

**AN ASSESSMENT OF HEAVY METAL POLLUTION NEAR AN OLD COPPER
MINE DUMP IN MUSINA, SOUTH AFRICA**

by

Ndinannyi Kenneth Singo

submitted in accordance with the requirements for the degree of

Master of Science

in the subject

Environmental Management

at the



Supervisor: Prof SJ Moja

Co-supervisor: Mr KW Maphangwa

June 2013

DECLARATION AND COPYRIGHT

I declare that “An assessment of heavy metal pollution near an old copper mine dump in Musina, South Africa” is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

.....

SIGNATURE

Mr NK Singo

.....

DATE

DEDICATION

I dedicate this research work to

My wife Elelwani Siaga-Singo

My daughter Rofhenya Tshinakaho Singo

My parents Madigana Samson Singo and Tshinakaho Elisa Magoro-Singo

I gratefully thank the Lord God for all His blessings, generosity and mercy upon me

ACKNOWLEDGEMENTS

- I would like to give special thanks to my supervisors Prof. SJ Moja and Mr. KW Maphangwa who reviewed and commented on the entire manuscript with good faith, incredible patience and guidance as my supervisors.
- Thanks are given to Mr. K Matshusa for all his help in the laboratory at the University of Venda, Ms LA Nemitamba of Eskom Kriel Power Station laboratory and Mr. PM Masipa of the Madzivhandila College of Agriculture for their laboratory assistance.
- My appreciation goes to my field assistants, TA Singo, NM Mualusi, and R Netshifume who assisted me with soil and water sampling.
- The community of Musina Municipality and the municipal spokesperson Mr. W Dzebu are thanked for their much needed support and guidance.
- Sincere thanks also go to my family, relatives and friends who showed me love and gave me courage in this venture which may look simple, but which was both intriguing and challenging. These include my beloved wife Mrs. E Siaga-Singo, little daughter RT Singo, my mother TE Magoro, my father Mr. MS Singo and all my brothers and sisters namely; Norman, Radzilani, Patrick, Konanani, Tshililo and those whose names I have not mentioned.
- If this project has any merit, it is due to the wise counsel and contribution of the above – mentioned people. Its shortcomings, whether of style or arrangement, errors of facts or of interpretation are all mine.

ABSTRACT

Heavy metal pollution in water and soil is a serious concern to human health and the associated environment. Some heavy metals have bio-importance but the bio-toxic effects of many of them in human health are of great concern. Hence, there was a need for proper understanding of the concentration levels of these heavy metals in ground water and soil around the community residing in the vicinity of the defunct mine. Mining has become prominent in this area because of the existence of copper lodes, veins and veinlets. It was therefore necessary to assess these selected metals associated with copper mining as their concentration has a tendency to affect the environment and human health. The objective of this study was to establish the levels of lead (Pb)-zinc (Zn)-copper (Cu)-arsenic (As)-nickel (Ni) metals in ground water and soil associated with an old copper mine in the vicinity of the township and to compare them with the South African and international standards in order to safeguard the health of the community using such water for drinking purpose.

Clean sampling plastic bottles were used to collect water from five water boreholes being used at present. Water samples were filtered using membrane filtration set LCW (0.45 μm). The samples were digested sequentially with different procedures for the total metal concentration. Concentrations of four metals commonly associated with Cu mining were examined at five different water boreholes which are used for drinking and industrial purposes. Flame Atomic Absorption Spectrophotometer (Perkin Elmer S/n 000003F6067A, Singapore) was used to analyze metals in water samples at Eskom Ga-Nala Laboratory: pH, electrical conductivity and turbidity were analyzed using an auto titrator meter (AT-500, Japan), conductivity meter (Cole-parmer[®] YO-19601-00) and turbidity meter (AL 250T-IR, Agua lytic, German) respectively.

Soil samples were collected from the selected areas where human health is of a serious concern, and a hand held auger drill was used to recover samples, while shovels were used to prepare the sampling area. The samples were sieved up to 63.0 μm particle size and digested with aqua-regia. Flame Atomic Absorption Spectrophotometer (Model: AA400; Year: 2008; Manufacturer: Perkin Elmer; Germany; Serial no: 201S6101210) was used at the University of Venda Laboratory to analyze soil from the study area for possible heavy metal contamination due to the defunct Cu mine in the area.

The results showed variation of the investigated parameters in water samples as follows: pH, 6.0 to 7.51; EC, 70.0 to 96.40 $\mu\text{S}/\text{cm}$ and turbidity, 1.05 to 4.56 NTU. The mean concentration of the metals increased in the following order: $\text{Pb} < \text{Cu} < \text{As} < \text{Ni}$. Ni is the most abundant in the ground water determined with value of (6.49 $\mu\text{g}/\text{g}$). The observations have confirmed that most ground water contains an appreciable quantity of Ni. The mean value of As in water is (4.20 to 4.84 $\mu\text{g}/\text{g}$), Pb and Cu have (2.13 to 2.58 $\mu\text{g}/\text{g}$) and (1.52 to 2.52 $\mu\text{g}/\text{g}$) respectively. For soil samples, the mean concentration of the metals increased in the following order: $\text{Pb} < \text{Cu} < \text{Zn} < \text{As} < \text{Ni}$. Pb ranged from (0.023 to 0.036 $\mu\text{g}/\text{g}$) followed by Cu (0.28 to 0.45 $\mu\text{g}/\text{g}$) then Zn (0.026 to 0.053 $\mu\text{g}/\text{g}$), the mean range of As in soil ranged from (0.054 to 0.086 $\mu\text{g}/\text{g}$). However, some studies show much higher contamination of As from the natural sources and Ni with (0.057 to 0.144 $\mu\text{g}/\text{g}$) lastly. Accumulation of heavy metals in soil is of concern due to their toxic effects on human and animals.

The quality of ground water from the five boreholes studied was satisfactory with turbidity (T), electrical conductivity (EC) and heavy metals (HM's) below the WHO limit. The water therefore may, according to the WHO Standards be safely used as a drinking water. The concern lies on pH which was slightly (0.5) below the standard. There is a serious need to monitor the ground water which is now used for drinking purposes.

This study revealed that heavy metal pollution in soil from the abandoned Cu mine in Musina is a threat to the health of the community. Although pollution was between medium and low in the contamination index, it is therefore important for the Musina Municipality or mine owner of Musina (TVL) Development Co Ltd copper mine to advocate possible remedial actions which will safeguard the environment and human health.

The tailing at Musina's old Cu mine have high pH and they lack normal soil stabilization processes, as a result the tailing does not develop a good plant cover. Pollution of the ground water resources is also evident in the study area where there is seepage or ingress of polluted water to the underground aquifers. Small-scale mining in Musina is causing further degradation to the environment but it supports the South African Waste Hierarchy by promoting the reuse and recycling of the tailing and mine dumps for the production of bricks. Mine workers are exposed to the above mentioned toxic heavy metals daily. Medicine will not help stop the poisoning. The only way to stop the metal poisoning is to stop being exposed to the heavy metals.

CONTENTS

	PAGE
DECLARATION AND COPYRIGHT.....	i
DEDICATION.....	ii
ACKNOWLEDGEMENTS.....	iii
ABSTRACT.....	iv-v
CONTENT.....	vi-xiv
LIST OF FIGURES.....	xv-xvii
LIST OF TABLES.....	xviii
GLOSSARY OF TERMS.....	xix-xxii
ACRONYMS AND ABBREVIATIONS.....	xxiii-xxiv
 CHAPTER ONE: INTRODUCTION	
1.1 Background to Ancient Mining activities.....	1
1.1.1 Mining activities in Limpopo Province.....	1-2
1.1.2 Social, environmental and economic impacts of mining.....	3
1.1.3 Impact of mining on human and environmental health.....	4-5
1.2 The Statement of the Problem.....	6
1.3 Need for the Research.....	6

1.4 Aims and Objectives.....	7
1.4.1 General aims.....	7
1.4.2 Specific objectives.....	8
1.5 Concluding Thought.....	8
References.....	9-11

CHAPTER TWO: LITERATURE REVIEW

2.1 General Aspect of Mining.....	12
2.1.1 Extraction operation.....	12
2.1.2 Surface mining.....	13
2.1.3 Underground mining.....	14
2.1.4 Beneficiation operation.....	15
2.1.5 Mineral processing operations.....	16
2.2 Mine Waste.....	16
2.2.1 Tailings.....	16-18
2.2.2 Mine dumps.....	18
2.2.3 Ore stockpiles.....	19
2.2.4 Slags.....	19
2.3 Heavy Metals.....	20-21
2.3.1 Cadmium.....	22

2.3.2 Arsenic.....	23
2.3.3 Mercury.....	24
2.3.4 Lead.....	25-27
2.3.5 Nickel.....	27
2.3.6 Copper.....	28
2.3.7 Zinc.....	29
2.3.8 Manganese.....	30
2.4 Harmful Effects of Heavy Metal on Human and Environment.....	31
2.5 Impacts of Abandoned Mines.....	32
2.5.1 Acid mine drainage.....	32-34
2.5.1.1 The role of micro-organisms in acid mine drainage.....	35-37
2.5.2 Land disturbance.....	38
2.5.3 Habitat destruction.....	39
2.5.4 Water quality.....	39
2.5.5 Social and development issues at a mining area.....	40
2.6 South African Policy and Legislation Frame work.....	41
2.6.1 National Environmental Management Act 107 of 1998.....	42
2.6.2 Mineral Act 50 of 1991.....	42
2.6.3 Mine closure and post-operational waste management.....	42
2.6.4 Mineral and Petroleum Resources Development Act 28 of 2002.....	43

2.7 Sampling Methods.....	43
2.7.1 Water sampling.....	43
2.7.1.1 Tap water (reticulated town water, tank water, and other storage facilities with a tap outlet).....	43
2.7.1.2 Groundwater (bores, wells-pump operated).....	44
2.7.1.3 Surface waters – shallow and deep (lakes, rivers, creeks, streams)..	44
2.7.1.4 Depth water samples	45
2.7.2 Soil sampling.....	46
2.7.2.1 Auger.....	47
2.7.2.2 Split spoon.....	47
2.7.2.3 Shovel.....	48
2.8 Review of Sample Treatment Methods.....	48
2.8.1 Grinding of samples.....	48
2.8.1 Acid decomposition.....	48
2.9 Review of Physico-Chemical Parameter.....	49
2.9.1 Mine tailings slope features and vegetation cover.....	49
2.9.2 pH.....	50
2.9.3 Electrical conductivity.....	50
2.9.4 Turbidity.....	51
2.9.5 Total metal content.....	51

2.10 Review of instrumental Techniques for Metal Analysis.....	52
2.10.1 Graphite furnace atomic absorption (GFAA).....	53
2.10.2 Flame atomic absorption (FAA).....	53-54
References.....	55-68

CHAPTER THREE: MATERIALS AND METHODS

3.1 Study Area and Sample Handling.....	70
3.1.1 Location.....	70
3.1.2 Geology.....	71
3.1.3 Soil.....	71
3.1.4 Climate.....	72
3.1.5 Topography.....	72
3.1.6 Land use and land capability.....	73
3.1.7 Vegetation.....	73
3.1.8 Surface water.....	73
3.1.9 Air quality.....	74
3.1.10 Noise pollution.....	74
3.1.11 Cultural heritage.....	74
3.1.12 Social and economic environment.....	75
3.2 Sampling Sites.....	76

3.2.1 Review of background information.....	76
3.2.2 Background samples.....	76
3.2.3 Reconnaissance survey.....	77
3.2.4 Water sampling.....	77
3.2.5 Soil sampling.....	78-81
3.3 Sampling Period and Frequency.....	82
3.4 Meteorological Parameters.....	83
3.4 Reagent and Methods.....	83
3.4.1 Water samples.....	83
3.4.2 Soil samples.....	84
3.5 Methods.....	85
3.5.1 Quality assurance, method validation and detection limit.....	85
3.5.2 Data analysis.....	86
3.5.3 Wind and precipitation data.....	87
3.5.4 Determination of physico-chemical parameters.....	88
3.5.4.1 Mine tailings slope features and vegetation cover.....	88
3.5.4.2 Paste pH analysis.....	88
3.5.4.3 Electrical conductivity.....	89
3.5.4.4 Turbidity.....	89
3.5.4.5 Total metal content.....	89

3.6 Concluding Thought.....	90
References.....	91-92

CHAPTER FOUR: RESULTS AND DISCUSSIONS

4.1 Review of Meteorological Data.....	93
4.1.1 Precipitation and temperature data.....	93-95
4.1.2 Wind speed and direction data.....	95-99
4.2 Quality Control, Detection Limit and Method Validation.....	100
4.3 Control Samples Data.....	101
4.3.1 External control data.....	101
4.3.2 Internal control data.....	102-103
4.3.3 Evaluation of soil pollution.....	104
4.4 Measurements of Physico-Chemical Parameters.....	105
4.4.1 Mine tailings slope features.....	105
4.4.1.1 Tailing profile logging.....	105-111
4.4.2 Vegetation cover.....	112
4.4.2.1 Erosion.....	112
4.4.2.2 Rehabilitation of disturbed land.....	113-115
4.4.3 Small-scale mining and brick-making business.....	115-117

4.4.4 pH data.....	118
4.4.4.1 pH data in water samples.....	118-119
4.4.4.2 pH data in soil samples.....	119-120
4.4.5 Conductivity in water samples.....	121
4.4.6 Turbidity in water samples.....	122-123
4.4.7 Total metal content.....	124
4.4.7.1 Total metal content in water samples.....	124-127
4.4.7.2 Total metal content in soil samples.....	128-135
4.4.8 Mean metal, standard deviation and coefficient of variation concentrations of field samples.....	135
4.4.8.1 Water sample.....	136
4.4.8.2 Soil samples.....	137-138
References.....	139-141

CHAPTER FIVE: SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary.....	142-143
5.1.1 Rehabilitation strategies to be developed.....	144
5.1.1.1 Re-vegetation strategy.....	144
5.1.1.2 Minimisation of risks to the public safety.....	144

5.1.1.3 Stabilisation of the high walls of the tailing and ensuring resistance to erosion.....	144
5.1.1.4 Encouragement of small-scale miners to practice rehabilitation.	145
5.2 Conclusions.....	145-146
5.3 Recommendations.....	147
APPENDICES.....	148
Appendix 1 Idealized/deviation response curves for FAAS.....	149
Appendix 2 Calibration curve as shown on the computer during analysis.....	149
Appendix 3 Ethics Clearance (Ref. Nr.: 2012/CAES/015).....	150
Appendix 4 Expected Outcomes of the Research.....	151

LIST OF FIGURES

	PAGE
Figure 2.1 Different steps of a surface mining activity (adopted from BRGM, 2001)...	13
Figure 2.2 Underground mine workings (adopted from BRGM, 2001).....	15
Figure 2.3 Photomicrographs 1 (left), 2 (centre) and 3 (right): Thiobacilli from bacterial generator (no flagella) - left and centre - and grown on ferrous iron (flagella) - right....	37
Figure 2.4 Waste Hierarchies (Kalule, 2009).....	41
Figure 2.5 Sampling protocol (DWAF, 2000 & SANS 5661-1:2000).....	45
Figure 3.1 Materials and Methods flow chart.....	69
Figure 3.2 Locality map of Musina and the study area (Adopted from DWAF, 2001)....	70
Figure 3.3 (A) & (B) Showing the water samples.....	78
Figure 3.4 A map showing the location of the Town and Sampling points (Modified from DWAF, 2001).....	80
Figure 3.5 Approach used for sampling plan (adopted from ASTM, 1987).....	81
Figure 3.6 (A) & (B) Depicting soil and tailing samples collected during field work, samples were transported by private car to the laboratories.....	82
Figure 3.7 Sample analysis with FAAS at the Department of Mining and Environmental Geology laboratory.....	90
Figure 4.1 Total rainfalls recorded between sampling periods.....	94
Figure 4.2 Minimum and maximum temperature recorded between sampling months...	95

Figure 4.3 Maximum wind speed recorded between January and February 2013.....	97
Figure 4.4 Maximum wind speed recorded between March and April 2012.....	97
Figure 4.5 Maximum wind speed recorded between May and June 2012.....	98
Figure 4.6 Maximum wind speed recorded between July and August 2012.....	98
Figure 4.7 The predominant wind direction during the sampling period.....	100
Figure 4.8 Variations of pollution index for selected metals in soil samples.....	105
Figure 4.9 (a): Profile exhibiting six different layering in the tailing dump from the North Note: Brownish steins resulting from steel dumped in layer C.....	107
Figure 4.9 (b): Representative profile along the middle of the tailings. Note: High metal dumped into layer B.....	109
Figure 4.9 (c): North-west profile representing pure tailing materials.....	111
Figure 4.10 (A) The influence of slope on the intensity of erosion. (B) High walls waiting to collapse posing danger to nearby inhabitants. (C) Tailing erosion and field sampling assistants standing near approx 3.0 m vertical wall of tailing. (D) A steep-side gully or donga created by erosion.....	113
Figure 4.11 (A) & (B) Shows re-vegetated trees in a row. (C) & (D) Shows the remaining components of an irrigation system decomposing due to the exposure to the direct prolonged sunlight.....	115
Figure: 4.12 (A & B) Mine equipment includes heavy trucks, a bull dozer and conveyor belts. (C) Land degradation resulting from the current mining activities. (D) Female mine workers collecting precious stones near copper dump.....	117
Figure 4.13 Measurements of pH from the water samples.....	119

Figure 4.14 pH ranges for the selected samples.....	121
Figure 4.15 Measurements of electrical conductivity in water sample.....	122
Figure 4.16 Turbidity obtained at all sites collected.....	123
Figure 4.17 (a) Measurements of heavy metals in water samples between January and March 2013.....	125
Figure 4.17 (b) Measurements of heavy metals in water samples between April and June 2012.....	125
Figure 4.17 (c) Measurements of heavy metals in water samples between July and August 2012.....	126
Figure 4.18 (a): Total As distribution per site.....	129
Figure 4.18 (b): Total Cu distribution per site.....	131
Figure 4.18 (c): Total Ni distribution per site.....	132
Figure 4.18 (d): Total Pb distribution per site.....	134
Figure 4.18 (e): Total Zn distribution per site.....	135

LIST OF TABLES

	PAGE
Table 3.1 Concentrations of calibration standards prepared from 0.10 ($\mu\text{g/g}$) stock solution.....	86
Table 3.2 Classification standards of soil pollution evaluation.....	87
Table 4.1 Average daily wind directions during sampling period.....	99
Table 4.2 Validation of method against soil certified values material.....	101
Table 4.3 Background levels of selected trace metals near the study area.....	102
Table 4.4 Internal background values.....	103
Table 4.5 Background levels against samples levels and their pollution index.....	104
Table 4.6 Mean metal concentration in water samples in both winter and summer period.....	136
Table 4.7 The mean concentration for selected metals over the entire span of the sampling sites.....	137

GLOSSARY OF TERMS

- Acid Mine Drainage:** The seepage of sulphuric acid solutions from mines and tailings, produced by interaction of oxygen in the ground, surface water, and sulphide minerals exposed by mining (DME, 2006:4).
- Concentration:** The purpose of concentration is to separate those particles with high values (concentrate) from those with lower values (Vick, 1983:6)
- Contamination:** An introduction of any poisonous or polluting substance into an environment (Parson, 2004 & Oxford, 2002).
- Dam:** The term includes any settling dam, slurry dam, evaporative dam, catchment or barrier dam and any other form of impoundment used for the storage of unpolluted water or water containing waste (DWAF, 1999).
- Deposit:** A dump, heap, pile or filling which usually projects above the natural ground level. Deposit includes terms such as slimes dams, tailing impoundments, mineral tailings, course water and waste rock dumps (Blight & Du Preeze, 1999).

Dispersion: Dispersion is the measuring of spreading and mixing due to microscopic variations in vocatives within and between pores (Vick, 1983:6).

Ecosystem: Organisms living together with their abiotic environment forming an interacting system, inhabiting and identifiable space (Oxford, 2004).

Effluent: A liquid fraction of the tailings slurry or pulp with the soluble chemicals (Oxford, 2004).

Environmental Impact: Is any change in the state of any component of the environment whether adverse or beneficial of the environment such as water, air and natural resources, flora, fauna and that which results or partially results from projects or departments (DEAT, 2002).

Erosion: Erosion includes a group of processes by which soil is entrained and transported across a given surface through the action of water, wind, ice or other agents, including the substance of soil (CARA,1983).

Fauna: The animals' life of the region (Oxford, 2004).

Flora: The plants' life of the region (Oxford, 2004).

- Ground water:** Also known as sub-surface water. Is water occurring below the ground in the saturated zone (Bear, 1979).
- Habitat:** Type of environment in which fauna and flora live (Oxford, 2004).
- Land Capability:** This is the extent to which land can meet the needs of one or more uses under defined conditions of management (Marsden, 1986).
- Land Use:** Is the human use of land. Land use involves the management and modification of natural environment or wilderness into built environment such as fields, pastures, and settlements. It also has been defined as "The arrangements, activities and inputs people undertake in a certain land cover type to produce, change or maintain it" (LI, 2002)
- Leaching:** It involves removed off, by direct contact with solvent usually strong acid or alkaline solution depending on the type of ore (Vick, 1883:8).

Mining Waste:	Mining waste comprises mined rock which has no economic ore, tailings which are sand-like residues after the mineral or minerals have been extracted from the rock and slag: the solid residue from the smelting process (DME, 2004).
Particulates:	Fine, solid particles which remain individually dispersed in air (UNEP, 2005).
Pollution:	Pollution is the contamination of resources such as water, air, soil and land (UNEP, 2005).
Reclamation:	The return of a disturbed site to an agreed-upon land use (UNEP, 2005).
Rehabilitation:	The return of disturbed land to a stable, productive and self-sustaining condition, after taking into account beneficial uses of the site and surrounding land (Marsden, 1986).
Tailings:	Tailings is any fine-grained waste materials from metallurgical processing including slimes and residues. It comprises mainly finely ground rock and many contain process chemical residues (DME, 2006; UNEP, 2005).

ACRONYMS AND ABBREVIATIONS

Au	Gold
As	Arsenic
°C	Degrees Celsius
COG	Council of Geoscience
CM	Chamber of Mines
DEAT	Department of Environmental Affairs and Tourism
DME	Department of Mineral and Energy
DWAF	Department of Water Affairs and Forestry
EC	Electrical Conductivity
FAAS	Flame Atomic Absorption Spectrometry
GFAAS	Graphite Furnace Atomic Spectrometry
GPS	Geographical Positioning System
HMs	Heavy Metals
mm	millimeters
Ni	Nickel
NWMS	National Waste Management Strategy
Pb	Lead
SAIMM	South African Institute of Mining and Metallurgy
SANS	South African National Standards

SAWS	South African Weather Services
TDS	Total dissolved solids
USA	United States of America
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation
Zn	Zinc

CHAPTER ONE: INTRODUCTION

1.1 Background to Ancient Mining activities

The discovery of the main gold-bearing conglomerate on Langlaagte Farm near Johannesburg in 1886 set off the gold rush of freelance diggers (CM, 1990). Fortuitously, the discovery of diamonds in Kimberley in 1871 had already attracted substantial capital from British and European banks to finance the emerging diamond mining houses created by Cecil Rhodes, Alfred Beit and Barney Barnato, who eventually united to form De Beers Consolidated Mines. Thus, powerful entrepreneurs were already on hand to exploit the gold (CM, 2002).

1.1.1 Mining activities in Limpopo Province

Limpopo is well-endowed with a wide variety of minerals (CM, 2002). The Minerals Bureau has records of just over 70 operating mines in the province, 50 of which are small to medium scale mines. The larger mining operations in the province include De Beers' Venetia diamond mine, the Exxaro Grootegeluk and Tshikondeni collieries, Anglo American Platinum's Amandelbult, Northam and mines in Potgietersrust, Musina, Lebowa, Marula and Modikwa platinum mines and the copper and phosphate operations at Phalaborwa. These deposits accounted for approximately 80% of the provinces mineral revenue in the year 1999/2000 (Wilson, 2000).

According to Stayt (1969) the ancient miners and smelters of Musina were Vha-Lemba, who worked under the patronage of the Venda chiefs. The Vha-Venda later learnt the art of smelting from the Vha-Lembas. Thomson (1972) corroborates this theory, and states: "According to Vha-Venda tradition, when the tribe moved across the Limpopo about 200 years ago, to settle in their present territory in the Northern Limpopo Province they found the Vha-Lemba mining the copper lodes near the Limpopo River; Vha-Lemba taught them how to smelt copper; but the Vha-Lemba were a very secretive people, and it was a long time before they parted with the knowledge of copper smelting". The Vha-Lemba are said to have stated that their ancestors were the first people to mine copper near the Limpopo River and that they taught members of other tribes how to smelt copper (SAIMM,1974). The closure of the copper workings came about shortly before the death of the Venda chief, Ramabulana, in 1864, who is said to have ordered his headman, Musina Vha-Leya, to close down production.

However, Van Warmelo (1940) has a different version of the origin of the Musina miners. This is based on the information given by a certain M. F. Mufamadi, whose genealogy can be traced back to the Musina copper workers. This clan, which had the name of Musina, originally came from across the Lebombo Mountains and settled in the vicinity of what is today Phalaborwa, in the north-eastern Limpopo Province (SAIMM,1974).

In November 2007, the human remains excavated at Mapungubwe in 1932 were symbolically handed over to Tshivhula, Lishivha and Matshete clans. These were the clans whose ancestor lived in Musina and Mapungubwe (National Government, 2008).

1.1.2 Social, environmental and economic impacts of mining

The social impact of large-scale mining projects is controversial and complex (Thomson, 1980). Mineral development can create wealth, but it can also cause considerable disruption. Mining projects may create jobs, roads, schools, and increase the demand for goods and services in remote and impoverished areas, but the benefits and costs may be unevenly shared. Despite economic success of the mining industries in Zambia in the recent past, a majority of Zambians continue to suffer extreme poverty (Cronje, 2008).

Exxaro Resources has spent ZAR140.0 million on community developments in Limpopo, De Beers South Africa has established a skills development centre linked to its Venetia mine. The centre is not only for mine employees, but also local schools and the Adults Learning Centre for the community of Alldays town (Limpopo Provincial Government, 2012). If communities feel they are being unfairly treated or inadequately compensated, mining projects can lead to social tension and violent conflict (ELAW, 2010).

Mining is an expanding industry that can provide sustainable economic, environmental, and social benefits to the communities and regions in which it operates. However, mining has a tendency to have a devastating impact and by its very nature has deleterious effects on the land, water, fauna and flora, and on surrounding communities (Thomson, 1980).

Acid mine drainage at inactive mines, degrades water quality and the impacts persist for a long time. In addition, acid mine drainage inhibits plant growth (Salomon *et al.*, 1995). Mining generates large volumes of solid waste such as waste rocks and tailings. Erosion occurs during rainy seasons and tailings and sediments are transported into nearby water bodies (Thomson, 1980).

Mining has taken place for thousands of years. Abandoned mines are a local phenomenon. Their major impacts are largely local but not always and dispersion of heavy metals can be regional or even global (Allan, 1988). The threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury, and arsenic. These metals have been studied and their effects on human health regularly reviewed by international bodies such as the World Health Organization (Salomon *et al.*, 1995).

Heavy metals have been used by humans for thousands of years, for an example in medicines. Although several adverse health effects from heavy metals have been known for a long time, exposure to heavy metals continues, and is even increasing in some parts of the world, particularly in less developed countries like Mozambique. Heavy metals are notable for their high toxicity (Clark, 1989).

1.1.3 Impact of mining on human and environmental health

Mining of certain minerals, including gold, copper, and nickel, is associated with acid drainage problems that can cause long-term impairment to waterways and biodiversity. Furthermore, some effluents generated by mining contain large quantities of toxic substances, such as cyanides and heavy metals, which have serious human health and ecological implications (Lombard, 1956).

Besides mining being a major contributor to the economic activity of a region, it is also a major degrader and polluter of the environment. Environmental impacts as a result of mining activities include land dereliction, acid mine drainage, heavy metals contamination, erosion and land degradation. These eventually lead to safety, health and social problems (Robbins, 1996).

Some past tailings dam failures have claimed lives and may have caused considerable environmental damage in China. Impacts from tailings disposal include transport of tailings solids into adjacent environments by wind and water erosion, pollution of ground and surface water by toxic substances such as cyanides, sulphates or dissolved metals from the tailings (Pieryznski *et al.*, 1994).

Tailings are disposed for the duration of an operation's design life. Their disposal affects the surrounding environment by means of emission and or discharges and often tends to lead to structural, artificial and contaminated land sites. These sites are usually unstable, they are prone to erosion, endanger life and contaminate ground water (Lombard, 1956).

Toxic effects from chronic exposures to heavy metals are far more common than acute poisonings. Chronic exposure may lead to a variety of conditions depending on the kind of exposure, metabolism and the storage of the specific element in question. For example, chronic exposure to cobalt dust has been associated with the development of pulmonary fibrosis that can lead to corpulmonale (Samara, 2006).

The hard metal pneumoconiosis has been described for other metal dusts. Chronic inhalation of high levels of cadmium also causes both fibrotic and emphysematous lung damage, but it also has major effects on bones and the kidneys. Exposure to copper can lead to its accumulation in liver, brain, kidney, and cornea, leading to the classic impairment and stigmata of Wilson disease and Indian childhood cirrhosis (Samara, 2006).

Heavy metal toxicity represents an uncommon, yet clinically significant medical condition. If unrecognized or inappropriately treated, heavy metal toxicity can result in significant morbidity and mortality. Many metals are however, essential to biochemical processes.

Others have found therapeutic uses in medicine. Latrogenic metal toxicity may occur with bismuth, gold, gallium, lithium, and aluminium. Intentional or unintentional ingestion of arsenic has been notorious as a means of suicide and homicide respectively (Samara, 2006).

1.2 The Statement of the Problem

Heavy metals are particularly problematic as they do not chemically break down in the environment. They settle at the bottom of streams or persist in streams or land for long periods of time, providing a long-term source of contamination to the surrounding inhabitants, and to the people that inhale them. These heavy metals have the potential to harm the environment and human health as they could continue causing damage long time after mining has ceased (Chao *et al.*, 2007). Due to the deterioration of water and soil quality due to the impacts of heavy metals, there was a need to study the heavy metals around the defunct copper mining at Musina to establish their levels of concentration and dispersion in the area.

1.3 Need for the Research

Mining operations routinely modify the surrounding landscape by exposing previously undisturbed earth materials. Erosion of exposed soils, extracted mineral ores, tailings, and fine material in waste rock piles can result in substantial sediment loading in surface waters and drainage ways. In addition, spills and leaks of hazardous materials and the deposition of contaminated windblown dust can lead to soil contamination (Davydora, 2005).

