determined by physical enumeration and calculation. Microsoft Excel 2010 was used for processing and plotting the data obtained from the questionnaire analysis.

3.3.5 Limitations to the study

The questionnaire was lengthy in nature, so it required more time to complete. Furthermore the technical nature of the questionnaire left some questions not be to completely answered. Additionally uncertainty of locating the interviewees in case the questionnaires were left behind for completion of answering resulted in interviewees not being given the leisure of time to complete questionnaires.

3.4 Results and discussions

3.4.1 Demographic characteristics of the respondents

Table 3.1 shows the profile (demographic characteristics) of the respondents to the questionnaires.

Table 3.1 Demographic characteristics of respondents

Characteristics	Respondents n (%)	Characteristics	Respondents n (%)
GENDER		**RACIAL ORIGIN**	
Female	34 (36 %)	Black	93 (99 %)
Male	60 (64 %)	Asians	1.0 (1 %)
AGE GROUP		**EDUCATIONAL LEVEL**	
<18	24 (26 %)		
18 – 30	42 (45 %)	Non	2.0 (2 %)
31 – 39	13 (14 %)	Primary	1.0 (1 %)
40 – 49	10 (11 %)	Junior secondary	10 (11 %)
50 -64	5.0 (5 %)	Senior secondary	36 (38 %)
		Tertiary	45 (48 %)
NATIONALITY			
		RELIGIOUS GROUPING	
South African	92 (98 %)		
Nigerians	1.0 (1 %)	Christians	93(99 %)
Asians	1.0 (1 %)	Moslems	1.0 (01%)

Tables 3.2 to 3.4 present the summary of the statistical results of the questionnaire investigation.

A total of 94 questionnaires were completed and returned by randomly selected respondents. These were to be correctly filled and suitable for analysis to derive the relevant information sought by this study. Table 3.1 indicates that respondents' ages ranged between 18 and 64 and most were of a Christian faith. A majority of the respondents fell within the 18 – 30 age group (42 %), followed by the < 18 age group (24 %). The males (64 %) formed the bulk of the respondents, almost double the next largest group of respondents - the females, (36 %). All respondents were of black race (100 %) and 98% were of South African nationality. The highest number of the respondents had tertiary education or were tertiary graduates (48 %), whereas (38 %) were senior secondary qualification. Only 11% of the respondents had junior secondary and 1% primary school level of education. Only 2% of respondents did not have any formal education (Table 3.1).

From Table 3.2, it is clear that most people 72 % were quite knowledgeable about mining activities taking place in the area. More than half of the respondents (79 %), have a good knowledge about the minerals mined in the area. Respondents (57 %) were aware of the environmental concerns due to mining activities with about51 %) concerned about food pollution in the area. Only about (38 %) of the inhabitants knew about the hazardous materials (chemicals) used in mining operations, with cited hazardous materials ranging from chemicals (mainly acids), explosives, dust, smoke, mud, etc. Certainty about the entry of the mining chemicals into the environment is not firm, suggesting that residents do not blame pollution in the area entirely on the mining activities taking place in the area.

Problems relating to mining waste may be rated as second only to global warming and stratospheric ozone depletion in terms of ecological risk. The release to the environment of mining waste can result in profound, generally irreversible destruction of ecosystem (Durand, 2012). The effluent produced by Acid Mine Drainage (AMD) enters the surface water bodies and the ground water and pose threat to humans, domesticated animals and ecosystem in general. Mine effluent affected by Acid Mine Drainage (AMD), decimate the aquatic life in the water bodies into which the effluent is discharged (Roback and Richardson, 1969; Adendorff, 1997; Jooste and Thirion, 1999). The salinity of river systems that receive mine effluent is greatly affected by the volume of sulphates contained in the effluent.

Table 3.2 Public awareness of the impacts of mining activity(ies) on environment

	Response, n (%)		**Response, n (%)**
Question Statements	**Yes**	**Question Statements**	**Yes**
Knowledge about:		**Knowledge about**	
1. Mining activities in the area	68 (72 %)	7. Seasonal variation i n the pollution level	44 (47 %)
2. Number of mining companies operating in the area	39 (42 %)	8. Seasonal variation in sicknesses suffered in the area	54 (57 %)
3. Minerals being mined	74 (79 %)		
4. General concern about the environmental pollution	54 (57 %)	9. Health impact of these materials in the environment	51 (54 %)
5. Concerns about food pollution	48 (51 %)	10. Wind contribution to pollution level in the area	65 (69 %)
6. Seasonal variation in the nature of pollutants	45 (48 %)		

With regard to knowledge of any seasonal variation in the nature of pollutants, (48 %) admitted to the observation of variation in nature of pollutants depending on the season, with (47 %) observing a variation in pollution level in different seasons.

Only 37 (39 %) people admitted to the knowledge of the use of hazardous materials and chemicals in the mining activities in the area with about 33 (35 %) accepting that the hazardous chemicals polluted the environment. With numerous mountain heaps of slime around the area, only 55 (59 %) of respondents knew they were mine wastes.

Percentage of respondents that indicated that the drinking water, soil, underground water and plants were 63 %, 74 %, 58 % and 66 % respectively were most polluted. Tables 3.3 elaborated on the hazardous nature of materials/chemicals used and introduced to the environment through mining activities as well as the nature of sicknesses suffered by the inhabitants of the area as a result of the effect on the people. Table 3.4 on the other hand summarizes the responses with regard to questions relating to the pollution of different environmental segments with chemicals emanating from mining activities in the area.

Most residents (58 %) were concerned about the environmental pollution in the area citing bad smell of the ponds, sewerage dump, sicknesses, animal deaths, bad taste of drinking water. as some of their reasons. Results from the questionnaire pointed out that residents (52 %) in the Lejweleputswa Municipal District (LMD) are fearful that the pollution in the area is widespread, contaminating the water, food, soil, plants. About 55 (59 %) of respondents expressed concern about the chemical nature/content of the rainwater and even more concerns expressed about pollution of drinking water by about 59 (63 %) of the respondents. The percentage of respondents that expressed concern about the chemical pollution in soil, plants, animals/meat and food was 74 %, 66 %,59 % and 42 % respectively, as a result of mining activities. Figure 3.3 presents the response pattern with regard to the pollution of different environmental segments with chemicals used in mining activities in the Lejweleputswa District Municipality.

Table 3.3 Percentage of respondents' on knowledge of impacts/ effects of hazardous material on human health (n=94)

	Response, n (%)		**Response, n (%)**
Question Statements	**Yes**	**Question Statements**	**Yes**
Knowledge about:		**Knowledge about:**	
11. Hazardous materials/chemicals		15. Reports of environmental concerns to Authorities	
used in mining	37 (39 %)	16. Reports on miscellaneous issues on mining impact	44 (47 %)
12. Entry of hazardous materials in		on the society	
the environment	33 (35 %)	17. Positive response from authorities	43 (46 %)
13. Slime dumps as mine waste	55 (59 %)		27 (29 %)
14. Sicknesses suffered in the area			
attributable to mining activities:	33 (35 %)		
Tuberculosis	32 (34 %)		
Cancer	38 (40 %)		
Asthma	9.0 (10 %)		
Diarrhorea	17 (18 %)		

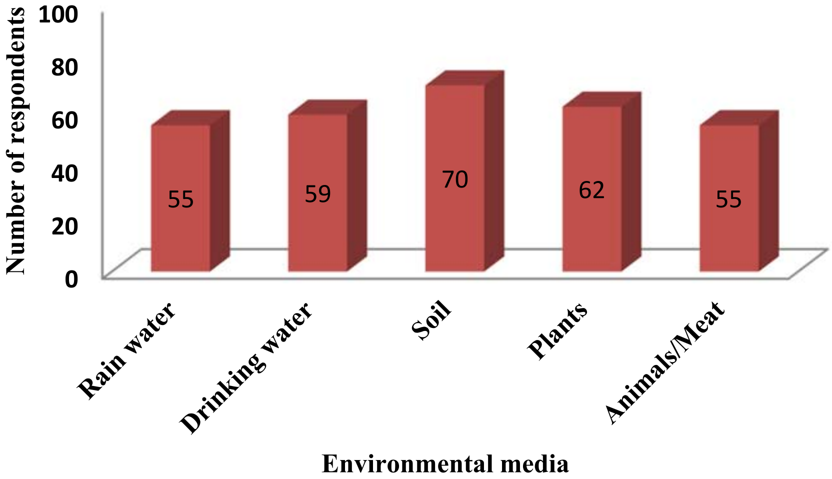

Figure 3.3 Number of respondents attributing pollution from mining activities in different environmental segments

Approximately 35 % of the respondents attributed some of the sicknesses suffered in the area to the environmental pollution due to the mining activities with cancer and tuberculosis ranking the highest among diseases. The prevalent sicknesses suffered in area and the number of respondents attributing their occurrence due to the pollution resulting from mining operations in the area is shown in figure 3.4.

Run-offs from slime dams, rock dumps, mine voids via seeps and decanting form the pathway through which metals enter the river system. Metals also enter the ground water by means of seepages of rainwater through mine dumps and the decanting of mine effluent from the slime dams into the ground water (Kleywegt, 1977; Jones *et al*., 1988; Naicker *et al*., 2003). Acid Mine Drainage containing metals can also seep through shallow holes and cracks in the dolomites linking the surface run-off to the water table and directly from the mine void into the Karst system above as the ground water level rises (Swart *et al*., 2003).

Gold mines in general generate Acid Mine Drainage containing high concentrations of metals such as manganese, aluminium, iron, nickel, zinc, cobalt, copper, lead, radium, thorium and uranium (Venter, 1995; Coetzee *et al*., 2006).

About (51 %) of the respondents expressed concern about food pollution due to mining activities, linking it to the negative health impact on inhabitants of the area. Heavy metals, including radionuclides accumulate in the sediments affected by mine effluent (Coetzee *et al*., 2006). Plants, including grass, vegetables, fruits and other agricultural products, absorb metals through their roots when exposed to such metals in the soil.

Depending on the concentration of the metal and the duration of exposure to the metal, exposure to any of the trace-elements could be fatal to organisms including humans (Smith and Heath, 1979; Venter, 1995; Adendorff, 1977; Jooste and Therion, 1999).

Forty eight percent of respondents reported that the nature of pollutants depended on seasons. Respondents (47 %) indicated observing variation in levels in different seasons, whereas (48 %) indicated that there was variation in pollutants in different seasons. There is also, a clear seasonal trend in sicknesses suffered by residents with about (61 %) of the respondents in agreement and (33 %) disagreeing.

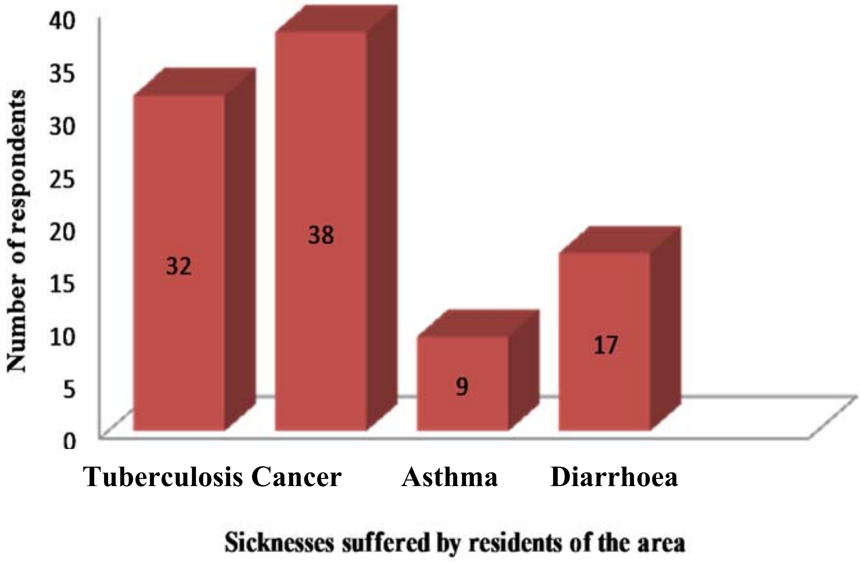

Figure 3.4 Number of respondents attributing sickness to the mining activities in the Lejweleputswa Municipal District

In the area, (57 %) of the respondents believe it depended on the season in the area. Fifty four percent of the respondents attributed health problems to material introduced to the environment as a result of mining activities. Respondents (69 %) agreed that wind direction and speed in the area contributed to the elevation of pollution level in the area. Wind condition is obviously a strong factor affecting pollution level in the area. Wind condition was suggested to play significant role in exacerbating the spread of pollution by eroding mine/slime dumps, blowing and transporting pollutants all around the vicinity.

There are however, suggestions of seasonal trend in pollutants levels in the area. Air pollution level seems to peak during winter due to burning of woods, coals and charcoal to warm up homes. Lack of grass on the ground during winter was stressed as primary reason for dust pollution in the atmosphere. Also, autumn – a period just succeeding the winter, blends gradually with winter presenting with drastic increased dust particles in the atmosphere due to escalated wind action.

In light of the extent of pollution resulting from the mining activities in the Lejweleputswa Municipal District, 59 (63 %) of residents in this district of the Free State, South Africa admitted to the knowledge of the negative effect of the pollution on the members of the public resident in the area. Residents occasionally report issues of environmental pollution to relevant authorities with emphasis on pollution related to mining activities. However, it was that there were clearly no positive responses from authorities to address the concerns of residents. There seems to be lethargy on part of residents and authorities to address the environmental issues. The questionnaire also indicated that illegal mining operation appears to be rife and that perpetrators seem to be making decent living out of the practice.

To address issues of environmental impact of mining activities on the environment, it could be suggested that the mining companies should all have a training program for all their staff on environmental issues, develop safe and good waste disposal mechanisms. Mining companies should therefore be urged to adopt green methods by ensuring the use of good and quality materials that are safe for the environment by cutting down drastically on the use of hazardous chemicals and other materials/equipment. Clear emphasis is placed on joint involvement of the communities to address environmental issues with strong engagement on community education on the impact of mining activities on human health and the environment.

3.5 Conclusions

The results of the current study suggest that the environment around the Lejweleputswa area of the Free State experiencing extensive degradation due to the mining activities taking place in the area. There are obvious effect of the environmental pollution on the residents of the area is the prevalence of sicknesses such as tuberculosis, skin diseases, rashes, respiratory infections etc. The excessive mine waste dust blown into the atmosphere by wind is a major concern to residents around the vicinity of the mine dumps.

The underground water in the area and subsequently, the drinking water, is not safe and of the sanitary standard that would be expected. There was explicit expression by residents that neither the government nor the mine officials are doing enough to bring the pollution in the area under control. Responses on efforts by mining companies and government to address issues of pollution in the environment in the area tend to suggest that there are also not enough programs in place to address the plight of the residents of the area with regard to the pollution of the environment and education of the public thereof.

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CHAPTER 4

EVALUATION OF TRACE ELEMENTS IN THE ENVIRONMENT AROUND THE LEJWELEPUTSWA AREA OF THE FREE STATES, SOUTH AFRICA

4.1 Abstracts

Soil, leaves, water and sediment obtained from six locations in six towns in the Lejweleputswa District Municipality (LDM) area of the Free State, South Africa were analyzed for trace elements using an ICP-OES. Analysis was conducted on monthly basis for six months – Oct-Dec 2012 and April-June 2013. The soil analysis showed that Calcium was the most prominent pollutant in the soil in all the studied towns. Fe was the second most abundant pollutant in the soil, followed in the order of abundance by Magnesium, Sulphur, and Phosphorus. The results obtained from Acacia Karroo leaves confirmed the migration of pollutants from the soil to plants. The leaves analysis also indicated Calcium as the most prominent pollutant in the leaves. The highest concentration of Calcium (100ppm) in the leaves in all the studied towns was observed in Allenridge in April, 2013 and Brandfort, Theunissen and Welkom in June, 2013. The lowest concentrations of calcium (0.38 %) in the leaves occurred in Theunissen in November, 2012. The second most abundant element in the leaves was Magnesium with concentrations greater than 1.0 ppm. The lowest and highest concentrations of Mg in the leaves of 0.05 % and 0.2 % occurred in Virginia during the month of April, 2013 and October, 2012 respectively. Iron, Suphur and Phosphorus also, occurred quite significantly, strongly indicating the occurrence of pyrite (FeS) in the area.

The analysis of water obtained from water bodies (streams) indicated that Ca was also by far the most predominant pollutant in the water bodies in the district. Magnesium was the second most abundant trace element in the water in the area was, followed by Sulphur. The water bodies in Allenridge were the most polluted in the municipality, followed by those

in Welkom and then Virginia. Allenridge, also, had the highest average Ca concentration, followed by Odendaalsrus, then Welkom and Virginia. The highest Mg concentration in the water bodies also occurred in Allenridge, followed by Welkom. Generally, Mg and S were the second most dominant pollutants in the water bodies in the area.

Sediment obtained from the waterbeds of the water bodies in the area also showed that the major pollutants in their order of occurrence were Ca, Fe, Mg and S. Calcium presented as the major pollutant, followed by Fe and then Mg. Al, S and Mn also featured prominently in the sediment. The highest average concentrations of Ca in sediment occurred in Welkom at 2.57 % and Mg in Brandfort at 0.60 %.

The high trace element concentration in sediment emanate from the deposition of soil content of trace elements to waterbeds. Calcium distribution in sediment occurred the highest in Welkom and Allenridge, whereas Mg distribution occurred highest in Brandfort. Subsequently, Ca and Mg concentration ratio is highest in Welkom followed by Allenridge.

4.2 INTRODUCTION

Lejweleputswa Municipal District (LDM) area of the Free State is one of the most mined areas in South Africa. Rich in gold and diamond, there are about five mining companies (Goldfieds, Harmony, star Diamond) operating in the area. In light of the enormous amount of chemicals used in mining activities and due to the disposal of tailings, the environment around mining areas is often polluted with trace elements (Antwi-Agyei *et al*., 2009). Knowledge of the spatial and temporal distribution of trace elements in the environment gives insight into the impact of the mining activities in an area (Taylor *et al*., 2011*)*. Drainage from abandoned or inactive mines and tailings from active mines contribute large quantities of toxic trace elements to the environment. Gold mining in recent times has become unpopular as it is regarded as a significant source of trace elements such as Hg, Pb and heavy metal contamination of the environment owing to activities such as mineral exploitation, ore transportation, smelting and refining, disposal of the tailings and waste waters around the mines (Essumang *et al*., 2007; Hanson *et al*., 2007; Singh *et al*., 2007).