Human health and environmental risks from soils generally fall into two categories: contaminated soil resulting from windblown dust and soils contaminated from chemical spills and residues. Fugitive dust can pose significant environmental problems at some mines. The inherent toxicity of the dust depends on the proximity of environmental receptors and the type of ore being mined (Chao *et al.*, 2007). High levels of arsenic, lead, and radionuclide's in windblown dust usually pose the greatest risk. Soils contaminated from chemical spills and residues at mine sites may pose a direct contact risk when these materials are misused (Zhang *et al.*, 1996).

Mine waste poses a threat to human health. In most cases the extent of this threat is never known as the heavy metals level is sometimes not established. Daily exposure to mine waste may lead to chronic or acute disease. Some of the heavy metals cause disease after a long period of exposure to them; whereas some affect the health of those exposed within a few days of exposure (Sainio *et al.*, 2001).

The project scope was to establish the concentration of lead (Pb), zinc (Zn), copper (Cu), arsenic (As) and Nickel (Ni) within and in the vicinity of mine residues left by past mining activities in Musina. The mine dumps are now used for brick making. The project will determine the consequences of the contamination to the brick workers.

1.4 Aims and Objectives

1.4.1 General aims

The research aimed at studying the characteristics of mine residues in Musina by investigating their geology, physical characteristics, current use and their potential harm to their surroundings.

1.4.2 Specific objectives

- ✓ To survey and observe tailings slope features and vegetation cover at an old copper mine in Musina.
- ✓ To evaluate the extent and impact of acid mine drainage in the surrounding area.
- ✓ To establish the levels and distribution of selected heavy metals in soil and water samples associated with the defunct mine.
- ✓ To assess the current economic activities (reprocessing, brick making) taking place at the old mine.
- ✓ To assess environmental degradation and human health impacts associated with activities at the old mine.
- ✓ To identify mitigation measures to reduce the negative impacts of waste on the environment and enhance positive environmental impacts.

1.5 Concluding Thought

Mining conditions and its effect might depend on the location, type of mineral being mined and the size of the mining operations. By understanding mining's threat to human health and the long-term effect on the environment and by taking precautions to reduce harm in all mining environments, miners and other people in mining communities can protect their health and improve their lives. The following chapter will discuss in detail the aspect of mining and its effects, but is not limited to heavy metals reviews and their health effect.

References

Allan RJ 1988: *Mining activities as a source of metals and metalloids to the hydrosphere, Impact through mining and industry and Prevention Technology*. Pub: UNESCO, Paris.

CARA 1983: Conservation of agriculture resources acts no 43 of 1983. Government gazette GN 1044 NO 9238, Pretoria, RSA.

Chamber of Mines (CM) 2002: South African Mining Introduction; South African Transition 1990 to 2001.

Chao W, Xiao CL, Pei FW & Zhi YG 2007: Pb, Cu, Zn and Ni concentrations in vegetables in relation to their extractable fractions in soils in suburban areas of Nanjing, China. *Polish J. Environ. Stud.* 2007, 16, 199-207.

Clark T 1989: Mercury. In: Trace Metals in Human and Animal Nutrition. Vol. 1. (Ed. W. Mertz) Academic press, Florida.

Cronje F, Changa C & Van Wyk J 2008: *Corporate social responsibility in Zambian mining industries*.

Davydova S 2005: Heavy metals as toxicants in big cities. *Microchemistry Journal*. 2005, 79, 133-136.

Department of Water Affairs and Forestry (DWAF) 2001: Waste generation in South Africa; Water Quality Management Series. Pretoria.

Department of Environmental Affairs and Tourism (DEAT) 2002: Intergraded environmental management series 1, Department of Environmental Affairs and Tourism, Pretoria, RSA SABS, 1998.

Director: Mineral economics, Pretoria. <http://www.dine.gov.za/> publication /Ref annual reports Vicks S.G.1983. Planning design and analysis of tailing dams.

ELAW 2010: Environmental Law Alliance Worldwide (ELAW), Guidebook for evaluating mining project EIAs, Eugene 97403 by Environmental Law Alliance Worldwide.

Landscape Institute (LI) 2002: *Guidelines for landscape and visual impact assessment*. Press, London, UK, 166pp.

Limpopo Provincial Government 2012: www.limpopo.gov.za.

Lombard AF 1956: Report on Klein Letaba Gold Fields, North-eastern Transvaal: Klein Letaba Mining Co. STK 06560012, unpublished report.

Mamadi MF 1940: The copper miners of Musina, Government printers, Pretoria (1940) Ed 2008.

Marsden DD 1986: The current limited impact of Witwatersrand gold-mine residues on water pollution in the Vaal River System. *The Journal of South African Institute for Mining and Metallurgy*.

Oxford 2004: The Oxford English dictionary, Oxford dictionary unit for London English. Oxford University press, London, UK.

Oxford (Ed) 2002: The San Concise Oxford English dictionary, Oxford dictionary unit for san English, Oxford University press South Africa, Cape Town.

Robbins J 1996: The Significance of Acid Mine Drainage in South Africa, in Acid Mine Drainage short course.

Sainio EL, Jolanki R, Hakala E & Kanerva L 2001: Metals and arsenic in eye shadows. *Contact Dermatitis*, 42(1), 5-10

SAIMM 1974: National Cultural History and Open Air Museum. Pretoria, *Journal of South African Institute of Mining and Metallurgy*.

Samara MD 2006: Staff Physician, Department of Emergency Medicine, State University of New York, Downstate Medical Centre.

Solomon W, Forster U & Pavel M 1995: *Heavy metals (Ed.), problems and solution*. New York: Springer-verlag.

Stayt WF 1969: The origin of the Musina people, original transcript in Van Warmelo, *The copper miners of Musina*.

Thompson L 1972: The copper miners of Musina (Translation by N.J Van Warmelo), Copper miners of Musina and their early history in Soutpansberg.

Warmelo NJ 2007: Manuscript Collection-Inventory (Unpublished) National Archives of South Africa, Pretoria.

Wilson MGC 2000: A Summarised Mineral Profile of the Limpopo Province, Council for Geosciences

Vick 1986:6: The role of engineering geology and environmental geology in the reconstruction and development programme for South Africa.

Zhang M & Gong ZT 1996: Contents and distribution of some heavy metal element in the vegetable cultivated soil in China. *Acta Pedologica Sinica* 1996, 33, 85-93.

CHAPTER TWO: LITERATURE REVIEW

This chapter aimed to give an overview of the environmental impacts of the abandoned mines, giving incidences that occurred before, and the impact on the community around the area of such mines.

2.1 General Aspect of Mining

In order to maximize the extraction efficiency of valuable components from ore bodies, extraction starts with the removal of non-economic materials which are deposited near the mine site. Depending on the type of commodity, different processes include mechanical and chemical methods, which are used to separate minerals of interest from the non-economic ones. In the subsequent processing stages, impurities remaining in the concentrates can either be recovered as valuable products or disposed of as waste (Solomon *et al.*, 1995). This constitutes the main source of pollution that contaminates underground water through leaching processes, and surface water through run-off from waste dumps and contaminated soil (Kelly, 1998).

2.1.1 Extraction operation

Several factors (location, geometry, morphology, depth, economics, environment, and even mining traditions), underlie the choice of methods for mining a specific ore deposit. Depending on these methods, and on the size of the mine site, the projects display different ore-extraction capacities, and consequently larger or smaller quantities of mining waste. From the environmental standpoint, a major difference can also be demonstrated in the composition of the waste associated with the mining method employed (Giammar, 1997).

2.1.2 Surface mining

There are many alternative mining methods within open pits and quarries, but the principles are identical. Most industrial materials and shallow metallic deposits (< 300.0 m deep) are mined by this method, which in practice is the cheapest. The scale of the projects, and particularly their depth, is determined by the economic threshold above which it is better to continue mining through underground workings (Chadwich, 1996).

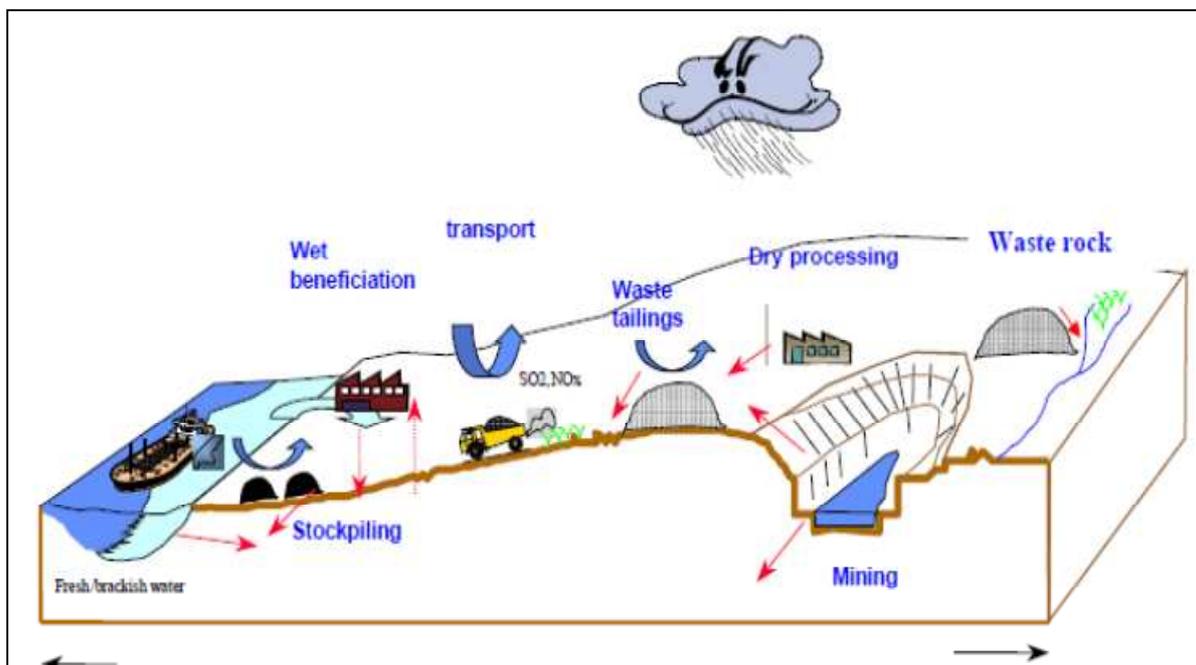


Figure 2.1 Different steps of a surface mining activity (adopted from BRGM, 2001).

As a rule, after the stripping operations (removal of the soil and superficial horizons), actual mining is carried out in successive steps, imparting a roughly conical shape to the mine (Figure. 2.1). The mining of each step or bench produces a tonnage of extracted material corresponding to the overburden surrounding the deposit, which is sent directly to the waste dump, and a tonnage corresponding to the ore that is selectively routed either for storage or directly to the processing plant (Rivas & Cendrero, 1996).

In general, overburden is removed as efficiently and rapidly as possible, usually with little combinations. Overburden piles compose the largest volume of waste generated by surface extraction activities (BRGM, 2001).

Advantages of surface mining operations, as compared to underground operations, include flexibility in production rates without deterioration of workings, relative safety for workers, and the ability to practice selective mining and grade control and low cost per ton of ore recovered. Surface mining also has lower development and maintenance costs than underground mining because it requires fewer specialized systems. During expanded development, however, some surface mines with large amounts of pre-stripping waste could have higher costs than established underground mines (BRGM, 2001).

2.1.3 Underground mining

All the operations conducted in the ore are connected to one another and to the surface by a series of passages, all opened in the overburden surrounding the deposit: these include shafts, inclines, drifts, chutes and cross-cuts for personnel and machine access, for removal of ore and drainage water, as well as for ventilation (Rivas & Cendrero, 1996).

Underground mining methods are usually employed to mine richer, deeper, and smaller ore bodies where open-pit methods would be impractical. Underground mining operations are complex combinations of tunnelling, rock support, ventilation, electrical systems, water control, and hoists for the transportation of people, ore and materials. The three main underground mining methods used to mine metal ore, are stoping, room-and-pillar, and block caving. All of these methods can be used in several variations, depending on the characteristics of the ore body (Giammar, 1997).

Mining in the Musina was undertaken through the stoping mining method. Unlike backfilling mining where waste rocks are used as support for excavated voids, this method allows for the removal of all materials to the surface.

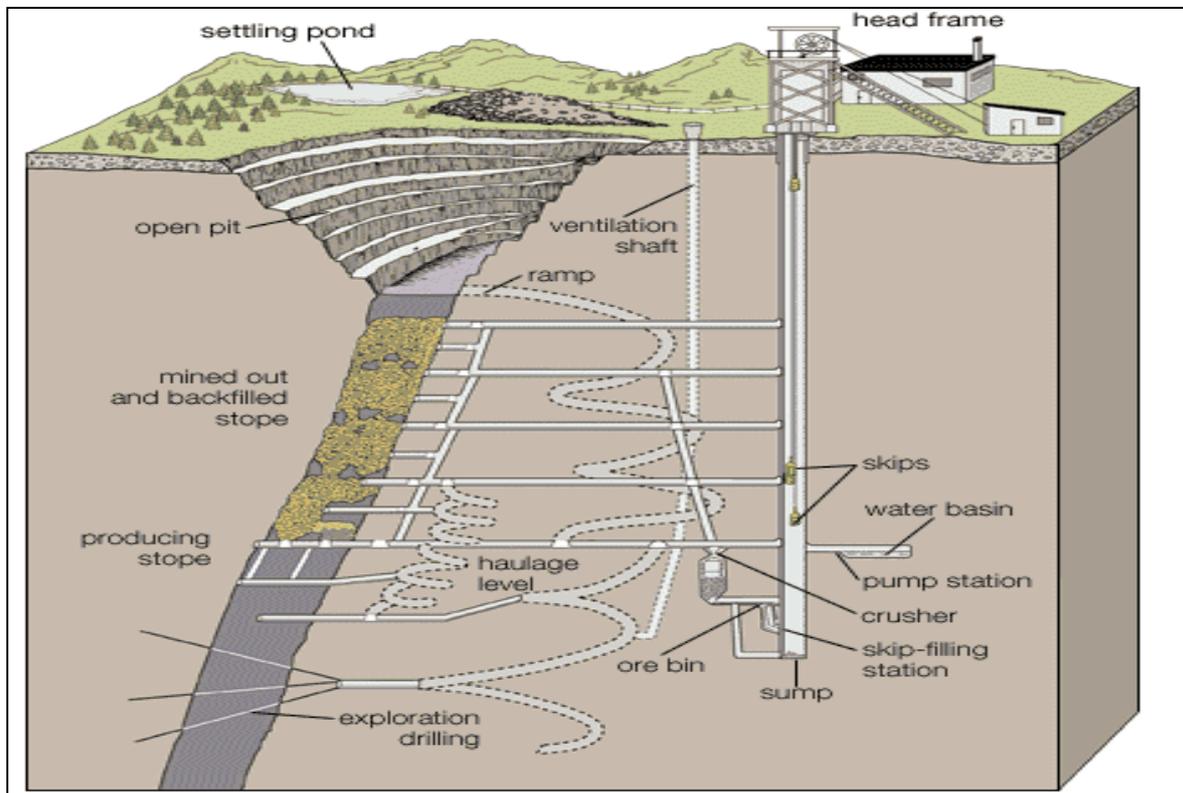


Figure 2.2 Underground mine workings (adopted from BRGM, 2001).

2.1.4 Beneficiation operation

Beneficiation of ores and minerals is defined as including: crushing, grinding, washing, filtration, sorting, sizing and gravity concentration. In essence, beneficiation operations typically serve to separate and concentrate the mineral values from waste material, remove impurities, or prepare the ore for further refinement.

Beneficiation activities generally do not change the mineral values themselves other than by reducing (crushing or grinding), or enlarging (palletizing or briquetting) particle size to facilitate processing. A chemical change in the mineral value does not typically occur in beneficiation (Rivas & Cendrero, 1996).

2.1.5 Mineral processing operations

Mineral processing operations generally follow beneficiation and serve to change the concentrated mineral value into a more useful chemical form. This is often done by using heat or chemical reactions to change the chemical composition of the mineral. In contrast to beneficiation operations, processing activities often destroy the physical and chemical structure of the incoming ore or mineral feedstock, such that the materials leaving the operation do not closely resemble those that entered the operation. The two major processes employed in mineral processing operations are classified as either pyrometallurgical methods, or hydrometallurgical methods (Kelly, 1998).

2.2 Mine Waste

2.2.1 Tailings

Tailings are the finely ground rock that is left over after the ore has been treated in the concentrator. Tailings are a combination of fine grained (typically silt sized, in the range from 0.001 to 0.60 mm), solid material remaining after the recoverable metals and minerals have been extracted from mined ore and the remaining process water. The chemical and physical nature of tailings solids is very similar to common river sand and silt and their characteristics also vary with the nature of the ore (BPEM, 1999).

Tailings tend to accumulate considerable amounts of heavy metals, which were uneconomic to extract, but may be leached for many years after the mining has ceased. In the long run, the geochemical reaction of tailing materials results in acid mine drainage and the release of heavy metals that impact on human health and the environment (Davies & Rice, 2001). The potential for acid generation in tailings has long been recognized. The concern is generally that acid drainage may develop after the mine has been abandoned, when the facilities are no longer in use or maintained (Faulkner, 1991).

Mine tailings are large piles of crushed rock that are left over after the metals of interest like lead, zinc, copper, silver, gold and others, have been extracted from the mineral rocks that contained them. Tailings, also known as pile, tails or leach residue are the materials left over after the processes of separating the value fraction from the worthless fraction of ore. Tailings are non-economic materials produced after the ore has been processed (Davis & Rice, 2001).

These materials are either placed back into open pits or underground workings where they come from or into engineered stockpiles or storage dam facilities. The composition of tailings is directly dependent on the ore. The mineral separation process, especially in older mining operations, is only partially efficient. As a result, after the crushing and grinding processes, some of the metal-containing minerals are left behind as small tailings particles (Davies & Rice, 2001).

In arid and semi-arid areas, mine tailings and their associated metal contaminants, such as arsenic, lead, and cadmium are prone to wind (aeolian) dispersion and water erosion. Wind dispersion occurs because the fine tailing particles, (silt or sand-like material) and their associated contaminants are easily suspended in the atmosphere by wind and dispersed throughout the environment as dust particles.

The spread of metal toxicants in association with tailings particles, through a combination of wind dispersion and water erosion, has been shown to result in measurable elevated levels in wildlife and human systems even at some significant distance from the tailings site (Davies & Rice, 2001).

These problems are extensive and can persist for decades, because these sites have low pH and lack normal soil stabilization processes. As a result these sites do not develop normal soil structure or support the establishment of plant cover. Many of these mining areas were worked during the last century, and as a result, are now located next to large urban populations. Thus, both human and ecological health impacts can occur from exposure to dust that is blown from these sites. These issues are of particular concern with regard to children in nearby communities and for sensitive riparian or wildlife refuge areas (Bowders & Chiado, 1990).

Tailings are generally a public relations challenge for the mining industry. While the global demand for mined products continues to rise, the negative image of mine tailings grows in spite of a sound record of environmental stewardship with mine tailings in the past twenty years, for example, changing natural landforms. These tailings dumps can be reduced by using them for road construction and brick-making (Teutsch *et al.*, 2001).

2.2.2 Mine dumps

Mine dump are waste rock or unused extraction products that are generally stored indefinitely in a landfill site. They are usually located in the immediate vicinity of the main mining centre due to transportation costs. The quantity of mining waste that can be stored at a mining centre varies considerably and depends mainly on the mining method selected.

As a rule, opencast pits and quarries generate more mining waste than an underground mine. The main type of waste rock is generated by surface (or barren rock) stripping to expose the shallow ore (BRGM, 2001).

This is the rock that is weathered to varying degrees, although increasingly fresh with depth and showing the geological characteristics of the local surrounding rock material. The largest (in tonnage) quantity of barren rocks comes from stripping for opencast mines. In underground mines, these barren rocks are generated by the passages (shafts, crosscuts) (BRGM, 2001).

2.2.3 Ore stockpiles

Intermediate storage of products and ore stockpiles is not waste. They are normally temporary dumps of lean ore at the mine site, depending on the cut-off content, which may vary with time. This management requires maintenance on the mine site for a period sometimes longer than a decade (Szymanski, 2004).

The ore stockpiles are materials selected by grade. These ores have a metal or mineral content which can be stored and get treated at a later stage when the plant is not processing at full capacity (Szymanski, 2004).

2.2.4 Slags

In many old copper, iron or gold mines, the ore or concentrate was burned or smelted nearby to remove certain components like sulphides in order to produce a purer marketable product. In this case, slag heaps can be found on these old sites, forming a specific type of waste.

Ash produced by cleaning furnaces or smoke stacks is frequently associated with them. These oxidised products are found either accumulated near the mine, if smelting was conducted nearby, or stacked in heaps near the smelter (BRGM, 2001).

2.3 Heavy Metals

Heavy metals are simply a certain class of metallic elements. The human body requires trace amounts of some heavy metals, including zinc, copper, iron, cobalt and others, but these can be dangerous at high levels. Other heavy metals such as mercury, lead, arsenic and cadmium have no known benefits and their accumulation over time can cause serious illness and even premature death. The industrialization of the world dramatically increased the overall environmental load of heavy metal (McBride, 1994).

The periodic table contains 105 elements, of which 80 are considered metals. Toxic effects in humans have been described for less than 30 of these. Many metals are essential to biochemical processes, and others have found therapeutic uses in medicine. Latrogenic metal toxicity may occur with bismuth, gold, gallium, lithium, and aluminium species (Ball, 1982).

The tailings, sands and waste rocks deposited close to the mining area are the main sources of heavy metals in the environment. When these deposits contain sulfides, for example pyrite, and if there is access to oxygen and water, acid mine drainage results. Transformation of sulphides and a shift to more acidic conditions enhances the mobility of elements such as manganese (Mn), iron (Fe), zinc (Zn), copper (Cu), and cadmium (Cd) (Salomon, 1995).

Heavy metals are abundant in air, soil and even drinking water. They are present in virtually every area of modern life, from construction materials to cosmetics, medicines, food, fuel, and even personal care (Goyer,1996). It is very difficult for anyone to avoid exposure. However, steps can be taken to understand and minimize the threat through acts of prevention and treatment. These acts will help to lessen the negative impact on family health. Heavy metals are dangerous as they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical concentrations in the environment. Generally, heavy metals have higher densities (Alloyways & Ayres, 1993).

Because they cannot be degraded or destroyed, heavy metals are persistent in all parts of the environment. Contamination of soil is a constant danger. Effects of soil pollution by heavy metals can make it infertile and unsuitable for plants. This affects the organism in the food-web (Alloyways & Ayres, 1993). Copper and zinc are essential in small, but critical concentrations for the normal healthy growth of either plant or animals.

They are toxic at high concentrations. Agricultural productivity on large areas of land in many parts of the world can be limited by deficiencies of essential trace elements or heavy metals (micronutrients), such as zinc, copper and manganese in the case of crops and in the case of livestock cobalt, copper and zinc (McBride, 1994).

Arsenic, nickel, copper, cadmium and chromium can be harmful to crops even at low concentrations. Heavy metals which are known to affect human health are arsenic, mercury, lead, and cadmium (Alloyways & Ayres, 1993).

2.3.1 Cadmium

Cadmium occurs naturally in the environment. Some of its presence in the environment is the result of natural processes such as forest fires, volcanic emissions, and weathering of soil and bedrock. Its presence is mostly the result of human activities, particularly metal production, fuel burning, transportation, solid waste disposal, and sewage sludge treatment (Environment Canada & Health Canada, 1994a).

It is mostly used to make nickel-cadmium batteries, but is also used in pigments, including those for ceramic glazes, polyvinyl chloride (PVC) plastics, industrial coatings, hair and body products (Environment Canada & Health Canada, 1994a). Cadmium from body and hair creams can be absorbed into the human body through contact via the skin (Ayenimo *et al.*, 2010).

Cadmium is absorbed into the body, accumulating in the kidney and the liver, although it can be found in almost all adult tissues (Elinder, 1985). The total amount absorbed by humans has been estimated to be between 0.2 and 0.5 µg/day (Health Canada, 2010b), with absorption via skin estimated to be 0.5 per cent (Health Canada, 2009a). Little absorbed cadmium is eliminated with humans getting rid of 50 per cent of cadmium from the body only 10-12 years after exposure (Hamer, 2003).

Cadmium and cadmium compounds are considered to be “carcinogenic to humans” by the International Agency for Research on Cancer (IARC, 2010) and are considered “toxic” in Canada because of their carcinogenicity and environmental effects (Environment Canada & Health Canada, 1994a). It and its compounds are also classified as known human carcinogens by the United States Department of Health and Human Services (ATDR, 2008).

2.3.2 Arsenic

Arsenic is a metal that naturally occurs in the earth's crust and may enter water sources (Agency of Toxic Substances and Disease Registry, 2007a). However, it is used in various products including textiles, preservatives, and pigments (Health Canada, 2010b). It is released into the environment through metal production, use of pesticides, burning fossil fuels, particularly coal, and waste disposal (Environment Canada & Health Canada, 1993).

Humans are mostly exposed via food, but other sources include drinking water, soil, ambient air (Environment Canada & Health Canada, 1993). According to Rasmussen, Subramanian & Jessiman (2001) it can be found in house dust as well. Schneider & Krivna (1993) state that it can be even found in cigarette smoking. It was found at a maximum of 2.3 ppm in a study on its presence in 88 different colours of eye shadow (Sainio *et al.*, 2001).

Ingested arsenic compounds are readily absorbed in the gastrointestinal tract and distributed throughout the body, including fetuses (Environment Canada & Health Canada, 1993). It can mostly be found in the liver, kidneys, lungs, spleen, and skin within 24 hours (WHO, 1988). Humans are said to be able to get rid of about 50.0% of Arsenic from their bodies between two and 40 days after ingestion, although it tends to accumulate in skin and hair over time (Environment Canada & Health Canada, 1993).

Arsenic may also be inhaled (Environment Canada & Health Canada, 1993) or dermal exposure through the skin, although US FDA study has predicted that dermal exposure to arsenic may contribute less than 1 per cent of the exposure from ingestion (WHO, 1988).

The ingestion of drinking water with very high arsenic levels has been blamed as increasing the risk of cancer in internal organs like the bladder, liver, and lungs (WHO, 1988; ATSDR, 2007a). Long-term exposure via ingestion has also been associated with skin cancer, skin thickening or discolouration (Environment Canada & Health Canada 1993). According to Health Canada (2006a), Arsenic can cause decreases in blood cell production, blood vessel damages, numbness in feet and hands, nausea and diarrhoea (Health Canada, 2006a).

Long-term exposure through inhalation causes some of the skin effects, circulatory and peripheral nervous disorders and an increased risk of lung cancer (ATSDR, 2007a), and a possible increase in risk to the gastrointestinal tract and the urinary system cancers (Gibb & Chen, 1989). Long-term skin contact is not likely to lead to any serious internal effects (ATSDR, 2007a).

Canada and other countries have imposed certain limits on arsenic levels for drinking water and food. In Canada, the maximum acceptable concentration (MAC) is 0.010 mg/L for drinking water, while the acceptable oral ingestion limit for arsenic impurities is 0.1 ppm for foods (WHO, 1988). It is also limited to 1000 mg/kg in paints or other coatings used on toys and other children's products (Health Canada, 2003).

2.3.3 Mercury

Mercury occurs primarily in two forms: organic mercury and inorganic mercury. Inorganic mercury and elemental mercury are both toxins that can produce a wide range of adverse health effects. Inorganic mercury is used in thermometers, barometers, dental fillings, batteries, electrical wiring and switches, fluorescent light bulbs, pesticides, fungicides, vaccines, paint, skin-tightening creams, antiseptic creams, pharmaceutical drugs, and other ointments (Waalkes, 2000).

Once it has become absorbed into the bloodstream, humans have the ability to convert this inorganic mercury to an organic form. Organic mercury is known to bioaccumulate due to the body's inability to process and eliminate it (Holum, 1983).

Mercury has recently been implicated as being a contributing factor in the increasing prevalence of autism in American children. The Autism Research Institute has focused on mercury containing vaccines and their relationship to autism. Over 2.0 million individuals are afflicted with autism, a neurodevelopment syndrome that typically produces impairment in sociality, communication, and sensory/perceptual processes. Horsfall (1999) reported that there is a positive correlation between complications seen in autistics and complications seen in mercury poisoned individuals.

2.3.4 Lead

Lead, like other metals, occurs naturally in the earth's crust (Health Canada, 2009b). While a little may enter through natural processes (for example, erosion), human industrial activities such as metal smelters or refineries are responsible for the bulk of its presence in the environment (Environment Canada, 2010b). Lead has been and continues to be used extensively, particularly in the making of lead-acid batteries (Environment Canada, 2010a).

It is also used to make lead shot and fishing weights, sheet lead, solder, some brass and bronze products, pipes, professional paints (other than paints for use by children), some ceramic glazes, dyes in paints and pigments, medical equipment (radiation shields), scientific equipment, and military equipment (ATSDR, 2007b).

Lipstick can become contaminated with lead through the use of contaminated raw materials or the use of pigments that contain lead (USDOL, 2004). Lead exposure in Canada has decreased since the 1970's, although everyone is exposed to trace amounts through air, soil, household dust, food, drinking water and various consumer products (Environment Canada, 2010a). If lead is ingested, adults will absorb about 10 per cent into their blood, while children will absorb about 40 to 50 per cent (Ziegler *et al.*, 1978; ATSDR, 2007b; Health Canada, 2009b) and of the 30 to 50 per cent of available particulate matter that is inhaled, adults will absorb 80 per cent (Health Canada, 2009b).

Skin contact with lead occurs every day, and the routine handling of inexpensive jewellery containing high levels can transfer lead to the skin (ATSDR, 2007b). Some lead has been found to be absorbed through the skin (Health Canada, 2009a). Dermal absorbed lead has been shown to be distributed throughout the body (Rastogi & Clausen, 1976; Lilley *et al.*, 1998). Pregnant women and young children are particularly vulnerable because lead can cross the placenta with ease and enter the foetal brain (USDOL, 2004). Lead can also be transferred to infants via breastfeeding (ATSDR, 2007b). Lead stored in bone serves as a source of foetal lead exposure (Rothenberg *et al.*, 2000).