The soil mainly acquire trace elements through inheritance from soil parent materials or input through human activities (anthropogenic source) involved in the transformation, e.g., use of fertilizers, organic manure, industrial activities, municipal waste, irrigation and wet and / or dry depositions. Soil contamination with heavy metals can also be as a result of the disposal of metalliferous tailing from mines. Acid ore tailings also contribute high concentrations of metals and low pH leachates to the soil shortly after exposure to the air. The problem of the release of high concentration of trace metals to the environment is peculiar to coal mines and can lead to severe pollution to the local soils. Trace metal accumulation in the soil could also be due to atmospheric deposition, and from point and non-point sources. Polluted soil can contain metal concentration of 100 – 1000 times greater than their background (Jiang *et al*., 2004). The soil metal retention is dependent on the geology of an area, presence of water soluble metals and insoluble metals in association with soil water movement through the vadose zone to groundwater (Mclean and Bledose, 1992). The soil origin and the pedogenetic processes leading to the soil formation largely determine the level of the metal content of the soil (Herediaa and Cirellib, 2008a).

Trace metal mobility in the soil is dictated by a number of factors such as the metal properties, the quantity and type of adsorption places, pH, concentration of complexing anions (organic and inorganic) and cations in the soil solution (Alloway, 1995). Upon contact with the soil, metal absorption does not occur to a great extent until metal retention capacity of the soil is overloaded, or until metal interaction with the associated organic matter enhances mobility (McLean and Bledose, 1992).

Metals occur in the soil in different forms such as in solution, due to dissolution in the soil, occupying exchange sites on inorganic soil constituents, specifically adsorbed on inorganic soil constituents, associated with insoluble soil organic matter, precipitated as pure or mixed solids, present in the structure of secondary minerals, or present in the structure of primary mineral. The soil attenuation index parameters such as clay content, organic carbon, CEC and soil pH are determined by the landscape position and phreatic depth (Heredia and Cirellib, 2008 a, b).

Plants on the other hand, are a good environmental quality indicator and respond directly to air, soil and water quality (Diaz and Massol-Deya, 2003; Kabata-Pandias, 2000).The chemical composition of plants can thus be used as an indicator of the degree of pollution or chemical proliferation in an area when compared with background values from a relatively unpolluted area (Ramamurthy and Kannan, 2009). Heavy metals are known to get into plants through adsorption (the binding of materials on the surface) or absorption (the penetration of metals into the inner matrix) or the occurrence of both mechanisms concurrently.

Excessive amount of trace elements lead to the toxicity of the plants leading to change in the physical appearance such as change in the colour of the leaves, inhibition of seed germination, stunted growth or even death (Ramamurthy and Kannan, 2009). lso, excessive intake of some trace elements by plants can lead to the inhibition of the uptake of other essential elements leading to the deprivation of essential elements to the plants by absorption through the soil (Ramamurthy and Kannan, 2009). Furthermore, trace elements accumulation in plants could have a negative influence on the physiological activities such as photosynthesis, gaseous exchange and absorption of nutrients. Consequently, crops could suffer from stunted growth and a reduction in dry matter accumulation and yield (Suciu *et al*., 2008).

Chemical toxicity in plants could also result when certain ions are taken up with the soil-water and accumulate in the leaves to a concentration that can damage the plant. The degree of damage depends upon time, concentration, crop sensitivity and crop water use, and if damage is severe enough, crop yield is reduced. Toxicity symptoms can appear on almost any crop if concentrations are high enough. Toxicity often accompanies or complicates a salinity or infiltration problem and may also occur even when salinity is low. Leaf absorption speeds up the rate of accumulation of toxic ions and may as well be a primary source of toxicity. Many trace elements, in addition to sodium, chloride and boron, are toxic to plants at very low concentrations.

Subsequently plants can be analyzed to determine the level of environmental pollution in an area as their elemental composition reflects the chemical composition of growth medium (soil, air and solutions) (Diaz and Massol-Deya, 2003; Kabata-Pendias, 2000). Trace metal absorption through the plant roots is dependent on the speciation of metal and soil characteristics and type of plants species. The effects of soil contamination on plants metal uptake as well as translocation and toxicity or ultra-structural alterations can be approximated by the extent of metal mobility and plant availability (Luo and Rimmer, 1995, Sresty and Madhva Rao, 1999; Chandra Sekhar *et al*., 2001). Plant absorption of trace metals is dependent on a number of factors such as the environmental availability of the elements, plant characteristics such as the species, age, health etc. and factors such as temperature, moisture availability, substrate characteristics, etc. (Baker, 1983).

In aquatic ecosystems, heavy metals are among the most persistent pollutants because of their resistance to decomposition under natural condition (Khan, 2011). High concentration of trace metals can be released into the aquatic environment as a result of leaching from bed rock, atmospheric decomposition, water - drainage run off from river banks and discharges from urban and industrial waste water (Rabee *et al*., 2011). Both anthropogenic pressure and natural processes account for degradation of surface and ground water quantity and quality (Carpenter *et al*., 1998). Industrial effluents, agricultural runoff, transport, burning of fossil fuel, animal and human excretion, geochemical weathering and domestic wastes could all contribute trace elements into the water bodies (Rabee *et al*., 2011).

The quantity of surface water depends mainly on the topography of the area, weather, as well as seasonal conditions (Canli and Atli, 2003). The geochemical signature of a water body is linked to the mineralogical and chemical composition of the aquifer formation, the chemical characteristics of infiltration water such as Hydrogen ion concentration (pH), Redox potential (Eh) and Partial pressure of Carbon dioxide (pCO_2), the surface exchange, the physical and biogeochemical conditions prevailing in the aquifer and the interaction between water and rock. The presence of any trace elements in the aquatic ecosystem interferes with the beneficial use of water bodies because of toxicity. There is however, no single mechanism or process that exhaustively explains the various processes occurring in water, hence, trace elements in water behave in a typical manner (Akhilesh *et al*., 2009).

With regard to sediments, metals are absorbed onto and incorporated into sediments, resulting in higher concentrations (Chan, 1995 ab; Cheevaporn *et al*., 1995; Borg *et a*l., 1996; Jeon *et al*., 2003; Schmitt, 2003). The mobility of solid phases from soils to sediments depends on the physiographic characteristics of the basin, such as topography, land use and vegetation cover (Batista, 2012). Reduced circulation or dispersion of sediment bound heavy metals makes sediments susceptible to contamination (Güngüm *et al*., 1994). Sediments are subsequently, considered to be the ultimate sink for many contaminants and therefore pose the highest risk to aquatic environment as a source of pollution (Bervoets *et al*., 1994; Forbes *et al*., 1994). Sediments are usually composed of a combination of lithogenic, authigenic and biogenic components such as mineral grains, organic matter, sulfides and carbonates. Heavy metals may be attached to any of these phases in proportions which depend on the physicochemical conditions of the sediment and associated water (Coetzee, 1993; Baeyens *et al*., 2003). The mobilization of chemical elements within the mining areas is mainly due to the physical processes associated to particulate matter, the transportation as suspension, or even, as chemical species in solution and later the deposition in sediments or the precipitation, respectively (Batista *et al*., 2012).

In recent times, trace element analysis is conducted primarily to assess whether trace elements are present in the environment at concentrations that are detrimental to aquatic biota or human health (Forster *et al*., 1996). It has been shown that sediment contamination is widespread and that metals are among the contaminants most often identified. Trace elements enter the terrestrial and aquatic environment via the atmospheric deposition and through point and non-point source releases to surface water. Trace elements in the atmosphere are often derived from natural sources such as through volcanic emissions

(Richardson, 2002) and anthropogenic activities such as combustion of municipal solid waste (Germani and Zoller *et al*., 1994), power plants releases from metal smelters, automobile emission and biomass burning (Rice, 1999). Point sources of trace elements include municipal sewage sludge, effluent to surface waters, coal- fired power plants, direct releases to water courses from industrial activities, and in some areas, acid mine drainage (Rice, 1999).

Non-point sources of trace elements include natural weathering of geologic materials and anthropogenic sources such as runoff of manure and artificial fertilizers from farm fields, releases from wear of automobile parts (Rice, 1999), and irrigation return flow (Stephen, *et al*., 1999). Trace elements emanating from industrial activities and sources include: from agriculture (As, Cu, Hg, Pb, Se and Zn); electrical power (As, Cd, Cu, Hg, Pb, Ni, Se, and Zn), metallurgy (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn); and wood and pulp (As, Cd, Cr, Cu, Hg and Pb) (Rice, 1999; Stephen, *et al*., 1999). Due to the extensive use of chemicals in mining operations, the environment around mining areas, are often polluted with different types of chemicals. Whereas trace elements such as Fe, Mn, Cu, Zn, Co, Ni etc. are very important for proper functioning of the biological system and their deficiency or excess in humans can result in health disorder and others such as Pb, As, Hg, etc., are not only biologically non essentials but definitely toxic. According to Akhilesh *et al*.; (2009).Cr, Pb, Cu and Zn are well known to cause health hazard in animals.

Lejweleputswa area of the Free State is extensively mined for gold and to a lesser extent diamond and the soil, plants, water and sediment in the areas are subsequently expected to be polluted with chemicals. The main purpose of this study was to quantify the trace elements in the environment in light of the numerous mining activities taking place in the area.

4.3 MATERIALS AND METHODS (FOR ENVIRONMENTAL ANALYSIS)

4.3.1 Study areas

The study was conducted around the Lejweleputswa area (district municipality) of the Free State, located at 27° 58´S 26° 44´E 27.967°S 26.733°E, in Free State, South Africa (Figures 3.1, 3.2 in the previous chapter and 4.1). The Lejweleputswa area is situated in the north western part of the Free State and borders, North West Province to the north; and Northern Cape Province to the West. The district is composed of 5 local municipalities and covers an area of 31930.28 square kilometers of the province's 129480 square kilometers. The population of the district is recorded at 627626 with 183163 households (5.74 per km^2) (Statistic SA, 2011). The various local municipalities in the district with the towns situated in them include: Masilonyana local municipality (Theunissen, Brandfort, Winburg, Soutpan and Verkeedevlei), Matjhabeng local municipality (Welkom, Virginia, Odendaalsrus, Hennenman, Ventersburg and Allenridge), Nala local municipality (Bothaville and Wesselsbron), Tokologo local municipality (Boshof, Dealesville and Hertzogville), Tswelopele local municipality (Bultfontein and Hoopstad). Lejweleputswa area is extensively mined for gold and to a lesser extent diamond. Most of the mining activities take place in the Matjhabeng local municipality in the towns of Welkom, Virginia, Odendaalsrus and Allenridge.

For the studythe towns of major focus Brandfort, Theunissen, Virginia,Welkom, Odendaalsrus and Allenridge. Apart from Brandfort and Theunissen, the other towns are all typical mining towns and with intensive mining activities. No mining activities are taking place in Brandfort and Theunissen. Brandfort falls under the 'Salt region' for the fact that it contains some salt pans, where salt is extracted whereas Theunissen is more an agricultural town. The towns of Brandfort and Theunissen are therefore taken to be the 'control' areas for the study.

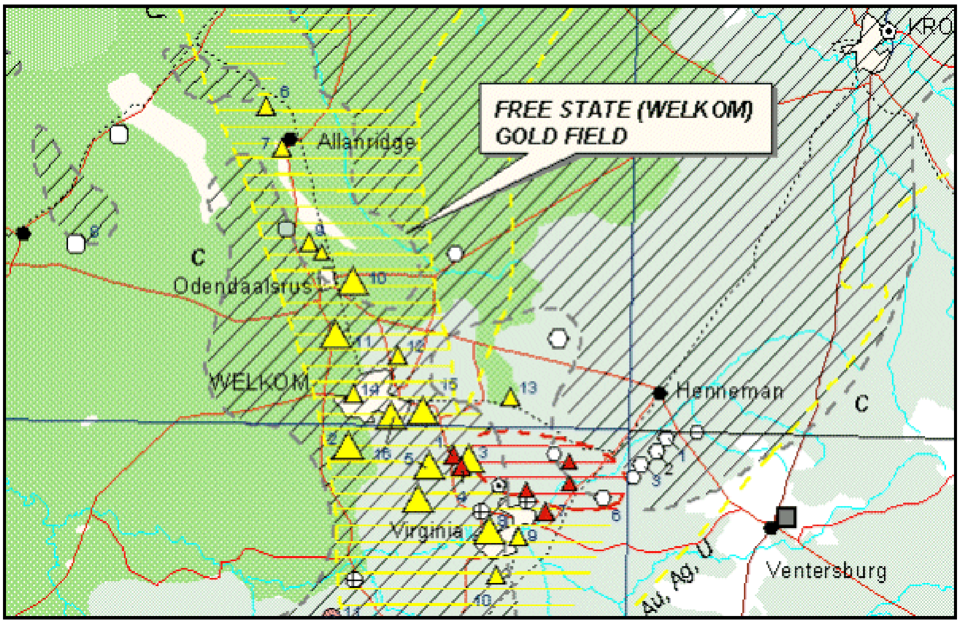

Figure 4.1 Map depictions of some of the towns under study

4.3.2 Environmental Sampling Procedure (Sample collection)

Sample procedure was done according to procedure by Motsara and Roy (2008). The environmental samples of soil, leaves, water and sediment for the study were collected from the towns of Allenridge, Odendaalsrus, Welkom, Virginia, Theunissen and Brandfort. Brandfort and Theunissen were taken as controls due to the fact that no mining activities/ operations take place in the area. The sampling points in the various towns were identified after surveillance trips to the areas and were as follows: Brandfort – at the bank of Kerrom River; Theunissen – at the bank of Jeppe River; Welkom – St Hellena River; Allenridge – Stink River. At the towns of Virginia and Odendaalsrus, sampling was conducted at unnamed 'Small River'banks by the roadsides.

The environmental samples (soil, leaves, water and sediments) were collected on monthly basis from October, 2012 to December, 2012 and from April, 2013 to June, 2013. The October to December period fall within the summer season whereas April to June, the winter season. The idea was to observe variation, if any, in the environmental trace elements concentrations between the two main seasons (the summer and winter) in the region. A central objective of the sampling criteria and procedure for individual samples were to obtain samples representative of the studied area. Hence, the sampling of the environment was carried out with utmost care as follows:

4.3.2.1 Soil To ensure enough coverage, an entire surface and depth of between 0 – 25 cm of soil was collected using a small spade (soil auger) from a number of spots in each of the sampling areas/locations. Collected soil samples were mixed and placed in clean polyethylene (plastic) bags free from any contamination.

4.3.2.2 Leaves A predetermined representative number of plants from a homogeneous sampling unit in each of the sampling locations contributed to the composite approximately

500 g of fresh Acacia Karroo leaves. During the sampling expedition, factors such as: crop nature (i.e. seasonal or perennial) and economic factor were taken in to consideration. Subsequently, leaves were collected from few (4 – 6) representative Acacia Karroo plants in each of the sampling locations in the different studied towns.

4.3.2.3 Water Water was sampled from specific central water body in each of the selected towns. Water was collected in polyethylene bottles with polypropylene caps. The bottles were previously pretreated - soaked for 24 hours in diluted nitric acid

4.3.2.4 Sediment In light of the fact that sediment is frequently heterogeneous due to small scale changes in hydrological regime and geomorphologic changes in the catchment areas (IAEA, 2003), a number of sediment samples (5 - 6) from a particular sampling area were mixed together in a composite sample (Darnley *et al*., 1995). Heterogeneity was examined by collecting multiple samples at a particular sampling area (Ramsey and Argyraki, 1997). Surface sediment of between 0 – 3 cm depth was collected with a hand shovel (Keith, 1995; Golterman *et al*., 1983).

4.3.3 Sample preparation and analysis

The soil, leaves, water and sediment samples were analyzed for trace elements concentrations at the University of the Free State Chemistry Department using the Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES), SHIMADZU, Model - ICPS – 7510 - Sequential Plasma Spectrometer (figure 4.2).

Fig. 4.2 ICP – 7510 (ICP – OES) Sequential Inductively Coupled Plasma Optical Emissions Spectrometer (Shimadzu ICPS – 7510, Japan).

The methods employed in the analysis of the different environmental samples of soil, leaves, water and sediment for trace elements contents were as follows:

4.3.3.1 Soil

An amount of the soil sample was dried, ground and sieved. To approximately 1.5 g of the dry soil sample, 10 ml concentrated HNO_3 was added and the mixture left to stand overnight. The volume of the mixture was reduced on a hotplate through evaporation and left to cool. To the cooled solution sample, 10 ml distilled water was added. The sample was then filtered, and the residue washed with 0.1 M HNO_3 and made into a 100 ml solution. The resulting solution was subsequently analyzed for trace elements using an Inductively Coupled Plasma Optical Emissions Spectrometer (ICP-OES).

4.3.3.2 Leaves

A 1.0 g leaves (Acacia Karoo leaves) sample was dried, and ashed for 4 hours at 550°C and left to cool for 2 hours. To the cooled sample, 1 ml concentrated HNO_3 was added. To this, 10 ml 1 M HNO_3 was added. The volume was reduced on a hotplate and left to cool. To the cooled sample, 10 ml distilled water was added. The sample was filtered, and the residue washed with 0.1 M HNO_3 and made up to 100 ml solution. An amount of the solution was analyzed for trace elements using an ICP-OES. The choice of Acacia Karoo leaves for the study was due to the fact that Acacia Karoo plant grew throughout the year in all the towns covered by the study. This attribute was necessary for proper understanding of the trace elements variation throughout the duration of the study in all the area covered in the study.

4.3.3.3 Water

An amount of the water sample was filtered and 10 ml concentrated HNO_3 added and left to stand overnight. An amount of the solution was analyzed for trace elements using an ICP-OES.

4.3.3.4 Sediment

The sediment sample was dried overnight at 120°C and left to cool. To 1.5 g of the dried and sieved sediment sample, 10 ml concentrated HNO_3 was added and left to stand overnight. The volume was reduced on a hotplate and left to cool. To the cooled sample, 10 ml distilled water was added. The aliquot was filtered and the residue washed with 0.1 M HNO_3, and made into a 100 ml solution. An amount of the solution was analyzed for trace elements using an ICP-OES.

The various trace elements concentrations obtained for the different samples for each month over the period of the study are presented in preceding chapters in which the sample trace elements concentration variation is discussed.

4.3.4 DATA ANALYSIS

Experimental data was analyzed using the general linear model of SAS statistical software version 1.2 (SAS, 2008) to determine the ‘analysis of variance’ (ANOVA). The Turkey’s least significant difference (LSDt), was used to determine the significant results between varied statistical difference between treatment means was determined at the $P = 0.05$ probability levels.

4.4 RESULTS AND DISCUSSIONS

4.4.1 SOIL

Table 4.1 outlines the concentration ranges in part per million (ppm) of the different trace elements that occurred in the soil samples in the studied towns/area. Soil was analysed for trace elements and the results are shown in table 4.1.

Table 4.1 summarizes the trace elements concentrations ranges in ppm in the soils of the six towns covered in the study. Table 4.2 presents the percentage concentration values determined for Ca and Mg in the soil during the period of the study. Calcium (Ca) was the dominant pollutant in the soil, followed by Mg, Fe, S, P and Al. These elements were also found to be quite prominent in the environment. The highest concentrations of Ca (7.3 %) and Mg (2.17 %) occurred in Allenridge in October, 2012. Figure 4.3 illustrates the percentage calcium distribution in the soils in the studied in the Lejweleputswa Municipal District.

The second highest concentration of Ca was observed in Welkom, at 1.98 % (1.23 ppm) in April, 2013, and Mg in Brandfort at 0.90 % (0.47 ppm) in June, 2013. Odendaalsrus and Virginia showed lower average concentrations of trace elements than the controls – Brandfort and Allenridge. The reason is attributable to perhaps, proper adherence to government policies with regard to management of mine wastes and general operations in the mining companies.

Table 4.1 Concentrations of calcium and magnesium (%) and concentration (ppm) ranges of other trace elements in Lejweleputswa Municipal District

Dates	**Towns**											
	Allenridge				**Brandfort**				**Odendaalsrus**			
	% Ca, Mg	>10ppm	>1ppm	>0.1ppm	% Ca, Mg	>10ppm	>1ppm	>0.1ppm	% Ca, Mg	>10ppm	>1ppm	>0.1ppm
Tues 9th Oct, 2012	7.30, 2.17	Ca, Mg, Fe	Al, S, Fe, Sr	Si, P, Ti, Mn, Zn, Ba	0.18, 0.16	Ca	Mg, Al, P	Si, S, Ti, Mn, Cu, Ba, Pt	0.10, 0.01	Ca	Mg, P, S	Al, Fe, Si
Thurs 8th, Nov. 2012	0.58, 0.10	Ca	Mg, P, S	Fe, Si, Sr	0.52, 0.16	Ca	Mg, P, S	Fe, Si, Sr	0.25, 0.05	Ca	P, S	Mg, Fe
Sat 8th Dec, 2012	0.78, 0.45	Ca	Ca, S, P	Mg, Fe, Al, Si	0.80, 0.54	Ca	Ca, S, P	Mg, Fe, Al, Si	0.13, 0.03	Ca	Mg, P, S	Al, Si, Sr, Fe
11th April, 2013	0.18, 0.07	_	Ca, Fe	B, Mg, Al, Si, S, Mn, Zn	0.92, 0.54	Ca, Fe	Mg, Al	Si, S, Mn, Sr, Ba	0.76, 0.17	Ca, Fe	Al, P, S	B, Mg, Si, Mn, Zn, Sr,Ba
17th May, 2013	0.23, 0.11	-	Al, Ca, Fe	Mg, Si, S, Mn, Zn	0.72, 0.54	Ca, Fe	Mg, Al	Si, S, Mn, Sr, Ba	0.12, 0.03	_	Ca, Fe	Mg, Al, Si, S
12th June, 2013	0.10, 0.04	_	Ca, Fe	Mg, Al, Si, S, Mn, Zn	0.96, 0.90	Ca, Fe	Mg, Al	P, Mn	0.18, 0.04	_	Ca, Fe	B, Mg, Al, Si, P, S, Mn

Table 4.1 continues

Dates	Towns											
	Theunissen				Virginia				Welkom			
	% Ca, Mg	>10ppm	>1ppm	>0.1ppm	% Ca, Mg	>10ppm	>1ppm	>0.1ppm	% Ca, Mg	>10ppm	>1ppm	>0.1ppm
Tues 9th Oct, 2012	0.31, 0.13	Ca	Mg, P, S	Fe, Sr	0.42, 0.12	Fe	Mg, Al, S, Ca	Si, P, Mn, Ba	0.98, 0.11	Ca	Mg, Al, P, S, Fe	Ti, Mn, Zn, Sr, Ba
Thurs 8th, Nov. 2012	0.27, 0.15	Ca, Fe	Mg, Al	Si, P, Ti, Mn, Ba	0.50, 0.18	Ca, Fe	Mg, Al	Si, P, S, Mn, Sr, Ba	0.93, 0.12	Ca	Mg, S, Fe	Al, Si, Mn, Sr, Ba
Sat 8th Dec, 2012	0.54, .0.24	_	Ca, Fe	Mg, Al, P, Si, S, Mn	0.12, 0.09	_	Ca, Fe	Mg, S, P, Al	0.98, 0.15	Ca	Al, P, Fe	Mg, Si, Mn, Sr, Ba, S
11th April, 2013	0.65, 0.17	Ca, Fe	Mg, Al	Si, P, S, Mn, Ba	0.14, 0.06	_	Ca, Fe	B, Mg, Al, Si, S, Mn	1.98, 0.26	Ca	Mg, Al, S, Fe	Si, P, Mn, Sr, Ba
17th May, 2013	0.26, 0.15	Fe	Ca, Mg, Al	Si, P, S, Ti, Mn, Ba	0.11, 0.04	_	Ca, Fe	B, Mg, Al, Si, S	0.83, 0.18	Ca	Al, S, Fe	Mg, Si, Mn, Sr, Ba
12th June, 2013	0.38, 0.15	_	Ca, Fe	Mg, Al, P, S, Mn, Ba	0.15, 0.06	_	Ca, Fe	B, Mg, Al, Si, P, S, Mn	1.66, 0.14	Ca	Fe	B, Mg, Al, Si, P, S, Mn, Sr, Ba

Table 4.2 Concentration of Calcium and magnesium (%) in the soil collected from six mining towns in the Lejweleputswa Municipal District (LDM)

Dates	**09/10/2012**	**08/11/2012**	**08/12/2012**	**11/04/2013**	**17/05/2013**	**12/06/2013**
Towns	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**
	Ca, Mg	**Ca, Mg**	**Ca, Mg**	**Ca, Mg**	**Ca, Mg**	**Ca, Mg**
Allenridge	7.30, 2.17	0.58, 0.10	0.78, 0.45	0.18, 0.07	0.23, 0.11	0.10, 0.04
Brandfort	0.18, 0.16	0.52, 0.16	0.80, 0.54	0.92, 0.54	0.72, 0.54	0.96, 0.90
Odendaalsrus	0.10, 0.01	0.25, 0.05	0.13, 0.03	0.76, 0.17	0.12, 0.03	0.18, 0.04
Theunissen	0.31, 0.13	0.27, 0.15	0.54, 0.24	0.65, 0.17	0.26, 0.15	0.38, 0.15
Virginia	0.42, 0.12	0.50, 0.18	0.12, 0.09	0.14, 0.06	0.11, 0.04	0.15, 0.06
Welkom	0.98, 0.11	0.93, 0.12	0.98, 0.15	1.98, 0.26	0.83, 0.18	1.66, 0.14

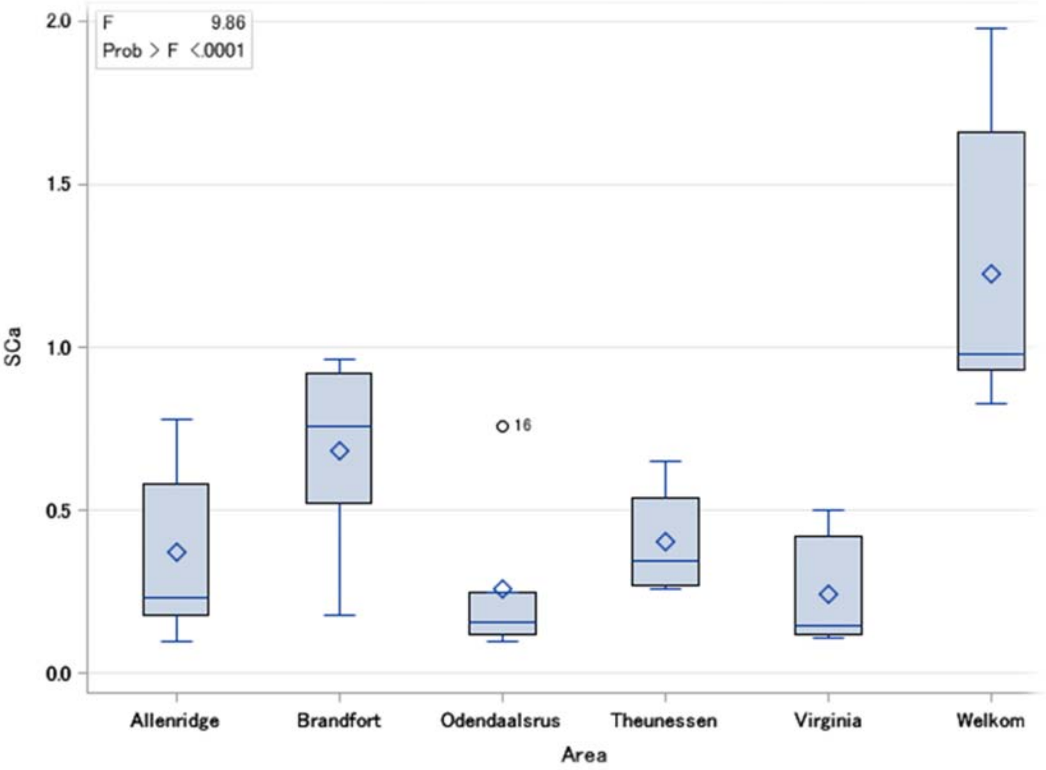

Figure 4.3 Calcium percentage (SCa) concentration in the soil collected from six towns in the mining Lejweleputswa District Municipality (LDM)

Subsequently, Ca concentration in the soil were significantly the highest (P = 0.01) in Allenridge, Welkom and Brandfort. Lower concentrations were recorded in Odendaalsrus (Fig.4.3). Also, Mg concentration levels in the soil were significantly (P = 0.001) higher in Allenridge and Brandfort. Odendaalsrus, Theunissen, Virginia and Welkom had approximately the same level of Mg in the soil.

The predominance of Ca as major pollutant in the area is first and foremost attributable to the naturally occurring minerals in the area in which calcium forms one of the prominent constituents of the minerals (Appendix B, p. 164). However, other than the natural occurrence of calcium as mineral in the environment, the regular liming operations increase the concentrations of Ca. Lime water ($Ca(OH)_2$) and $CaSO_4$ are used to neutralize excessive sulphuric acid due to acid mine drainage resulting from mining operations, thus contributing to the high concentration of calcium in the environment. With regard to the presence of Mg, other than from the natural occurrence, could also have resulted from the occasional use of $MgSO_4$ for liming purposes to neutralize the high acidity of the soil.

Incidentally, significantly high levels of Magnesium occurred in Welkom soil where high levels of Ca also occurred. The high acidity of the soil and the environment in general of gold mining areas often resulting in acid mine drainage is due to the often occurrence of Pyrite (FeS) with gold ores in the soil. The excess sulphuric acid is therefore, a result of dissolution of sulphur in the pyrite (FeS) content of gold ore in water generating sulphuric acid of very high concentration in the environment. The drainage of the high concentrated sulphuric acid in the environment is what leads to acid mine drainage (AMD) mostly in gold mined areas. The occurrence of S and Fe in the soil Lejweleputswa Municipals District is significant from our results, occurring at concentrations above 1.0 ppm in most of the studied towns. Figure 4.4 depicts soil magnesium distribution in the different studied towns.

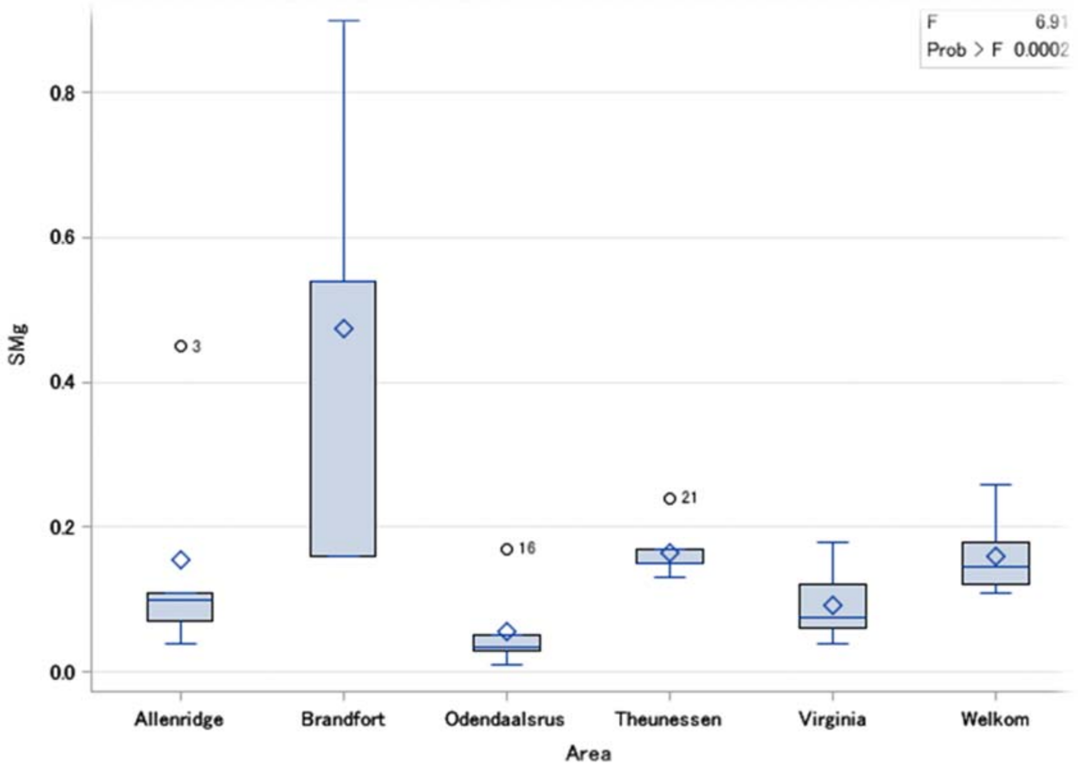

Figure 4.4 Magnesium percentage (SMg) concentration in the soil collected from six towns in the mining Lejweleputswa District Municipality

Also, the high presence of Ca and Mg could also be related to the mineralization and its host rock and later anthropogenic dispersion (Loredo *et al*, 2006). Fe, Cr and V are elements of analogous geochemical behavior and considered geogenic elements with a homogeneous distribution within the studied area. Mn, Co, Ni and Zn, elements with a similar chemical structure, are usually linked in nature, but not associated to the ore (Loredo *et al*., 2006; Adriano, 1986).

Other prominent metals in the soil in the studied towns included Fe, S, Al and P (Table 4.1). Fe and S could have originated from pyrite (FeS) contained in the rock bearing the gold ore in the area. Also, the wide spread occurrence of Ca in the soil in all the studied towns suggests that there is possibly a considerable amount of $CaCO_3$ in the soil in the Lejweleputswa District Municipality of the Free State, South Africa.

The highest average (mean) concentration of Ca in the soil occurred in Welkom (1.2267), followed by Brandfort (0.6833). In light of the fact that Brandfort has not experienced the kind of extensive mining activities like Welkom, Allenridge, the high average Ca concentration is ascribed, mainly, to the naturally occurring minerals in Brandfort. Calcium concentration percentage distribution in the soil was highest in Welkom. Allenridge and Brandfort appear equal but higher than Theunissen and Virginia which also have similar percentage distribution of Ca. Odendaalsrus has the least distribution of Ca in the soil.

The highest average occurrence of Mg in the soil was observed in Brandfort (0.47), followed by Theunissen (0.17) and then Welkom (0.16). Brandfort also had the highest distribution of Mg in the soil. Virginia and Welkom had similar distribution of Mg, but higher than Allenridge with higher distribution than Odendaalsrus and Theunissen. Apart from Brandfort, Mg occurrence in all the studied towns could be considered statistically the same suggesting that Mg occurrence in Lejweleputswa District is mainly due to the mineral occurrence in the area.

The soil Ca – Mg ratio (fig. 4.5) was highest in Allenridge and Welkom (0.79) where high levels of Ca occurred, followed by Odendaalsrus (5.38) and statistically the same for all the other towns. Figure 4.5 illustrates the calcium/magnesium percentage concentration ratios in the different studied towns.

4.4.2 LEAVES

Table 4.3 Shows the concentration ranges in part per million (ppm) of the different trace elements that occurred in the leaves collected from the studied towns/area. The results of the trace elements content in the Acacia Karroo leaves obtained in the studied towns over the period of the study are shown in table 4.3. Table 4.4 presents concentration percentage values for Ca and Mg in the leaves obtained from different towns over the period of the study.

Calcium was the predominant elemental content of the leaves in all the towns. The highest concentration of calcium of 100 ppm occurred in Allenridge in April, 2013. In Brandfort, Theunissen and Welkom, the highest concentration of calcium of 100 ppm occurred in June, 2013. In the other towns, calcium, also, present as the predominant pollutant in the leaves, occurring at concentrations greater than 10 ppm. The second most abundant element in the leaves was Mg, occurring at concentrations greater than 1.0 ppm. S and P also occurred mostly at concentrations greater than 1.0 ppm in the leaves in all the towns.

The Ca content in the leaves is most likely to have been absorbed from the soil in light of the fact that pollutants in the soil usually affect the plants as they are introduced into the plants via deposited contaminants in the soil or via ingestion through leaves (Altaf, 2006).