After immediate exposure, humans are able to get rid of 50 per cent of the lead within two to six weeks (Health Canada, 1992), but it takes 25 to 30 years to get rid of 50 per cent of lead that has accumulated in the body over time (ATSDR, 2007b; Health Canada, 2007). No safe blood level of lead is known, with even the lowest levels having been shown to affect a foetus and the central nervous systems in children (CDCP, 2010).

Small amounts are recognized as being hazardous to human health (Environment Canada, 2010a). Infants, toddlers, children, foetuses, and pregnant women are most susceptible to its chronic low-dose effects (Health Canada, 2009a; Health Canada, 2010b).

Chronic low-level exposure may affect the kidneys, cardiovascular system, blood, immune system, and especially the central and peripheral nervous systems (ATSDR, 2007b). IQ deficits have been associated with high blood lead levels (ATSDR, 2007b), and also those of low levels (Sprinkle, 1995). Lead exposure has also been linked to miscarriages, hormonal changes, reduced fertility in men and women, menstrual irregularities, delays in puberty onset in girls (CSC, 2007), memory loss, mood swings, nerve, joint and muscle disorders, cardiovascular, skeletal, kidney and renal problems (Aremu, 2008). Lead and inorganic lead compounds have been classified as possible and probable carcinogenic to humans, respectively (IARC, 2010).

It was also one of the first substances to be considered “toxic” in Canada (Environment Canada, 2010a). High-level acute exposures can cause vomiting, diarrhoea, convulsion, coma, and death (Health Canada, 2007). In Canada, lead is restricted in gasoline and controlled when released from secondary lead smelters and steel mills (Health Canada, 2010b).

2.3.5 Nickel

Nickel occurs naturally and may be an essential element in humans (Environment Canada & Health Canada, 1994b). It has many uses, from metal coins and jewellery, to heat exchangers, batteries, and ceramic colouring among others (Environment Canada & Health Canada, 1994b). Given its abundance, everyone is exposed to small amounts, mostly through food, although also through air, drinking water, soil, household dust, and skin contact with products containing it, including cosmetics (ATSDR, 2005; Health Canada, 1994b).

Foetal exposures can also occur and it can also be passed to breast-fed infants. High levels of exposure can lead to health effects depending on route and the kind of nickel exposed to (Health Canada, 2010b). Certain types of nickel ("oxidic", "sulphuric", and "soluble" nickel) were considered to be "toxic" because of concerns about health due to carcinogenicity, and in some cases, the effect on the environment.

In Canada, metallic nickel was not considered a concern for human health (Environment Canada & Health Canada, 1994b). Metallic nickel and alloys have been classified as possibly carcinogenic to humans (IARC, 2010). Also, allergy to nickel is common and it can cause severe contact dermatitis (Health Canada, 2010b), in fact being one of the most common causes of such (Sainio *et al.*, 2001). Ten years ago, the first case of nickel allergy caused by eye shadow was reported and it has been reported that even 1 ppm may trigger a pre-existing allergy (Sainio *et al.*, 2001).

2.3.6 Copper

Copper is a metal that occurs naturally throughout the environment; in rocks, soil, water, and air. Copper is an essential element in plants and animals (including humans), which means it is necessary for us to live. Therefore, plants and animals must absorb some copper from eating, drinking, and breathing. Copper is used to make many different kinds of products like wire, plumbing pipes, and sheet metal (Sainio *et al.*, 2001).

Copper is also combined with other metals to make brass and bronze pipes and faucets. Copper compounds are commonly used in agriculture to treat plant diseases like mildew, for water treatment and as preservatives for wood, leather, and fabrics (ATSDR, 2004).

Copper is released into the environment through mining, farming, manufacturing operations and through waste water released into rivers and lakes. It is also released from natural sources like volcanoes, windblown dusts, decaying vegetation, and forest fires. When released into the environment it usually attaches to particles made of organic matter, clay, soil, or sand. Copper does not break down in the environment (ATSDR, 2004).

2.3.7 Zinc

Zinc is a metallic chemical element found in reasonable abundance around the world. It is classified among the transition metals, along with nickel and mercury, among others. The metal is used in a variety of alloys and compounds which have a range of uses, from sunscreen to fine art. Living organisms also rely on it as a valuable nutritional trace element; many foods are excellent sources, including seeds and whole grains (Newchurch & Kahwa, 1984).

Pure zinc is a bluish white, lustrous metal. It is extremely brittle at average room temperature, although when it is heated it becomes soft, malleable, and easily worked. When burned, it yields a bright blue to green flame, and the metal is reactive, combining readily with an assortment of other elements. On the periodic table of elements, zinc is identified by the symbol Zn, and the metal has an atomic number of 30 (ATSDR, 2004).

Humans have been using zinc for thousands of years; the element was used extensively in India in particular. Around the 1500s, it began to be imported into Europe, where it was a costly and unusual metal. Allegedly, zinc was named by Paracelsus, after the German *zinke*, "jagged," to describe the way it behaved in a furnace (WisegEEK, 2012).

2.3.8 Manganese

Manganese is a pinkish-grey, chemically active element. It is a hard metal and is very brittle. It is hard to melt, but easily oxidized. Manganese is reactive when pure, and as a powder it will burn in oxygen, it reacts with water (it rusts like iron) and dissolves in dilute acids (Bailey & Rada, 1984).

Manganese is essential to iron and steel production. Manganese dioxide is also used as a catalyst. Manganese is used to decolorize glass and make violet coloured glass. Potassium permanganate is a potent oxidizer and used as a disinfectant.

Other compounds that find applications are manganese oxide (MnO) and manganese carbonate (MnCO₃): the first goes into fertilizers and ceramics; the second is the starting material for making other manganese compounds (Birge *et al.*, 1977).

Manganese is one of the most abundant metals in soils, where it occurs as oxides and hydroxides, and it cycles through its various oxidation states. Manganese occurs principally as pyrolusite (MnO₂), and to a lesser extent as rhodochrosite (MnCO₃). The main mining areas for manganese ores are South Africa, Russia, Ukraine, Georgia, Gabon and Australia (Briggs & Ficke, 1978).

2.4 Harmful Effects of Heavy Metal on Human and Environment

Lead in the environment is mainly particulate bound with relatively low mobility and bioavailability. Lead does, in general, not bio-accumulate and there is no increase in concentration of the metal in food chains. Lead is not essential for plant or animal life. In the general non-smoking adult population, the major exposure pathway is from food and water. Airborne lead may contribute significantly to occupational exposure and exposure to smokers (WHO, 1995).

Cadmium and cadmium compounds are, compared to other heavy metals, relatively water soluble. They are therefore also more mobile in soil, generally more bio-available and tend to bioaccumulate. Cadmium is not essential for plant or animal life (WHO, 1995b; WHO, 1989a).

Cadmium accumulates in the human body and especially in the kidneys. According to current knowledge, kidney damage (renal tubular damage) is probably the critical health effect, both in the general population and in occupational exposed workers (Järup *et al.*, 1998). The accumulation of cadmium in the kidney (in the renal cortex) leads to dysfunction of the kidney with impaired reabsorption of, for instance, proteins, glucose, and amino acids.

It is estimated that 1.0% of all smoking women in Sweden with low body iron stores, may today experience adverse kidney effects due to the cadmium load (Järup *et al.*, 1998). Both human and animal studies indicate that skeletal damage (osteoporosis) may be a critical effect of cadmium exposure, but the significance of the effect in the Swedish population is, according to (Järup *et al.*, 1998) still unclear.

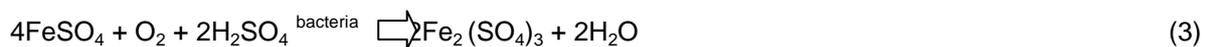
Everyone must absorb small amounts of copper every day because copper is essential for good health. High levels of copper can be harmful. Breathing high levels of copper can cause irritation of the nose and throat. Ingesting high levels of copper can cause nausea, vomiting, and diarrhoea. Very high doses of copper can cause damage to the liver and kidneys, and can even cause death (WHO, 1992a; WHO, 1992b).

2.5 Impacts of Abandoned Mines

2.5.1 Acid mine drainage

The water flowing on the surface of the earth (creeks, rivers, lakes and many other water bodies) and below the surface (groundwater) contains many chemical compounds in very small amounts. Many of these chemicals have natural sources, some are anthropogenic and others are derived from a combination of natural and anthropogenic sources.

The following chemical reactions describe the oxidation of pyrite (FeS_2) to the products that constitute the contaminants generically termed Acid Rock Drainage (ARD), although similar equations may be written for the oxidation of pyrrhotite (FeS) (Trudinger, 1971).



It may be seen that Equations 3 and 4 contain the term "bacteria" in addition to chemical formulae. The bacteria, which are usually site-specific strains of *Thiobacillus ferrooxidans*, utilize the sulphur present as their source of energy. They are autotrophic, obtaining their nutritional needs from the atmosphere (nitrogen, oxygen, carbon dioxide and water) and from minerals (sulphur and phosphorus). While these bacteria are not catalysts by definition, they do act as accelerating agents if their habitat conditions are at or close to optimal and they are an important factor in the generation of ARD. They are also capable of adaptation by mutation if their habitat is markedly changed (Trudinger, 1971).

It is thought that in the absence of bacteria (usually *T. ferrooxidans*) Equations 1, 2 and 5 predominate, while in the presence of bacteria reactions are best described by Equation 5, which can be regarded as a combination of Equations 1 and 3, or 2, 3 and 4, or 1, 2, 3 and 4.

The formulae representations are:

FeS_2 - pyrite; H_2O - water; O_2 - oxygen; S - sulphur; H_2SO_4 - sulphuric acid; FeSO_4 - ferrous sulphate; $\text{Fe}_2(\text{SO}_4)_3$ - ferric sulphate.

It may be seen that in addition to pyrite, the presence of both oxygen and water is required for process progression. This has important ramifications in that removal of the oxygen source (by total submersion under water) or the water source (conditions of aridity) will halt ARD production.

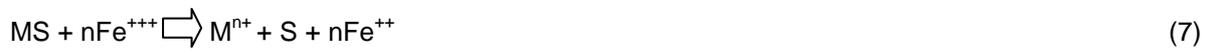
ARD production would also be considerably slowed or halted by the termination of *T. ferrooxidans* reproduction by a bactericidal agent. The end products are sulphuric acid and ferric sulphate. Also, sulphuric acid is an important intermediate product. From the onset of pyrite oxidation, pH falls (acidity increases) quickly and then stabilizes, typically at values around pH 2.5 to 3.0. The pH of stabilization is normally determined by the optimal habitat requirement of the site-specific strain of bacteria (Trudinger, 1971).

If pyrite and/or pyrrhotite are the only sulphide minerals open to atmospheric oxidation then the products of the oxidation process are those described above. Depending upon the availability of water and oxygen, reactions may not always approach completion as indicated by equations 1 to 6, and in such cases intermediate phases of chemical compounds or minerals may remain at the oxidation site (Trudinger, 1971).

If metallic minerals such as galena (lead sulphide, PbS), chalcopyrite (iron-copper sulphide, FeS.CuS), sphalerite (zinc sulphide, ZnS), in addition to pyrite and pyrrhotite are present as is usually the case in the natural oxidation of a mineral deposit and the oxidation of products from the mining of a mineral deposit then there may be a secondary effect of the oxidation of the iron-sulphur minerals to sulphuric acid and ferric iron (ARD, 2012).

The stable pH developed (2.5 to 3.0) and the products of sulphuric acid and ferric sulphate create conditions where the ferric iron ion itself can act as an oxidant (above about pH 3.0 the ferric ion is itself hydrolyzed to ferric hydroxide, which precipitates as the familiar rust-coloured stain associated with ARD). In the absence of ferric iron at pH 2.5-3.0, sulphuric acid will dissolve some heavy metal carbonate and oxide minerals, but has little reactive effect on heavy metal sulphides (Walsh & Mitchell, 1972).

However, the ferric iron ion is capable of dissolving many heavy metal sulphide minerals, including those of lead, copper, zinc, and cadmium, by the general reaction (ARD, 2012).



Where: MS \rightleftharpoons solid heavy metal sulphide; Fe⁺⁺⁺ \rightleftharpoons aqueous ferric iron ion; Mⁿ⁺ \rightleftharpoons aqueous heavy metal ion; S \rightleftharpoons sulphur; Fe⁺⁺ \rightleftharpoons aqueous ferrous iron ion.

2.5.1.1 The role of micro-organisms in acid mine drainage

Micro-organisms (most frequently bacteria) are often integrally involved in the chemical alteration of minerals. Minerals, or intermediate products of their decomposition, may be directly or indirectly necessary to their metabolism. The dissolution of sulphide minerals under acidic conditions (ARD), the precipitation of minerals under anaerobic conditions, the adsorption of metals by bacteria or algae, and the formation and destruction of organometallic complexes are all examples of indirect micro-organism participation. Where minerals are available as soluble trace elements, serve as specific oxidizing substrates, or are electron donors/acceptors in oxidation-reduction reactions, they may be directly involved in cell metabolic activity (Dutrizac & MacDonald, 1974).

There are three categories of oxidation-reduction reactions for minerals with micro-organisms:

- ✓ Oxidation by autotrophic (cell carbon from carbon dioxide) or mixotrophic (cell carbon from carbon dioxide or organic matter) organisms. Energy derived from the oxidation reaction is utilized in cell synthesis.
- ✓ Electron acceptance by minerals (reduction) for heterotrophic (cell carbon from organic matter) and mixotrophic bacteria. Chemical energy is used to create new cell material from an organic substrate.
- ✓ Electron donation by minerals (oxidation) for bacterial or algal photosynthesis (reaction is fuelled by photon energy).

Oxidation of sulphur or sulphides for energy production is restricted to the bacterial genus *Thiobacillus*, the genus *Thiomicrospira*, and the genus *Sulfolobus*. These bacteria all produce sulphuric acid (i.e. hydrogen ions, H^+ , and sulphate ions, SO_4^-) as a metabolic product. Extensive reviews of these bacteria and their behaviour have been written by Brearley (1978) and Trudinger (1971).

Under suitable conditions it is these bacteria that are known to accelerate the generation of ARD from pyritic and pyrrhotitic rocks. Evangelou & Zhang (1995) report that sulphide oxidation catalysed by bacteria may have reaction rates six orders of magnitude (i.e. 1,000,000 times) greater than the same reactions in the absence of bacteria. Photomicrographs 1, 2 and 3, from Le Roux, North & Wilson (1973) illustrate the shape and appearance of *T. ferrooxidans*: The bacteria develop flagella only if they are required for mobility in accessing energy sources.

ARD is the product formed by the atmospheric (i.e. by water, oxygen and carbon dioxide) oxidation of the relatively common iron-sulphur minerals pyrite and pyrrhotite in the presence of (catalysed by) bacteria (*Thiobacillus ferrooxidans*), and any other products generated as a consequence of these oxidation reactions.

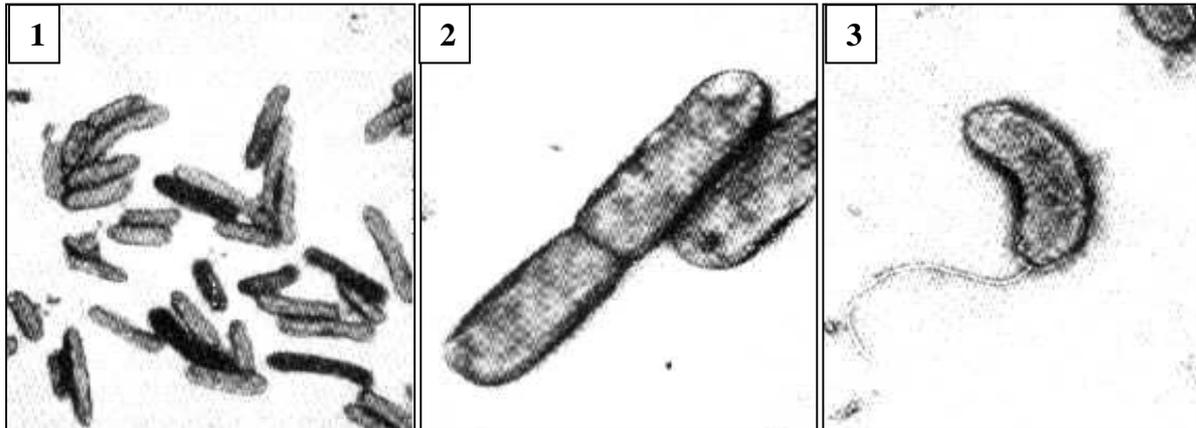
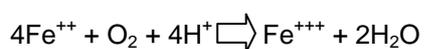


Figure 2.3 Photomicrographs 1 (left), 2 (centre) and 3 (right): *Thiobacilli* from bacterial generator (no flagella) - left & centre - and grown on ferrous iron (flagella) - right. Magnification about X 5000 (left), X 20, 000 (centre), X 15000 (right) (from Le Roux, North & Wilson, 1973).

An important reaction involving *T. ferrooxidans* is the oxidation of ferrous to ferric iron (Fe^{++} to Fe^{+++})



Ferric iron is a powerful oxidizing agent. Even at a $\text{Fe}^{+++}/\text{Fe}^{++}$ ratio of 1:1,000,000, a Redox potential of greater than +0.4 V is generated, which is sufficient for the attack of most base metal sulphides (Dutrizac & MacDonald, 1974). The general equation for the ferric ion reaction with base metal sulphides is:



Consequently *T. ferrooxidans*, in generating Fe^{+++} , is indirectly responsible for the dissolution of base metal sulphide minerals and the mobilization of metallic cations such as Cu^{++} , Zn^{++} , Pb^{++} and Cd^{++} . Base metal sulphides react only very slowly with sulphuric acid in the absence of ferric iron (Roman & Benner, 1973).

The importance of Redox potential in determining metal solubility and transport can be clearly seen for copper in the Eh-pH diagram for the $Cu-H_2O-O_2-S-CO_2$ system. Effects of bacteria upon the rate of dissolution of copper from chalcopyrite are highly pronounced, as demonstrated by Malouf & Prater, 1961.

2.5.2 Land disturbance

As compared to underground mining methods, surface mining causes greater disturbances on surface areas and produces larger amounts of solid waste; and the use of this method continues in many countries. Underground mining is frequently conducted in such a manner that it causes rocks above the extracted seams to collapse down wards to fill the void left after removing the ore.

If these mines are relatively close to the surface, this collapse can be evident on the surface as land subsidence. Subsidence can result as cracks in the land surface, unevenness in roads, inundation of waterfront land or damage to buildings located above or close to the area (ELAW, 2010).

2.5.3 Habitat destruction

Wildlife species live in communities that depend on each other. Survival of these species can depend on soil conditions, local climate, altitude, and other features of the local habitat. Mining causes direct and indirect damage to wildlife. The impacts stem primarily from disturbing, removing, and redistributing the land surface. Some impacts are short-term and confined to the mine site; others may have far-reaching, long-term effects (USEPA, 1994).

The most direct effect on wildlife is destruction or displacement of species in areas of excavation and piling of mine wastes. Mobile wildlife species, like game animals, birds, and predators, leave these areas. More sedentary animals, like invertebrates, many reptiles, burrowing rodents, and small mammals, may be more severely affected (USEPA, 1994).

2.5.4 Water quality

Perhaps the most significant impact of a mining project is its effects on water quality and availability of water resources within the project area. Mine water pollution in South Africa's largest city, Johannesburg, is a major problem. It faces the looming threat of toxic water spewing out of idle mines as early as 2013-2014, unless government steps in to prevent an environmental disaster (McCarthy, 2011). Negative impacts of mining in Canada vary from the sedimentation caused by poorly built roads during exploration through the sediment and disturbance of water during mine construction (EMCC, 2000).

Key questions are whether surface and groundwater supplies will remain fit for human consumption, and whether the quality of surface waters in the project area will remain adequate to support native aquatic life and terrestrial wildlife (ELAW, 2010).

Acid mine drainage also dissolves toxic metals, such as copper, aluminium, cadmium, arsenic, lead and mercury, from the surrounding rock. These metals, particularly the iron, may coat the stream bottom with an orange-red coloured slime called yellow-boy. Even in very small amounts, metals can be toxic to humans and wildlife. Carried in water, the metals can travel far, contaminating streams and groundwater for great distances. The impacts to aquatic life may range from immediate fish kills to sub-lethal impacts affecting growth, behaviour or the ability to reproduce (ELAW, 2010).

2.5.5 Social and development issues at a mining area

The displacement of settled communities is a significant cause of resentment and conflict often associated with large-scale mineral development. Entire communities may be uprooted and forced to move elsewhere, often into purpose-built settlements not necessarily of their own choosing. Besides losing their homes, communities may also lose their land and thus their livelihoods. Community institutions and power relations may also be disrupted (IIED, 2002).

Displaced communities are often settled in areas without adequate resources or are left near the mine, where they may bear the brunt of pollution and contamination. Forced resettlement can be particularly disastrous for indigenous communities who have strong cultural and spiritual ties to the lands of their ancestors and who may find it difficult to survive when these are broken (IIED, 2002).

2.6 South African Policy and Legislation Framework

Waste management in South Africa is based on the principles of the White Paper on Integrated Pollution and Waste Management (IP&WM), and the National Waste Management Strategy (NWMS), published by the Department of Environmental Affairs and Tourism in 1999 and 2000, respectively and the subsequent enhancements of the new National Environmental Management: Waste Act, 2008 (Act No. 59 of 2008).

South Africa supports the waste hierarchy (Figure. 2.4) in its approach to waste management, by promoting cleaner production, waste minimisation, reuse, recycling and waste treatment with disposal seen as a last resort in the management of waste. The waste hierarchy is supported under the South African Policy (White Paper and the National Waste Management Strategy).

Cleaner Production	Prevention
	Minimisation
Recycling	Re-Use
	Recovery
	Composting
Treatment	Physical
	Chemical
	Destruction
Disposal	Landfill

Figure 2.4 Waste Hierarchies (Kalule, 2009).

2.6.1 National Environmental Management Act 107 of 1998

The National Environmental Management Act (Act No. 107 of 1998) emphasizes the avoidance of the disturbance of ecosystems and loss of biological diversity. This applies to mining activities where ecosystems are disturbed and there is a loss of biodiversity during mining and where there is acid mine drainage in coal and gold mines. The Act also indicates that the use of non-renewable resources, such as minerals, should consider the consequences of depletion of these resources (DMR, 2006).

2.6.2 Mineral Act 50 of 1991

Mineral Act (Act No.50 of 1991) encourages the mining houses or companies to have a full Environmental Management Programme Report (EMPR). This helps to regulate environmental impacts during prospecting, exploration, mining and processing of minerals. The Act requires the mining companies to rehabilitate their sites during prospecting, mining and afterwards. The environmental management programme looks at different environmental impacts that emanate from mining operations and also include mitigating strategies of those impacts (DMR, 2006).

2.6.3 Mine closure and post-operational waste management

Many mine-related environmental impacts often continue after mining operations have ceased. Amongst the more pronounced post-closure impacts is landscape scarring, in the form of un-rehabilitated waste rock dumps, mine tailing dams, discard dumps, old shafts and underground mine water ingress to fresh water.

In addition, continuing environmental damage from polluted waters (including acid mine drainage), wind-blown dusts and the dispersal of contaminated solid waste is a feature of mines throughout the world (Pulles, 1992).

2.6.4 Mineral and Petroleum Resources Development Act 28 of 2002

Where the holder of reconnaissance permission, prospecting rights, mining rights, retention permit or mining permits, as the case may be, or his or her successor in title, is deceased or cannot be traced or, in the case of a juristic person, has ceased to exist, has been liquidated or cannot be traced, the Department of Environmental Affairs and Tourism, may instruct the Regional Manager concerned to take the necessary measures to prevent pollution or ecological degradation of the environment or to rehabilitate dangerous health and social occurrences or to make an area safe (DMR, 2006).

2.7 Sampling Methods

2.7.1 Water sampling

2.7.1.1 Tap water (reticulated town water, tank water, and other storage facilities with a tap outlet)

If there are several taps in testing area, the one which is frequently used must be chosen subject to the removal of any external fitting such as filters and contaminants. Remove any external fittings such as filters and remove any contaminants (for example grease, slime, sediment build-up), around the spout with a clean cloth. Tap cleanliness is particularly important with microbiological testing (Clarkson, 1987).

Tap outlets which are suspected of being contaminated must be disinfected first before taking a sample. Disinfect by swabbing the outside of the tap and as much of the inside as possible with a 0.1% sodium hypochlorite solution (Munn, 1970). Prepare the 0.1% solution by diluting commercially available sodium hypochlorite solution (approx. 10%), by a factor of 100.0. Allow to stand for a few minutes (to allow full disinfection), before proceeding (Munn, 1970).

2.7.1.2 Groundwater (bores, wells-pump operated)

Operate the pump to flush out stagnant water from the pipe. Operation time will depend on the depth of the bore and diameter of the pipe-work (CSIRO, 2009). Do not sample a newly drilled bore/well or a rarely used one unless the facility has been pumped for more than 48.0 hours.

Obiri (2007) said one should collect the sample from a tap, which should be located on the discharge side of the pump (do not collect the water sample from a tap located on the inlet side to the pump as this will not be representative of the water reaching the users).

2.7.1.3 Surface waters—shallow and deep (lakes, rivers, creeks, streams)

National River Authority (1994) stress that for surface water sample, simply hold the bottle firmly and plunge the neck downwards to a depth of about 0.5 m. Turn the bottle until the neck points upward and mouth is directed towards the current (if present). If a sample is taken from a boat, always collect the sample from the upstream side of the boat. Alternatively, a clean bucket (of about 10 L capacity), or other suitable vessel such as a large beaker can be used to collect the surface sample. Dip the bucket or beaker into the stream, withdraw and then transfer to the laboratory sample container (Vega *et al.*, 1998).

The sampling protocol was adopted from DWAF Quality of Domestic Water Supplies Volume 2: sampling guide, 2000. The protocol is also in line with SANS 5667-1:2008 Water Sampling part 1.

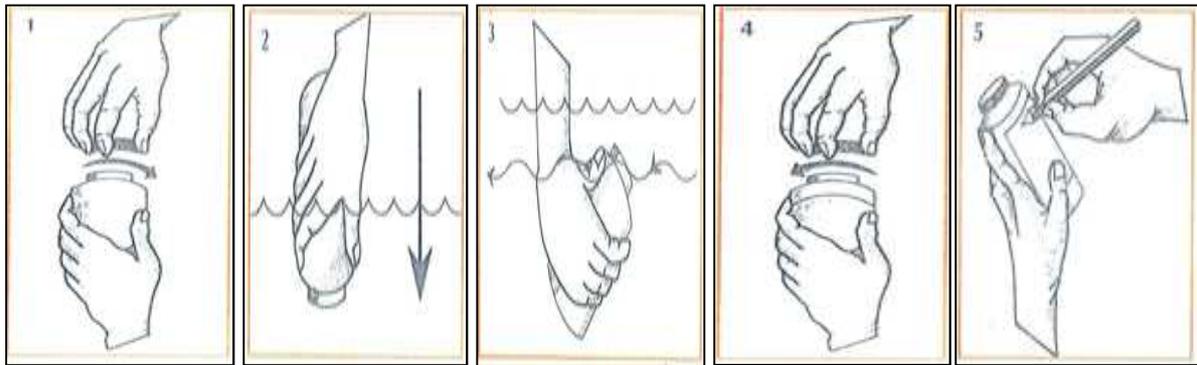


Figure 2.5 Sampling protocol (DWAF, 2000 & SANS 5661-1:2000).

The bottle must be labelled. Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with the sample first prior to filtration. Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (Teflon). Optional: If the sample contains a lot of particulate matter then it may be necessary to pre-filter a sample using a glass fibre (GF/C) filter paper GFC 1.2 μm (APHA, 1998).

2.7.1.4 Depth water samples

Collect the water sample using a suitable depth sampling device (hosepipe, grab, pump and many more). Be careful not to disturb bottom sediment. If a composite sample is to be submitted for analysis, pour equal portions of freshly collected samples into the appropriate container (Obiri, 2007).

2.7.2 Soil sampling

Soil sampling and testing provides an estimate of the capacity of the soil to supply adequate nutrients to meet the needs of growing plants (Harold, 2000). Traditionally, the goal of soil sampling is to develop a representative estimate of the average nutrient needs for a field so that the best single rate of application can be determined (Harold, 2000).

The most commonly used sampling design for many field studies is systematic sampling using either transects or grids (Cannon *et al.*, 1994). Systematic sampling designs are often criticized by statisticians but the ease with which they can be used and the efficiency with which they gather information makes them popular in the field of earth sciences.

Ideally the initial point of transect or grid and or its orientation should be randomly selected. The major caution in the use of systematic sampling with constant spacing is that the objects to be sampled must not be arranged in an orderly manner, which might correspond to the spacing along transect or the grid (Cannon *et al.*, 1994).

The collection of the most solid phase samples in the vicinity of tailings impoundment requires access to the subsurface soils (Keely & Boateng, 1987). The different kinds of extraction methods can be applied as follows;

2.7.2.1 Auger

The auger penetrates the subsurface sediments through a combination of rotation and downward force, as rotation occurs, cuttings are brought to the surface on the auger flights. Augers are relatively fast penetrating in fine sediments, particularly unconsolidated tailings. Solid samples are easily obtained from auger flight (Keely & Boateng, 1987).

A hand auger is a tool for boring holes consisting of a shank with crosswise screw with a cutting head which is essentially a small scale, hand operated version until the auger flight is full. The auger is then withdrawn, cleaned and reinserted into the original hole for further augering (NUTP, 1985).

2.7.2.2 Split spoon

The split spoon is a thick-walled sampler which is mounted on drill rods and extended to the bottom of the borehole. The sampler is advanced by a hammer into the subsurface material to obtain the sample. The sampler is intended for unconsolidated material and it is sometimes necessary to use retainers in the shoe of the sampler to prevent loss of the sample (NUTP, 1985). The disadvantages of this method are that the sample size is limited due to relatively short length and samples may be altered from their in-situ state.

2.7.2.3 Shovel

A shovel is a hand implement consisting of broad scoop or a hollowed out blade with a handle. The shovel is used to dig pits down to depths of around one metre. This technique is successful in unconsolidated materials and highly broken rock (EPRI, 1985).

The good thing about a shovel is that it is light and portable. The shallow samples can be obtained relatively fast. But it has a number of limitations; samples can only be obtained from shallow depth. Penetration of unbroken and coarse ground sediments is not feasible. Collection of large quantities of samples is time consuming.

2.8 Review of Sample Treatment Methods

2.8.1 Grinding of samples

At least 2.0 kg of each soil sample needed to be divided in half and dried overnight at 110 °C using a bench mounted laboratory oven. The 1.0 kg of sample should be removed and allowed to cool. The sample should then milled to 80.0 % or <75.0 µm fine (Chauke, 2011).