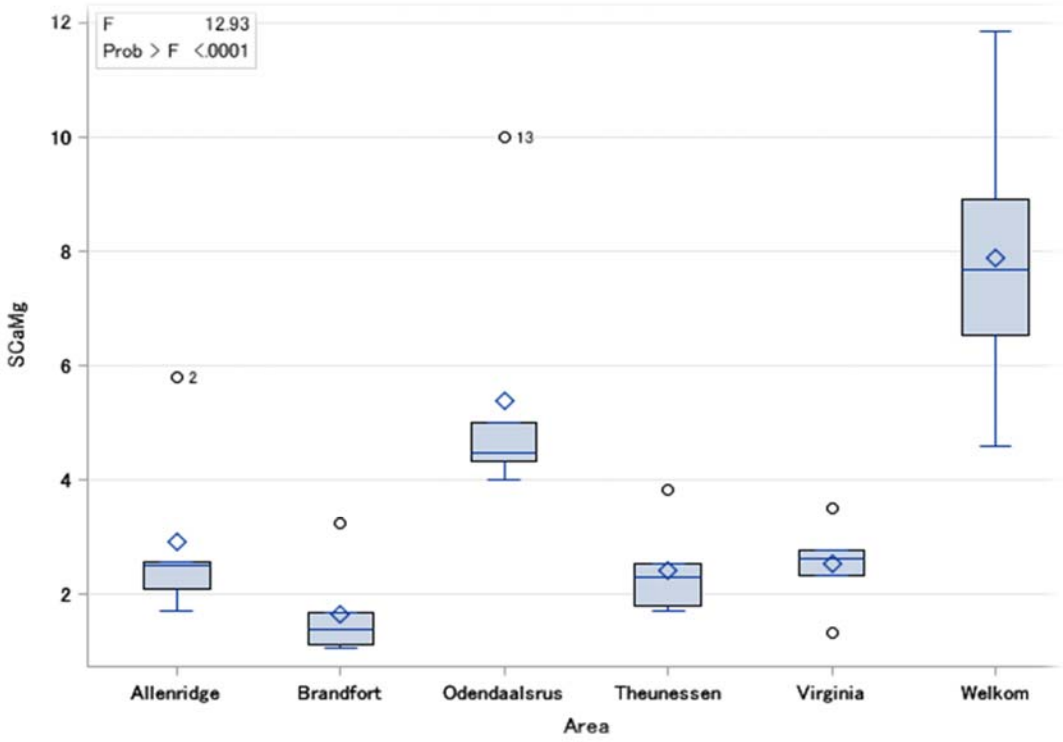

Figure 4.5 Calcium- magnesium (SCaMg) percentage concentration ratio in the soil in six towns in the mining Lejweleputswa District Municipality

Table 4.3 Trace elements concentration occurrence ranges in plant leaves collected from six towns in the mining Lejweleputswa Municipal District Area

Dates	**Towns**											
	Allenridge				**Brandfort**				**Odendaalsrus**			
	100ppm	>10ppm	>1ppm	>0.1ppm	100ppm	>10ppm	>1ppm	>0.1ppm	100ppm	>10ppm	>1ppm	>0.1ppm
Tues 9th Oct, 2012	_	Ca	Mg, P, S	Si, Sr, Fe	_	Ca	Mg, Si, P, S	Al, Fe, Sr	_	Ca	Mg, P, S	Fe, Sr
Thurs 8th, Nov. 2012	_	Ca	Mg, P, S	Al, Si, Fe, Sr	_	Ca	P, S	Mg; Al, Si, Fe, Sr	_	Ca	Mg, P, S	Al, Si, Fe, Sr
Sat 8th Dec, 2012	_	Ca	Mg, P, S	Al, Si, Fe, Sr	_	Ca	Mg, P, S	Fe, Si, Sr	_	Ca	Mg, P	Fe, Sr
11th April, 2013	Ca	_	Mg, S	B, Al, P, S, Fe, Sr, Ba	_	Ca	Mg, Si	B, P, S, Fe, Sr	_	Ca	Mg, Si	B, P, S, Fe, Sr
17th May, 2013	_	Ca	Mg	P, S, Fe	_	Ca	Si	Mg, P, S, Fe	_	Ca	Mg	Si, P, S, Fe, Sr
12th June, 2013	_	Ca	Si	B, Mg, P, S, Fe, Sr	Ca	_	Mg, Si, S	P, Fe, Sr	_	Ca	Mg, Si	P, S, Fe, Sr

Dates	**Towns**											
	Theunissen				**Virginia**				**Welkom**			
	100ppm	>10ppm	>1ppm	>0.1ppm	100ppm	>10ppm	>1ppm	>0.1ppm	100ppm	>10ppm	>1ppm	>0.1ppm
Tues 9th Oct, 2012	_	Ca	Mg, P, S	Al, Fe, Si	_	Ca	Mg, P, S	B, Al, Si, Fe, Zn, Sr	Ca		Mg, P, S	Al, Si, Fe, Sr
Thurs 8th, Nov. 2012	_	Ca	P, S	Mg, Fe	_	Ca	Mg, P, S	Al, Fe, Si, Sr, Zn	_	Ca	Mg, P, S	Fe, Si, Sr
Sat 8th Dec, 2012	_	Ca	Mg, P, S	Al, Si, Sr, Fe	_	Ca	Mg, P, S	Al, Si, Fe, Sr	_	Ca	P, S	Mg, Fe, Al, Si
11th April, 2013	_	Ca	Mg, Si	B, P, S	_	Ca	_	B, Mg, Si, P, S	_	Ca	Mg, Si	B, P, S, Fe, Sr
17th May, 2013	_	Ca	Mg	P, S	_	Ca	_	Mg, Si, P, S	_	Ca	Si	Mg, P, S, Fe, Sr
12th June, 2013	Ca	_	Mg, S	Si, P	_	Ca	_	Mg, Si, P, S, Fe	Ca	_	Mg	Al, P, S, Fe, Sr

Table 4.4 Concentration of Calcium and magnesium (%) in plant leaves collected from six mining towns in the Lejweleputswa Municipal District (LDM)

Dates	**09/10/2012**	**08/11/2012**	**08/12/2012**	**11/04/2013**	**17/05/2013**	**12/06/2013**
Towns	**(%)** **Ca, Mg**	**(%)** **Ca, Mg**	**(%)** **Ca, Mg**	**(%)** **Ca, Mg**	**(%)** **Ca, Mg**	**(%)** **Ca, Mg**
Allenridge	1.35, 0.21	0.95, 0.19	1.15, 0.21	2.12, 0.23	1.06, 0.11	1.49, 0.11
Brandfort	0.76, 0.16	0.79, 0.09	1.47, 0.14	1.08, 0.11	0.72, 0.09	2.00, 0.21
Odendaalsrus	1.00, 0.20	1.45, 0.13	1.95, 0.19	1.47, 0.16	1.43, 0.13	1.46, 0.14
Theunissen	0.76, 0.16	0.38, 0.11	0.97, 0.15	1.06, 0.13	1.60, 0.14	1.85, 0.14
Virginia	1.07, 0.26	1.50, 0.17	1.16, 0.16	0.68, 0.05	0.96, 0.07	0.85, 0.10
Welkom	2.10, 0.19	1.30, 0.18	0.81, 0.14	1.32, 0.14	1.03, 0.10	2.08, 0.19

Generally, the origin of trace metals in plant leaves is attributed to the accumulation due to atmospheric deposition (Air accumulation factor - AAF) or transfer from soil (Concentration factor - CF) or both. The variation in AAF and CF values can be due such factors as the chemical speciation of trace metals, atmospheric and soil concentrations and variations in uptake (Vousta *et al*., 1996). Trace elements are often deposited on plant surfaces by rain and dust. The relationship between the atmospheric element deposition and elevated elements concentration in plants and topsoil, especially in cities and in vicinities of emitting factories have been well established (Vousta *et al*., 1996 and Srinivas *et al*., 2002). Also, the elevated concentrations of various trace elements in local crops, and other plants as a consequence of anthropogenic emissions have been widely reported (Zarcinas *et al*., 2004ab; Wong *et al*., 2001). Subsequently, the accumulation of trace elements in leaves is due to atmospheric deposition or transfer from soil or both.

Although, seasonal accumulation trends of elements concentration in leaves - often referred to as 'Accumulative Bio-monitors' have been well reported for many plant species (Bargali, 1998; Kim and Fergusson, 1994; Piczak *et al*., 2003), this trend was not obvious from the current results for calcium and magnesium which were the most prominent pollutants in the soil in the studied areas. The presence of elements in the soil does not necessarily imply that they are available to plants. Generally, plant – to - soil concentration ratio is far from a linear function (Bargali, 1998; Kabata-Pendias *et al*., 1984).

The average (mean) concentration of Ca in the leaves (table 4.4) was highest in Odendaalsrus at 1.46 and closely followed by Welkom at 1.44 and Brandfort at 1.31. The highest average (mean) concentration of Mg in leaves occurred in Odendaalsrus (0.33), followed by Allenridge (0.17) and then Welkom (0.16) and Brandfort (0.15).

Calcium percentage concentration distribution was highest in Brandfort, followed by Welkom and then Theunissen. The percentage concentration distribution of calcium in Virginia was a little higher than that in Allenridge. However, the calcium concentrations in the two towns are comparable. Odendaalsrus had very little distribution of calcium in the environment. Magnesium concentration distribution in the leaves in all the towns was quite small with the least distribution occurring at Theunissen.

The leaves Ca-Mg ratio was highest in Virginia at 0.9365, followed by Welkom (9.123), (table 5.2). However, since, the difference in Ca – Mg ratio is not significant between the studied towns, the Ca –Mg ratio is statistically the same in the leaves for all the towns.

Table 4.5 Mean Ca, Mg and CaMg concentrations in leaves in the different towns over the period of the study.

	N	LCa		LMg		LCaMg	
Area		**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**
Allenridge	**6**	1.223	0.205	0.173	0.053	7.783	3.291
Brandfort	**6**	1.310	0.645	0.153	0.059	8. 462	1.997
Odendaalsrus	**6**	1.460	0.301	0.325	0.410	8.185	4.099
Theunissen	**6**	1.103	0.541	0.138	0.017	7.910	3.808
Virginia	**6**	1.067	0.296	0.140	0.088	9.365	3.685
Welkom	**6**	1.440	0.537	0.157	0.036	9.123	2.157
Probability (P) value		0.5484		0.4320		0.9443	

In final analysis, with regard to leaves study, Ca and Mg concentrations and CaMg concentration ratio in leaves were generally non-significant as illustrated in table 4.5. The low mean value of Ca and Mg occurrence in the leaves in all the studied towns. Hence, the plants and more likely other food crops grown in the area (Lejweleputswa Municipal District), are probably not excessively contaminated by trace elements present in the environment around the Lejweleputswa Municipal District Area of the Free State, South Africa.

4.4.3 WATER

Table 4.6 presents the concentration ranges in parts per million (ppm) of the different trace elements that occurred in the water bodies in the studied towns/area. Magnesium (Mg), Sulphur (S) and to a reasonable extent Silicon (Si) were quite prominent in the water bodies in all the studied towns. The highest concentrations of Ca, Mg and S occurred in Allenridge of higher than 100 ppm in December, 2012 and April to June, 2013. Magnesium (Mg) occurred in the range between 1.0 and 10 ppm. Welkom had the second highest concentration of Ca and Mg in the water bodies to Allenridge.

Trace elemental contents in the water bodies in the different towns are presented in table 4.6. Table 4.7 presents the concentration percentage values for Ca and Mg in the water bodies studied in the different towns during the period of the study. Calcium (Ca) was the predominant pollutant in the water bodies in the area. Figure 4.6 shows the percentage calcium distribution in the water in the studied towns in the Lejweleputswa Municipal District.

Table 4.6 Trace elements concentrations occurrence ranges (ppm) in water collected from studied towns in the mining Lejweleputswa Municipal District

Dates	**Towns**											
	Allenridge				**Brandfort**				**Odendaalsrus**			
	100ppm	>10ppm	>1ppm	>0.1ppm	100ppm	>10ppm	>1ppm	>0.1ppm	100ppm	>10ppm	>1ppm	>0.1ppm
Tues 9th Oct, 2012	_	S, Ca	Mg	Sr	_	_	Ca	Mg, Si, S	_	_	Ca	Si, S, Fe
Thurs 8th, Nov. 2012	_	S, Ca	Mg	B, Sr	_	_	Ca	Mg, Si, P, S, Fe	_	Ca	Mg, S	Si, Sr
Sat 8th Dec, 2012	S, Ca	Mg	Sr	Si, P, B	_	_	Ca	Mg, Si, S,	_	_	S, Ca	Mg
11th April, 2013	S	_	B	P, Ca, Fe	_	Ca	_	B, Mg, Si, P, S, Fe	_	Ca	Mg, S	B, Si, Fe
17th May, 2013	S	Ca	B, Mg	Fe	_	Ca	_	B, Mg, Si, P, S	_	Ca	Mg, S	B, Si, Sr
12th June, 2013	S, Ca	Mg	B, Sr	Si, P, Fe	_	Ca	Mg, Si, S, Fe	Al, P, Ti	_	S, Ca	Mg	B, Si, Sr

Dates	**Towns**											
	Theunissen				**Virginia**				**Welkom**			
	100ppm	>10ppm	>1ppm	>0.1ppm	100ppm	>10ppm	>1ppm	>0.1ppm	100ppm	>10ppm	>1ppm	>0.1ppm
Tues 9th Oct, 2012	_	Ca	Mg, Si, S	_	_	Ca	Mg, S	Si	_	S, Ca	Mg,	B, Si, Fe, Sr
Thurs 8th, Nov. 2012	_	_	_	Ca	_	Ca	Mg, S	Si, Sr	_	Ca	Mg, S	Si, Sr
Sat 8th Dec, 2012	_	Ca	Mg, S	Si	_	_	Ca	S	_	_	Ca	S
11th April, 2013	_	Ca	Mg, Si, S	B	_	Ca	Mg, S	B, Si	_	S, Ca	Mg, Fe	B, Si, P, Sr
17th May, 2013	_	_	Mg, S, Ca	Si	_	Ca	S	B, Mg, Si	_	Ca	S	B, Mg, Si
12th June, 2013	_	Ca	Mg, Si, S	B	_	Ca	Mg, S	Si	_	S, Ca	Mg	B, Si, Sr

Table 4.7 Concentration of Calcium and magnesium (%) of water collected from six mining towns in the Lejweleputswa Municipal District (LDM)

Dates	**09/10/2012**	**08/11/2012**	**08/12/2012**	**11/04/2013**	**17/05/2013**	**12/06/2013**
Towns	**(%)** **Ca, Mg**	**(%)** **Ca, Mg**	**(%)** **Ca, Mg**	**(%)** **Ca, Mg**	**(%)** **Ca, Mg**	**(%)** **Ca, Mg**
Allenridge	637, 195	967, 278	850, 249	02, 00	60, 19	1262, 421
Brandfort	19, 07	53, 20	13, 02	23, 08	26, 10	53, 24
Odendaalsrus	23, 07	63, 23	54, 19	35, 10	123, 33	126, 32
Theunissen	66, 65	06, 08	53, 44	33, 33	34, 67	49, 59
Virginia	70, 30	66, 28	15, 05	29, 13	62, 32	70,30
Welkom	103, 66	60, 56	10, 06	71, 43	66, 67	62, 65

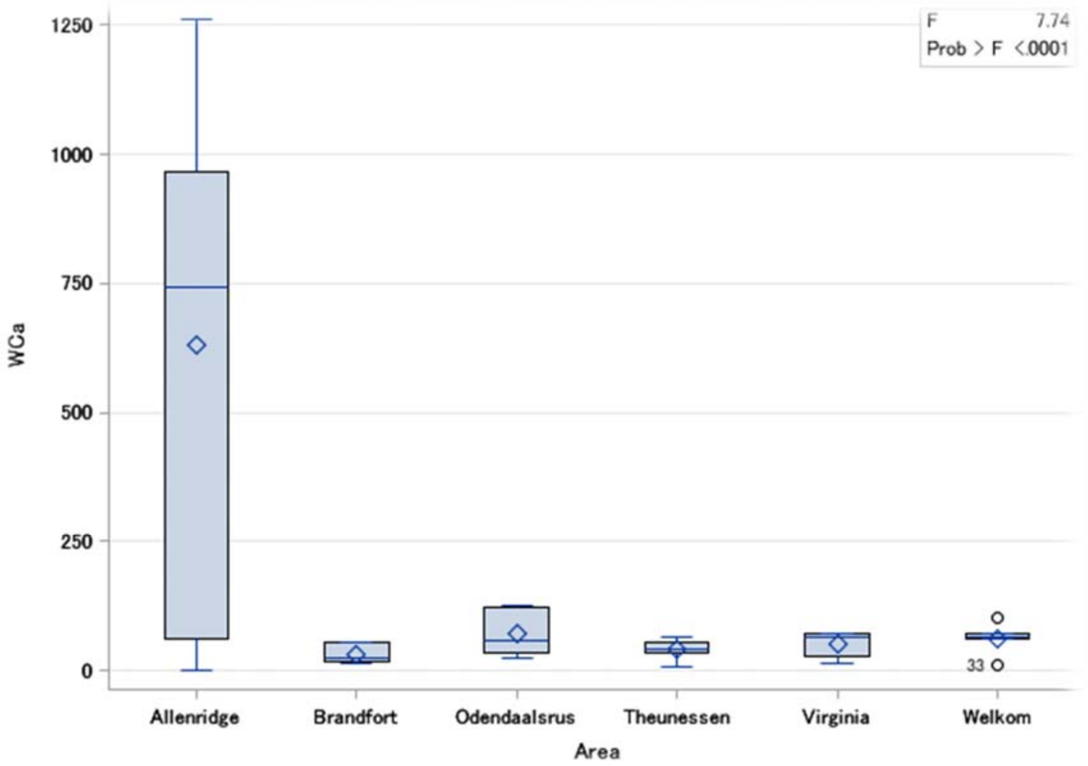

Figure 4.6 Calcium percentage (WCa) concentration in the water collected from six towns in the mining Lejweleputswa District Municipality (LDM)

In Brandfort, Odendaalsrus, Welkom, Theunissen and Virginia, Ca occurred at concentrations higher than 10 ppm with Mg, S and Si occurring at concentrations greater than 1.0 ppm. Other pollutants in the water bodies at much lower concentrations of above 0.1 ppm were B, Fe and Sr. Figure 4.7 presents the magnesium occurrence in the water bodies' located Lejweleputswa Municipal District area, South Africa.

The percentage distribution of Ca in Allenridge was the highest (fig. 4.6). The distribution of Mg was also highest in Allenridge, although, much lower than Ca. All the other towns had approximately similar levels of distribution of Mg in their water bodies with Mg concentrations in Theunissen water slightly more pronounced than in the other towns (fig. 4.7).

The highest occurrence of calcium and sulphur in Allenridge is attributable to the flow of the '*Stink River*' – a man-made sewerage river carrying mine and human wastes from the whole area and settling in Allenridge. According to the BIS and ICMR, the maximum allowable concentration and the permissible concentration of Fe in drinking water is between 1.0 and 0.3 ppm respectively (Akhilesh *et al*., 2009).

The predominance of calcium as major pollutant in the area could be attributed to liming in which lime water ($Ca(OH)_2$), $CaSO_4$ and $MgSO_4$ are used to neutralize the excess sulphuric acid resulting from the dissolution of sulphur content of gold ore in water. This often leads to acid mine drainage (AMD) in areas mined for gold resulting in high acidity of the soil. The occurrence of S and Fe is significant, occurring in concentrations above 1.0 ppm in most of the towns.

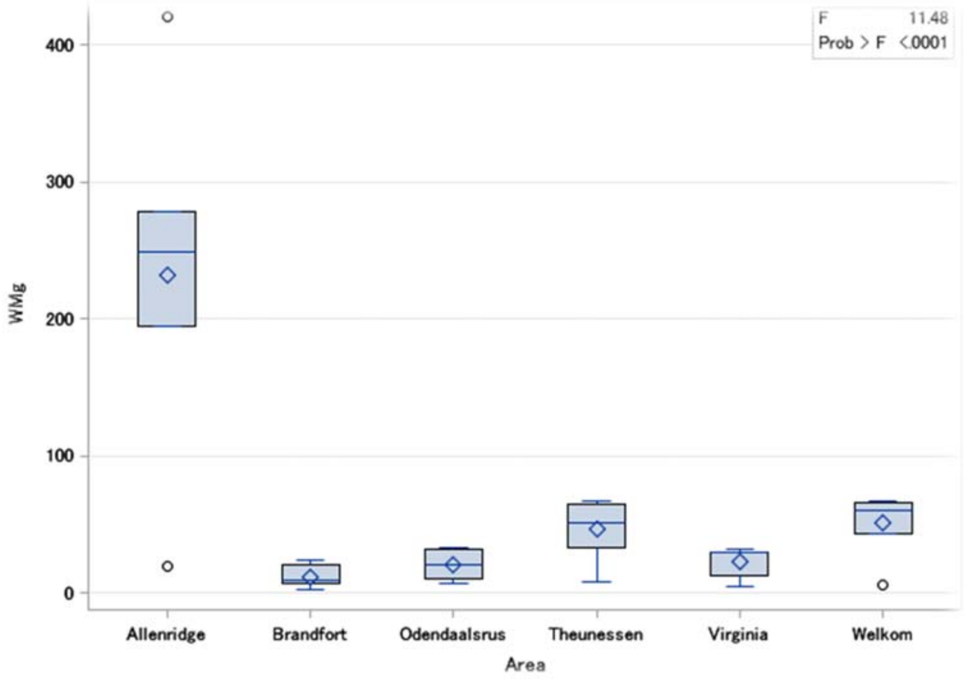

Figure 4.7 Magnesium percentage (WMg) oncentration in the water collected from six towns in the mining Lejweleputswa District Municipality (LDM)

The significant presence of Mg is also attributed to the regular liming exercise in which $MgSO_4$ in conjunction with $Ca(OH)_2$ and $CaSO_4$ are used as major agents in the neutralization of the soil of its high acidity resulting from acid mine drainage. Also, the high occurrence of Ca and Mg could predominantly also be related to the mineralization and its host rock and later anthropogenic dispersion. This is mainly due to the natural occurrence of Ca and Mg bearing minerals in the area (Appendix B). Iron (Fe), Chromium (Cr) and Vanadium (V) are elements of analogous geochemical behaviour and considered geogenic elements with a homogeneous distribution within the studied area. Manganese (Mn), Cobalt (Co), Nickel (Ni) and Zinc (Zn), elements with a similar chemical structure, are usually linked in nature, but not associated to the ore (Loredo *et al.*, 2006; Adriano, 2001; Shacklette and Boerngen, 1989).

The average (mean) concentration of Ca found in the water was about 629.7 % in Allenridge. Water obtained from in Odendaalsrus had the second highest Ca (70.7 %), followed by that obtained from Welkom at 62 5 % (table 5.1). Apart from Allenridge, the mean Ca concentration in the water is statistically equal for water in all the other towns. Also, the highest mean concentration of Mg in water was in Allenridge, with Odendaalsrus and Welkom coming second and third respectively (table 5.1). The mean Mg concentrations for the rest of the towns seem to be statistically equal.

The mean percentage Ca–Mg ratio was highest in Odendaalsrus at 3.3400, but statistically equal (not significantly different) for Brandfort and Allenridge (table 5.2). The Ca-Mg ratio for Virginia and Welkom are less but also statistically equal. Figure 4.8 shows the calcium – magnesium concentration ratios in the water in the studied towns in the Lejweleputswa Municipal District area, South Africa.

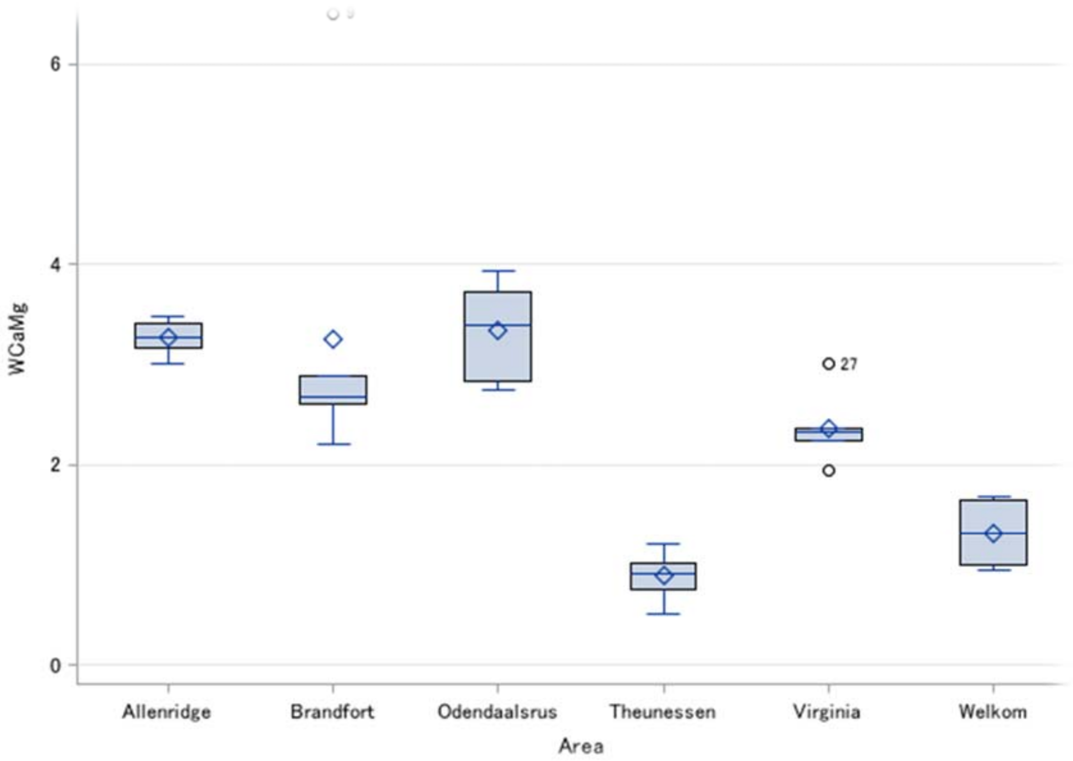

Figure 4.8 Calcium - magnesium (WCaMg) percentage concentration ratio in the water collected from six towns in the mining Lejweleputswa District Municipality (LDM)

4.4.4 SEDIMENT

Table 4.8 presents the concentration ranges in parts per million (ppm) of the different trace elements that occurred in the sediments that occurred in the water beds of water bodies in the studied towns/area.

Tables 4.8 and 4.9 present the trace elements concentration ranges and the exact concentrations of Ca and Mg in the sediment in the different towns investigated over the period of the study. The study revealed that the major pollutants in the sediment were Ca, Fe and S, occurring mainly at concentrations above 10 ppm in all the towns studied. Figure The percentage calcium distribution in the sediment in the studied towns in the Lejweleputswa Municipal District are shown in Figure 4.9.

The sediments obtained in Welkom had the highest (5.16 %) occurrence of Ca in the sediments. On the average, the highest occurrence of calcium in the sediment was in Welkom. The highest occurrence of Mg occurred in Brandfort. The highest occurrence of Mg in Brandfort could be because Brandfort is a salt region and may naturally be rich in some of the alkali metals often bonded to the different salt minerals occurring in the area. Figure 4.10 illustrates the magnesium concentration occurrence in the sediment in the studied towns in the Lejweleputswa Municipal District area of the Free State, South Africa.

Virginia was the least polluted with respect to both calcium and magnesium. Aluminum (Al), Phosphorus (P) and Zinc (Zn) also featured significantly in the sediment in all the towns, occurring at concentrations above 1.0 ppm in most of the towns. The occurrence of Ca, Mg and Sr, other than due to liming activity, to neutralize the soil of its high acidity, could also be related to the mineralization and its host rock and subsequent anthropogenic dispersion. The widespread occurrence of calcium in the sediment suggests the presence of $CaCO_3$ in the soil of the Lejweleputswa.

Iron sulphide (FeS) – pyrite- seems to be an important metalliferous mineral in the area and decomposes to release iron (Fe) and sulphur (S) in the soil and sediment under oxidizing condition despite their stable condition under reducing conditions in which they are stable. Also, the rate of decomposition of FeS varies with grain size of the sediment particles as observed by Loredo *et al*., (2006).

The occurrence of Mn is attributable to the presence of Mn oxide in the sediment. Also, the presence of Mn in the calcite in the sediments indicates the accumulation of these sediments under oxic conditions as observed by others (Calvert and Pedersen, 1993). Co-precipitation of calcite – manganese phase was suggested in the light of the unique Ca-Mn association. The occurrence of Sr in concentrations greater than 10.0 ppm in Allenridge and Welkom could also, be related to the presence of biogenic carbonates in the area as observed by Rubio *et al*., (2000).

The highest mean concentration of Ca in sediment occurred in Welkom at about 2.57, significantly higher than the average Ca concentration in the other towns. The mean Ca concentration in Allenridge (1.31), Theunissen (0.96) and Brandfort (0.79) are not significantly different, hence, are statistically equal and significantly less than that of Welkom. Odendaalsrus at 0.22 and Virginia at 0.11, have the least concentrations of Ca in the sediment.

The highest mean concentration of Mg in the sediment was at Brandfort (0.58), followed by Theunissen (0.39). Welkom at 0.27, Allenridge (0.14) and Odendaalsrus (0.09) are statistically equal as they are not significantly different. The comparative sediment Ca-Mg (DCaMg) ratio was highest in Welkom at 9.84, followed by Alllenridge (8.57) which could be considered statistically equal. Virginia at 2.52 is the third highest ratio, followed by Theunissen at 2.41 and then Odendaalsrus at 2.58, not significantly different. Figure 4.11 shows the calcium – magnesium concentration ratios in the sediment in the studied towns in the Lejweleputswa Municipal District area, South Africa.

Table 4.8 Trace elements' concentrations occurrence ranges in sediment collected from six locations each in one of the six towns in the mining Lejweleputswa Municipal District Area

Dates	**Towns**											
	ALLENRIDGE				**BRANDFORT**				**ODENDAALSRUS**			
	100ppm	>10ppm	>1ppm	>0.1ppm	100ppm	>10ppm	>1ppm	>0.1ppm	100ppm	>10ppm	>1ppm	>0.1ppm
Tues 9th Oct, 2012	_	Ca, S, Fe	Mg, Al, P, Zn	Si, Mn, Co, Ni, Cu, Sr, Ba	_	Ca, Fe	Mg, Al	Si, Mn, Ba, Ti, Cu, Ba	_	_	Ca, Fe	Al, P, Mn,
Thurs 8th, Nov. 2012	_	_	Al, S, Ca, Fe	_	_	_	Ca, Fe	Mg, Al, P, Mn	_	Ca	Fe	Mg, Al, Si, Mn, Ba, Ti
Sat 8th Dec, 2012	_	Ca	S, Fe	Al, Si, Zn	_	Ca, Fe	Mg, Al	Si, P, S, Mn, Zn, Ba	_	Ca, Fe	Mg, Al, S	Si, P, Mn, Sr, Ba
Thurs11th April, 2013	_	Ca, S, Fe	Mg, Al, P, Zn	Si, Mn, Co, Ni, Cu, Sr, Ba	_	Ca, S	Mg, Al, P, Fe, Zn	Si, Mn, Co, Ni, Cu, Sr, Ba	_	Ca, Fe	Mg, Al	Si, Mn, Ba, Ti, Cu
Fri 17th May, 2013	_	Ca	Fe	Mg, Al, P, S, Sr	_	_	Al, S, Ca, Fe	_	_	_	Ca, Fe	Mg, Ai, P, Mn
Wed12th June, 2013	_	Ca, Fe	Mg, Al, S	Si, P, Mn, Zn, Sr, Ba	_	Ca	S, Fe	Al, Si, Zn	_	Ca, Fe	Mg, Al	Si, P, S Mn, Zn, Ba

Dates	Towns											
	THEUNISSEN				**VIRGINIA**				**WELKOM**			
	100ppm	>10ppm	>1ppm	>0.1ppm	100ppm	>10ppm	>1ppm	>0.1ppm	100ppm	>10ppm	>1ppm	>0.1ppm
Tues 9th Oct, 2012	_	Ca,	Mg, Al, Fe	Si, Mn,	_	_	S, Ca, Fe	Al, Si	_	Ca	Fe	Mg, Al, P, S, Sr
Thurs 8th, Nov. 2012	_	Ca, Fe	Mg, Al	Si, P, S, Mn	_	_	Ca, Fe	_	_	Ca, Fe	Mg, Al, S	Si, P, Mn, Zn, Sr, Ba
Sat 8th Dec, 2012	_	Ca, Fe	Mg, Al, S	Si, P, Ti, Mn	_	_	Ca, Fe	Mg, Al, P, S	_	Ca	Mg, Al, S, Fe	Si, P, Mn, Sr, Ba
Thurs 11th April, 2013	_	_	Ca, Fe	Al, P, Mn	_	Ca	Mg, Al, Fe	Si, Mn	_	_	S, Ca, Fe	Al, Si
Fri 17th May, 2013	_	Ca	Fe	Mg, Al, Si, Mn, Ba, Ti	_	Ca, Fe	Mg, Al	Si, P, S, Mn	_	_	Ca, Fe	_
Wed 12th June, 2013	_	Ca, Fe	Mg, Al, S	Si, P, Mn, Sr, Ba	_	Ca, Fe	Mg, Al, S	Si, P, Ti, Mn	_	_	Ca, Fe	Mg, Al, P, S

Table 4.9 Concentrations of Calcium and magnesium (%) in the sediment collected from six mining towns in the Lejweleputswa Municipal District (LDM)

Dates	**09/10/2012**	**08/11/2012**	**08/12/2012**	**11/04/2013**	**17/05/2013**	**12/06/2013**
Towns	**Ca, Mg**	**Ca, Mg**	**Ca, Mg**	**Ca, Mg**	**Ca, Mg**	**Ca, Mg**
Allenridge	4.30, 0.26	0.32, 0.15	0.17, 0.04	0.68, 0.18	1.38, 0.14	1.04, 0.07
Brandfort	0.96, 0.54	0.65, 0.52	0.65, 0.44	0.94, 0.71	0.75, 0.58	0.83, 0.70
Odendaalsrus	0.24, 0.12	0.16, 0.08	0.60, 0.22	0.08, 0.04	0.18, 0.07	0.09, 0.03
Theunissen	0.45, 0.26	0.95, 0.36	1.78, 0.54	0.98, 0.34	0.94, 0.38	0.68, 0.46
Virginia	0.15, 0.06	0.19, 0.05	0.10, 0.04	0.08, 0.04	0.08, 0.04	0.07, 0.03
Welkom	2.06, 0.30	2.73, 0.25	2.34, 0.30	5.16, 0.44	1.58, 0.11	1.54, 0.21

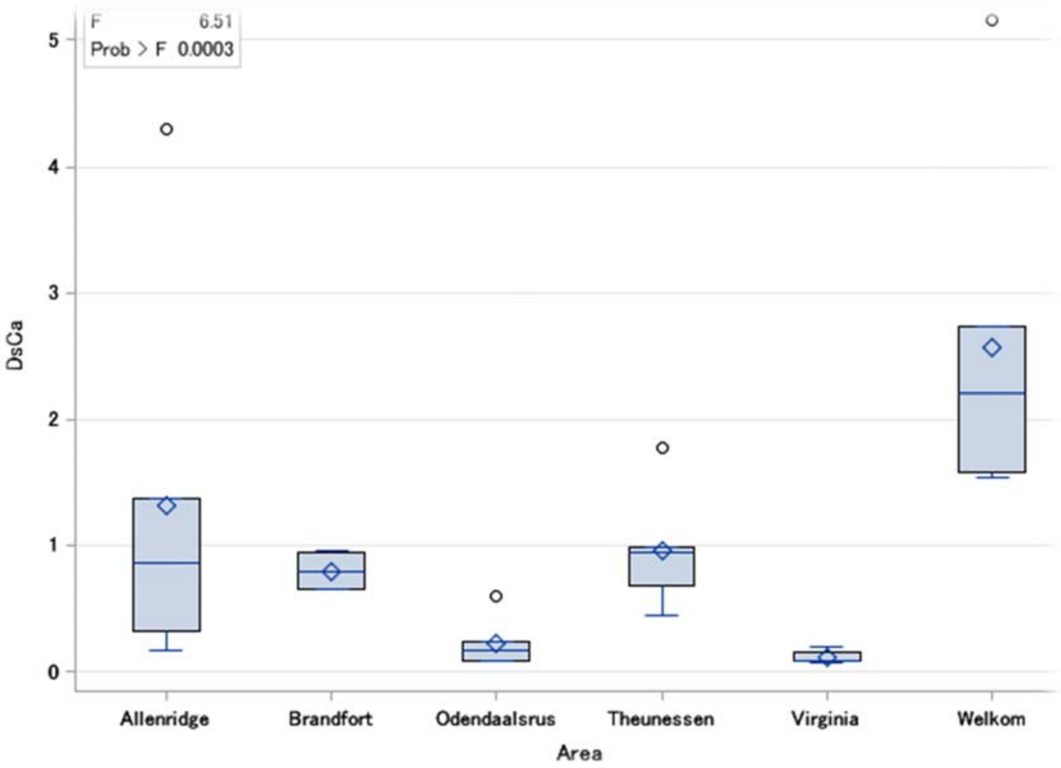

Figure 4.9 Calcium percentage (DsCa) concentration in the sediment collected from six towns in the mining Lejweleputswa District Municipality (LDM)