2.8.1 Acid decomposition

Weigh 5.0 g of each milled sample. Pour it into a 500.0 ml beaker. Add 20.0 ml of nitric acid and 60.0 ml of hydrochloric acid into the beaker. Place the beaker on a hot plate for at least 40.0 minutes to allow digestion to take place. Transfer the contents from the beaker into a 100.0 ml volumetric flask and fill it with de-ionised water. Mix the contents properly to ensure homogenous mixing (Chauke, 2011).

2.9 Review of Physico-Chemical Parameter

2.9.1 Mine tailings slope features and vegetation cover

Normally the outside of tailing slopes should be 30° to 45°. Provided the angle of the slope of the side of the tailing is not steeper than 27°, then according to Clausen (1973) the sides will be permanently covered by vegetation.

Soil texture is the relative proportion of different-sized mineral particles (clay, silt and sand) in soil or soil horizon respectively (SSS, 1999). Soil texture is a fundamental physical property of soil that influences how the soil responds to different stresses, such as compatibility and erosion. In practice soil texture is also used as a basic indicator of soil chemical properties (McSweeney & Jansen, 1984).

Water and erosion are dominant degrading processes on tailings. Mrost (1974) estimated that the annual water erosion induced loss of material from the surface of tailings 30.0 to 40.0 m high and with a slope of about 35°, amounts to a layer of approximately 100.0 mm. This result in hundreds of tonnes of soil lost every year in an area, which has an average annual rainfall of 700.0 mm.

The ideal vegetation cover consists of trees and shrubs that can act as a windbreak to the tailings during the dry winter months and additional strong grass cover to ensure complete surface protection. Trees are much more acid-tolerant than grass; whereas grass prefers alkaline or neutral soil; trees grow better in acid soil (Hill, 1973).

2.9.2 pH

The pH is a measure of how acidic or basic water is. The range goes from 0 to 14.0, with 7.0 being neutral. The pH of less than 7.0 indicates acidity, whereas pH of greater than 7.0 indicates a base. Pollution can change water's pH, which in turn can harm animals and plants living in water (USGS, 2013).

The levels of water acidity can be changed by human practices and the alkaline environment conditions may neutralise these acids. The pH of water does not have direct consequences except at extremes. The adverse effects of pH result from the solubilisation of toxic heavy metals and protonation or deprotonation of other ions (Ayers, 1985).

Soil pH affects the concentration of arsenic in the soil solution, solubility decreases with increasing pH. At high pH values, in the presences of calcium and magnesium, oxy-anions of arsenic are precipitated (Berman, 1980).

2.9.3 Electrical conductivity

The EC is the capacity of the material to carry electric current. In water it is generally used as a measure of the mineral or ionic concentration. Michaud (1991) defined EC as the total amount of dissolved ions in water and is used to estimate the amount of total dissolved salts (TDS) in water. Only ionisable material contributes to conductivity.

Conductivity will vary with water source; ground water, water drained from agricultural fields, municipal waste water, rainfall. Conductivity can indicate ground seepage or a sewage leak (RCB, 2004).

2.9.4 Turbidity

Turbidity is the amount of cloudiness in the water. This can vary from a river full of mud and silt where it would be impossible to see through the water (high turbidity), to spring water which appears to be completely clear (low turbidity) (USEPA, 2003a). Drinking water should have a turbidity of 5.0 NTU or less according to the South African Department of Water Affairs and the SABS (24-1:2011 Edition 1). Turbidity diffuses sunlight and slows photosynthesis. Plants begin to die (Ziegler, 2002).

Weather and seasons can contribute to turbidity. High turbidity can quickly block filters and stop them working effectively. High turbidity will also fill tanks and pipes with mud and silt, and can damage valves and taps (ASTM, 1973). The following turbidity guidelines for drinking water apply in the US, and are very similar to the standards limits in South Africa. Drinking water should have a turbidity of 5.0 NTU or less and where water is chlorinated, turbidity should be less than 5.0 NTU and preferably less than 1.0 NTU for chlorination to be effective.

2.9.5 Total metal content

Although the great majority of quality problems with community drinking water are related to faecal contamination, a significant number of serious problems may occur as a result of chemical contamination from a variety of natural and man-made sources. In order to establish whether such problems exist, chemical analyses must be undertaken (Kleinmann, 1985).

However, it would be extremely costly to regularly undertake the determination of a wide range of parameters, particularly in the case of supplies that serve small numbers of people. Fortunately, such parameters tend to be less variable in source waters than faecal contamination, so that alternative strategies can be employed (CSIRO, 2009).

Vega *et al.*, (1998) indicated that the range of health-related parameters may include: fluoride (where it is known to occur naturally), nitrate (where intensification of farming has led to elevated levels in groundwater), lead (in areas where it has been used in plumbing), chromium (in areas where it is mined), arsenic (in areas where it is known to occur naturally), pesticides (where local practices and use indicate that high levels are likely).

If these or any other chemicals of health significance are thought to be present, they should be monitored and the results examined in view of the WHO guideline values and any relevant national standards. If this is done, the reagents must be of high quality and carefully standardized. Other parameters require conventional laboratory analysis by spectrophotometer, atomic absorption spectroscopy, or chromatography, using standard methods (NRA, 1994).

2.10 Review of instrumental Techniques for Metal Analysis

Metal analysis is done by atomic absorption (AA) spectrometry. This method describes both flame atomic absorption (FAA) spectroscopy and graphite furnace atomic absorption (GFAA) spectroscopy. Of the two methods, the detection limit for GFAA is about two orders of magnitude better than FAA (USEPA, 1999).

2.10.1 Graphite furnace atomic absorption (GFAA)

The technique uses an electrically heated graphite tube inside a graphite furnace for vaporization, ashing and atomization of the sample solution. Lower detection limits can be achieved because the whole sample is exposed to the atomization process.

Sometimes a platform is inserted at the base of the graphite tube where the sample drop is placed for atomization. The platform slows down the atomization and enhances the reproducibility of the results. Errors are usually higher than those for flame atomization by a factor of 5-10 (Elliot & Stever, 1973).

2.10.2 Flame atomic absorption (FAA)

The FAA relies on a flame to provide the heat necessary to evaporate the solvent and break molecular bonds in order to produce a cloud of free atoms in the path of an atomic absorption spectrophotometer. The method is rapid, sensitive, and free from inter-element interferences.

The trace metal to be detected is dissociated from its chemical bonds by flame and is put into an unexcited or "ground" state. The metal is then capable of absorbing radiation at discrete lines of narrow bandwidth (Jon, 1980).

A hollow cathode or electrode-less discharge lamp for the determined metal provides a source of the characteristic radiation energy for that particular metal. The absorption of this characteristic energy by the atoms of interest in the flame is measured and is related to the concentration of the metal in the sample (Jon, 1980).

A series of known standard solutions are used by the analyst for the calibration of the instrument (i.e., preparation of the analytical curve) (Elliot & Stever, 1973). The solutions are not subject to the preparation method but contain the same matrix as the sample preparations to be analysed. Working standards are prepared by appropriate single or multiple dilutions of the standard solutions. Mixed standards should be prepared with chemical incompatibilities in mind. For those metals that indicate chemical or ionization interferences, the final dilution shall contain 2.0% (v/v) of the 50.0 mg/ml cesium and lanthanum solutions (Jon, 1980).

References

Acid Rock Drainage (ARD) 2012: <http://www.lenntech.com/periodic/elements/cu.htm#ixzz1qVnvTjCf>.

Agency of Toxic Substances & Disease Registry (ATSDR) 2004: Toxicological Profile for Copper. November 1, 2011, <http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=245&tid=44>.

Agency of Toxic Substances & Disease Registry (ATSDR) 2007a: Toxicological Profile for Arsenic. November 5, 2011, from <http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=22&tid=3>.

Agency of Toxic Substances & Disease Registry (ATSDR) 2007b: Toxicological Profile for Lead. November 5, 2011, from <http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=96&tid=22>

Agency of Toxic Substances & Disease Registry (ATSDR) 2008: Toxicological Profile for Cadmium. November 5, 2011, from <http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=48&tid=15>

Alloway BJ 1996: Soil pollution and land contamination. In pollution causes, effects and control (unpublished report).

Alloway BJ & Ayres DC 1993: *Chemical Principles of the Environmental Pollution*. Glasgow: Blackie Academic and Professional.

APHA 1998: *Standard methods for the examination of water and wastewater* (20th Ed.). Greenberg AE and Eaton AD (Eds.): American Public Health Association. Washington DC.

Aremu MO 2008: in *Environment, Health and Nutrition: Global Perspective*, Basu, S.K.; Datta, B. (Eds.), A.P.H. Publishing Inc.: New Delhi, India; 2008, pp. 79–96.

Ayenimo JG, Yusuf AM & Adekunle AS 2010: Heavy Metal Exposure from Personal Care Products. *Bulletin of Environmental Contamination and Toxicology*, 84(1), 8-14.

Bailey PA & Rada RG 1984: Distribution and enrichment of trace metals (Cd, Cr, Cu, Ni, Pb, Zn) in bottom sediments of navigation Pools 4 (Lake Pepin), 5, and 9 of the Upper Mississippi River, in Wiener JG, Anderson RV and McConville DR eds., *Contaminants in the Upper Mississippi River*. Boston, Butterworth Publishers, p. 119-138.

Ball H 1982: Arsenic Poisoning and Napoleon's Death. *New Scientist* October 1982; 101-104.

Bécharde G 1996: Natural Resources Canada, personal communication to Mills C.

Best Practice Environmental in Mining (BPEM) 1999: Water Management in Mining Australia.

Bellinger DC 2008: Very low lead exposures and children's neurodevelopment. *Current Opinion in Paediatrics*, 20(2), 172-177.

Bhatti TM, Bigham JM, Vuorinen A & Tuovinen OH 1994: Alteration of mica and feldspar associated with the microbiological oxidation of pyrrhotite and pyrite, in Alpers CN, & Blowes DW (Ed). *Environmental geochemistry of sulphide oxidation*: Washington, D.C. American Chemical Society Symposium Series 550, p. 90-105.

Birge W, Black JA, Westerman AG, Francis PC & Hudson JE 1977: Embryopathic effects of waterborne and sediment-accumulated cadmium, mercury, and zinc on reproduction and survival of fish and amphibian populations in Kentucky: U.S. Department of the Interior, Research Report 100, Washington, D.C., 28 p.

Bowders J & Chiado E 1990: Engineering Evaluation of Waste, Phosphatic Clay for Producing Low Permeability Barriers, in Proceedings 1990 Mining and Reclamation Conference and Exhibition, Volume 1, pp 11-18, West Virginia University.

Brearley CL 1982: Microbiological mining. *Scientific American*, v. 247, no. 2, p. 44-53.

Briggs JC & Ficke JF 1978: Quality of rivers of the United States, 1975 water year: U.S. Geological Survey Open-File Report 78-200, 436 p.

Bruyneel M, De Caluwé JP, des Grottes JM & Collart F 2002: Use of kohl and severe lead poisoning in Brussels, *Revue médicale de Bruxelles*, 23(6), 519-522.

Brearley CL 1978: Bacterial Leaching, *CRC Critical Reviews in Microbiology*, v6, Iss.3, 207-262.

Bruynesteyn A & Hackl RP 1984: Evaluation of acid production potential of mining waste materials, *Minerals and the Environment*, 4(1), 5-8.

BRGM 2001: Management of mining, quarrying and ore-processing waste in the European Union, 79 p., 7 Figs., 17 Tables, 7 annexes, 1 CD-ROM (Collected data)

Canadian Council of Resource & Environment Ministers (CCRE) 1987: Canadian Water Quality Guidelines.

Cannon ME, McKenzie RC, & Lachapelle G 1994: Soil salinity mapping with electromagnetic induction and satellite-based navigation methods. *Can. J. Soil Sci.* 74: 335–343.

Canwest News Service (CNS) 2008: Tories won't list leaded lipsticks. *Canada.com*. Retrieved from <http://www.canada.com/topics/news/national/story.html?id=4b8f58b0-c225-4925-8e6e-3b41a3687626>.

Centres for Disease Control & Prevention (CDCP) 2009: Lead: Prevention Tips. Retrieved November 5, 2011, from <http://www.cdc.gov/nceh/lead/tips.htm>.

Chauke RP 2011: Prediction of acid mine drainage generation and their remedial actions in tailings dam in an abandoned Louis Moore gold mine, unpublished thesis. University of Venda.

Centres for Disease Control & Prevention (CDCP) 2010: National Report on Human Exposure to Environmental Chemicals: Fact Sheet (Lead). Retrieved November 3, 2011, from http://www.cdc.gov/exposurereport/Lead_FactSheet.html.

Chadwich J 1996: Polish Lignite. *Mining Magazine*, March.

Colmer AR, Temple KL, & Hinkle ME 1950: An iron-oxidizing bacterium from the drainage of some bituminous coal mines: *Journal of Bacteriology*, v. 59, p. 317-32.

Cork DJ & Cusanovich MA 1979: Continuous Disposal of Sulphate by Bacterial Mutualism, *Dev. Ind. Microbiology.*, v20, 591-602.

CSIRO 2009: The Australian Methodology to derive ecological investigation levels in contaminated soil. CSIRO. Land and Water Sciences. Report 43/09

Davies MP & Rice S 2001: "An alternative to conventional tailings management –“dry stack” filtered tailings” and mine waste. January 2001, pp. 411-420.

Davydova S 2005: Heavy metals as toxicants in big cities. *Microchemistry Journal*. 2005, 79, 133-136.

Department of Justice, Food & Drugs Act (DJFG) 2008: Retrieved February 24, 2011, from <http://laws-lois.justice.gc.ca/eng/acts/F%2D27/>.

Department of Environmental Affairs & Tourism (DEAT) 1998: National Environmental Management Act No. 107, Government Printers, South Africa.

Department of Mineral & Energy (DME) 2006: Profit guideline towards management and closure of gold minerals resource deposits. Department of Minerals and Energy. Pretoria, RSA.

Department of Mineral & Energy (DME) 1991: Mineral Act No. 50, Government Printers, South Africa.

Department of Mineral & Energy (DME) 2002: Mineral and Petroleum Resources Development Act 28, Government Printers, South Africa.

Department of Mineral Resource (DMR) 2006: Draft Guideline towards management and closure of gold mine residue deposits, Pretoria, RSA.

Director: Mineral economics, Pretoria .<http://www.dine.gov.za/> publication /Ref annual reports Vicks S.G.1983. Planning design and analysis of tailing dams.

Dutrizac JE & MacDonald RJC 1974: Ferric Ion as a Leaching Medium, *Minerals Sci. & Eng.*, v6, n2, p59-100.

Electric Power Research Institute (EPRI) 1985: Field measurement methods for hydrogeologic investigations: a critical review of the literature. EPRI EA-4301 Project 2485-7, Palo Alto, CA.

Elinder CG 1985: Normal Values for Cadmium in Human Tissues, Blood, and Urine in Different Countries. In L. Friberg.

Elliot E V & Stever KR 1973: Atomic Absorption. *Newsletter*, 12, 60-67.

Ehrlich HL 1990: *Geomicrobiology* (2nd): New York, Marcel Dekker, Inc., 646 p.

Ehrlich HL & Brearley CL (Ed) 1990: *Microbial mineral recovery*. New York, McGraw-Hill, Inc., 454 p.

Environment Canada 2010a: Lead. Retrieved November 8, 2011, from <http://www.ec.gc.ca/toxiques-toxics/Default.asp?lang=En&n=98E80CC6-1&xml=D048E4B9-B103-4652-8DCF-AC148D29FB7D>.

Environment Canada 2010b: Toxic Substances List. Retrieved October 29, 2011, from <http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=0DA2924D-1&wsdoc=4ABEFFC8-5BEC-B57A-F4BF-11069545E434>.

Environment Canada & Health Canada 1993: Priority Substances List Assessment Report: Arsenic and its Compounds. Retrieved November 5, 2011, from http://www.hcsc.gc.ca/ewhsemt/pubs/contaminants/psl1lsp1/arsenic_comp/indexeng.Php.

Environment Canada & Health Canada 1994a: *Priority Substances List Assessment Report*. Cadmium and its Compounds. Retrieved November 5, 2011, from http://www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/psl1lsp1/cadmium_comp/index-eng.php.

Environment Canada & Health Canada 1994b: Priority Substances List Assessment Report: Nickel and its Compounds. Retrieved November 5, 2011 from http://www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/psl1-lsp1/compounds_nickel_composes/index-eng.php.

Environmental Mining Council of Canada (EMCC) 2000: Mining and waste pollution issues in BC, Rockefeller Brothers Fund, BC V8W2AS.

Evangelou VP & Zhang YL 1995: A Review: Pyrite Oxidation Mechanisms and Acid Mine Drainage Prevention. *Critical Reviews in Environmental Science and Technology*, v25, n2, p 141-199.

Faulkner BB & Skousen JG 1994: Treatment of Acid Mine Drainage by Passive Treatment Systems pp 250-270 in *Volume 2 of Proceedings of the international Land Reclamation and Mine Drainage Conference and the third Conference on the abatement of Acidic Drainage*. Pittsburgh, PA, April 24-29, 1994.

Garrels RM & Christ CL 1965: Solutions, *Minerals and Equilibrium*. Harper & Row, New York, 216-222.

Giammar D 1997: Surface Coal Mining and Environmental Degradation in the United States, 1997: [http://ftp.pku.edu.cn/departments/Caltechll-ge 148/199 7C/Report s/st](http://ftp.pku.edu.cn/departments/Caltechll-ge%20148/1997C/Reports/st).

Gibb H & Chen C 1989: Is inhaled arsenic carcinogenic for sites other than the lung? In U. Mohr, D.V. Bates, D.L.

Goyer RA 1996: Toxic effects of metals. In Casarett and Doull's toxicology, The basic science of poisons. Fifth Edition.

Greenberg AE, Clesceri LS, Eaton AD & Franson MAH (Ed) 1992: *Iron and sulphur bacteria*, in Standard methods for the examination of water and wastewater (18th): Washington, D.C., American Public Health Association, Section 9240.

Hamer G 2003: Solid waste treatment and disposal: Effects on public health and environmental safety. *Biotechnol. Adv.* 2003, 22, 71-79.

Harold DR 2000: Efficient Fertilizer Use: Soil Sampling for High Yield Agriculture.

Health Canada 2010d: Harper Government Takes Action to Protect Children from Lead Exposure. Retrieved November 30, 2011, from [http://www.hc-sc.gc.ca/ahc-asc/media/nr-cp/ 2010/2010_203-eng.php](http://www.hc-sc.gc.ca/ahc-asc/media/nr-cp/2010/2010_203-eng.php).

Hill 1973: The Zimbabwean approach to vegetating of soil slime dams. *J.S. Afri. Min. & Metal.* 74 (5): 197-208.

Holum JR 1983: Elements of General and Biological Chemistry, 6th Edition, John Wiley and Sons NY.

Horsfall MN Jr & Spiff AI 1999: Speciation of Heavy Metals in Intertidal Sediments of the Okirika River System (Nigeria). *Bull. Chem. Soc. Ethiop.* 13(1): 1–9.

International Institute for Environment & Development (IIED) 2002: Breaking New Ground: Mining, Minerals and Sustainable Development: Chapter 9: Local Communities and Mines, Breaking New Grounds. <http://www.iied.org/pubs/pdfs/G00901>.

Ingles J & Scott JS 1987: State-of-the-Art of Processes for the Treatment of Gold Mill Effluents, unpubl. Report, Environmental Protection Service, Ottawa, 6-32 to 6-46.

Järup L, Berglund M, Elinder CG, Nordberg G & Vahter M 1998: Health effects of cadmium exposure - a review of the literature and a risk estimate.

Jon CVL 1980: *Analytical Atomic Absorption Spectroscopy*. Selected methods; Academic Press. New York. 141. ISBN No, 0-12-714050-6.

Kalule SK, 2009: Evaluation of Climate Change impact of waste mining options, (WMSA Mining Conference, East London, August 2009.

Keely JF & Boateng 1987: Monitoring well installation, purging and sampling techniques Part 1: Conceptualisation, Ground water.

Kelly DP 1988: Evolution of the understanding of the microbiology and biochemistry of the mineral leaching habitat, in Norris PR & Kelly DP (Ed), *Biohydrometallurgy-Proceedings of the international symposium Warwick 1987*: Kew, Surrey, Great Britain, Antony Rowe Ltd., Science and Technology Letters, p. 3-14.

Kelly J 1998: *Trace Metals in Agriculture*. In: *Effect of Heavy Metal Pollution on plants*, Vol II. (Ed) Lepp, N.W. Applied Science Publishers London & New Jersey.

Kleinmann RLP 1985: Treatment of Acid Mine Water by wetlands: Control of Acid mine drainage, IC-9027, 1985.

Lawrence RW & Sadeghnobari A 1986: Investigation of predictive techniques for acid mine drainage. Report on DSS Contract No. 23440-7-9178/01-SQ, Energy Mines and Resources, Canada, MEND Report 1.16.1 (a).

Leathen WW, Barley SA & McIntyre LD 1953: The role of bacteria in the formation of acid from certain sulfuric constituents associated with bituminous coal, II. Ferrous-iron oxidizing bacteria: *Applied Microbiology*, v. 1, p. 65-68.

Leduc LG & Ferroni GD 1994: The Need for Thiobacillus Ferrooxidans Strain Selection in Applications of Bioleaching, Proc. Biominet, 10th Ann. Gen. Meet., Minister of Supply and Services Canada, Ottawa, 25-42.

Le Roux NW, North AA & Wilson JC 1974: Bacterial Oxidation of Pyrite, Proc. *10th Internat. Min. Proc. Congr. 1973, Inst. Min. Met.*, London, 1051-1066.

Lizama HM & Suzuki I 1987: Bacterial leaching of a sulphide ore by Thiobacillus ferrooxidans and thiooxidans, I. Shake flask studies. *Biotechnology and Bioengineering*, v. 32, p. 110-116.

Lilley SG, Florence TM & Stauber JL 1998: The use of sweat to monitor lead absorption through the skin.

Malouf EE & Prater JD 1961: Role of Bacteria in the Alteration of Sulphide. *J. Metals*, New York, v13, p353-356.

McBride MB 1994: *Environmental chemistry in soils*. Oxford University Press, Oxford.

McCarthy T 2011: Sinking Solutions for the Mining Water Pollution, (www.watersafe.co.za/posted_on_March_7, 2011).

McSweeney K & Jansen IJ 1984: Soil texture and associated rooting behaviour in mine soils. *Soil. Sci. Soc. Am. J.*, 48: 607-612.

Michaud JP 1991: A citizen's guide to understanding and monitoring lakes and streams: Olympia, Washington state department of ecology publication 94-149, pp66.

Mine Environment Neutral Drainage Program (MEND) 1990: Assessment of Existing Natural Wetlands affected by low pH, Metal Contaminated Seepages (Acid Mine Drainage), MEND Report No. 3.12.1a, Natural Resources Canada, Ottawa.

Mine Environment Neutral Drainage Program (MEND) 1993: Treatment of Acidic Seepages using Wetland Ecology and Microbiology: Overall Program Assessment, MEND Report No. 3.11.1, Natural Resources Canada, Ottawa.

Munn RE 1970: *Biometeorological Methods*. New York Academic press, 1970. Pp53.

Mrost M 1974: Slimes disposal at South African gold mines. *J.S Afr. Int. Min & Metal*, pp. 285-291.

Natural River Authority (NRA) 1994: Abandoned mine and the water environment. Natural rivers Authority water quality series. No. 14. HMSO, London.

Natural Uranium Tailings Program (NUTP) 1985: Uranium Tailings Sampling Manual. NUTP-IE Energy, Mines and Resources Canada.

Newchurch EJ & Kahwa IA 1984: Heavy metals in the Lower Mississippi River. *Journal of Environmental Science and Health*, v. A19, no. 8, p. 973-988.

Obiri S 2007: Determination of heavy metals in boreholes in Dumasi in the Wasswa West District of Western Region of Republic of Ghana.

Pieryznski GM, Sims JT & Vance GF 1994: *Soils and Environmental Quality*. Boca Raton, Florida: Lewis Publishers.

Pulles W 1992: Water pollution; Its Management and Control in the South African Gold Mining Industry. *Journal of the Mine Ventilation Society of South Africa*, 45(2): 18-36.

Rastogi SC & Clausen J 1976: Absorption of lead through the skin. *Toxicology*, 6(3), 371-376.

Rastogi V 1985: The effects of particle size distribution on the rate of mine acid formation and its mitigation by bacterial inhibitors, Proceedings of 1985 ASSMR, Denver, Colorado

Rastogi V 1984: Laboratory methods for determining the effects of bactericide on acid mine drainage, Proceedings of 1984 Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation, Lexington, Kentucky.

Resource Control Board (RCB) 2004: The clean water team guidance compendium for watershed monitoring and assessment state water resources control board. FS-3.1.1.30.

Rivas V & Cendrero A 1996: Assessment of the Effects of Mining and urbanisation on Earth Surface Process in Northern Spain. Universidad de Cantabria, Santander.

Rothenberg SJ, Khan F, Manalo M, Jiang J, Cuellar R & Reyes S 2000: Maternal Bone Lead Contribution to Blood Lead during and after Pregnancy. *Environmental Research*, 82(1), 81-90.

Roman RJ & Benner BR 1973: The Dissolution of Copper Concentrates. *Minerals Sci. & Eng.*, v5, n1, p3-24.

RTI 1999: Toxicological profile for lead. Research Triangle Institute for U.S, Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta.

Scand J 1998: Work Environmental Health, 24 suppl. 1:52p.

Schneider G & Krivna V 1993: Multi-Element Analysis of Tobacco and Smoke Condensate, March 7, 2011, http://www.who.int/entity/water_sanitation_health/dwq/GDW12rev1and2.pdf.

Silverman MP & Lundgren DG 1959: Studies on the chemolithotrophic iron bacterium *Ferrobacillus ferrooxidans*-1. An improved medium and a harvesting procedure for securing high cell yields. *Journal of Bacteriology*, v. 77, p. 642-647.

Soil Survey Staff 1999: Soil taxonomy: basic system of soil classification for making and interpreting soil surveys. Agric. Handbook No. 436. 2nd Ed. US DA-NRCS. US Govt. print. Office. Washington DC.

Solomon W, Forster U & Pavel M 1995: heavy metals (Ed.), problems and solution, New York: Springer-verlag.

Steffen, Robertson & Kirsten (B.C.) Inc. (1991), Sulphate Reduction as a Water Treatment Alternative at the Faro Mine, report for Curragh Resources Inc., 64p.

Szymanski MB & Davies MP 2004: Tailings dams: design criteria and safety evaluations at closure. British Columbia Mine Reclamation Symposium 2004. <http://www.infomine.com/publications/docs/Szymanski2004.pdf>.

Temple KL & Colmer AR 1951: The autotrophic oxidation of iron by a new bacterium, *Thiobacillus ferrooxidans*. *Journal of Bacteriology*, v. 62, p. 605-611.

Teutsch N, Erel Y, Halicz L & Banin 2001: A Distribution of natural and anthropogenic lead in mediterranean soils. *Geochim. Cosmochim. Acta* 2001, 65, 2853-2864.

Trudinger PA 1971: Microbes, Metals and Minerals. *Minerals Sci. & Eng.*, v3, n4, p13-25.

United States Department of Labour (USDOL) 2004: Occupational Safety and Health Administration (OSHA); Safety and Health Topics: Heavy metals, USDOL Publication, Washington, D.C. (www.osha.gov/SLTC/metalsheavy/index.html).

United States Environmental Protection Agency (USEPA) 1994: Technical Report: Design and Evaluation of Tailings Dams. <http://www.epa.gov/osw/nonhaz/industrial/special/mining/techdocs/tailings.pdf>

USEPA 1999: Centre for Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268 June 1999.

USGS 2013: Water properties, the USGS Water Science School. www.usgs.com.

Vega M, Pardo R, Barraado E & Deban L 1998: Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Water Research* 32: 3581-3592.

Vermeulem NJ 1981: The competitive and state of gold tailings, PHD Thesis, UP, RSA.

Voet E, Van der JB, Guinée HA & Udo de Haes (Ed) 2000: *Heavy Metals: A Problem Solved? Methods and Models to Evaluate Policy Strategies for Heavy Metals*. Kluwer Academic Publishers, Dordrecht

Waalkes MP 2000: Mercury carcinogenesis in review. *Inorganic Biochemistry* 79: 240-244.

Walsh F & Mitchell R 1972: A pH Dependent Succession of Iron Bacteria. *Environmental Science and Technology*, v6, n9, p.809-812.

Warkentin DD & Rowley MV 1994: Britannia Mine site A.R.D. *Biosulphide Demonstration Project - Interim Report - Laboratory Testing*, NTBC Research Corp., Richmond, B.C., 21p.

WHO 1989a: Lead - environmental aspects. Environmental Health Criteria 85. World Health Organisation, International Programme on Chemical Safety (IPCS), Geneva, Switzerland.

WHO 1992: Cadmium. Environmental Health Criteria 134. World Health Organisation, International Programme on Chemical Safety (IPCS), Geneva, Switzerland.

WHO 1995a: Cadmium-environmental aspects. Environmental Health Criteria 135. World Health Organisation, International Programme on Chemical Safety (IPCS), Geneva, Switzerland.

WHO 1995b: Inorganic lead. Environmental Health Criteria 165. World Health Organisation, International Programme on Chemical Safety (IPCS), Geneva, Switzerland.

WHO 1988: Environmental Health Criteria 61. World Health Organisation, International Programme on Chemical Safety (IPCS), Geneva, Switzerland.

Ziegler EE, Edwards BB, Jensen RL, Mahaffey KR & Fomon SJ 1978: Absorption and Retention of Lead by Infants. *Pediatric Research*, 12 (1), 29-34.

CHAPTER THREE: MATERIALS AND METHODS

This chapter presents the methods, procedures and equipment employed during the course of the study. The work was divided into three stages, namely; desktop, fieldwork and laboratory work. A summary of procedures and stages is presented in Figure 3.1.