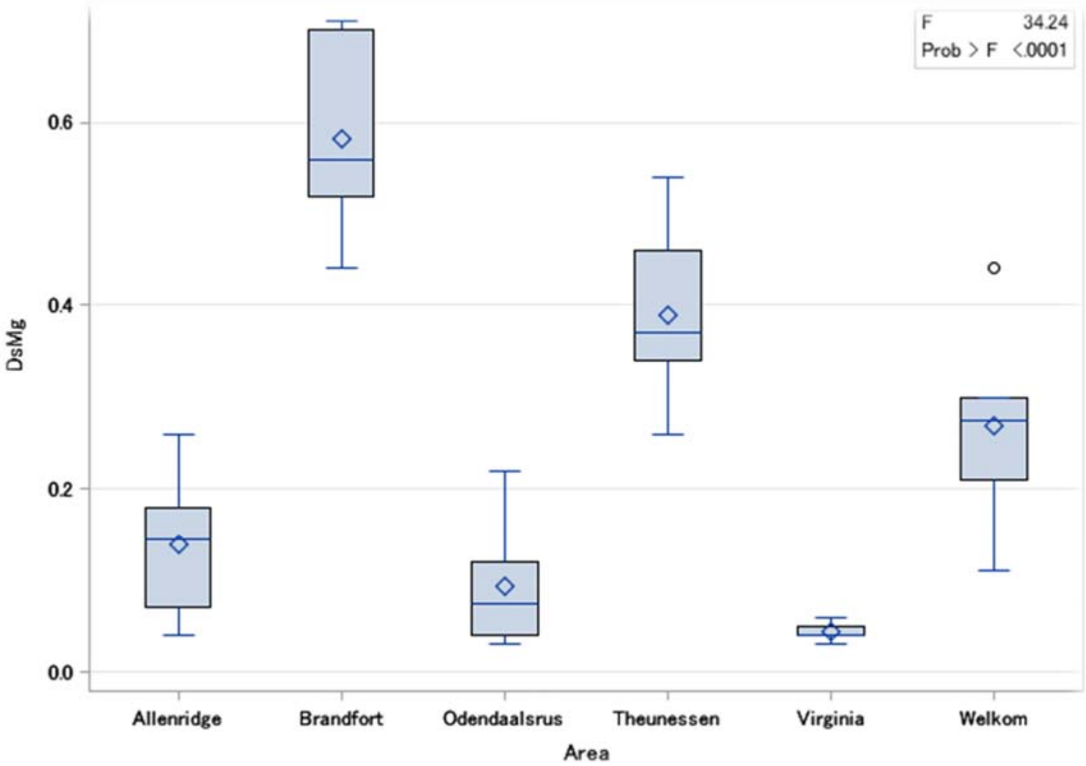

Figure 4.10 Magnesium percentage (DsMg) concentration in the sediment collected from the six mining towns in Lejweleputswa District Municipality (LDM)

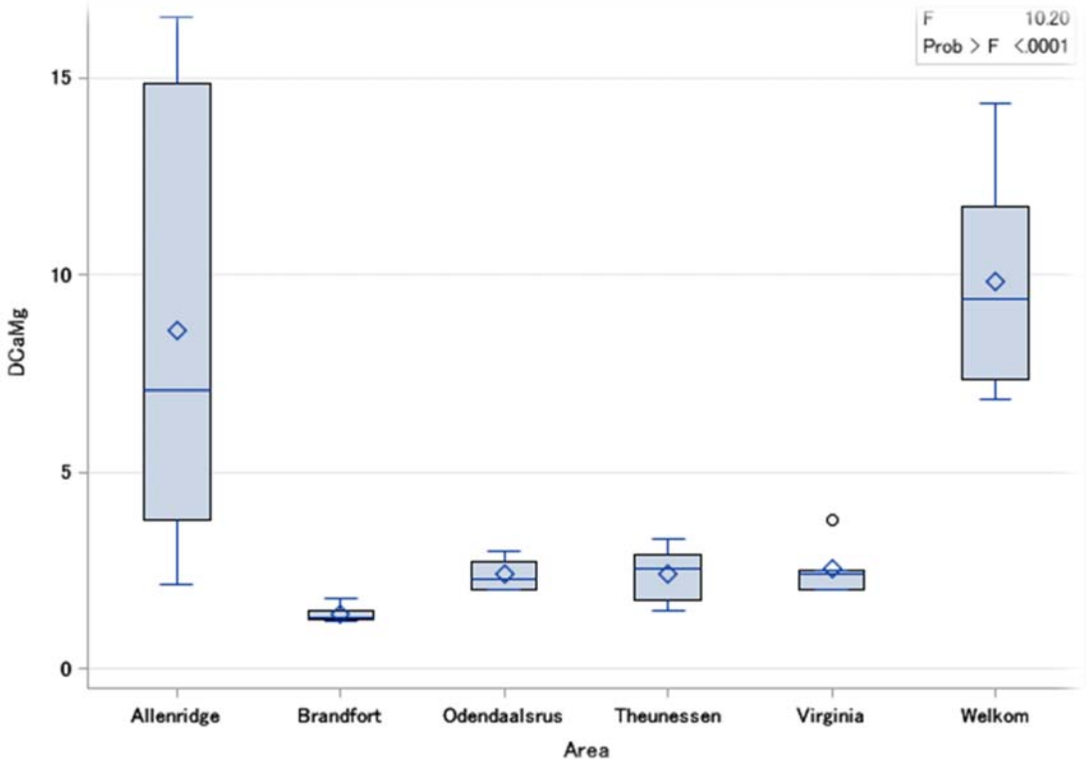

Figure 4.11 Calcium - magnesium (DCaMg) percentage concentration ratio in the sediment collected from six towns in the mining Lejweleputswa District Municipality (LDM)

4.5 Conclusions

It can be concluded from this section that water obtained from water bodies (streams) indicated that Ca was by far the most predominant pollutant in the water bodies in the district. Magnesium was the second most abundant trace element in the water in the area was, followed by Sulphur. The water bodies in Allenridge were the most polluted in the municipality, followed by those in Welkom and then Virginia. Allenridge, also, had the highest average Ca concentration, followed by Odendaalsrus, then Welkom and Virginia. The highest Mg concentration in the water bodies occurred in Allenridge, followed by Welkom. Generally, Mg and S were the second most dominant pollutants in the water bodies in the area. Sediment obtained from the waterbeds of the water bodies in the area showed that the major pollutants in their order of occurrence were Ca, Fe, Mg and S. Calcium presented as the major pollutant, followed by Fe and then Mg. Al, S and Mn also featured prominently in the sediment. The highest average concentrations of Ca in sediment occurred in Welkom at 2.57 % and Mg in Brandfort at 0.60 %. The high trace element concentration in sediment emanate from the deposition of soil content of trace elements to waterbeds. Calcium distribution in sediment occurred the highest in Welkom and Allenridge, whereas Mg distribution occurred highest in Brandfort. Subsequently, Ca and Mg concentration ratio is highest in Welkom followed by Allenridge.

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CHAPTER 5

GENERAL DISCUSSION FOR TRACE ELEMENTS OCCURRENCE IN THE ENVIRONMENT, EVALUATION OF THE STUDY, CONCLUSIONS AND RECOMMENDATIONS

5.1 General Discussions

In light of the extensive mining activities taking place in the Lejweleputswa District Municipality (LDM) area of the Free State, South Africa, and associated environmental implications of such activities which result in among others, the proliferation of the environment with chemicals. This study was conducted to quantify the levels of various trace elements concentrations in the environment (i.e., soil, leaves, water and sediment). Subsequently, soil, leaves, water and sediment samples collected on monthly basis over a period spanning six months covering partly summer and winter periods, from six locations in six different towns of Allenridge, Odendaalsrus, Welkom, Virginia, Theunissen and Brandfort in which most of the mining activities take place in the district, were analyzed for trace elements using an Inductively Coupled Plasma Optical Emissions Spectrometer (ICP-OES).

Results obtained from the analysis revealed that the most common pollutants in the soil, leaves, water and sediment in all the studied towns, in their order of dominance were, for the - Soil: Ca, Fe, Mg, Al and S (table 4.1), Leaves: Ca, Mg, P and S with significant concentration of Si (table 4.3), Water: Ca, S, Mg with significant concentration of Si (table 4.6) and Sediment: Ca, Fe, Mg, Al, S with significant concentration of Si and other elements (table 4.8).

Table 5.1 The average calcium and magnesium percentage concentration values in the different media and towns.

AREA	SOIL		LEAVES		WATER		SEDIMENT	
	Ca	**Mg**	**Ca**	**Mg**	**Ca**	**Mg**	**Ca**	**Mg**
Allenridge	$0.3740^{B,C}$	0.15400^{B}	1.2233^{A}	0.1733^{A}	629.7^{A}	232.4^{A}	1.3150^{B}	0.14000^{D}
Brandfort	0.6833^{B}	0.47333^{A}	1.3100^{A}	0.1533^{A}	31.2^{B}	11.83^{B}	0.7967^{BC}	0.58167^{A}
Odendaalsrus	0.2567^{C}	0.05500^{B}	1.4600^{A}	0.3250^{A}	70.7^{B}	20.67^{B}	0.2250^{C}	0.09333^{D}
Theunissen	$0.4017^{B,C}$	0.16500^{B}	1.1033^{A}	0.1383^{A}	40.2^{B}	46.00^{B}	0.9633^{BC}	0.39000^{B}
Virginia	0.2400^{C}	0.09167^{B}	1.0667^{A}	0.1400^{A}	52.0^{B}	23.00^{B}	0.1117^{C}	0.04333^{D}
Welkom	1.2267^{A}	0.16000^{B}	1.4400^{A}	0.1567^{A}	62.0^{B}	50.50^{B}	2.5683^{A}	0.26833^{C}
Error(Std deviation)	0.08571	0.019201	0.202953	0.030641	43380.88	3165.892	0.736171	0.007334
LSD	0.3514	0.1663	0.5312	0.2064	245.59	67.538	1.0117	0.101

*Mean **%** values with similar/same letter superscripts (A, B, C and/or D) are considered statistically equal/not significantly different.

*LSD – Least Significant Difference

Calcium was the most concentrated pollutant in the soil in the Lejweleputswa District Municipality (LDM). In Allenridge, the most concentrated pollutant was calcium with concentration range between 10 and 100 ppm. The highest concentration of Ca and magnesium in the soil occurred in Allenridge in October, 2012, at approximately 7.30 % for Ca and 2.17 % for Mg. Allenridge also, had the highest average concentration of Ca and Mg in the soil of about 1.53 % Ca and 0.49 % Mg for the period of the study. Calcium was the second highest concentrated element observed in Welkom at 1.98 % in April 2013 and the second highest average concentration of Ca was also at Welkom at 1.23 ppm. With regard to Mg, the second highest concentration occurred in Brandfort at 0.9 mg in June, 2013. Brandfort also had the second highest average concentration of Mg at 0.47 %.

With regard to the average percentage concentrations of calcium and magnesium in the soil, calcium occurred in the soil in the different towns in the following decreasing order of concentration:

The average percentage order of occurrence of calcium in the soil is as follows:

Allenridge (1.53 %) > Welkom (1.23 %) > Brandfort (0.68 %) > Theunissen (0.40 %) > Odendaalsrus (0.26 %) > Virginia (0.24 %)

The average percentage order of occurrence of magnesium in the soil is follows:

Allenridge (0.49 %) > Brandfort (0.47 %) > Theunissen (0.17 %) > Welkom (0.16 %) > Virginia (0.09 %) > Odendaalsrus (0.06 %)

Calcium (Ca) and Iron (Fe) were observed as the predominant and most concentrated pollutants in the soil, with Mg closely following Fe in dominance and concentration. Aluminium (Al) and Sulphur (S) were also presence in the soil in the area.

Iron (Fe) also occurred in the range above the 10 ppm in October, 2012 representing the highest occurrence of iron in Allenridge whereas the highest occurrence of calcium occurred in the months of October, November, and December, 2012. In the region > 1 ppm (i.e. > 1ppm region), Al, S, P and Fe occurred in October, 2012 in the concentration range greater than 1.0 ppm. Most occurrence of trace elements in the soil occurred in the 0.1ppm concentration level including elements such as Ba, B, Al, S, Fe, Sr, Mn, P, S, and Zn. Brandfort soils' also had calcium as the predominant pollutant with Iron featuring very significantly, almost at the same concentration as calcium. Elements such as Mg, Al, S, and P occurred mainly in the 1.0 ppm concentration level in the soil. Most elements such as Si, Ti, Vu, Ba, Pt, Sr and Mn mainly occurred in the 0.1 ppm concentration range. Brandfort had higher concentrations of Fe, Al and Mg than Allenridge and Odendaalsrus. B, Ba and Sr occurred in the > 0.1 ppm concentration range in the three towns of Allenridge, Brandfort and Odendaalsrus.

Odendaalsrus soils', also had Ca as the dominant pollutant with Ca concentration falling within the concentration > 10 ppm. The concentration and distribution of Fe is very closely related to that of Ca in the soil with other elements such as Mg, S, P and Al being quite significant in concentration (i.e. falling within the > 0.1ppm concentration levels).

In Theunissen, Ca and Fe were most prominent pollutant in the soil occurring at concentrations higher than 10 ppm. Mg occurred at mainly concentrations above 1.0 ppm whereas Si, Mn, Ti, Ba and Sr occurred at concentrations greater than0.1 ppm. In Virginia, Ca and Fe were the biggest pollutants in the soil occurring mainly at concentrations above 1.0 ppm. Mg, Al and S occurred occasionally at concentrations higher than 0.1 ppm. Other pollutants in the soil in Virginia occurring at concentrations above 0.1 ppm were Mn, Si, P, Ba and occasionally, S, Al, and Mg, fluctuating in concentrations between 0.1 ppm and 1.0 ppm. Calcium is clearly the major pollutant in the soil in Welkom occurring at concentration above 10 ppm. Other pollutants included: Mg, Al, P, S, Fe, Mn, Si and Sr.

With regard to soil Ca-Mg concentration inter-comparison, in the different towns, the highest Ca/Mg concentration ratio occurred in Welkom. There is, however, no clear trend observed for the variations in concentrations of Ca and Mg between the summer and winter seasons. Table 5.2 presents the mean CaMg ratio in the different media (soil, plants, water and sediment).

The Ca/Mg concentrations in the different towns occurred in the decreasing order as shown below:

Welkom (7.88) > Odendaalsrus (5.38) > Allenridge (2.94) > Virginia (2.53) > Theunissen (2.42) > Brandfort (1.66).

In leaves, Ca was the predominant trace element content occurring in the concentration range between 10 and 100 ppm in all the studied towns in the Lejweleputswa District Municipality area of the Free State, South Africa. Magnesium (Mg), Phosphorus (P), Sulphur (S) and occasionally Silicon (Si) collectively occurred in concentrations above 1.0 ppm in the leaves in all the towns. Most of the other trace elements contents of the leaves occurred in the concentration range between 0.1 and 1.0 ppm and included Fe, B, Sr, Al, Ba, P and Si in almost all the towns. It was only in Odendaalsrus and Virginia where Ca concentration did not reach the 100 ppm concentration level.

In Allenridge, Ca was the dominant trace element in the leaves with concentrations mainly above 10 ppm except for the month of April, 2013 in which the concentration reached 100 ppm and thus the highest Ca concentration occurrence in leaves was in Allenridge. In Brandfort, Theunissen and Welkom, the highest concentration of calcium of 100 ppm occurred in June, 2013. In the other towns (Virginia and Odendaalsrus), calcium, also, was the predominant pollutant in the leaves, but at much lower concentration, occurring at concentrations greater than 10 ppm. Magnesium (Mg), Phosphorus (P), Sulphur (S) and Silicon (Si) were also present in the leaves at concentrations above 1.0 ppm. In the range

Table 5.2 Mean calcium and magnesium percentage concentration ratios in the different media and towns

AREA	SOIL	LEAVES	WATER	SEDIMENT
	SCaMg	**LCaMg**	**WCaMg**	**DCaMg**
Allenridge	2.9380^{C}	7.783^{A}	3.2640^{A}	8.570^{A}
Brandfort	1.6600^{C}	8.462^{A}	3.2583^{A}	1.385^{B}
Odendaalsrus	5.3833^{B}	8.185^{A}	3.3400^{A}	2.383^{B}
Theunissen	2.4183^{C}	7.910^{A}	0.8850^{C}	2.417^{B}
Virginia	2.5317^{C}	9.365^{A}	2.3650^{B}	2.522^{B}
Welkom	7.8800^{A}	9.123^{A}	1.3150^{C}	9.835^{A}
Mean standard deviations	1.12349995	1.04178598	1.93028291	1.11344633
Error Mean Square	2.585923	10.72469	0.539574	7.936795
LSD	1.9302	3.8614	0.8817	3.3218

*Mean **%** values with similar/same letter superscripts (A, B, C and/or D) are considered statistically equal/not significantly different.
*LSD – Least Significant Difference.

between 0.1 ppm and 1.0 ppm, Si, Sr, Fe, Al and B were also found to be present in the leaves. The second most abundant element in the leaves was Mg, occurring at concentrations greater than 1.0 ppm. S and P also occurred mostly at concentrations greater than 1.0 ppm in the leaves in all the towns covered but not at the same frequency as Mg.

In Brandfort, other than in June, 2013, in which Ca concentration was determined at about 100 ppm, Ca concentrations was above 10 ppm for all the other months of the study (table 4.3). Magnesium (Mg), Phosphorus (P), Sulphur (S) and Silicon (Si) were determined and occurred within the concentration levels above 1.0 ppm, while Al, Fe, Sr and B, all occurred at concentrations above 0.1 ppm.

The leaves obtained from Odendaalsrus contained Ca in the concentration levels of above 10 ppm throughout the period of the study, whereas Mg, P, S and Si occurred at concentrations above 1.0 ppm. Fe, Sr, Al and Si were all above 0.1 ppm. Calcium was also the dominant pollutant in the leaves in Theunissen with the highest concentration occurring in June, 2013 at about 100 ppm. Calcium concentration was above 10 ppm for the rest of the period of the study. Mg, P, S and Si were all determined at concentration levels above 1.0 ppm whereas Al, Fe, Sr, B were above 0.1 ppm.

In Virginia, the leaves contained contain calcium as the major trace element at concentrations above 10.0 ppm throughout the period of the study. Magnesium (Mg), Phosphorus (P) and Sulphur (S) were observed at concentrations above 1.0 ppm. The majority of the trace elements in the leaves such as: B, Al, Si, Fe, Zn and Sr occurred at concentrations greater than 0.1 ppm. In Welkom, Ca was also the predominant pollutant in the leaves and was determined at concentrations above 100 ppm in the months of October, 2012 and June, 2013. During the other periods, calcium concentrations in the leaves in Welkom was above 10 ppm. Magnesium (Mg) and Phosphorus (P) occurred at concentrations above 1.0 ppm, whereas Al, Si, Fe, Sr and B, all occurred at concentrations above the 0.1 ppm.

The order of occurrence of calcium in leaves in the studied towns is indicated below:

Odendaalsrus (1.46 %) > Welkom (1.44 %) > Allenridge (1.35 %) > Brandfort (1.14 %) > Theunissen (1.10 %) > Virginia (1.07 %)

The average percentage order of occurrence of magnesium in the leaves is:

Allenridge (0.18 %) > Odendaalsrus (0.16 %) > Welkom (0.16 %) > Theunissen (0.14 %) > Virginia (0.14 %) > Brandfort (0.13 %)

The leaves Ca-Mg ratio occurred in the order: Virginia (9.37) > Welkom > (9.12) > Brandfort (8.46) > Odendaalsrus (8.19) > Theunissen (7.91) > Allenridge (7.78)

In water, the most abundant chemical pollutant was calcium with S showing great prominence as the second most prominent trace element pollutant. Magnesium (Mg) was also greatly prominent and more prominent than sulphur in Theunissen and Virginia. In Allenridge, Ca and S were observed at 100 ppm concentration level whereas the highest occurrence of Ca in Brandfort was greater than 10 ppm.