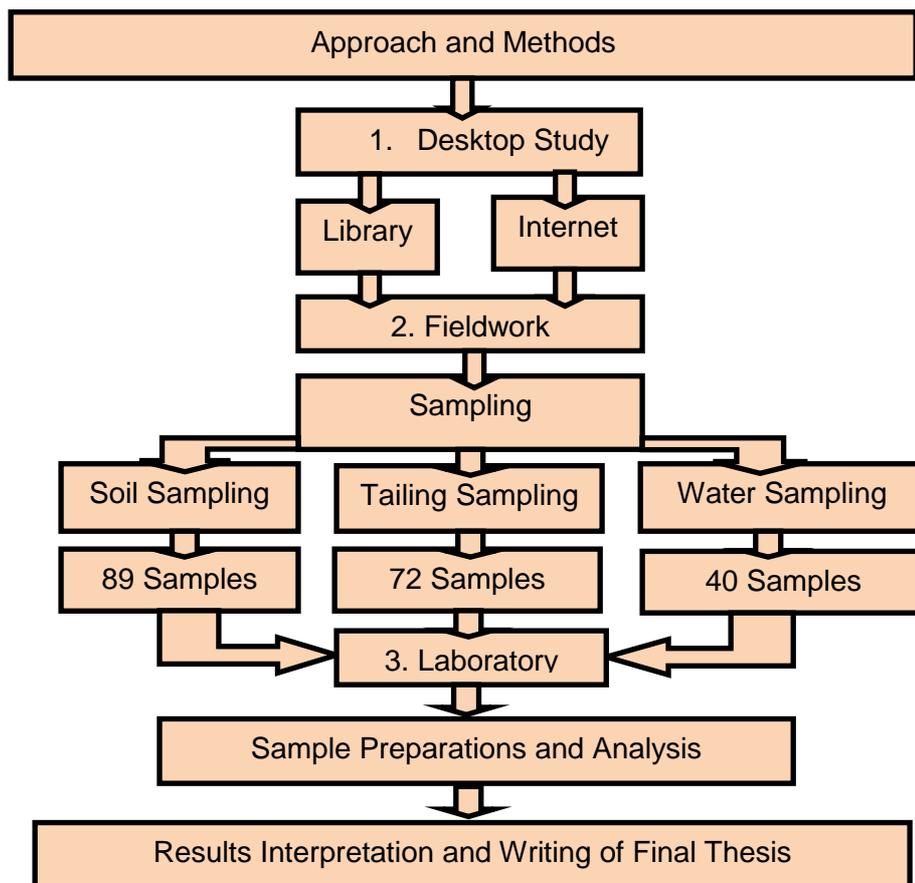


Figure 3.1 Materials and Methods flow chart.

3.1 Study Area and Sample Handling

3.1.1 Location

Musina is the northernmost town in Limpopo province of South Africa located at coordinates; 22° 20' 17"S 30° 02' 30"E / 22 33806°S 30 04167°E (Musina Municipality, 2012). It is located near the confluence of the Limpopo River and the Sand River and the border of Zimbabwe (SAN parks, 2003). Iron ore, coal, magnetite, graphite, asbestos, diamonds, semi-precious stones and copper are mined in the region (Barnes, 1998).

Musina Copper Mine is situated at the Eastern part of Musina town, close to the local hospital. It is about 60.0 km from Louis Trichardt (Makhado) and 89.0 km from De Beers Venetia diamond mine. Figure 3.2 shows the location of the Musina Copper Mine.



Figure 3.2 Locality map of Musina and the study area (Adopted from DWAF, 2001)

3.1.2 Geology

The oldest rocks belong to the Sand River Gneiss and have a minimum age of 3 790 Million years. They formed the basement to a sequence of cover rocks, the Beit Bridge Complex, which, according to their dominant lithology, are subdivided into the Mount Dowe, Malala Drift and the Gumbu Groups. These were intruded by the Musina Suite 3 150 Million years ago (Brandl, 1981).

The Sand River Gneiss and the Beit Bridge Complex were subsequently subjected to several periods of high grade metamorphism and intense deformation. South of the Soutpansberg grey gneisses with associated leucocratic material are developed. Scattered occurrences of sedimentary and ultramafic rocks, belonging to the Giyani Group, are present. Metamorphism is of low to medium grade (Brandl, 1981).

3.1.3 Soil

The area is characterized by shallow stony soils associated with calcrete or granite gneisses and deeper soils are found at the foot of slopes and at valley bottom. There is sufficient soil to meet top soiling requirements, in some areas soil depth is as much as 2500.0 mm (SAN parks, 2003).

Although the region has diverse soils, poorly developed shallow soils on hard to weathered rock are common. Soils are generally red in colour and weakly structured. North of the Soutpansberg, accumulation of sediments from the mountain range has resulted in deep sandy soils (> 750.0 mm).

Further north the soils are not as deep (450.0 mm to 750.0 mm), but are more strongly structured. Clay content is generally less than 15.0% although areas with as much as 35.0% clay are known (Hemming, 2009).

3.1.4 Climate

Temperatures in the study area vary dramatically according to topography and seasonal conditions. The climate of the area is typical of the northern regions of South Africa. Summers are hot and humid, receiving the majority of the rainfall. Winters are warm and dry and droughts are not uncommon. Average summer temperatures are highest in January, averaging above 44.0 °C (MED, 2007).

Winter lows are experienced in July with average minimum temperatures of around 0 °C. Frost occurrences not recorded. Average annual rainfall for the area is between 300.0 to 340.0 mm. Precipitation falls mostly in December and January, often falling as heavy thunder showers (Hemming, 2009).

3.1.5 Topography

The major topographical features in the region are the Soutpansberg mountain range and the Blouberg Massif (Hemming, 2009). They are surrounded by typical gentle slopes and the undulating Bushveld Complex of the Limpopo Midveld. The area has a maximum elevation of about 560.0 m above mean sea level (SAN parks, 2003).

3.1.6 Land use and land capability

The main land use in the area includes livestock grazing, game farming and cultivation. Human settlement is the predominant land use in the area. Properties are generally shacks and farming is mainly cattle based with many properties used for game farming. Game farms, tourist lodges and hunting operations are still common. There are no major industrial developments within Musina town.

3.1.7 Vegetation

The Baobab species forms part of the vegetation; no endangered species were found in the area. The Musina Mopani Bushveld is from open woodland to moderately closed shrub land. The balance of species is dependent on the underlying soils. Common trees include *Acacia nigrescens*, *Adonsonia digitata* and *selerocarya birrea*. The grassy and herbaceous layers are poorly developed. These vegetation types are extensive, but poorly protected (Hemming, 2009).

3.1.8 Surface water

The Sand River drains the central and eastern areas to the Limpopo River in the north east. These rivers are all fed by numerous, non-perennial tributaries that meander across the Limpopo valley. There is no river near Musina town.

3.1.9 Air quality

Visual regional air quality is generally good as there are limited industrial and no active mining developments within the town. Air quality in the immediate area is generally good to very good. During winter particulate matter from fires, ploughing activities and exposed agricultural land have a potential to contribute to the increased dust levels in the area. Dust fallout from vehicles travelling on gravel roads and uncultivated lands also contributes to air pollution.

3.1.10 Noise pollution

The Musina area is rural in nature and generally very quiet. Noise that is generated there is typical of agricultural areas and comes from vehicles and machinery in the central business district. Vehicles and limited train traffic pass through the town, which may result in slightly higher noise levels.

3.1.11 Cultural heritage

The area is composed largely of communities running large commercial farms. It is clear that there are grave sites located outside the locations and town. Prior to the occupation of the region by the current day settlers the area was used by the San people (Hemming, 2009).

These hunter-gatherer peoples from the Stone Age roamed the region leaving stone tools. The Limpopo Province has many Iron Age sites, although most of the sites are located closer to the Limpopo River.

The Musina community continues to live in a very rural and traditional manner (Hemming, 2009). The Mapungubwe Heritage site is found within the western part of Musina town.

3.1.12 Social and economic environment

The population of Musina municipality is approximately 160 000 people. Musina town is the largest residential area in the municipality and the majority of the residents are farm workers residing on farms. More than half of the population is under 19 years old. The remaining part of the population is characterized by people mostly below the age of 44 (Barnes, 1998).

Racial makeup: Black; 82.6%, Coloured; 0.8%, Indians/Asians; 0.1% and White 16.5%. First languages: Tshivenda 48.6%; Northern Sotho 16.9%; Afrikaans 14.1%; Sotho 6.7% and other languages (Shangaan, Zulu, Shona and Nyungwe) 13.7% (Musina Municipality, 2012).

Levels of service provision such as water, sanitation and electricity within the municipality are generally poor. The majority of households depend solely on fire wood as a primary source of energy for heating and cooking. Candles are still a popular alternative source of light. Access to water, sanitation and refuse removal is poor. Household income levels are very low (Barnes, 1998). The area comprises both formal and informal settlements. The majority of informal settlers are immigrants from Zimbabwe.

3.2 Sampling Sites

3.2.1 Review of background information

To obtain the existing status of the area, the collected background information was reviewed. The status review was aimed at providing data on the exact location and ease of access to the site, climate, activities (businesses, residential and farming), possible contamination sources, existing data and other details which could help in the preparation of an appropriate sampling plan.

3.2.2 Background samples

The internal control samples were collected at three “uncontaminated” sites outside the town centre at an open area that has no streets or industries close-by. These sites were located in the “rural” areas, near Madimbo (BS1) village in the east, outside Nancefield (BS2) location in the west and Matswale (BS3) location in the northwest of the town, respectively.

The second group named “external control” samples were obtained from the Council of Geoscience, but their sampling program only cover Polokwane to Makhado which is 60.0 km from Musina town.

3.2.3 Reconnaissance survey

The work was undertaken in the Musina area and incorporated visual observation of the tailings and mine dumps, informal interviews with the community, and on-site training for volunteers, field samplers and sample collection. The informal interviews with the community were part of the community consultation to establish any concerns about previous mining activities.

A reconnaissance survey was conducted to see whether there was access to the study area with the aim of finding areas where detailed surveys could be conducted. Due to the extensive expanse of the area and shortage of detailed available information about the mine, it was used to provide a general overview of the study area. This was to assess the problems faced by the community and the environment as a result of past mining activities.

3.2.4 Water sampling

Sampling plastic bottles were soaked overnight with dilute nitric acid solution (1.0 HNO_3), then washed in a soap bath, rinsed three times each in distilled water and then with water sample before it was collected. A total of 40 borehole ground water samples were collected into 1 L pre-washed polyethylene bottles randomly from the copper mine and surrounding communities. Samples were collected in duplicate and store in ice at the laboratory until analysis were completed within seven days. Ground water samples were primarily collected from the three boreholes used for brick-making and from two other sites from the boreholes within the townships. It must be noted that rivers are dry most of the time due to semi arid nature of the study area and that would also explain why boreholes are the primary source of water. Water samples were collected into clean plastic containers as illustrated in Figure 3.3.



Figure 3.3 (A) & (B) Showing the water samples.

The site survey revealed there was no water flowing from the old shaft or leakages from sewage system pipes between residential areas. Permission to sample water directly from the sewage dams was not granted by the municipality. That could have allowed the study to determine how much of the heavy metal pollution in the ground water came from the sewage system.

The samples were transported in a cooler box filled with ice tubes to Eskom Kriel power station in Ga-Nala (formerly Kriel) for analysis. The collected samples were stored in the refrigerator at 4.0 °C until sample testing time.

3.2.5 Soil sampling

Two territory types of sampling were selected because of the different types of soil contamination and different land uses. The two territories are: a) Soil forming the cover layer of the tailing dump and b) the soil used by inhabitants of the village for vegetable gardens, streets and roads.

The two territory types sampling adds up to 122 sampling sites as indicated in Figure. 3.4. All the sample sites are far away from the pollution sources such as landfills, petrol stations and factories. A hand held Garmin GPS 62s was used to record the geographical positions of the sampling points. A hand held auger drill was used to recover tailing and soil samples, while a shovel was used to prepare the sampling area.

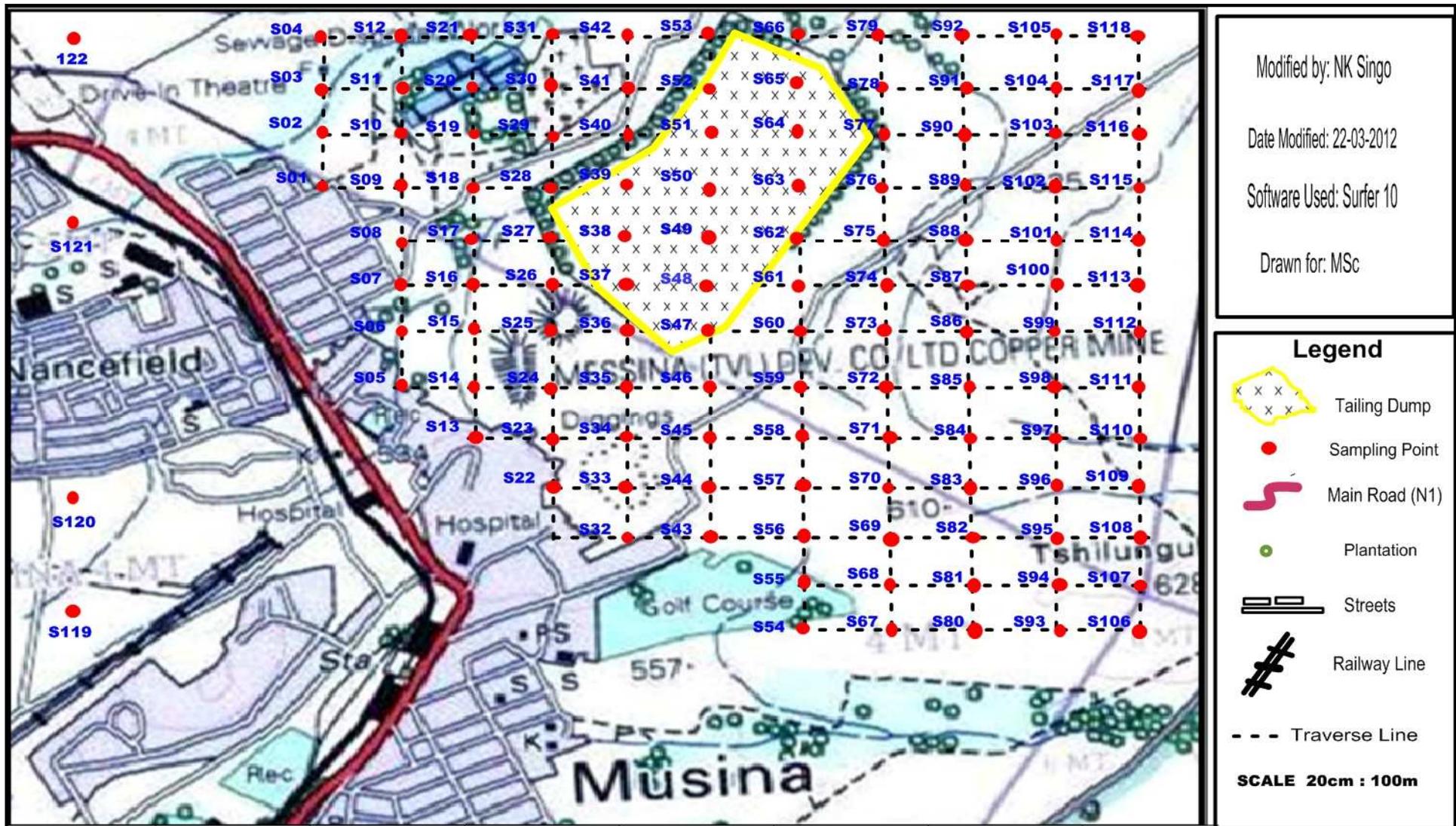


Figure 3.4 A map showing the location of the town and sampling points (Modified from DWAF, 2001).

Systematic grid sampling (Figure. 3.5) was commissioned in the study by using a square grid and collecting sample from the nodes (intersections of the gridline).

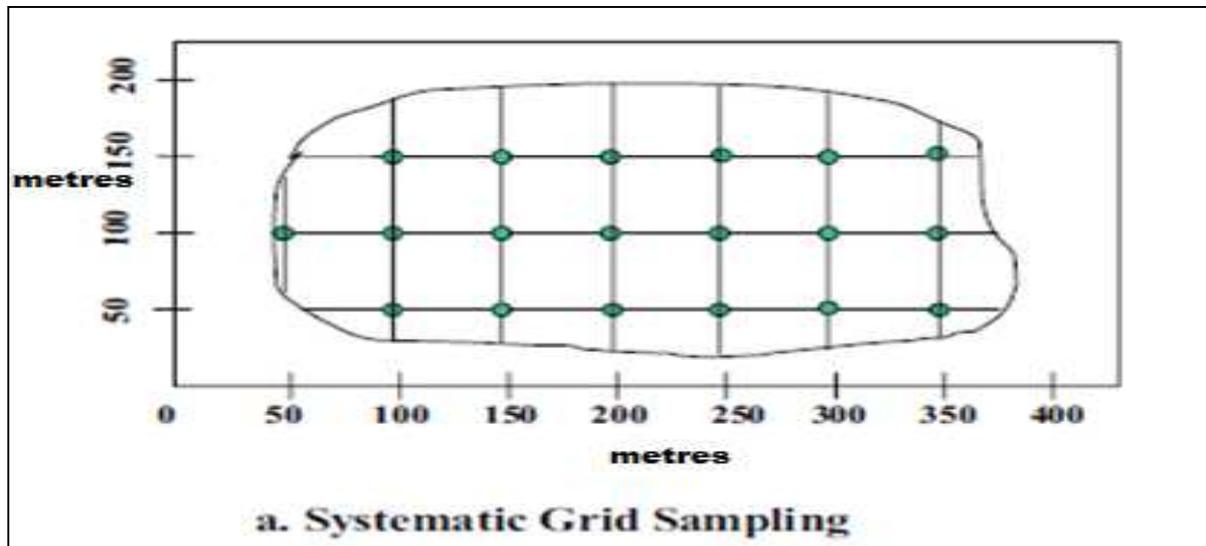


Figure 3.5 Approach used for sampling plan (adopted from ASTM, 1987).

Each soil sample was collected by grid from the sampling plot of about 1.5 Km by 1.5 Km with a total of 11 samples and 13 samples respectively. The spacing between the samples was 70.0 m. However, due to restrictions such as settlements, sewages, shutting ranges, a golf course and private game land, some of the samples were impossible to collect. This resulted in a total of 96 samples collected as opposed to the planned 122.

At each sampling point, the top layer sample (0 to 15.0 cm) was taken separately using a stainless steel sampling tube and stored in clean polythylene bags (Figure. 3.6) until they were analysed.



Figure 3.6 (A) & (B) Depicting soil and tailing samples collected during field work, samples were transported by private car to the laboratories.

3.3 Sampling Period and Frequency

Water samples were mainly collected in the mornings during weekends before the temperature rises. Sometimes water samples were collected throughout the day depending on the weather conditions and permitted time of sampling from the borehole owners. Five samples were collected monthly resulting in a total of 40 samples between April and August 2012. A second campaign covered the wet period and ranged from January to April 2013.

The soil samples were collected once at the end of each month during the dry / winter season (May to August) and wet / summer season (January to April) of 2012 and 2013, respectively.

3.4 Meteorological Parameters

It is important to consider wind and precipitation data during the interpretation of any pollution study (Tharaga C, SAWS Scientist, email communication, 2012). Pollution is in the first instance a local problem. However, the boundless atmosphere carries the pollutants away from town, over land and sea, and around the world. This is both an advantage and a disadvantage (WMO Consultant, 2005). Meteorology provides very useful data in pollution study since it influences human exposure to the pollutants (Infotox, 2000).

3.4 Reagent and Methods

3.4.1 Water samples

Sample preparation, treatment and analyse were done at Eskom Kriel power station laboratories in Ga-Nala. The pH, electrical conductivity and turbidity were analysed using auto titrator meter (AT-500, Japan), conductivity meter (Cole-parmer® YO-19601-00) and turbidity meter (AL 250T-IR, Agua lytic, German) respectively. The equipment consists of special probe connected to an electronic meter that measures and displays pH, EC, and Turbidity readings. Before testing, calibrations of the instrument were done in accordance with manufacturer's instructions.

Water samples were filtered using the membrane filtration set LCW 916 (0.45 µm). About 50.0 ml of the filtered water sample was pipetted into a 200.0 ml glass beaker, together with 10.0 ml of perchloric acid (70%, Saarchem) and 20.0 ml of nitric acid (55%, Saarchem).

The mixture was repeated in two other beakers to make triplicate samples. A fourth beaker was used to prepare a blank solution and it contained the same solvents as in the first three beakers, except that the 50.0 ml water sample was replaced with same amount of distilled water.

The four beakers with their contents were then placed on a hot plate and boiled until the volumes were reduced to about 25.0 ml. The samples were then transferred to 50.0 ml volumetric flasks which were filled to the mark with distilled water and their heavy metals contents were analysed by FAAS (Perkin Elmer S/n 000003F6067A, Singapore).

3.4.2 Soil samples

Soil and tailing samples were prepared at Madzivhandila College of Agriculture, and at the Department of Mining and Environmental Geology laboratory University of Venda. Soil samples were oven dried at a temperature of 105.0 to 110.0°C and left overnight to dry. The dried samples were removed from the oven and left to cool to room temperature (25.0 °C).

The samples were sieved using Retsch AS 200 basic sieve shaker of up to 63.0 µm particle size. Samples that were coarse were milled with a Retsch RS 200 milling machine for 10.0 minutes to obtain the required particle size (75.0 µm).

The milling pots were cleaned with quartz in between milling. The fine samples were produced to ensure homogeneity and liberation of mineral grains in the sample and to enable efficient digestion by acid. After sieving and milling, the samples were transferred to sample bags and labelled.

A weighing balance (Radwag ES 220/C/2) was used to weigh about 5.0 g of each sample and it was transferred into a 200.0 ml digestion beaker. A certified reference (SARM 1) soil standard of known metal values purchased from Mintek was also weighed and digested under similar experimental conditions as the samples (Personal communication 1, 2012).

About 80.0 ml of aqua-regia (60.0 ml HCl + 20.0 ml HNO₃) solution was added to a beaker containing a sample. The sample acid mixtures were repeated in three different 200.0 ml beakers. The contents of the beakers were boiled on a hot plate until about 20.0 ml of the digested solution were left and cooled at room temperature.

After cooling the samples digests were then quantitatively transferred to 100.0 ml volumetric flasks and made to the mark with de-ionized water before their metal contents were analysed by FAAS.

3.5 Methods

3.5.1 Quality assurance, method validation and detection limit

In order to plot a calibration curve on the FAAS, calibration standards for Pb, Zn, Cu, Ni, and As were prepared by extracting a known volume of a stock solution (0.10 µg/g) and diluting it to 100.0 ml with de-ionized water.

The calibration standards were marked to prevent mix-up during calibration. Standards concentrations ranged from 0.00050 to 0.10 µg/g (Table 3.1).

Table 3.1 Concentrations of calibration standards prepared from 0.10 µg/g stock solution for each element.

Standard concentrations (µg/g)	Dilution volume (ml)
0.0005	100.0
0.001	100.0
0.002	100.0
0.005	100.0
0.01	100.0

The concentrations obtained were recorded and subsequently converted to micrograms per gram (µg/g) using the following formula:

$$\mu\text{g/g} \Rightarrow (\text{Concentrations X Dilution}) / \text{Sample weight}$$

Standard methods for drinking-water analysis were tested under local conditions for accuracy and precision, agreed at national level, and applied universally. However, the use of standard methods does not in itself ensure that reliable and accurate results will be obtained. Regular review of the equipment was considered to ensure standardization. This was undertaken by supervisory staff from a control laboratory.

3.5.2 Data analysis

Data was organized and evaluated using MS Excel[®] spread-sheets. MS Excel also allowed mean (M) calculation, standard deviation (S²) and coefficient of variation (CV) of data to be plotted and visualized easily in the same environment.

To analyse pollution degrees of the heavy metals in different areas, the following formulae were used to calculate the comprehensive pollution index (Lian *et al.*, 2011):

Single Contamination Index method is: $P_f \Rightarrow C_f / S_f$

Where P_f is the Single Contamination Index of heavy metal pollutant, C_f is its real concentration and S_f is its regional background value. This calculation of the heavy metal pollution is according to the Environmental Quality Standard for soils, 1995-7-13.

Table 3.2 Classification standards of soil pollution evaluation

Classifications	P	Pollution grade
A	$P \leq 1.0$	Very low
B	$1.0 < P \leq 2.0$	Low
C	$2.0 < P \leq 3.0$	Medium
D	$3.0 < P \leq 5.0$	High
E	$5.0 < P \leq 10.0$	Very high
F	$P > 10.0$	Super high

(Environmental Standards of Soil Pollution, 1995)

3.5.3 Wind and precipitation data

Meteorological data during the sampling period were obtained from the South African Weather Services (SAWS) at Venetia mine Musina weather station (No. 08085672). The aim was to use the station at Musina town during these studies. This was impossible as the station in the area had stopped working in 2009 pending being fixed (Tharaga C, SAWS Scientist, email communication, 2012).

3.5.4 Determination of physico-chemical parameters

3.5.4.1 Mine tailings slope features and vegetation cover

Tape measure (30.0 m Micro-Tec ®) was used to measure the length and the width of the tailing. This was done by measuring the length and width of the bottom part of the tailing and also the top part. The height of the tailing was measured using GPS.

The clay and silt fraction (less than 2.0 micro millimetres to 63.0 micro millimetres), was measured by the pipette method according to Kohn (ISO DIS 11277: 06. 1994). The materials used for completing the tailing logging activities include; hand lens, field note book, log forms, protractor, pencil, knife and compass with altimeter (FCDSR, 2006).

To undertake logging in good working conditions, the tailing surface to be logged was assessed to see if was safe and that there were no rocks at top of the tailings that might fall. Before embarking on logging, the tailings surface was cleaned, using a broom. However, the use of a broom created problems in some parts as tailings were not firmly consolidated.

3.5.4.2 Paste pH analysis

A pH-Meter Basic 20+ was used to analyse the paste pH of soil and tailing. Prior to taking pH reading, the pH meter was calibrated with buffer solutions of 4.0, 7.0 and 10.0 at 25.0°C. The weigh 20.0 g of dried earth was put into 100.0 ml beaker, then 50.0 ml of distilled water. It was shaken for 2.0 hours and the eletrode was immersed in the upper part of suspension. The pH measurements were taken after the pH meter has stabilised (accuracy 0.1 unit).

3.5.4.3 Electrical conductivity

Electrical conductivity was analysed using an auto titrator meter (AT-500, Japan).

3.5.4.4 Turbidity

A turbidity meter (AL 250T-IR, Agua lytic, German) was used for the operation.

3.5.4.5 Total metal content

The tailings and soil samples were analysed for Pb, Zn, Cu, Ni and As using a flame atomic absorption spectrometer (Perkin Elmar S/n 000003F6067A, Singapore) at the Department of Mining and Environmental Geology Laboratory, University of Venda (Figure 3.7).

De-ionised water was used as a blank sample and analysed between the samples in order to increase the confidence level of the results. The accuracy of the results was assessed by analyzing blanks and replicated samples were independently analysed at Madzivhandila College laboratory.



Figure 3.7 Sample analysis with FAAS at the Department of Mining and Environmental Geology laboratory.

3.6 Concluding Thought

The correlation of the actual data and background values will suggest a possible source of pollution, and give an idea of how much anthropogenic contribution was made to the contamination of Musina water and soil. The anthropogenic sources suspected are from the defunct copper mining and heavy vehicles in the area. The following chapter will show actual data versus background data, review of meteorological data and its influence on the contamination.

References

ASTM 1987: Standard practice for reducing field sampling of aggregate to testing size (ASTM 702-87).

Barnes E (Ed.) 1998: The Important Bird Areas of southern Africa (Ed.). Birdlife South Africa, Johannesburg.

Brandl G 1981: The geology of the Messina area.

Chauke RP 2011: Prediction of acid mine drainage generation and their remedial actions in tailings dam in an abandoned Louis Moore gold mine, unpublished thesis. University of Venda

Clausen HT 1973: Ecological aspect of slimes dams construction, *Journal of South African Mining and Metallurgy*, pp178-183.

Field Classification, Description of Soil and Rock 2006: Yenington Mine Site Standard Operating Procedures. June 6. 2006. SOP 12.

Lian E, Feng GH & Wang YX 2011: Frontiers of Green Building, Materials and Civil Engineering. *Applied Mechanics and Materials*.

Hemming M 2009: Coal Bed Methane Exploration rights application, unpublished report.

Infotox CC 2000: Environmental Health Risk Assessment-Methylcyclopentadienyl Manganese Tricarbonyl. Document No. 009-2000. Final Report No. 7

Musina Development Strategy 2007: 14-16: Map of the Musina Municipality at the Northern boundary of South Africa.

Musina Municipality 2012: (<http://www.musina.gov.za>).

SAN Parks 2003: Integrated management plan for natural and cultural heritage resources in the Vhembe/Dongola National Park, incorporating the san parks preliminary management plan for Vhembe/Dongola National Park.

WMO Consultant 2005: Atmospheric Environment Service, Department of Environment, 4905 Dufferin Street, Ontario, 2005.

CHAPTER FOUR: RESULTS AND DISCUSSIONS

This chapter focuses on the results and interpretation of the research findings. The data is presented in the form of figures, tables or text for effective data and results presentation. Heavy metals are common pollutants in air, water and soil. Pollutants are emitted as a result of various industrial activities. The potential human health and environmental effects of heavy metals associated with an old copper mine in Musina were evaluated.

4.1 Review of Meteorological Data

Wind and precipitation data were evaluated with the intention of understanding the transport and distribution of pollutants from their main sources within the study area. Meteorological data during the sampling period were obtained from the South African Weather Services (SAWS) at Venetia mine Musina weather station (No. 08085672).

4.1.1 Precipitation and temperature data

The total amount of rainfall during the period of sampling is given in a Figure 4.1. No rain was recorded between March and August 2012. It rained for 28 days between January and April 2013 with a total of 136.0 mm.