In Allenridge, Ca concentration was at 100 ppm in December, 2012 and june, 2013 whereas S was at 100 ppm in December, 2012 and April, May and June, 2013. Calcium (Ca) and Sulphur (S) also occurred in the levels greater than 10 ppm for October and November and Ca also, in May, 2013. Magnesium (Mg) was present in the concentration levels greater than 1.0 ppm with the exception for the months of December, 2012 and June, 2013. B and Sr occurred between 0.1 ppm and 1.0 ppm in Allenridge and between 1.0 ppm and 10 ppm for Brandfort and Odendaalsrus. In most cases, S, Mg, Si and Fe occurred in the concentration levels above 0.1 ppm (table 4.6, p. 112). B and P and Al were obtained in the concentration range between 0.1 ppm and 1.0 ppm.

In Odendaalsrus, other than in October, 2012 in which Ca concentrations were between 1.0 ppm and 10 ppm, Ca concentrations were generally above 10 ppm in most cases. S occurred in the concentrations greater than 10 ppm only in June, 2013, but was in most cases at concentrations greater than 1.0 ppm except for October, 2012 when it occurred at concentrations greater than 0.1 ppm in the water bodies in the Lejweleputswa District Municipality.

In water, the highest concentrations of Ca, Mg and S occurred in Allenridge at concentrations higher than 100 ppm in December, 2012 and April to June, 2013. Mg occurred in the range from 1.0 and 10 ppm. Welkom has the second highest concentration of Ca and Mg in the water bodies to Allenridge. In Brandfort, Odendaalsrus, Welkom, Theunissen and Virginia, Ca was also the highest concentrated pollutant in water, whereas S showed great prominence in Welkom. Calcium (Ca) occurred at concentrations above 10 ppm with Mg, S and Si occurring at concentrations above 1.0 ppm in water. Other pollutants in water at much lower concentrations of above 0.1 ppm were B, Fe and Sr.

Other than in June, 2013 in which the highest concentration of S was recorded above 10 ppm, S concentrations ranged between 1.0 ppm and 10 ppm for the rest of the period of the study except for October, 2012 in which S concentration was below 1.0 ppm. Si, Sr and B in Odendaalsrus all recorded concentrations between 0.1 ppm and 1.0 ppm (i.e. below 1.0 ppm) in the water bodies in the Lejweleputswa Municipal District area of the Free State, South Africa.

In Theunissen, Virginia and Welkom, Ca occurred at concentrations above 10 ppm except for November, 2012 for Theunissen in which it occurred between 0.1ppm and 1.0 ppm in December, 2012. For Virginia and Welkom, Ca concentrations occurred between 1.0 ppm and 10.0 ppm in December, 2012. Magnesium (Mg) and Sulphur (S) occurred at concentrations greater than 1.0 ppm in Theunissen and Virginia with the exception for

December, 2012 when S occurred at concentrations greater than 0.1 ppm in Virginia and Welkom.

Magnesium (Mg) occurred in the concentration levels above 1.0 ppm with the exception for May, 2013 in which Mg occurred at concentrations between 0.1 ppm and 1.0 ppm. S concentration levels occurred above 1.0 ppm for all the towns except for Virginia and Welkom, in which it occurred greater than 0.1 ppm in December, 2012. Fe, B, Si, P and Sr all occurred in concentrations between 0.1 ppm and 1.0 ppm in Welkom and Si, Sr and B in Virginia and B in Theunissen.

The highest occurrence of Ca and sulphur in Allenridge were attributable to the flow of the '*Stink River*' – a man-made sewerage river carrying mine and human wastes in the whole area and settling in Allenridge. According to the BIS and ICMR, the maximum allowable concentration and the permissible concentration of Fe in drinking water is between 1.0 and 0.3 ppm respectively (Akhilesh *et al*., 2009).

The mean percentage order of occurrence of calcium in the water is indicated below:
Allenridge (630 %) > Odendaalsrus (71 %) > Welkom (62 %) > Virginia (52 %) > Theunissen (40 %) > Brandfort (31 %)

The average percentage order of occurrence of magnesium in the water is:
Allenridge (232 %) > Welkom (51 %) > Theunissen (46 %) > Virginia (23 %) > Odendaalsrus (21 %) > .Brandfort (12 %)

The water Ca-Mg ratio occurred in the order: Odendaalsrus (3.34 %) > Allenridge (3.26 %) > Brandfort (3.26 %) > Virginia (2.37 %) > Welkom (1.31 %) > Theunissen (0.89 %)

An assessment of trace elements pollution of the sediment in the environment around the Lejweleputswa area of the Free State revealed that the major pollutants in the sediment occurred in the order Ca greater than Fe with S, Al and Mg. the former trace elements were also observed in the sediment in all the studied towns and occurring at concentrations above 10 ppm in all the towns studied. Table 4.9 presents the percentage concentrations of calcium and magnesium in the sediment in the different towns for the period of the study.

In Allenridge, Ca was the major pollutant and occurred at concentrations above 10.0 ppm. Fe and S also occurred at concentrations above 10.0 ppm in October, and April, 2013. Zinc (Zn) occurred at concentrations above 1.0 ppm. The concentrations of Mg, Al, and P fluctuated between 0.1 ppm and 1.0 ppm while Co, Cu, Sr, Ba and Si, all occurred in the 0.1 ppm to 1.0 ppm concentration range in Allenridge, Brandfort and Odendaalsrus. In Brandfort and Odendaalsrus, Ca and Fe occurred in concentrations above 10 ppm and Mg and Al occurred in the concentration levels above 1.0 ppm. Phosphorus (P) occurred in the concentration levels above 1.0 ppm in Allenridge and Brandfort while P, Si and Mg occurred in the concentration range above 0.1 ppm in the sediment in all the towns.

In Theunissen, Virginia and welkom, Ca and Fe occurred mainly above the 10 ppm concentration range while Mg, Al, and S fluctuated between 0.1 ppm and 1.0 ppm concentration range. Mn, Ba, Sr and P occurred in the concentration range between 0.1 ppm and 1.0 ppm in the sediment in all the towns of Theunissen, Virginia and Welkom.

On the average, Welkom had the highest occurrence of calcium in the sediment. The highest occurrence of Mg occurred in Brandfort. This could be due to the fact that Brandfort is a salt region and may naturally contain some of the alkali metals emanating from the different salt content of the area. Virginia presented as the least polluted with regard to both calcium and magnesium. Al, P and Zn also featured significantly in the sediment in all the towns, occurring at concentrations above 1.0 ppm in most of the towns.

The occurrence of Mn is attributable to the presence of Mn oxide in the sediment. Also, the presence of Mn in the calcite in the sediments indicates the accumulation of these

sediments under oxic conditions (Calvert *et al*., 1993). Co-precipitation of calcite – manganese phase was suggested in the light of the unique Ca-Mn association (Ward *et al*., 1995). The occurrence of Sr in concentrations greater than 10.0 ppm in Allenridge and Welkom could be related to the presence of biogenic carbonates in the area (Rubio *et al*., 2000). The order of occurrence of calcium in the sediment is indicated below:
Welkom (2.57 %) > Allenridge (1.32 %) > Theunissen (0.96 %) > Brandfort (0.80%) > Odendaalsrus (0.23 %) > Virginia (0.112%)

The average percentage order of occurrence of magnesium in the sediment is: Brandfort (0.58 %) > Theunissen (0.39 %) > Welkom (0.27 %) > Allenridge (0.14 %) > Odendaalsrus (0.09 %) > Virginia (0.04 %)
The sediment Ca –Mg ratio occurred in the order: Welkom (9.84) > Allenridge (8.57) > Virginia (2.52) > Theunissen (2.42) > Odendaalsrus (2.38) > Brandfort (1.39).

The predominance of calcium as major pollutant in the soil in the whole region other than their natural occurrence in the soil in the area could be attributed to regular liming activities in the area. In liming activities, lime water ($Ca(OH)_2$) and $CaSO_4$are used to neutralize the excess sulphuric acid resulting from the dissolution of sulphur content of gold ore in water which often generates high concentration of sulphuric acid. This often leads to acid mine drainage (AMD) in areas mined for gold. The occurrence of S and Fe is significant, occurring at concentrations above 1.0 ppm in most of the towns. The presence of Mg, other than its natural occurrence in the minerals in the area is attributed to the regular liming exercise in which $MgSO_4$ is occasionally used in the neutralization of the soil of its high acidity that often result in acid mine drainage. Also, the high presence of Ca and Mg could also be related to the mineralization and its host rock and later anthropogenic dispersion (Loredo *et al*., 2006). Subsequently, the predominance of Ca in the area suggests that considerable amount of $CaCO_3$ and possibly, $CaSO_4$ occurs as mineral in the soil in the whole Lejweleputswa area (Bolormaa *et al*., 2012). Iron (Fe), Chromium (Cr) and Vanadium (V) are elements of analogous geochemical behavior and considered geogenic elements with a homogeneous distribution within the studied area. Mn, Co, Ni and Zn, elements with a similar chemical structure, are usually linked in nature, but not associated to the ore (Loredo *et al*., 2006; Adriano, 1986; Rose *et al*., 1979; Shacklette and Boerngen, 1989).

The Ca content in the leaves is mostly likely to have been absorbed from the soil in light of the fact that pollutants usually affect the plants as they are introduced into the plants via deposited contaminants in the soil or via ingestion through leave (Altaf, 2006).

Generally, the origin of trace metals in plant leaves is attributed to the accumulation due to atmospheric deposition (Air accumulation factor - AAF) or transfer from soil (Concentration factor - CF) or both. The variation in AAF and CF values can be due to such factors as the chemical speciation of trace metals, atmospheric and soil concentrations and variations in uptake etc (Vousta *et al*., 1996). The highest occurrence of Ca and S in the water in Allenridge is attributable to the flow of the '*Stink River'* – a man-made sewerage river carrying mine and human wastes in the whole area and settling in Allenridge. According to the BIS and ICMR, the maximum allowable concentration and the permissible concentration of Fe in drinking water is between 1.0 and 0.3 ppm respectively (Akhilesh *et al*., 2009).

In sediment, the occurrence of Mn is attributable to the presence of Mn oxide in the sediment. Also, the presence of Mn in the calcite in the sediments indicates the accumulation of these sediments under oxic conditions (Calvert *et al*., 1993). Co-precipitation of calcite – manganese phase was suggested in the light of the unique Ca-Mn association (Ward *et al*., 1995). The occurrence of Sr in concentrations greater than 10.0 ppm in Allenridge and Welkom could be related to the presence of biogenic carbonates in the area (Rubio *et al*., 2000). The mechanism that controls the mobility of Al and Fe is possibly associated to the Eh-pH seasonal variation that could facilitate the solubility or precipitation of Fe and Al bearing minerals such as oxyhydroxides (Violante *et al*., 2010).

5.2 Evaluation of the study

The study critically aimed to evaluate the major chemical pollutants in the environment in the form of trace elements in light of the intense mining activities taking place in the Lejweleputswa District Municipality, Free State, South Africa.

The first step in the study was to conduct a public awareness study in the area to evaluate the level of the public understanding of the impact of the mining activities in their area on the residents and the environment in general.

The study involving (36 %) female and (64 %) male of which (98 %) were South Africans resident in the area, with (38 %) having senior secondary qualification and (48 %) with tertiary educational qualifications revealed that (73 %) of inhabitants were aware of the mining activities in the area. (80 %) of people are knowledgeable about the minerals in the area. Approximately, (39 %) of inhabitants knew about hazardous materials, mainly chemicals used in the mining operations. Other hazardous materials emanating from the mining operations in the area include: explosives and wastes such as dust, smoke, mud. However, local residents of the area are not certain that the chemicals used in mining operations infiltrated into the environment. Subsequently, majority of residents (52 %) had up to secondary education and could not attribute the environmental pollution in the area to the mining activities.

The results obtained from the analysis of the soil, leaves, water and sediment collected from locations in six towns in the area (with two towns serving as the control adopting standard environmental practices) reveal that the major pollutants in the four environmental segments studied was Ca, with second most abundant being Fe and Mg for soil and Mg, S and P for leaves. In water, the second most abundant chemical pollutants were S and Mg (table 4.6) and in sediment, Fe, S, and Mg (table 4.8) featured significantly.

Other than the natural occurrence of most of the identified trace elements in the environment in the studied area, anthropogenic activities is identified to play a major role in the high concentration of some of the identified elements such as Ca, Mg, and to some extent S. The major anthropogenic activities leading to the introduction of trace elements such as Ca, Mg, etc., in the environment is attributed to regular 'Liming activities' in the area. The process of liming entails the use of $Ca(OH)_2$, $CaSO_4$ and $MgSO_4$ to neutralize the excess sulphuric acid generated in the environment and often associated with mining operations. Also, the natural occurrence of compounds such as $CaCO_3$, $CaSO_4$ and $MgSO_4$ in the soil in Lejweleputswa possibly explains why acid mine drainage does not constitute a serious problem in the area. This is due to the fact that $Ca(OH)_2$, $CaSO_4$, $MgSO_4$ and $CaCO_3$ in the soil dissolve in natural water in the area to form a strong alkaline (basic) solution capable of neutralizing the acid formed in the environment in light of the dissolution of pyrite (FeS) or sulphur occurring in minerals in the area in the natural waters (storm, pond, stream, underground etc.) in the environment.

Often, gold bearing reefs occur naturally with pyrite (FeS) and on contact with water, the S content of the pyrite reacts with water in the environment to produce a high concentration of sulphuric acid in the environment. Fe, Cr and V are geogenic elements of analogous geochemical behavior and seem to have homogeneous distribution within the studied area. Mn, Co, Ni and Zn, are elements with a similar chemical structure, are usually linked in nature, but not associated to the ore.

Origin of trace metals in plant leaves is attributed to the accumulation due to atmospheric deposition or transfer from soil or both. Trace elements are often deposited on plant surfaces by rain and dust. Link between atmospheric element deposition and elevated elements concentration in plants and topsoil, have well been established. Subsequently, a number of the trace elements' contents in the leaves could result from atmospheric deposition and transfer from the soil or both.

In the sediment, the occurrence of Mn is attributable to the presence of Mn oxide in the sediment. Also, the presence of Mn in the calcite in the sediments indicates the accumulation of these sediments under oxic conditions (Calvert *et al*., 1993). Co-precipitation of calcite – manganese phase was suggested in the light of the unique Ca-Mn association (Ward *et al*., 1995). The occurrence of Sr in concentrations greater than 10.0 ppm in Allenridge and Welkom could be related to the presence of biogenic carbonates in the area (Rubio *et al*., 2000).

5.3 General conclusions

At the start of the project, we aimed at unraveling the extent of pollution of the Lejweleputswa area of the Free State, South Africa with trace elements, such as, mercury, lead, nickel, arsenic – heavy metals that are of very serious environmental threat, especially to human health. Other than zirconium, there seem not to be any of the seriously dangerous heavy metals in the environment.

The reason for the non-proliferation of heavy metals in the environment could be due to proper adherence of the mining companies to the legislated laws, and hence, follow proper disposal methods of mine wastes and general mining regulations.

However, the common occurrence of calcium in the all the studied areas and in the media, is attributable to, other than the natural occurrence of the mineral in the soil, to the regular use of calcium sulphate ($CaSO_4$), calcium carbonate ($CaCO_3$) and calcium hydroxide ($Ca(OH)_2$) to neutralize the sulphuric acid contamination of the area due to acid mine drainage. Iron and sulphur in the environment are thought to come from the pyrite (FeS) that occurs with gold ore in the area. Magnesium could result from the Magnesium sulphate ($MgSO_4$) which is also used to neutralize the excess sulphuric acid in the environment that often leads to acid mine drainage. Some rock types in the area are known to also contain $CaCO_3$, $CaSO_4$ and $MgSO_4$ that can naturally neutralize the acid due to acid mine drainage. The occurrence of these compounds ($CaCO_3$, $CaSO_4$ and $MgSO_4$) in the soil in Lejweleputswa possibly explains why acid mine drainage does not constitute a serious problem in the area because the acid is neutralized in the soil by these compounds in solution.

5.4 General recommendations for the control of pollution in the Lejweleputswa District Municipality

- Sufficient number of trees need to be planted in the area, especially around the slime dumps
- A detailed operational instruction needs to be developed by government and served to the mining companies
- Regular government monitoring of adherence to instituted regulations needs to be observed
- Communities should be located at a minimum distance from slime dumps and mining operations in general
- Regular government inspection of mines and their operations is advised.
- A simple procedure for members of the public to relay their complaints to government needs to be developed and a better government interaction with public on issues pertaining to mining activities should be developed.
- A community forum should be developed to interact with mining officials and government on issues pertaining to the society with regard to mining activities in the area.
- Government routine engagement with mineworkers/unions for better understanding of problems with regard to operations and general improvement in areas, especially with respect to operations and reduction of casualties at work and conditions of work in general.

5.5 Recommendations for further studies

In view of the fact that in the current study, the soil, plant, water and sediment in the Lejweleputswa District Municipality (LDM), were covered in the study and analyzed for trace elements, further studies in the area of broader coverage is necessary to acquire a comprehensive view of the environmental situation of the environment of the Lejweleputswa area of the Free State, South Africa.

For further investigation into the environmental condition of the Lejweleputswa area with regard to the extensive mining activities taking place in and around the area, it could be recommended that subsequent studies of the environment around the Lejweleputswa area of the Free State South Africa should be to:

1 Conduct in-depth analysis of the various mine (slime) dumps in the area to have a clear understanding of their chemical composition and subsequent threat to the environment and the inhabitants of the area
2 Quantify the level of trace elements and trace gases in the atmosphere around the area.
3 Analyze animal parts and human excrements for trace elements contamination
4 Analyze radiation levels in the mines, public buildings and identified homes in the area
5 Analyze the area in general for radionuclides
6 Quantify the level of uranium proliferation in the environment in light of the fact that uranium is often associated with gold ore.

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APPENDIX

A QUESTIONNAIRE

PUBLIC AWARENESS OF THE ENVIRONMENTAL IMPACT OF MINING ACTIVITIES IN THE LEJWELEPUTSWA AREA OF THE FREE STATE, SOUTH AFRICA

CENTRALUNIVERSITY OF TECHNOLOGY, BLOEMFONTEIN, FREE STATE, SOUTH AFRICA (CUT)

PUBLIC AND MINE WORKERS/OFFICIALS LEVEL OF AWARENESS OF ENVIRIONMENTAL IMPACT OF MININIG ACTIVITIES IN THE AREA.