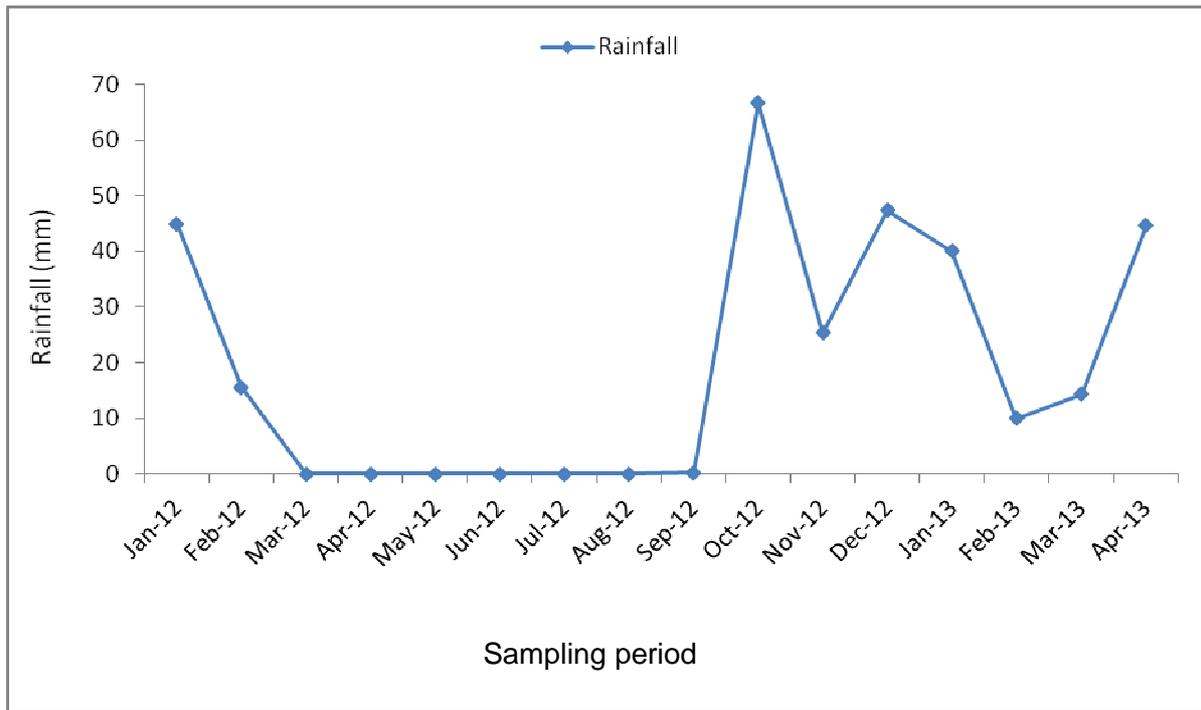


Figure 4.1 Total rainfalls recorded between sampling periods.

Few rainy days recorded was not surprising since Musina is semi-arid, characterised by low rainfall with a total of 33, 43 and 41 rainy days in the year 2010, 2011 and 2012 respectively (SAWS, 2010/2012). The total amounts of rainfall recorded in summer were 208.20 mm in 2010, 322.20 in 2011 and 200.20 mm for the year 2012 (SAWS, 2010/2012).

Fine particles of dust do not simply lie around until they are blown away by the wind; rather they stick together in clumps when they are wet. Moisture content is an important component of soil since it serves as a solvent for many processes (Okonkwo *et al.*, 2006).

The lack of rainfall in Musina could lead to low moisture levels in soil of the area, particularly during windy seasons and these increase the generation of airborne soil and dust materials and again increase human exposure through inhalation.

High temperatures are also common within this study area as shown by Figure 4.2. High temperatures cause increased evaporation from the soil. As the moisture content in the soil decreases, the cohesive force between the soil particles decreases and the rate of dust generation increases (Hoover, 1971).

During hot weather, a coating of dust on leaves could decrease transpiration. As a result of decreased transpiration, the loss of water through leaves in vegetation decrease.

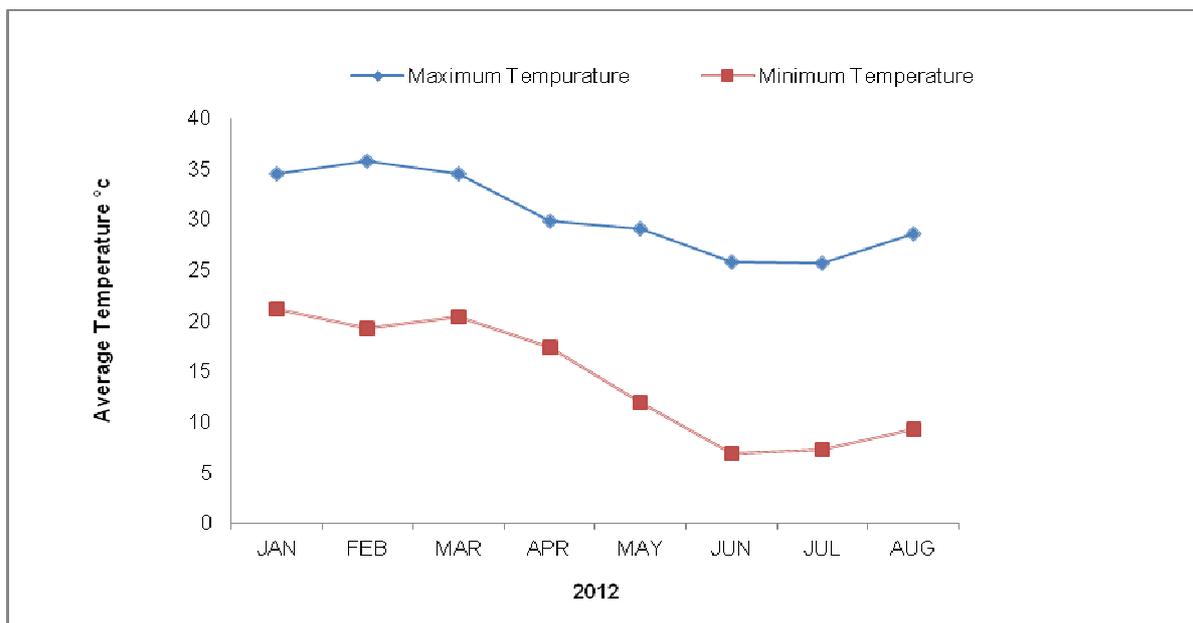


Figure 4.2 Minimum and maximum temperature recorded between sampling months.

4.1.2 Wind speed and direction data

Wind speed and direction in a given area determines the dust generation potential, the distance of downwind transport and the rate of dilution of certain pollutants (Annegarn *et al.*, 2002).

Maximum daily wind speeds recorded during the dry and wet sampling period are illustrated in Figures 4.3 to 4.6. The highest wind speed recorded was 6.2 m/s on the 2nd day of February 2013 and on the 4th day in April 2012, and 5.5 m/s on the 10th day of March and 4th day of July 2012.

The threshold wind speed 5.4 m/s has an ability to lift dust (Annegarn *et al.*, 2002). However this was seldom exceeded during the sampling periods which lead to a small amount of dust being generated and lifted into the air, which can contribute to less exposure of people to inhalation of the dust particles. Wind speeds greater than threshold wind speed were recorded on the 2nd, 5th and 9th days of February 2013. Other greater-than-threshold wind speeds were noted on the 2nd, 6th and 10th of March 2012.

Wind speeds exceeding the threshold were recorded on the 4th and 5th days of April 2012. In July 2012 only one day exceeding the threshold was recorded (the 4th). January 2013 and both May, June and August 2012 had shown wind speeds below the threshold. The high wind speed observed does pose a human health risk from dust inhalation.

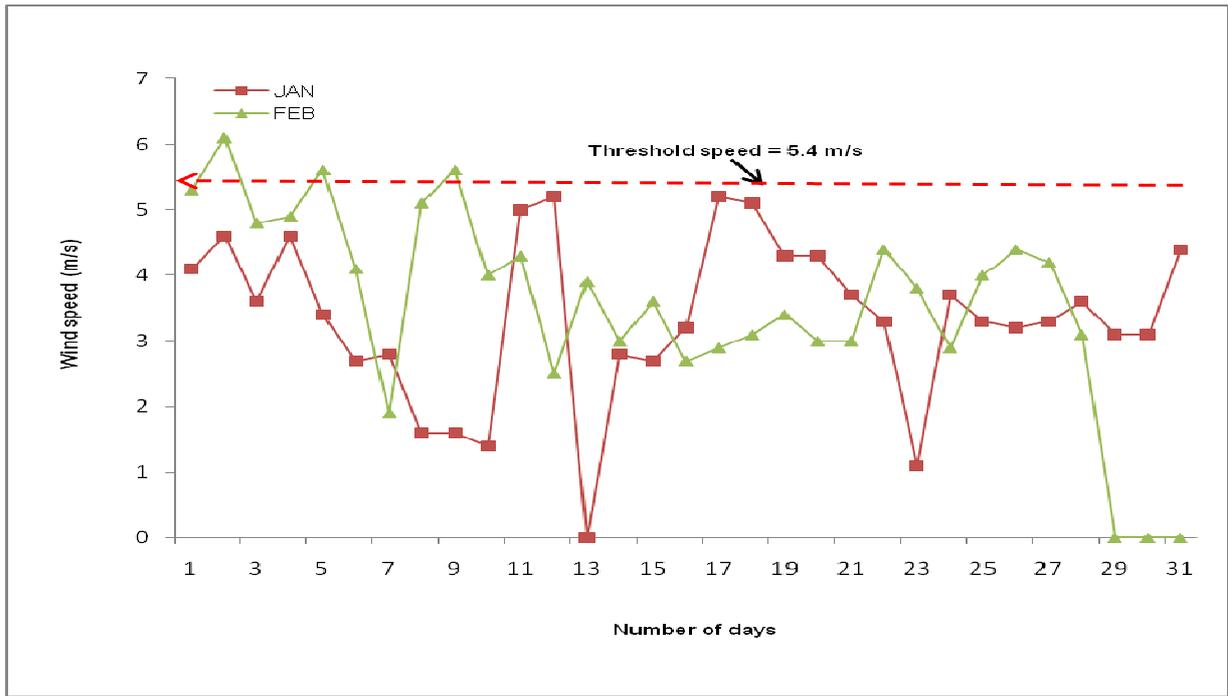


Figure 4.3 Maximum wind speed recorded between January and February 2013.

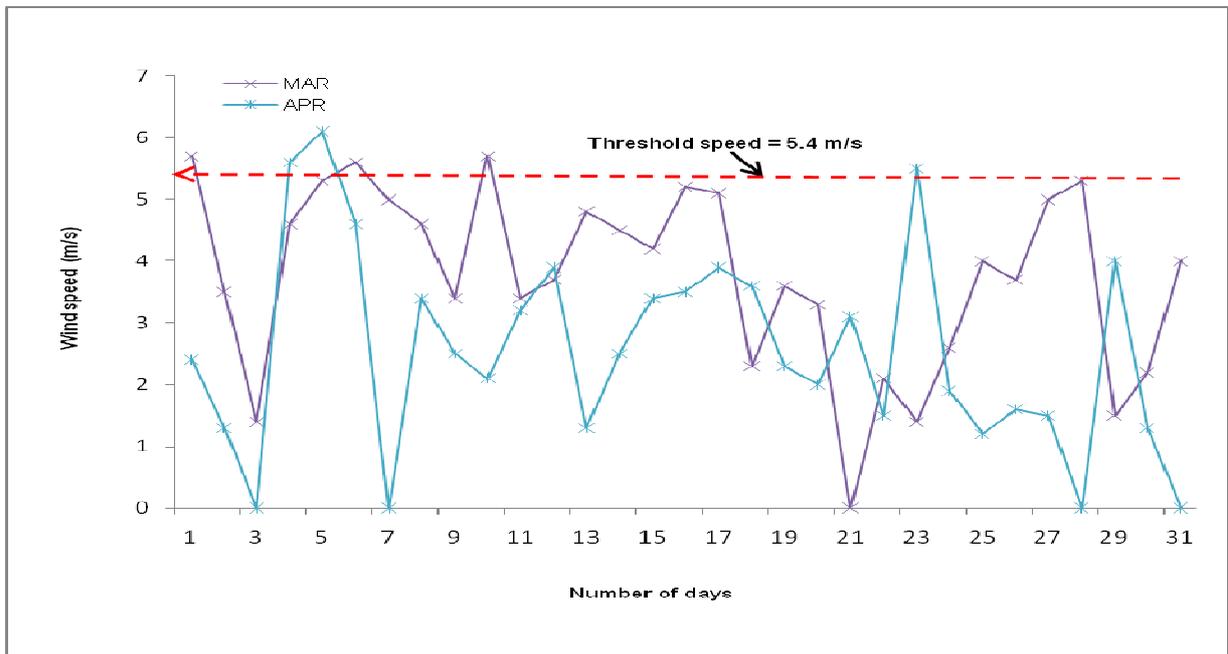


Figure 4.4 Maximum wind speed recorded between March and April 2012.

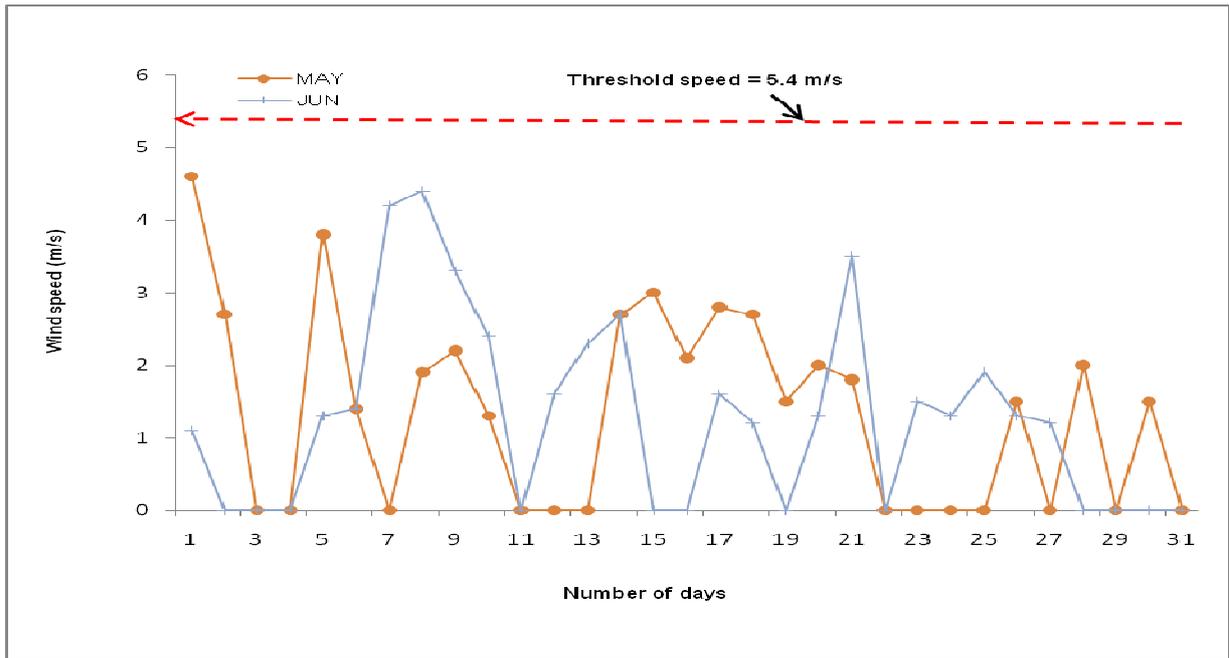


Figure 4.5 Maximum wind speed recorded between May and June 2012.

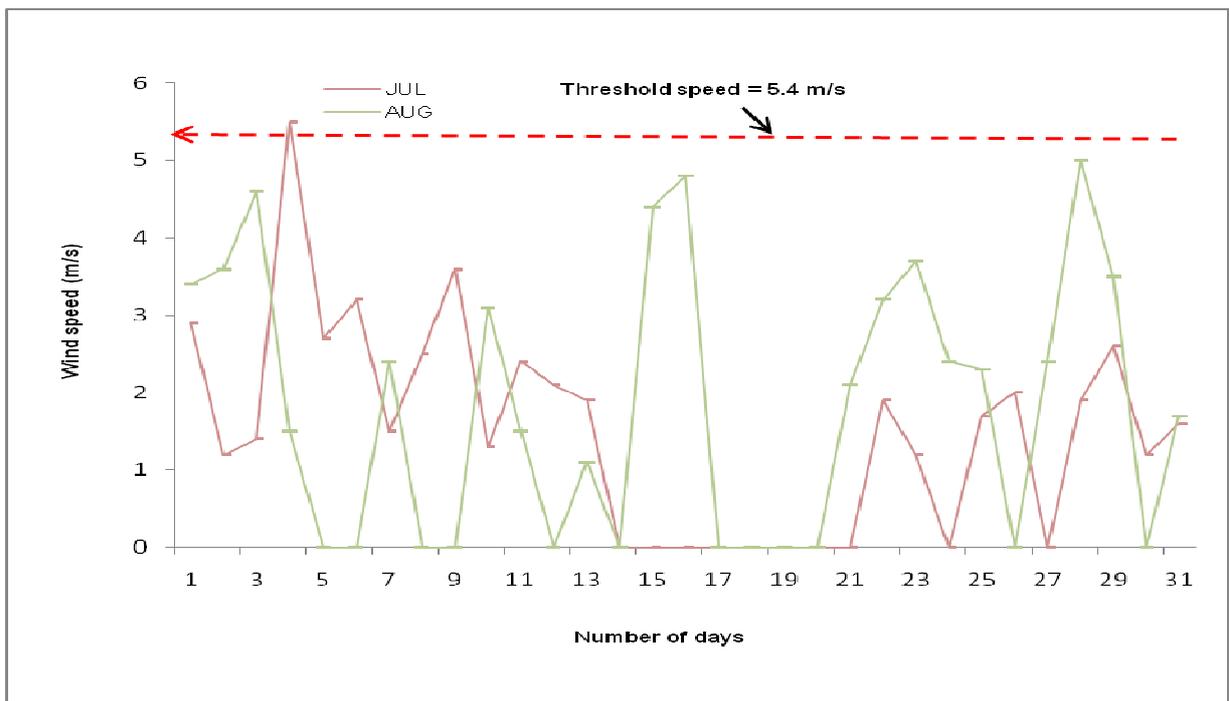


Figure 4.6 Maximum wind speed recorded between July and August 2012.

The maximum daily wind direction is indicated in Table 4.1. Wind directions ranging from 0 to 320.0 were recorded during the course of study. The main directions for January and February ranged from north-east to south-west, March ranged from north to south-west, April north to north-west and, north to south-west was recorded for the months of May, June, July and August. Figure 4.7 shows the predominant wind direction obtained during the sampling period. The main wind directions were north and south-west.

Table 4.1 Average daily wind directions during sampling period.

Month	Number of days															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	Wind direction															
JAN	140	100	110	120	140	100	120	110	90	100	100	110	110	130	120	80
FEB	80	100	110	80	110	110	110	80	110	90	200	110	90	60	120	100
MAR	110	120	60	0	130	110	80	150	110	100	80	80	120	90	70	80
APR	120	110	130	110	150	140	110	120	0	320	100	120	100	0	0	0
MAY	0	0	0	0	100	100	0	110	100	110	100	0	0	120	0	0
JUN	0	0	140	130	0	0	180	310	290	260	110	0	0	100	120	120
JUL	0	0	0	160	0	120	110	0	110	0	100	130	0	110	290	200
AUG	0	60	130	0	100	120	260	310	70	0	0	250	90	120	130	220

Month	Number of days															
	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	
	Wind direction															
JAN	230	0	120	130	80	110	110	50	110	100	60	110	90	100	110	
FEB	90	120	100	90	90	110	80	130	110	120	120	110	0	0	0	
MAR	220	140	100	100	110	90	110	110	100	100	100	110	110	100	0	
APR	100	100	100	80	100	150	120	120	120	80	0	0	120	110	0	
MAY	0	100	0	130	110	80	0	0	150	190	130	0	0	0	130	
JUN	70	130	120	180	120	90	100	290	260	100	0	100	0	0	0	
JUL	0	120	0	0	0	0	150	90	0	120	0	130	90	110	0	
AUG	130	100	0	170	100	130	120	130	0	110	100	90	180	120	120	

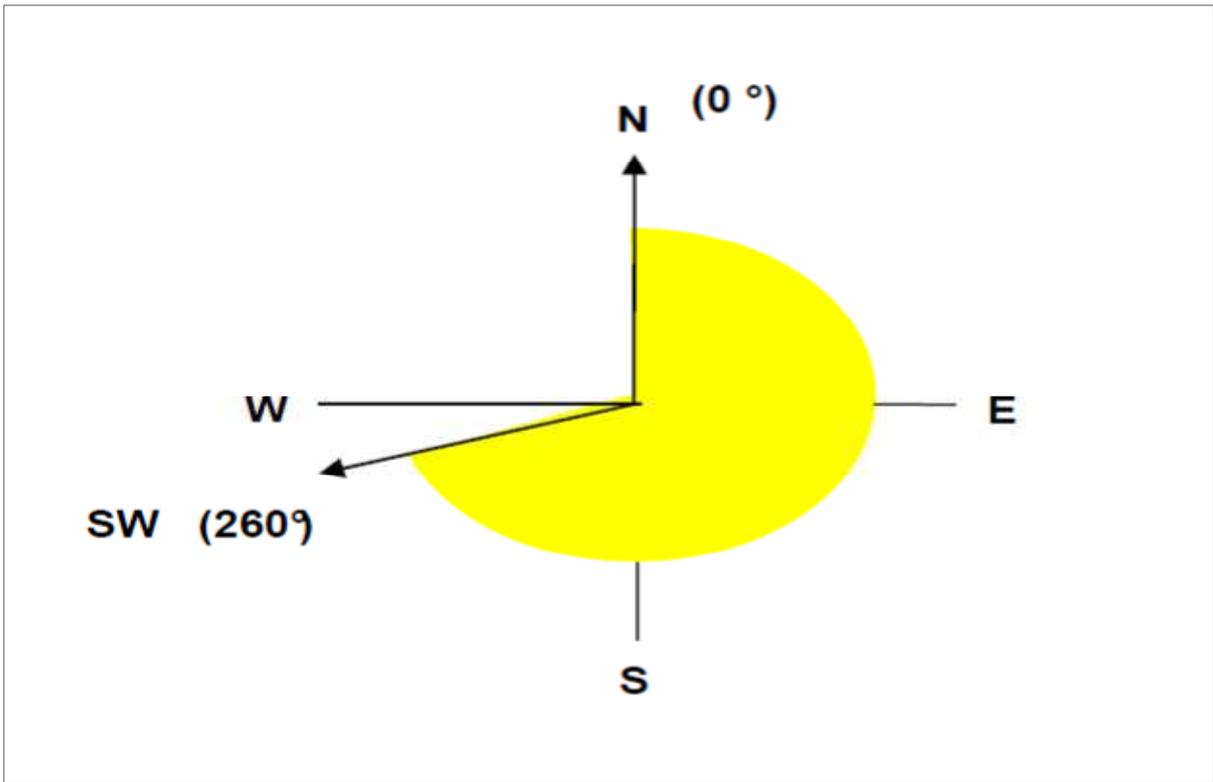


Figure 4.7 The predominant wind direction during the sampling period.

4.2 Quality Control, Detection Limit and Method Validation

The results of selected metals for certified soil value material are given in Table 4.2. The calibration values gave correlation coefficients of metals in the range of: As (0.54 to 0.86), Cu (0.28 to 0.45), Ni (0.57 to 0.144), Pb (0.23 to 0.36) and Zn (0.26 to 0.53). The calibration curves per metal had the following R-values: As (0.9951), Cu (0.9995), Ni (0.9888), Pb (0.9999) and Zn (0.9948) and the detection limits obtained for As, Cu, Ni, Pb and Zn were (0.04 $\mu\text{g/g}$), (0.02 $\mu\text{g/g}$), (0.02 $\mu\text{g/g}$), (0.02 $\mu\text{g/g}$) and (0.02 $\mu\text{g/g}$) respectively.

Table 4.2 Validation of method against soil certified values material.

Total metals	Concentration levels ($\mu\text{g/g} \pm \text{RSD}$)	Certified values ($\mu\text{g/g}$)
As	0.086 \pm 5.69	11.00
Cu	0.045 \pm 2.72	12.00
Ni	0.144 \pm 3.13	8.00
Pb	0.036 \pm 1.84	40.00
Zn	0.053 \pm 2.55	264.00

4.3 Control Samples Data

To determine the extent of pollution in soil as a result of heavy metal concentration, it is necessary to define the natural level of these metal (pre-civilisation level or pre-mining level), and then subtract it from the existing level for metal concentration, to thereby derive the total enrichment caused by anthropogenic impacts (Forstner,1983). Koranteng *et al.*, (2011) have a different approach to this matter; the contamination is the ration obtained by dividing the concentration of metal by the background level.

4.3.1 External control data

The total metal content of the soil samples retrieved from the study area were compared with concentrations levels from Polokwane, Dendron, Bandeliakop, Matoks and Louis Trichardt (Makhado), which are within 60.0 km from Musina and do not have mining activities. This data was obtained from the geochemical database of the Council for Geoscience (Doreen Van Der Walt, Geo-scientist, CG, email communication, 2013).

Table 4.3 shows the background levels of selected trace metals from areas near Musina. According to the Council of Geoscience geochemical database (2013), the highest As (0.014 µg/g) was obtained in Dendron, and the lowest recorded was in Polokwane (0.004 µg/g). Pb was not detected in Louis Trichardt and the highest was found to be (0.013 µg/g) in Dendron. The highest Cu level (0.054 µg/g) was reported in Matoks and the lowest value (0.029 µg/g) in Louis Trichardt. Ni levels increased from (0.037 µg/g) in Dendron to (0.086 µg/g) in Louis Trichardt. Zn levels increased from (0.056 µg/g) in Louis Trichardt to (0.094 µg/g) in Matoks.

Table 4.3 Background levels of selected trace metals near the study area.

Location	Lat	Long	Ni (µg/g)	Cu (µg/g)	Zn (µg/g)	As (µg/g)	Pb (µg/g)
Polokwane	-23.3256020	29.79868300	0.022	0.040	0.051	0.004	0.006
Dendron	-23.3712179	29.32679600	0.037	0.044	0.056	0.014	0.013
Bandeliakop	-23.0386020	29.90178900	0.091	0.042	0.087	0.013	0.010
Matoks	-23.4514220	29.67935500	0.067	0.054	0.094	0.003	0.006
Louis Trichardt	-23.8931030	29.45658100	0.086	0.029	0.056	0.011	0.000

(Council of Geosciences, 2013)

4.3.2 Internal control data

A total of three samples were analysed for background levels. These samples were collected between 5.0 and 25.0 km outside Musina town. Consideration was given to sample areas far away from industrial sites, main roads and mining areas as these anthropogenic sources could influence the outcomes.

Table 4.4 shows the total internal background values of selected metals. The highest As concentration (0.040 µg/g) was obtained in Nancefield, situated about 5.0 km west of Musina and the lowest (0.001 µg/g) in Madimbo, within 25.0 km east of the town. The highest Pb (0.035 µg/g) was recorded in Matswale which is within 15.0 km northwest of the town and the lowest (0.017 µg/g) recorded was in Nancefield. Ni concentration has been measured at a high concentration level (0.160 µg/g) in Madimbo and lowest (0.055 µg/g) in Matswale. The highest Cu (0.007 µg/g) was recorded in both Madimbo and Matswale, and the lowest (0.005 µg/g) in Nancefield. Zn has shown a high concentration level (0.061 µg/g) in Madimbo and the lowest recorded was (0.012 µg/g) in Nancefield.

The results obtained from both internal and the external control samples were further used to evaluate the pollution levels due to anthropogenic activities within the study area. However, much attention was given to the internal control samples since external control samples were taken a bit far away from the study area.

Table 4.4 Internal background values

Location	key	Distance (Km)	Metals (µg/g)				
			Ni	Cu	Zn	As	Pb
Madimbo	BS1	25.0	0.160	0.007	0.061	0.001	0.020
Nancefield	BS2	5.0	0.089	0.005	0.012	0.040	0.017
Matswale	BS3	15.0	0.055	0.007	0.035	0.020	0.035
Mean			0.101	0.007	0.036	0.020	0.035

4.3.3 Evaluation of soil pollution

Abandoned copper mines have been a health threat to the inhabitants of many mining communities worldwide (Koranteng *et al.*, 2011). The amount of metal contamination in the examined soil samples was quantified using the Single Contamination Index method. A brief description of the applied index is given below:

Single Contamination Index method is: $P_f \Rightarrow C_f / S_f$

The contamination index (P_f) is the ration obtained by dividing the concentration of metal by the background value. The concentration levels of the metals may be classified based on the Single Contamination Index (P_f) scale ranging from A to F (A-Very low, B-Low, C-Medium, D-High, E-Very high and F-Super high). The results of the quantification of the metal contamination of the soil samples using contamination index are shown in the Table 4.5. The pictorial impression of trends in the mutual pollution effect of the studied metals in the study area is presented in Figure 4.8.

Table 4.5 Background levels against samples levels and their pollution index

Sample type	Metals	External background levels ($\mu\text{g/g}$)	Internal background levels ($\mu\text{g/g}$)	Sample levels ($\mu\text{g/g}$)	Contamination Index	Pollution grade
Soil	As	0.009	0.061	0.086	1.4	Low
	Cu	0.040	0.020	0.045	2.3	Medium
	Pb	0.007	0.035	0.036	1.0	Low
	Zn	0.068	0.036	0.053	1.5	Low
	Ni	0.060	0.104	0.144	1.4	Low

The results of the determination of As, Cu, Pb, Zn and Ni contamination in soil has shown that pollution from the abandoned copper mine is low to medium. The pollution ranges as follows Cu<Zn<Ni<As<Pb. The interpretation has shown that Musina defunct mine and its surroundings is a relatively not pristine and but less contaminated area.

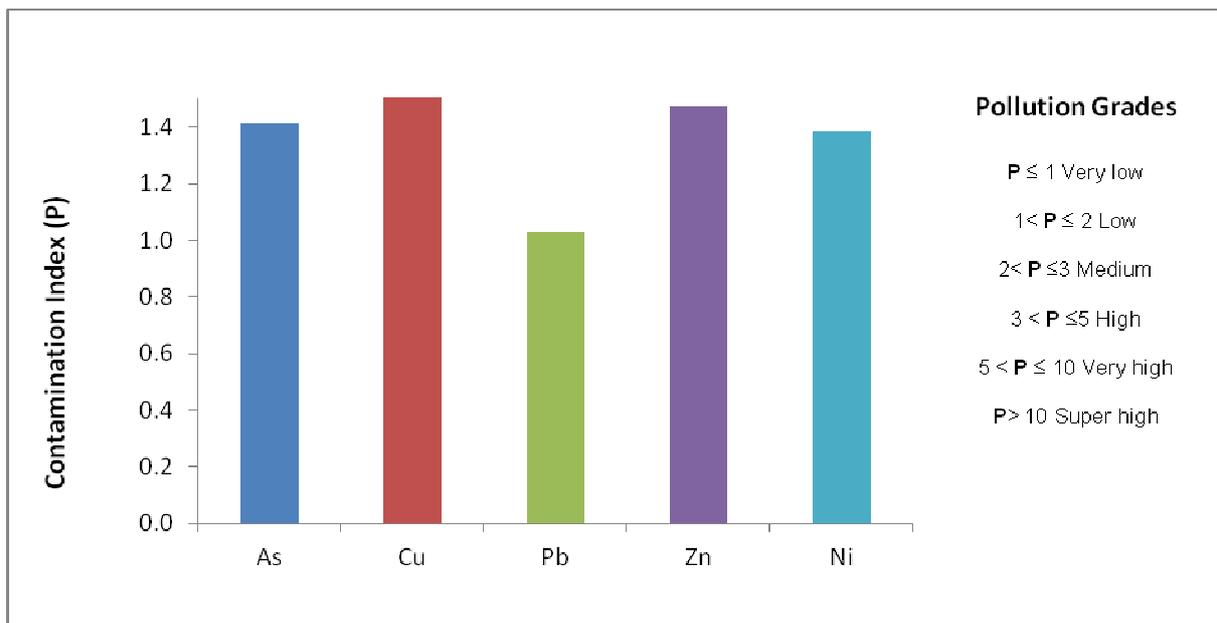


Figure 4.8 Variations of pollution index for selected metals in soil samples.