QUESTIONNAIRE FOR THE ASSESSMENT OF THE LEVEL OF KNOWLEDGE OF INDICIDUALS LIVING ARAOND LEJWELEPUTSWA AREA, OF THE ENVIRONMENTAL IMPACT OF MINING ACTIVITIES IN THE AREA

QUESTIONNAIRE FOR THE ENVIRONMENTAL IMPACT OF MINING SURVEY, DECEMBER, 2011 – JANUARY, 2012

Start Time:

Interviewer Introduces Herself/Himself and the institution – CUT

Interviewer's name:……………………………………………….

PURPOSE OF SURVEY

The effect of the state of the environment on the inhabitants of an area is recently becoming of serious concern to different governmental authorities around the globe. Mining activities is associated with serious environmental degradation and pollution.

The Lejweleputswa area of the Free State is among the most mined areas in South Africa. With growing interest on the effect of environmental condition on human and animal health and its overall impact on the environment as a whole, this survey seeks to ascertain the level of the impact of mining activities in the area, the public and mining officials / workers awareness level of the impact of mining activities on the environment and its inhabitants and efforts by government, mining authorities and the public to address the environmental impact of mining in the area.

The survey will be conducted around the Lejweleputswa area where the inhabitants would have had long experience of the impact of mining activities on the environment. The questionnaire is intended to assess the knowledge of the public, mining and government officials about the impact of mining activities on the environment and the effort by mining authorities and government to stem the impact of mining activities on the environment.

CONSENT

Kindly be certain that the information provided by you is correct to the best of your knowledge. You are however, not in any way compelled to answer any of the questions.

The questionnaire evaluates the general awareness level of individuals about the environmental impact of mining activities in their area. The information to be obtained from the questionnaire shall be used as part of the data to compile a thesis in fulfillment of requirement for the degree of 'Doctor of Technology' in Environmental Health.

CONFIDENTIALITY

All personal information gathered in this survey will be kept strictly confidential. Names and address of respondents shall not be included or divulged.

City/Town/Village Kgotla

QUESTIONNAIRE IDENTIFICATION NUMBER

SECTION A: BACKGROUND INFORMATION OF THE RESPONDENT

Date of interview	
District	
Name of town /village	
Name of business	
Business address	
Contact details	

A1 **Name of respondent……………………………………………………….**
A2 **Contact address…………………………………………………………….**
A3 **Contact telephone number………………………………**
A4 **Age of respondent 1) < 18 2) 18 – 39 3) 30-39 4) 40-49 5) 50-64 6) >64**
A5 **Gender 1) Male 2) Female**
A6 **Racial origin 1) Black 2) White 3) Asian 4) Others (specify)**
A7 **Nationality ……………………………………………………**
A8 **Religion 1) Christian 2) Muslim 3) Hindu 4) None 5) Others (specify)**
A9 **Educational level 1) No formal education 2) Primary 3) Junior secondary 4) Senior secondary 5) Tertiary education.**

SECTION B: MINE AND ALLIED WORKERS AWARENESS LEVEL OF THE CONSEQUENCIES OF MINING ACTIVITIES ON THE ENVIRONMENT

B1 **In which mine do you work? I……………….. 2………………. 3……………..4…………**
B2 **Do you live close to the mine? Yes………… No……………….**
B3 **How long have you been working in the mining sector?...**
B4 **What work do you do at the mine? ……………………………………………**
B5 **Have you always lived in this mining town? Yes………………. No………………….**
B6 **How long have you been living in this mining area…………………………**
B7 **Are you aware of mine wastes that could be hazardous to the environment?**
Yes……………. No……………..
B8 **Kindly list some hazardous substances you believe are contained in the mine waste?**
1………………………2…………………………3…………………………4………………
B9 **Do you know how mine wastes are disposed by your company? Yes……….No…………**
B10 **Are there some tailing dams in the area for mine waste disposal? Yes……….No…………**
B11 **How far is the tailing dam from the**
i) Mine………………..ii) Residential area……………….iii) City centre………………….

B11 Do you know how these hazardous materials get into the environment? Yes…….No……

B12 Kindly give a brief explanation of how you think the hazardous materials get into the environment?

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B13 How are mine wastes disposed by the mining companies?...

B14 Do you think the mining authorities are aware of the impact of their activities to the environment?

B15 Are there measures taken by the mining companies to reduce the amount of wastes that enter the environment? Yes………………….No……………………….

B16 Kindly outline the efforts by mining authorities to curb environmental pollution by the their company:……………………………………………………………………………………

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B17 Are you aware of government legislations or by-laws governing mining operations?
Yes……………………..No…………………………

B18 Are mining companies supervised by the government? Yes……………..No………………

B19 To what extent do you think these supervisions influence the mining authorities to comply with existing laws?...

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B20 Do you think the government is wining in effort to persuade the mining companies to bring environmental pollution to the barest minimum? Yes………………No………………….

B21 What extra measures would you advise the government to take to ensure that environmental pollution by mining companies is brought under control?...

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SECTION C PUBLIC AWARENESS OF CONSEQUENCIES OF MINING ACTIVITIES

C1 **Do you know of the mining activities taking place in this area? Yes……No……**

C2 **How many mining companies are operating in this area?..**

C3 **Kindly list the companies' names ……………………………………………………………**
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C4 **What minerals are mined in this area?**
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……………………………………………………………………………………………………
……………………………………………………………………………………………………

C5 **How are waste rocks from mining disposed?**

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C6 **Do you know of any hazardous materials used in mining operations? Yes………No……..**

C7 **What hazardous materials are these?1)…………………………………………………………...**
2)……………………………………….3)…………………………………………………………..
4)……………………………………….5)……………………………………………………..........
6)……………………………………….7)…………………………………………………………..

C8 **Do these hazardous materials enter the environment? Yes…………………..No……………**

C9 **Kindly indicate which of the following is affected by the hazardous materials from the mines.**

I	**Drinking water**	**Yes…………….No……........**
Ii	**Rain water**	**Yes…………….No……….....**
Iii	**Underground water**	**Yes…………….No…………**
Iv	**Soil**	**Yes…………….No…………..**
V	**Plants**	**yes……………..No…………**
Vi	**Animals**	**Yes……………..No…………**
Vii	**Foods**	**Yes……………..No…………**
Viii	**Public**	**Yes……………..No……….....**

C10 Have you felt concerned about the environmental pollution in the area? Yes……..No……….

C11 Kindly explain what led you to becoming concerned about the environment?
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C12 Are there concerns about food pollution due to environmental pollution from mining? Yes…….No…….

C13 Are you aware of any health impact of these materials in the environment? Yes……No……

C14 What sicknesses do people suffer as a result of environmental pollution?
i…………………………………………..
ii………………………………………….
iii…………………………………………
iv…………………………………………

C15 Is there an observable seasonal trend in the nature of pollution? Yes………..No………

C16 Is there an observable seasonal trend in pollution level? Yes……….No……………..

C17 Is there an observable seasonal trend in the sicknesses suffered by the members of the public? Yes……………….No…………………

C18 Does the wind condition affect the pollution level in the area? Yes………..No………………

C19 Can the environmental pollution be attributed to mining activities? Yes…………No…………
C20 Are you aware of reports to the authorities of environmental pollution? Yes………No………
C21 Were the complaints related to mining activities? Yes………..No…………….
C22 Did the authorities respond positively? Yes…………No……………………...
C23 Was there a follow up by the complainant? Yes……………No………………..
C24 Was there a follow up by the authorities? Yes…………..No………………….
C25 Are you aware of illegal mining activities? Yes…………No……………………
C26 Are illegal miners well-off from their dealings? Yes………..No……………….
C27 Could illegal mining be described a common practice by people? Yes……………No………………
C28 Are you aware of the consequences of obnoxious materials in the environment?

Yes	
No	

i. **Is rain water affected?**

Yes	
No	

ii. **Is the underground water?**

Yes	
No	

iii. **Is drinking water affected?**

Yes	
No	

iv. **Is the soil affected?**

Yes	
No	

v. **Are plants affected?**

Yes	
No	

vi. **Are animals affected?**

Yes	
No	

vii. **Are foods in the area affected?**

Yes	
No	

viii **Is the public affected?**

Yes	
No	

ix **Are there concerns about environmental pollution from mining activities that could affect food quality and safety?**

Yes	
No	

C29 **Have you ever felt concerned about the environmental pollution in this area?**

Yes	
No	

C30 **What prompted your concern about the environment?………………………**

C31 **Are you aware of any health impact of these materials in the environment?**

Yes	
No	

C32 **What sicknesses are these?**
i……………………………………..
ii…………………………………….
iii……………………………………
iv……………………………………

C33 **Are there observable seasonal trends in the pollutant level in the area?**
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C34 How does wind affect the pollution in the area?

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C35 How do pollutant levels differ between winter and summer seasons?

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C36 Are you aware of reports to the authorities of environmental pollution?

Yes	
No	

C37 Were the complaints related to mining activities?

Yes	
No	

C38 Was there a positive response?

Yes	
No	

C39 Was there a follow up by the complainant?

Yes	
No	

C40 Was there a follow up by the authorities?

Yes	
No	

C41 Do you know about illegal mining is?

Yes	
No	

C42 Do you know people who are not mine workers but go into the mines on their own to get minerals to sell?

Yes	
No	

C43 Are there many such people as in question 24 above?

Yes	
No	

C44 Are such miners wealthy from the practice?

Yes	
No	

C45 Are the youths influenced into such mining activities?

Yes	
No	

C46 What do you think the government can do to discourage such mining activities?

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C47 **What do you think the mining companies should do to control such miners not employed by the mining companies?**

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C48 **What can mining companies do to control the environmental impact of mining?**

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APPENDIX

B MINERAL OCCURRENCE IN THE LEJWELEPUTSWA DISTRICT MUNICIPALITY, FREE STATE, SOUTH AFRICA, THEIR CHEMICAL FORMULAE AND LOCALITIES *(mindat.org)*

	Mineral	Chemical formula	Locality
1	Albite-Anorthite Series	-	Roberts Victor Mine, Boshof, Lejweleputswa District
2	Analcime	$Na_2(Al_2Si_4O_{12}).2H_2O$	Robert Victor Mine, Boshof, Lejweleputswa District
3	Apatite	-	Star Mine, Theunissen kimberlite field, Theunissen
4	Aragonite	$CaCO_3$	President Brand Mine, Lejweleputswa District, Free State Province, South Africa
5	Augite	$(Ca, Na)(Mg, Fe^{2+}, Al, Fe^{3+}, Ti)[(Si, Al)_2O_6]$	Roberts Victor Mine, Boshof, Lejweleputswa, Free State, South Africa
6	Augitevar: Fassaite	-	Roberts Victor Mine, Boshof, Lejweleputswa District, Free State, South Africa
7	Bultfonteinite (TL)	$Ca_2(HSiO_4)F.H_2O$ Ref: AM 40 (1955), 900; HB2/1 (1995)	Bultfontein, Lejweleputswa, Free State, South Africa
8	Calcite	$CaCO_3$	Star Mine, Theunissen kimberlite field, Theunissen, Lejweleputswa District, Free State Province, South Africa; Robert Victor Mine, Boshof, Lejweleputswa District, Free State, South Africa; Loraine Mine, Welkom, Witwatersrand field, Lejweleputswa District,

			Free State Province, South Africa
9	Chromite	$Fe^{2+}Cr^{3+}_2O_4$	Robert Victor Mine, Boshof, Lejweleputswa District, Free State Province, South Africa
10	Coesite	SiO_2	Roberts Victor Mine, Boshof, Lejweleputswa District, Free State, South Africa
11	Corundum	Al_2O_2	Roberts Victor Mine, Boshof, Lejweleputswa District, Free State Province, South Africa
12	Diamond	C	Reported for at least 7 localities in this region
13	Diopside	$CaMgSi_2O_6$	Roberts Victor M ine, Boshof, Lejweleputswa District, Free State, South Africa
14	Freudenbergitevar: Ferrous freudenbergite	-	Bultfontein, Lejweleputswa District, Free State Province, South Africa
15	Garnet	$X_3Z_2(SiO_4)_3$	Star Mine, Theunissen Kimberlite field, Theunissen, Lejweleputsw District, Free State Province, South Africa Blaauwbosch Mine, Boshof, Lejweleputswa District, Free State, South Africa
16	Glass	-	Roberts Victor Mine, Boshof, Lejweleputswa District, Free State Province, South Africa
17	Gold	Au	Reported for at least 10 localities in this region
18	Graphite	C	Roberts Victor Mine, Boshof, Lejweleputswa District, Free State, South Africa

19	Grossular	$Ca_3Al_2(SiO_4)_3$	Roberts Victor Mine, Boshof, Lejweleputswa District, Free State Province, South Africa
20	Hornblende	-	Roberts Victor Mine, Boshof, Lejweleputswa District, Free State Province, South Africa
21	Iridium var: Osmiridium	-	Lorraine Mine, Welkom, Witwatersrand field, Lejweleputswa District, Free State Province, South Africa President Steyn Mine, Welkom, Witwatersrand field, Lejweleputswa District, Free State Province, South Africa President Brand Mine, Lejweleputswa District, Free State Province, South Africa
22	Isoferroplatinum	Pt_3Fe	Reported for at least 6 localities in this region
23	Kyanite	$Al_2(SiO_4)O$	Roberts Victor Mine, Boshof, Lejweleputswa District, Free State Province, South Africa Blaauwbosch Mine, Boshof, Lejweleputswa District, Free State, South Africa
24	Mannardite	$Ba(Ti^{4+}{}_6V^{3+}{}_2)O_{16}$	Star Mine, Theunissen kimberlite field, Theunissen, Lejweleputswa District, Free State Province, South Africa
25	Monazite	-	Bothaville, Lejweleputswa District, Free State Province, South Africa
26	Mountainite (TL) (Ref: Min. Mag.(1957) 31,	$KNa_2Ca_2[Si_8O_{19}(OH)].6H_2O$ (white fibre)	Bultfontein, Lejweleputswa District,

	611-623; Mineral of South Africa)		Free State Province, South Africa
27	Mullite	$Al_{4+2x}Si_{2-2x}O_{10-x}$	Roberts Victor Mine, Boshof, Lejweleputswa District, Free State Province, South Africa
28	Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Welkom, Witwatersrand field, Lejweleputswa District, Free State Province, South Africa
29	Olivine	$(Mg,Fe^{2+})_2SiO_4$	Star Mine, Theunissen kimberlite field, Theunissen, Lejweleputswa District, Free State Province, South Africa
30	Omphacite	$(Ca,Na)(Mg,Al)Si_2O_6$	Roberts Victor Mine, Boshof, Lejweleputswa District, Free State Province, South Africa
31	Perovskite	$CaTiO_3$	Star Mine, Theunissen kimberlite field, Theunissen, Lejweleputswa District, Free State, South Africa
32	Phlogopite	$KMg_3(AlSi_3O_{10})OH,F)_2$	Theunissen Kimberlite field, Theunissen, Lejweleputswa District, Free State Province, South Africa Star Mine, Theunissen Kimberlite field, Theunissen, Lejweleputswa District, Free State Province, South Africa
33	Priderite	$K(Ti^{4+}{}_7Fe^{3+})O_{16}$	Star Mine, Theunissen kimberlite field, Theunissen, Lejweleputswa District, Free State Province, South Africa
34	Pyrite	FeS_2	President Brand Mine, Lejweleputswa District,

			Free State Province, South Africa Welkom, Witwatersrand field, Lejweleputswa District, Free State Province, South Africa Star Mine, Theunissen Kimberlite field, Theunissen, Lejweleputswa District, Free State Province, South Africa
35	Pyrophyllite	$Al_2(Si_4O_{10})(OH)_2$	Welkom, Witwatersrand field, Lejweleputswa District, Free State, South Africa
36	Quartz	SiO_2	President Brand Mine, Lejweleputswa District, Free State Province, South Africa Lorraine Mine, Welkom, Witwatersrand field, Lejweleputswa District, Free State Province, South Africa Welkom, Witwatersrand field, Lejweleputswa District, Free State Province, South Africa Roberts Victor Mine, Boshof, Lejweleputswa District, Free State Province, South Africa Blaauwbosch Mine, Boshof, Lejweleputswa District, Free State Province, South Africa
37	Rhodesite (TL) (Ref: Min.Soc. Notice no. 95 (1956), and Min. Mag. (1957) 31, 607-610)	$KHCa_2Si_8O_{19}.5H_2O$	Bultfontien, Lejweleputswa District, Free State Province, South Africa

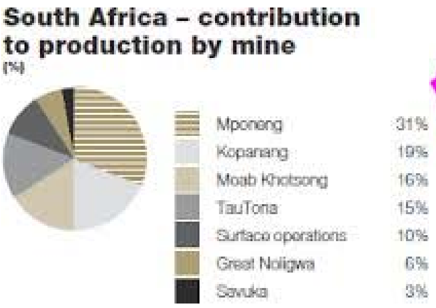
38	Rutile	TiO_2	Welkom, Witwatersrand field, Lejweleputswa District, Free State Province, South Africa
39	Sanidine	$KAlSi_3O_8$	Roberts Victor Mine, Boshof, Lejweleputswa District, Free State Province, South Africa
40	Spinel	$MgAl_2O_4$	Roberts Victor Mine, Boshof, Lejweleputswa District, Free State Province, South Africa Star Mine, Theunissen kimberlite field, Theunissen, Lejweleputswa District, Free State Province, South Africa
41	Stibiopalladinite	Pd_5Sb_2	President Brand Mine, Lejweleputswa District, Free State, South Africa
42	Sudoite	$(Mg,Fe^{2+})_2Al_3(AlSi_3O_{10})(OH)_8$	Welkom, Witwatersrand field, Lejweleputswa District, Free State Province, South Africa
43	Uraninite	UO_2	Welkom Mine, Welkom, Witwatersrand field, Lejweleputswa District, Free State, South Africa
44	Zircon	$ZrSiO_4$	Bultfontein, Lejweleputswa District, Free State Province, South Africa Bothaville, Lejweleputswa District, Free State Province, South Africa

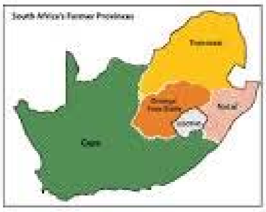
Appendix C Virginia town sampling point

Appendix D Welkom sampling point (St Helena)

	Mean Standard Deviations		
Trace elements	**Ca**	**Mg**	**CaMg**
Medium			
Soil	1.06538071	1.15790365	1.12349995
Leaves	1.03755864	2.92096006	1.04178598
Water	1.20916512	1.49493023	1.93028291
Sediment	1.24712134	1.04946138	1.11344633

Appendix E Mean standard deviations for trace elements content in the different media





Appendix F Map illustrations of industrial and mining areas, political and provincial demarcations of South Africa and demarcations of African countries within Africa.