4.4 Measurements of Physico-Chemical Parameters

4.4.1 Mine tailings slope features

4.4.1.1 Tailing profile logging

The height of the tailings was measured using a GPS receiver by taking the difference between the surface and the top elevation of the tailing.

The elevation of the top of the tailing was found to be 546.0 m whereas the ground elevation was 534.0 m. Therefore, the height of the tailing was found to be 12.0 m.

The tailings were deposited in layers. The tailings exhibit sequential layering that shows a dumping time scale. Each layer appeared to have enough time to consolidate before other materials were dumped. This resulted in stratified (banded), layering which is conspicuous in the profile. A total of three different profiles were identified and logged.

Figure 4.9 (a) shows the tailing dump located at X 246995.50 Y 31 009265.90 Z 531.0 coordinates. These coordinates were taken using the GPS system. It is slightly steep (30-35.0°) due to erosional activities. Exposure to sun and rainfalls lies around 180.0°S.

The topography of the surrounding area is gently undulating to near flat with little or no vegetation. When sampling, the layer C provided guidance on contaminated material not related to processing plant that might cause an unintended increase in metal content on the results. Layer C is due to dumped metals (steel) not oxidation of minerals. It was important to log the profiles of the sampling area before collecting samples so that the horizon associated with contamination can not be overlooked.



Profile Description

A-Profile: 0.0 to 20.0 cm, brown, dry, loam, fine platy, slightly calcareous (40%), no roots, no pores, clear contact with the next profile.

B-Profile: 20.0 cm to 150.0 cm, yellowish brown, dry, silty, clay loam, few rock fragments, fine to sub-angular, slightly hard, no roots, very few fine dendritic tabular, clear wavy boundary.

C-Profile: 150.0 cm to 180.0 cm, brown, slightly moist, silty clay loam, few pores.

D-Profile: 180.0 cm to 280.0 cm, yellowish brown, dry to moist, few rock fragments, fine sub-angular, slightly hard, very few fine dendritic tabular. Clear wavy boundaries.

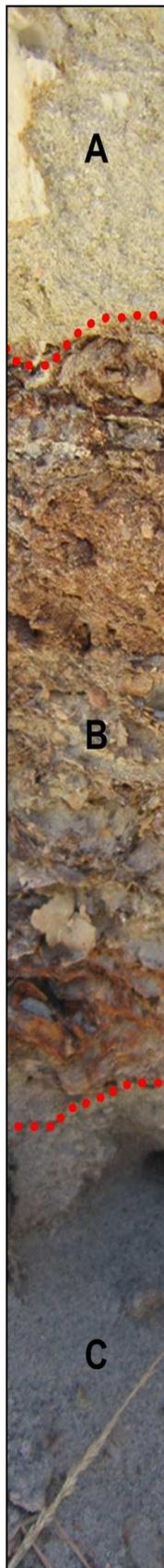
E-Profile: 280.0 cm to 380.0 cm, yellowish to brown-grey, silty clay loam, slightly calcareous (30%), moderately firm, no roots appeared.

F-Profile: 380.0 cm to 600.0 cm, yellowish olive, dry, silty loam, and no roots fragments, very fragmented rocks, very coarse platy, slightly hard, abrupt smooth boundary.

Figure 4.9 (a): Profile exhibiting six different layering in the tailing dump from the North

Note: Brownish steins resulting from steel dumped in layer C

Figure 4.9 (b) shows the tailing dump located X 246993.10 Y 31 009796.3 Z 548.0. It is moderately steep as it is less exposed to erosional activities. Exposure to sun and rainfalls lies around 270.0°S. This profile shows a highly contaminated zone of approximately 400.0 cm. This ranges from 200.0 cm up to 600.0 cm at top to the botom. Due to high contamination, it is advisable not to collect sample along this zone. The close proximity of layer B to both layer C and layer A makes it risky to collect any samples in this area. No vegetation recorded nearby this tailing profile.



Profile Description

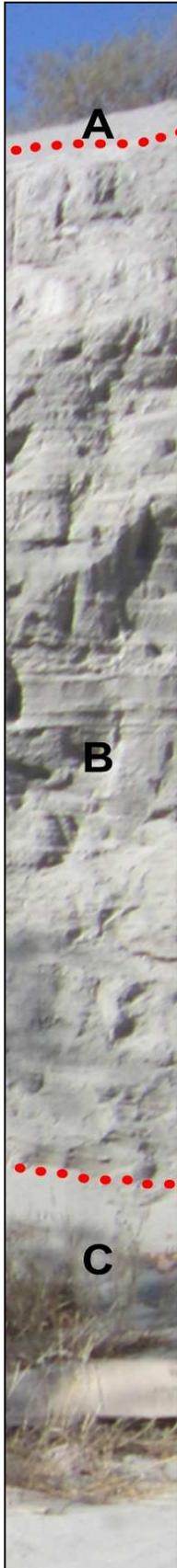
A-Profile: 0.0 to 200.0 cm, bright yellowish brown, dry, loam, rock fragments, fine sub angular, slightly hard, fine roots.

B-Profile: 200.0 cm to 600.0 cm, Dark reddish brown, dry, loam to sandy, rock fragments and steel remnants, very fine granular with lamellar structure, clear wavy boundary.

C-Profile: 600.0 cm to 680.0 cm, greyish-brown, loam, no rock fragments, sub-angular, slightly hard, 0.5 cm cracks, wide borrowing hole at base, clear wavy boundary.

Figure 4.9 (b): Representative profile along the middle of the tailings. Note: High metal dumped into layer B.

Figure 4.9 (c) shows the tailing dump located X 247019.40 Y 31 009822.20 Z 544.0. It is slopping due to erosional activities. Exposure to sun and rainfalls lies around 140.0° SE. The tailing is characterised by 40.0% grasses and trees in parts. This profile represents tailings material that is not polluted by any material that is not related to the mine processing plant. Sampling in this area is not limited to any zone due to the homogeneity of the material. This profile is regarded as a true representative of the tailings materials. These areas of uncontaminated tailing covers approximately 70.0% of the study area.



Profile Description

A-Profile: 0.0 to 29.0 cm, grey to brown, loam, very few rounded boulder, granular, fine roots, no course roots.

B-Profile: 29.0 cm to 500.0 cm, dark grey to brown, no rock fragments, sub-angular slightly hard, very few fine pores, abrupt smooth boundary.

C-Profile: 500.0 cm to 600.0 cm, brownish grey, slightly moist, no rock fragments, slightly calcareous.

Figure 4.9 (c): North-west profile representing pure tailing materials.

4.4.2 Vegetation cover

Vegetation cover is the percentage of soil which is covered by green vegetation. It is a key factor in land degradation (Wikipedia, 2013). Vegetation cover plays a very important role on protecting the soil surface from raindrop splashing and reducing surface water runoff (DISME, 2013).

4.4.2.1 Erosion

Heavy metal contamination of soil is a far more serious problem than air or water. Heavy metal can also be very quickly translocated through the environment by erosion of the soil particles to which they are adsorbed and re-deposited elsewhere (Moja, 2007). Wind erosion and water erosion are dominant environmental elements that have a degrading effect on tailing (Figure 4.10). Estimates from a study that was undertaken at the University of the Witwatersrand suggest the annual water erosion induces loss of material from the surface of the slime wall of about 30.0 to 40.0 m with a slope of about 36° (Mrost, 1974).

Normally the outside wall of the tailings dumps dips at about 30.0-45.0°. The tailings have partially flattened slopes to a dip of about 27.0° due to erosion. According to Clausen (1973) if the angle of the slope of the side walls is not steeper than 27.0°, the sides should become permanently covered by vegetation. The statement above was not confirmed by the observations made in this study, as shown in Figure 4.10 below. Soil erosion in the study area is mainly caused by having a high slope gradient and the lack of vegetation on the slopes that can be able to limit the loss of soil due to wind and rainfall.

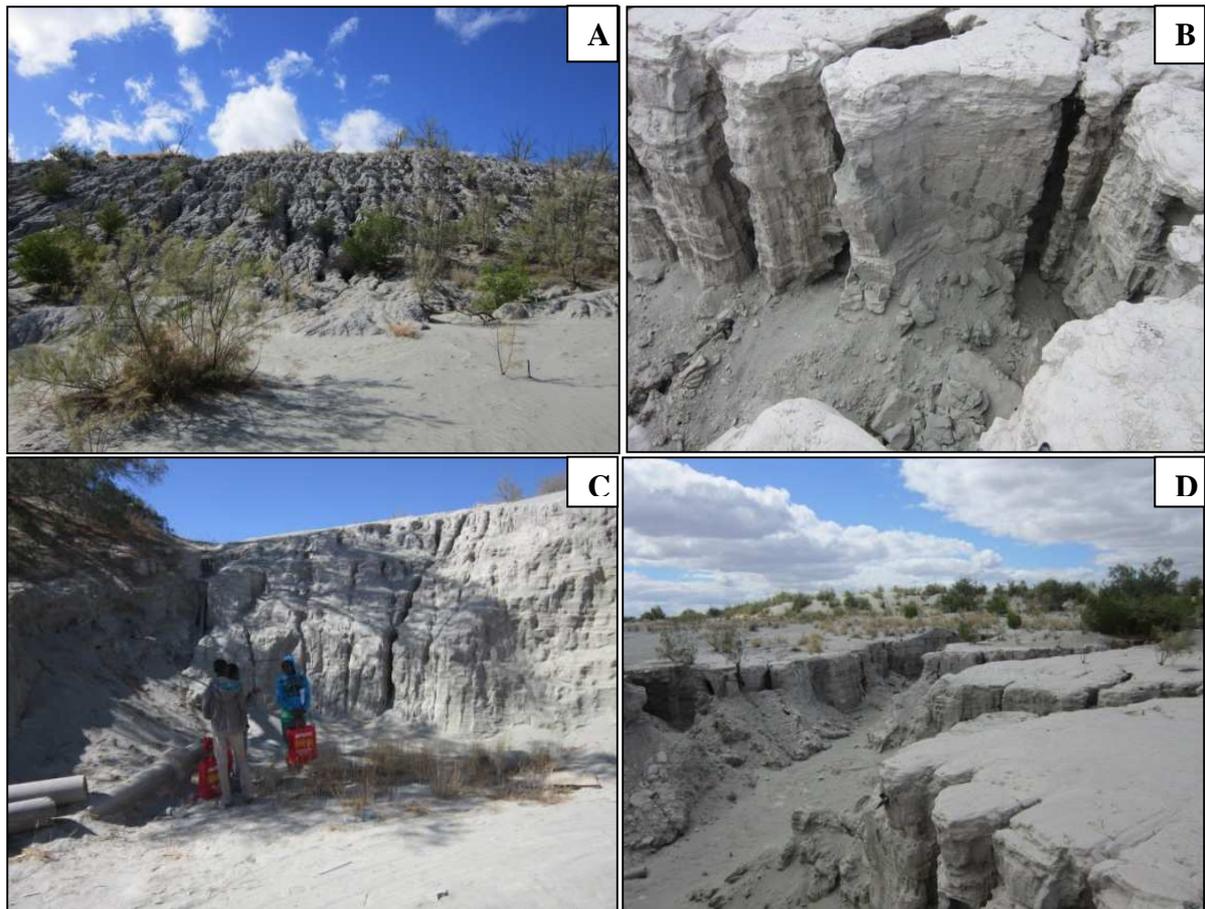


Figure 4.10 (A) The influence of slope on the intensity of erosion. (B) High walls waiting to collapse posing danger to nearby inhabitants. (C) Tailing erosion and field sampling assistants standing near approx 3.0 m vertical wall of tailing. (D) A steep-side gully or donga created by erosion.

4.4.2.2 Rehabilitation of disturbed land

Rehabilitation or re-vegetation of Musina's defunct copper tailing soil was not successful in preventing sediments and pollutants associated with the tailing from entering nearby surface areas.

The vegetation could not control soil erosion by dissipating the erosive force of raindrops, reducing the velocity of surface runoff, stabilizing soil particles with roots, and contributing organic matter to the soil, which increases soil infiltration rates. Erosion impact is more intensive in sparsely distributed re-vegetation, as shown in Figure 4.11.

It became clear from site observation that the planted vegetation adapts partially to the tailing conditions. Some grassland sods, shrubs and small trees, are struggling to grow on the tailing. This could be attributed to high pH conditions within the tailing.

The mine had irrigation systems on site to ensure enough watering. This seems to have stopped some years back as the pipes were damaged by the sun. This could mean that the rehabilitation process was not given enough time or was not maintained sufficiently for re-vegetation to survive on its own.

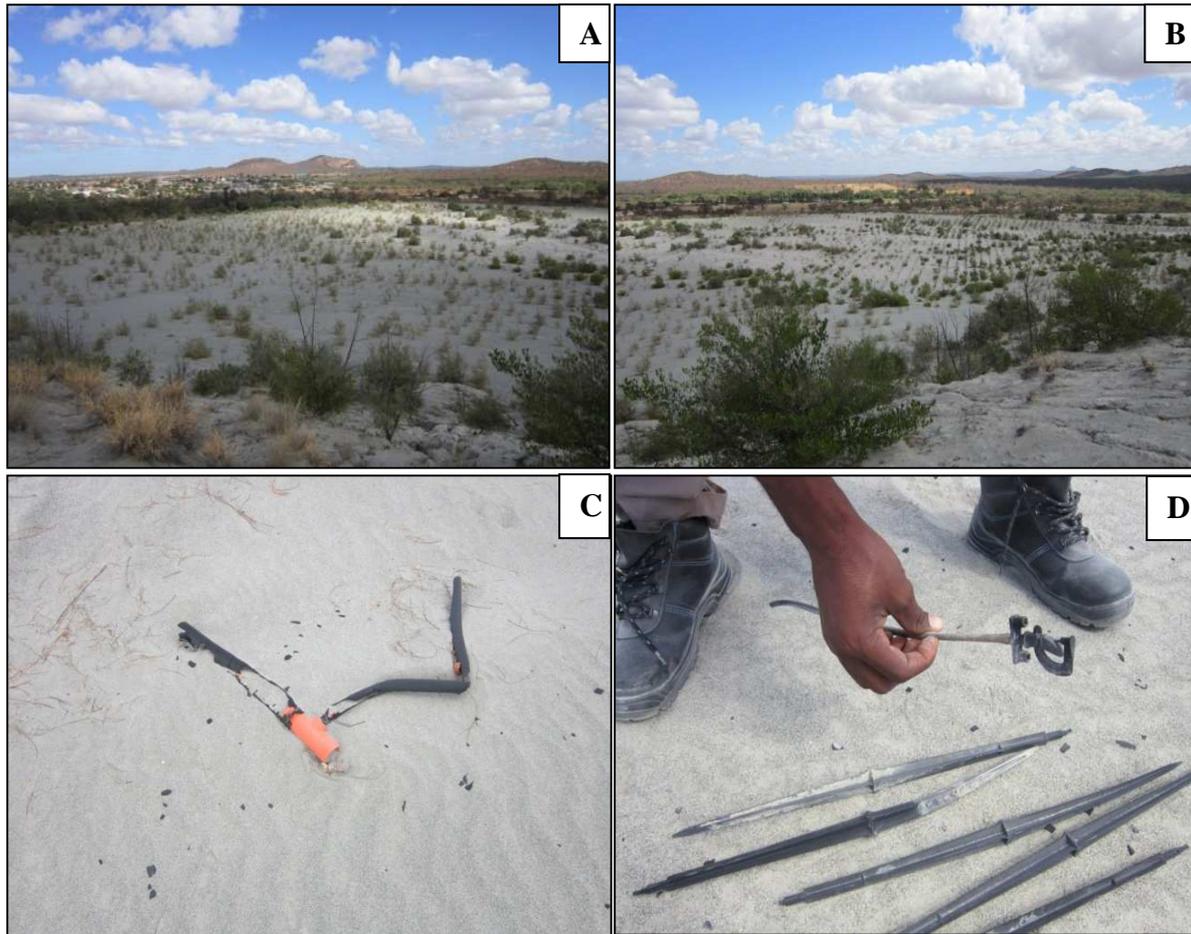


Figure 4.11 (A) & (B) Shows re-vegetated trees in a row. (C) & (D) Shows the remaining components of an irrigation system decomposing due to the exposure to prolonged direct sunlight.

4.4.3 Small-scale mining and brick-making business

Musina's abandoned copper mine was re-established around early 2008 for the process of making bricks from the old mine waste (Personal Communication 2, 2012). The mining operation is mechanised as they use equipment such as powered engine trucks, conveyer belt machines, excavators, tractors and other equipment for processing mine dumps.

The small-scale mine in Musina consists of largely unskilled workers that require technical assistance to perform the work. The major environmental problem occurring at the mine is dust generation and land degradation. Some of the the data collected during the reconnaissance survey suggest that most of the workers were unskilled and worked without any personal protective equipment.

Small-scale mining in Musina has led to the problem of dust pollution which is released while mining the waste dumps to make bricks out of it. These miners mine without giving any consideration to any mining legislative procedures or health and safety standards. This behaviour creates risks for the workers and for the community members in the vicinity of the mine. This statement is illustrated by Figure 4.12.



Figure: 4.12 (A & B) Mine equipment includes heavy trucks, a bulldozer and conveyor belts, (C) Land degradation resulting from the current mining activities. (D) Female mine workers collecting precious stones near the copper dump.

4.4.4 pH data

4.4.4.1 pH data in water samples

pH is an indicator of the acidity or alkalinity of the water. The levels of water acidity can be changed by human practices and alkaline environmental conditions may neutralise these acids. The pH of water does not have direct consequences except at extremes. The adverse effects of pH result from the solubilisation of toxic heavy metals and protonation or deprotonation of other ions (Ayers, 1985).

Figure 4.13 illustrates the pH values obtained from the entire study area which were within the acid range to slight alkaline of 6.0 to 7.51. The lowest recorded pH values were 6.0 at W1 during the month of May and the highest was 7.51 at W4 in the month of January 2013. The mean (average) values of pH of water ranged from 6.44 to 6.78. An increasing trend obtained was: $W3 < W2 < W5 < W4 < W1$. The mean values levels of W2 and W3 were below WHO optimum limits of between 6.5 and 8.5 (WHO, 1998 and 1993). pH values lower than 6.5 are considered too acidic for human consumption and can cause health problems such as acidosis (WHO, 1998).

“If too much acidity develops in human body, immune system can be slow to respond to attacks by harmful organisms. When your body is in an acidic state, this often leads to a slower metabolism and you can put weight. That, in turn, can cause stress and with lack of exercise can exhaust the body” - Sunday Times, 21 April 2013.

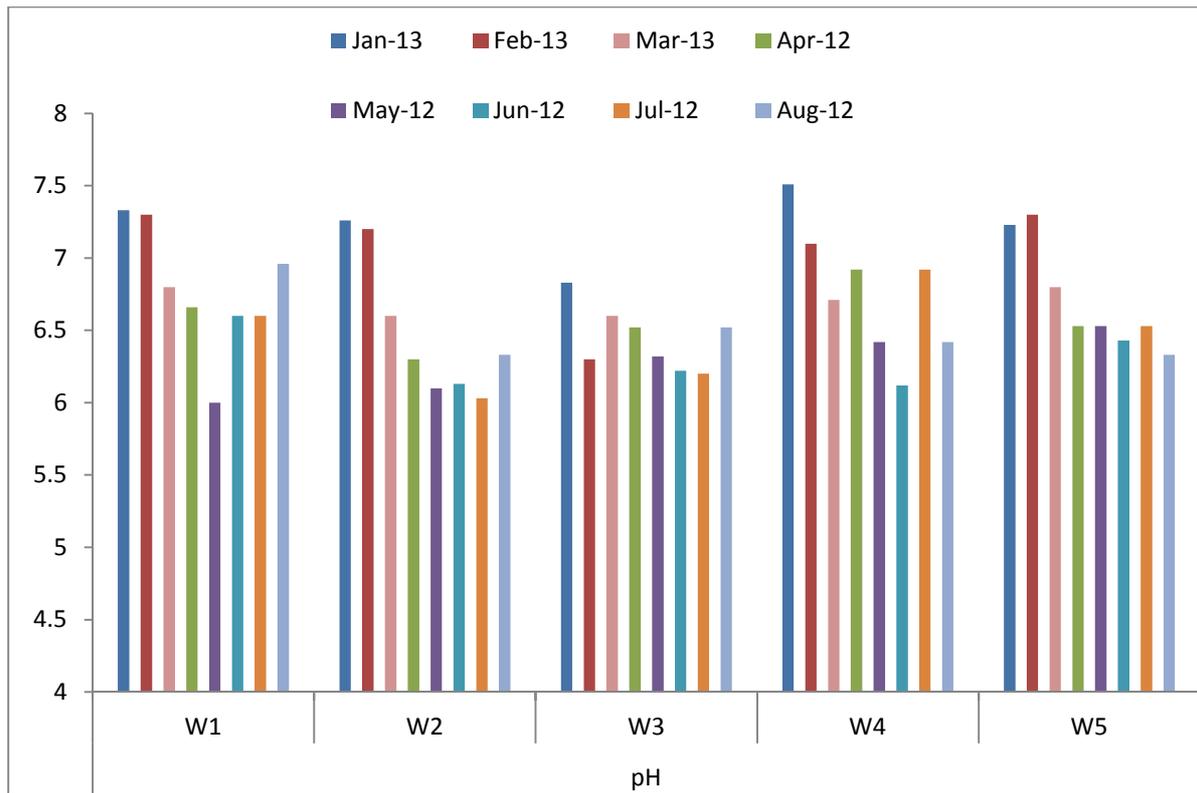


Figure 4.13 Measurements of pH from the water samples.

Biological activities and anthropogenic sources such as nutrients cycling and industrial discharge respectively can give rise to pH fluctuation (AWWA, 1971). Carbonate rich limestones are not reported in the study area at any source, this is a good example of high alkalinity, and what granite dominance in the area could have contributed. Slight metal solubility may occur at extremes of range (Aucamp and Vivier, 1990).

4.4.4.2 pH data in soil samples

The soil samples (S1 to S122) were analysed for pH concentration but only selected samples are presented and discussed in this section. It was vitally important that certain representative samples be selected that accurately represent soil in the areas that are likely affect human health in the study area.

The selected sites / samples were further analysed monthly. This was aimed at controlling the concentration changes on those specific sites. It must also be noted that number of samples in a study area determine the cost of the study, thus limited samples were used as mentioned above.

Figure 4.14 shows most pH values obtained in the soil samples were within the alkaline range of 7.10 to 9.47 and a few exceptions were within the acid range of 4.24 and 5.71. The high pH values may have originated from the lime applications used during the rehabilitation programme. These conditions have the capacity to neutralise acid added to the environment. However, these conditions tend to reduce the solubility or dissolution of substances and favour environmental health. The soil in a low rainfall condition tends to be basic with pH readings over 7.0. Summer rains contributed to slight acidity. Again, granitic rock groups have low alkalinity due to the absence of minerals that contribute to alkalinity (Moja, 2007).

It can be observed from all samples that the levels of pH were not similar from one sample to another. The lowest pH value obtained near the shopping mall could be as a result of more contamination by petroleum products. This could be the result of trucks leaking chemicals since the sample was taken near the entrance of the mall. The wide space at the mall entrance is used as a parking area for heavily loaded trucks from Zambia, Zimbabwe and Malawi, and also local trucks.



Figure 4.14 pH ranges for the selected samples

4.4.5 Conductivity in water samples

The EC is the capacity of material to carry current. In water it is generally used as a measure of the mineral or ionic concentration. Michaud (1991) indicated that the geology of certain areas determined the amount of ions that contributes to EC. The evaporation and loss of fresh water will increase the conductivity and salinity of a water body.

The EC concentration values measured ranged from (75.0 $\mu\text{S}/\text{cm}$) and (96.4 $\mu\text{S}/\text{cm}$) as shown in Figure 4.15. EC mean concentrations recorded in decreasing order were: W2 (88.7 $\mu\text{S}/\text{cm}$), (87.0 $\mu\text{S}/\text{cm}$) at site W3, (86.7 $\mu\text{S}/\text{cm}$) at site W4, (84.1 $\mu\text{S}/\text{cm}$) at site W5 and the lowest (81.6 $\mu\text{S}/\text{cm}$) at W1. The results indicated clearly that influence of seasonal changes and rainfall had the minimum impact on the ground water.

The high EC value could be due to the presence of high level of heavy metals that were found in the samples. Soil and rocks of Musina could have released ions into the ground water that flow through. The WHO permissible limit for EC of ground water is (300.0 $\mu\text{S}/\text{cm}$) (WHO, 2003). EC values of the samples are below the WHO permissible limit.

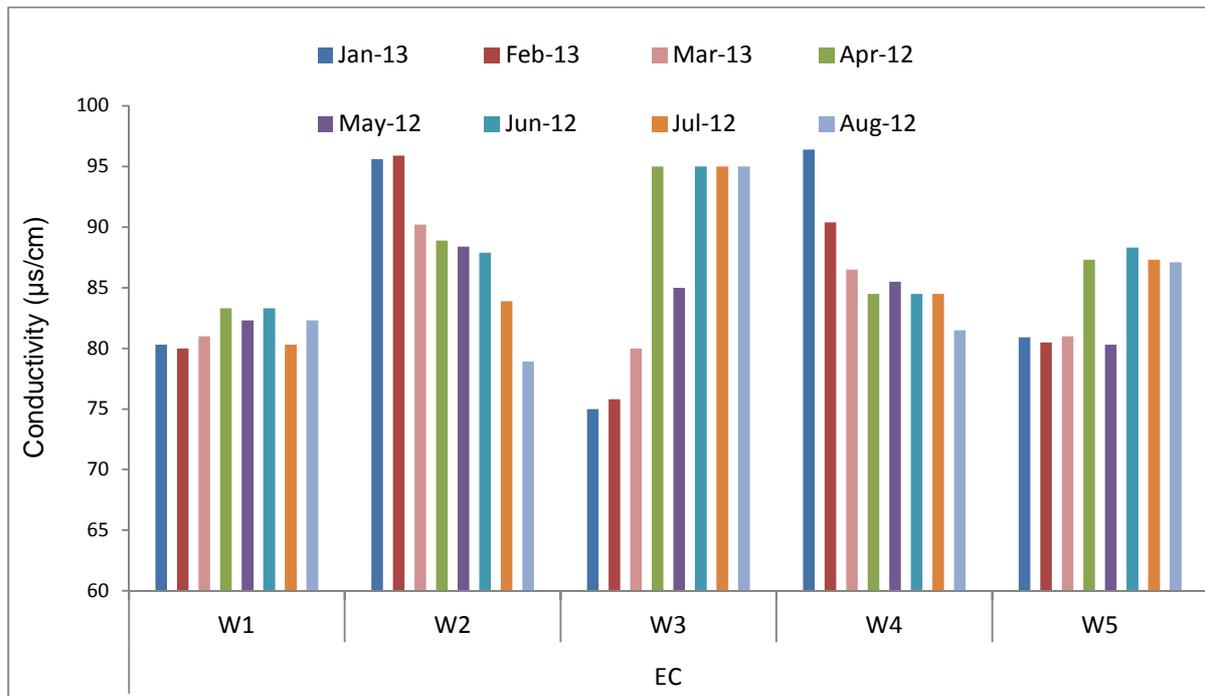


Figure 4.15 Measurements of Electrical Conductivity in water sample.

4.4.6 Turbidity in water samples

Turbidity is the amount of cloudiness in the water (USEPA, 2003a). Drinking water should have a turbidity of 5.0 NTU or less according to the South African Department of Water Affairs and the SABS (24-1:2011 Edition 1). Turbidity diffuses sunlight and slows photosynthesis. Plants begin to die (Ziegler, 2002).

In a total of 40 samples collected in the study area, none were higher than 5.0 NTU. They all ranged from 1.05 to 4.56 NTU as shown in the Figure 4.16. It was observed from the results that all samples fell within South African and US standards limits of 5.0 NTU or less.

The recorded increasing trend obtained was: $W1 < W4 < W3 < W2 < W5$. The lowest was 1.05 NTU at W5 and the highest 4.56 at W1. These were recorded during the month of July 2012 and February 2013 respectively. There was a slight change during the sampling time. These changes cannot be related much to the precipitation and wind as these water samples were not surface samples. It has been noted that a change of pH played role in the change of turbidity of water. The increase in pH is directly proportional to an increase in turbidity.

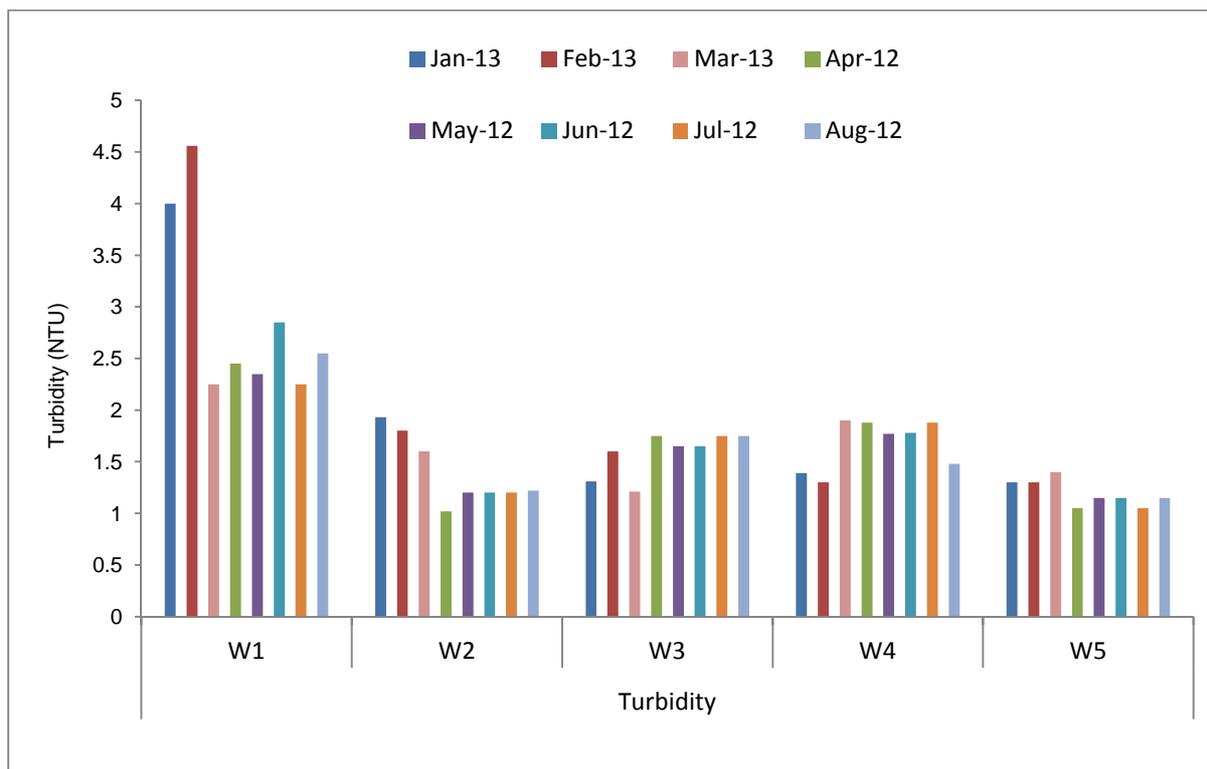


Figure 4.16 Turbidity obtained at all sites collected.

4.4.7 Total metal content

The natural water and soil analysis for physical and chemical properties including trace elements contents are very important for public health studies (Brenner *et al.*, 1993). Even if there are no anthropogenic sources of contamination, there is potential for natural levels of metals and other chemicals to be harmful to the environment and human health. Unfortunately, this problem arose because ground water in most cases was extracted without a detailed investigation.

4.4.7.1 Total metal content in water samples

Figure 4.17 (a) to 4.17 (c) shows the concentration levels of As, Cu, Ni and Pb per site obtained from water samples. The As is fairly widespread in the environment with average of (10.0 µg/g) in surface water (DWAF, 1996).

The highest values recorded were in January and February with values of (6.20 µg/g) and (6.45 µg/g) respectively. The mean concentration of As has recorded an increasing trend as: W5<W2<W4<W1<W3. As concentration levels were all below the South African Domestic Water guidelines (0-10.0 µg/g). According to the guidelines in South Africa, no health effects are expected within the range of (0-10.0 µg/g). Human health will seriously be at risk if As in potable water should exceed (10.0 µg/g) (SANS DWU, 1996).

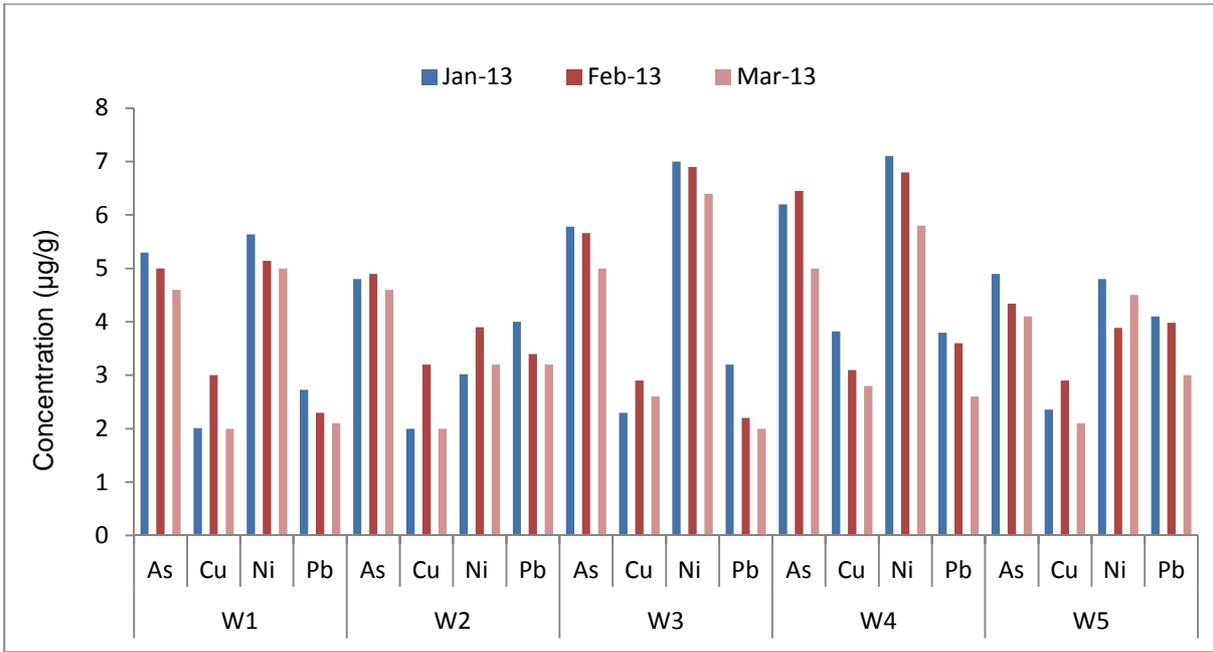


Figure 4.17 (a) Measurements of heavy metals in water samples between January and March 2013.

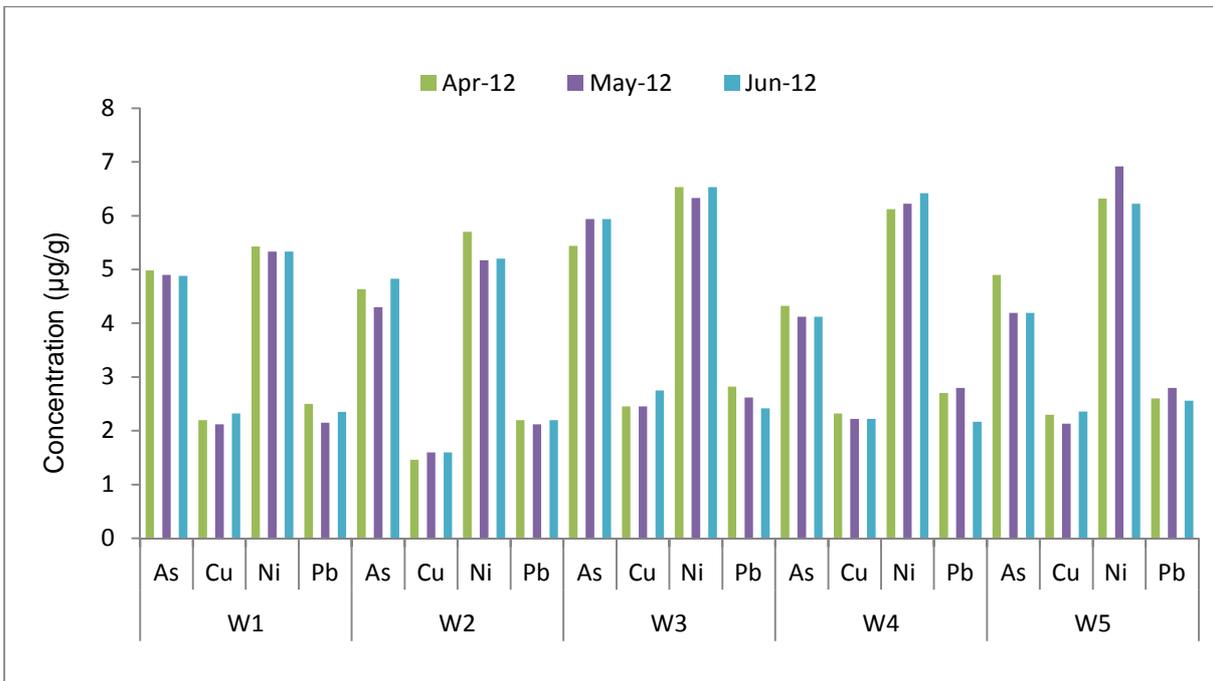


Figure 4.17 (b) Measurements of heavy metals in water samples between April and June 2012.

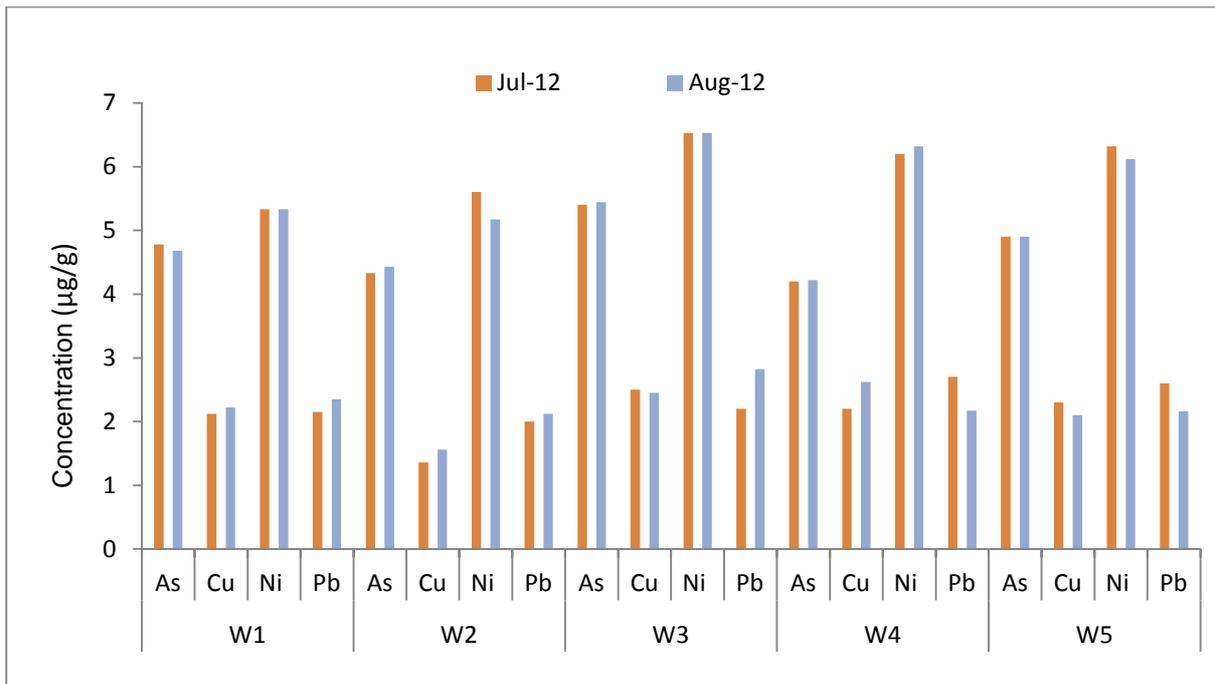


Figure 4.17 (c) Measurements of heavy metals in water samples between July and August 2012.

WHO (2008) and DWA (1996) reported that an average daily intake of Cu in diet and water is about (0.001 µg/g). A significant amount of Cu in domestic water results from dissolution of Cu from household plumbing systems (Tao, 1998).

The concentration of Cu showed the highest values during January and February, which were (3.82 µg/g) and (3.10 µg/g) respectively. The mean concentration trend of Cu showed: W2<W1<W5<W3<W4. All samples showed Cu concentrations were within the range (0.0 µg/g to 30.0 µg/g) for South African drinking water guidelines. It is recommended that the concentration of Cu in potable water should not exceed the (30.0 µg/g) as this is the threshold for acute poisoning with nausea and vomiting (SANS DWU, 1996).

DWAF (1996) stated that Pb is present in surface and ground water at a concentration level of less than (10.0 µg/g). The highest Pb concentration was reported in January and February with (4.10 µg/g) and (3.98 µg/g) respectively. An increasing concentration trend recorded as: W1<W3<W2<W4<W5. No samples exceeded the Pb guidelines of (0.0 µg/g to 10.0 µg/g) in the drinking water in South Africa. It is recommended that the concentration of (0-10.0 µg/g) has no danger of adverse effects.

The Pb guideline of (10.0 µg/g) should not be exceeded as it results in potentially acute and irreversible effects to human body (SANS DWU, 1996). However, SANS has advised that (10.0-50.0 µg/g) has no danger of any adverse health effects except for a slight risk of behavioural changes and possibility of neurological impairments, where the exposure to Pb from other sources such as food is not minimised.

Ni is associated with copper, chromium and cobalt rocks (DWAF, 1996). Ni concentration in surface water ranges from (0.003 µg/g) to (0.15 µg/g) and can be higher in mineralised areas (WHO, 2008). Given its abundance, everyone is exposed to small amounts, mostly through food, air, drinking water, soil, household dust, and skin contact with products containing it, including cosmetics (ATSDR, 2005; Health Canada, 1994b). The mean concentration recorded an increasing trend as follows: W2<W1<W5<W3<W4. The highest Ni concentrations were reported (7.10 µg/g) during the month of January and the (6.90 µg/g) in February. All the Ni concentrations measured were below the South African guidelines of (50.0 µg/g) and WHO of (70.0 µg/g).

4.4.7.2 Total metal content in soil samples

The investigation of heavy metal in the soil was restricted to the top sub-soil since sub-surface soils are better indicators of available uptake and the surface is available for human inhaling (Nyangababo and Hamya, 1986).

Out of the large number of sampling sites, the area of interest was selected and discussed in detail in this section. The selected samples represent the following sites in the study area: S1 (Industrial sites), S7 (Gravel road), S8 (Vegetable garden), S9 (Shrubs), S13 and S14 (Great North Mall), S15 (Mine dump), S16 (Brick yard), S17 (Human tracks), S18 (Stream sediments), S62 (Tailing dam).

The concentration of the each metal per site is illustrated in Figure 4.18 (a) to 4.18 (e). The results showed some variations in the concentration of metals in the soil. Arsenic metal is fairly widespread with average concentration of (0.002 µg/g) in soil environment (DWAF, 1996). According to the USEPA (1995) and WRC (2002), the guideline of As in soil is (0.021 µg/g) and (0.002 µg/g) respectively. Higher As concentration levels were recorded at all sites in the month of May, June, July and August 2012. This could be attributed to the dryness of the season.

The mean concentration of As levels obtained follow the increasing trend: S1 (Industrial sites) < S8 (Vegetable garden) < S9 (Shrubs) < S15 (Mine dump) < S7 (Gravel road) < S14 (Great North Mall) < S62 (Tailing dam) < both S17 and S18 (Human tracks and Stream sediments) < S16 (Brick yard).

As recorded for soil sample per site ranged from lowest (0.009 $\mu\text{g/g}$) to the highest (0.134 $\mu\text{g/g}$) value within the study area. The lowest As was obtained at S13 (Great North Mall) and was much higher than the level obtained from uncontaminated background sites in Musina (0.001 $\mu\text{g/g}$). All the observations suggest that As is above the background value in all sites. The guideline concentration for As is 0.002 $\mu\text{g/g}$ (WRC, 2002). The entire studied area exceeded the threshold guideline, this could cause effect in development of skin cancer, bladder and lung cancer (DWAF, 1996). WHO (1998) warn that single high does exposure to As may occur by inhalation and cause nausea, diarrhoea and with multi-organ failure.

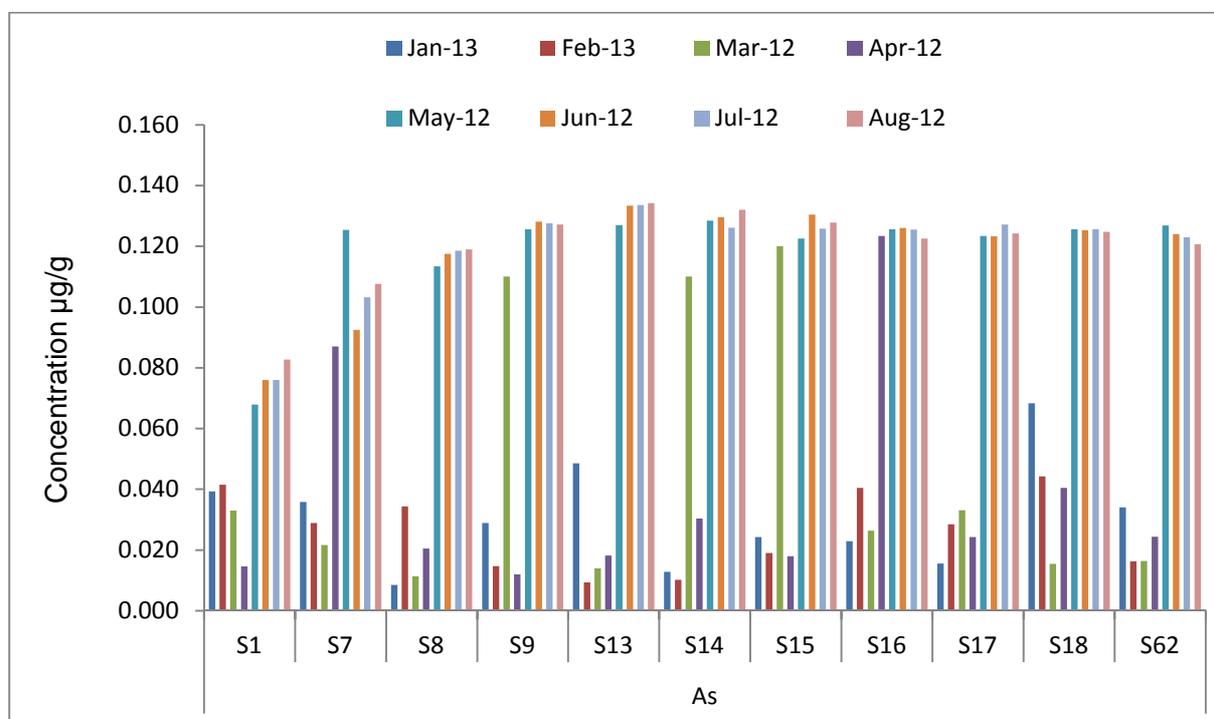


Figure 4.18 (a): Total As distribution per site.

DWAF (1996) reported copper levels in surface soil ranged between (0.030 $\mu\text{g/g}$) to (0.0117) $\mu\text{g/g}$. It was expected that the graph would show high levels of Cu at each sampling point as Cu was been mined at the area, but it was evident from the illustration below that this was not the case.

The mean concentration of Cu levels obtained follow the increasing trend: S13 (Great North Mall) < S1 (Industrial sites) < S16 (Brick yard) < S7 (Gravel road) < S8 (Vegetable garden) < S9 (Shrubs) < S15 (Mine dump) < S17 (Human tracks) < S62 (Tailing dam).

Cu recorded lowest concentration in both S9 (Shrubs) and S62 (Tailing dam) with about (0.003 µg/g) and the highest recorded (0.119 µg/g). However S14, S16, S17 and S18 show Cu below the detection limit during the month of January 2013. The guideline for Cu concentration on soil is (0.007 µg/g) (WRC, 2002). Exposure to the above threshold could result in gastrointestinal disturbances and possible liver, kidney and red blood cell damage (DWAF, 1996). Cu is an irritant of the respiratory tract and high levels of dust exposure may result in coughing and nausea (WHO, 1998).

Cu is easily adsorbed and precipitated in sediments at an alkaline pH (Dallas and Day, 1993). Cu availability to plants is reduced when the soil pH is high, organic matter is high and there is a high concentration of Zinc (Berman, 1980). The month of May has been responsible for elevated Cu concentration in almost all sites, surprisingly the wind speed was at lowest speed and the pH was just over 7.

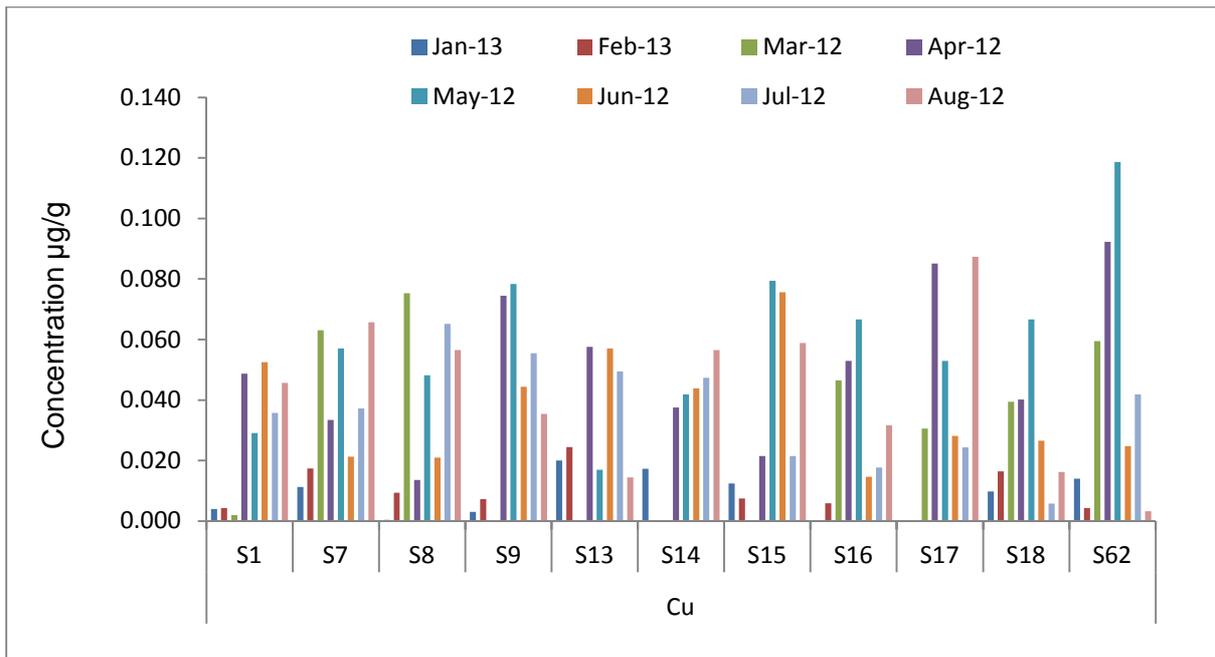


Figure 4.18 (b): Total Cu distribution per site.

Ni is relatively non-toxic and absorption following oral ingestion is poor (SANS AWU, 1996). Higher Ni concentrations may be found around mines where other ore contains Ni where mined. Soil pH has a major effect on the concentration of Ni in the soil. Its solubility decreases with increasing pH (Page and Chaug, 1990).

The mean concentration of Ni follows the increasing trend: S13 and S14 (Great North Mall) < S15 and S62 (Mine dump and Tailing dam) < S16 (Brick yard) < S18 (Stream sediment) < S8 (Vegetable garden) < S1 and S17 (Industrial sites and Human tracks) < S7 (Gravel road).

Ni concentration recorded an increase from (0.005 µg/g) to (0.078 µg/g), and the lowest recorded was at S15 (Mine dump) and highest at S7 (Gravel road). The guideline threshold of Ni in soil is (0.050 µg/g) (WRC, 2002). The majority of sites fell below the guideline and a few goes just above the guideline.

Soil ingestion makes the greatest contribution to the exposure to Ni in a community's health. The critical effects of ingested Ni are developmental effects on the offspring of females exposed during pregnancy (DWAF, 1996). WRC (2002) reported that Ni is a potent skin sensitizer and ingestion of Ni cause skin reactions in previously sensitized individuals.

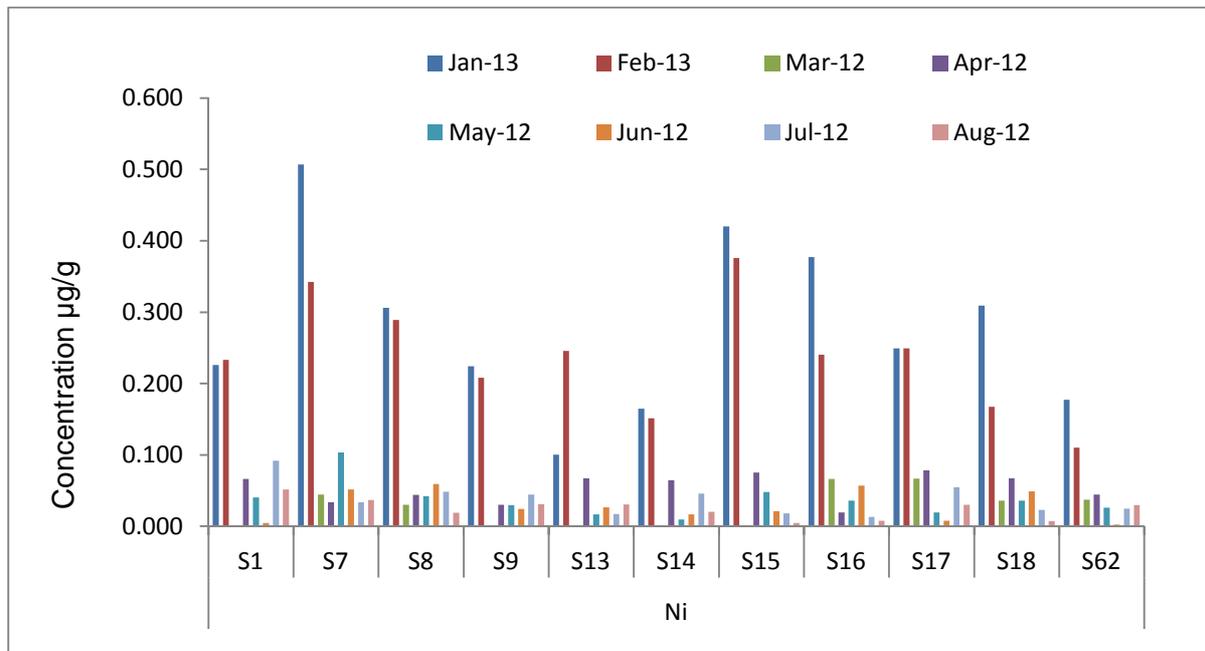


Figure 4.18 (c): Total Ni distribution per site.

Pb background concentration levels in surface soil ranged between (0.003 µg/g) and (0.66 µg/g) (DWAF, 1996). Adsorption is the primary factor responsible for low Pb concentration in soil. In the presence of clay suspensions at pH between 5 and 7, Pb is precipitated and adsorbed mostly as relatively hydroxides (DWAF, 1992). High levels of Pb in soil are found near roadways (Thomson, 2005).

An increasing mean concentration trend was obtained: S15 (Mine dump) < S9 (Shrubs) < S8 (Vegetable garden) < S1 (Industrial sites) < S7 (Gavel road) < S13 (Great North Mall) < S8 and S62 (Stream sediment and Tailing dam) < S16 (Brick yard) < S17 (Human tracks) < S18 (Stream sediment).

The lowest recorded Pb concentration (0.002 µg/g) was at S18 (Stream sediment), and the highest (0.086 µg/g) was at S9 (Shrubs). S17 has recorded Pb below the detection limit during the month of January and February 2013. The entire studied area exhibits higher Pb level above the guideline of (0.007 µg/g) (WRC, 2002). WHO (1998) warned that exposure to Pb, particularly in young children, should be minimised. At a relatively low concentration with continuous exposure, Pb can cause neurological impairment in young children and fetuses. Pb exposure may also cause anaemia (DWAF, 1996).

Data gathered from the study area have indicated major changes of Pb concentration in soil samples. The relative reduction of Pb concentration was reported in April and July, and an increase was reported in May and June due to the increase in wind speed. The largest decrease in Pb concentration was observed during the month of July, during this period the average wind speed was low and the pH was almost neutral.

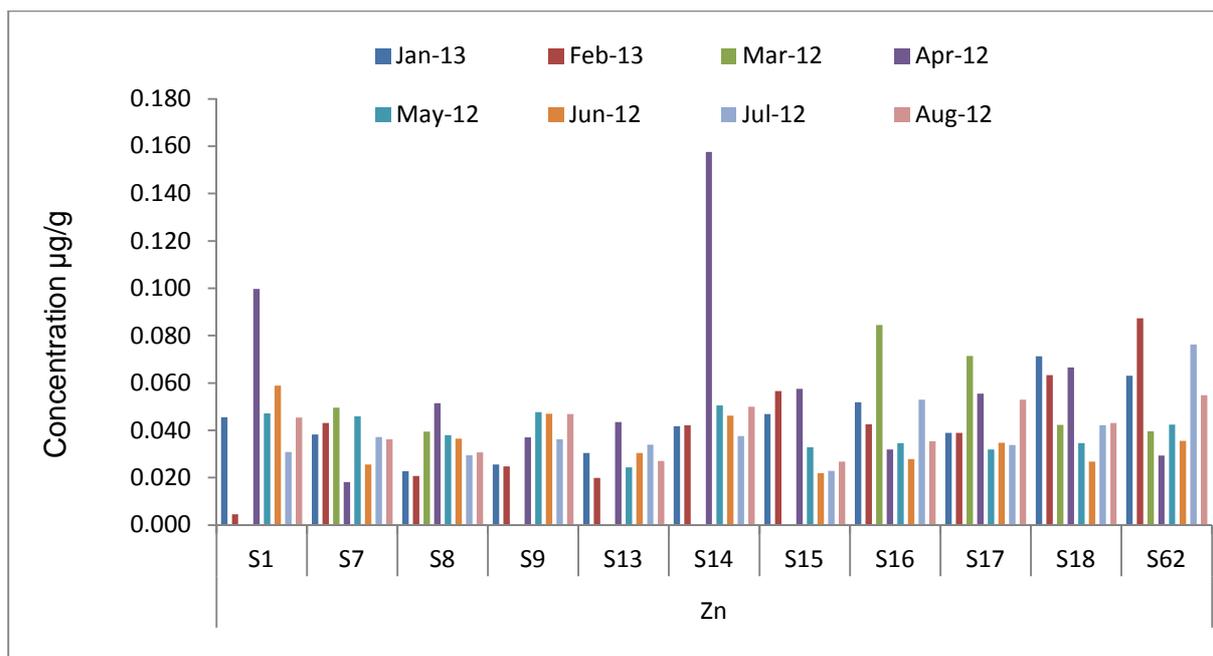


Figure 4.18 (d): Total Pb distribution per site.

Zn is the 23rd most abundant element in the earth's crust (Lenntech, 2013). Zn is commonly associated with Cu and Cd. It is an essential for animal and plants. Humans have a high tolerance of Zn (DWAF, 1996 & WHO, 2008).

The background concentration of Zn in soil is between (0.018 µg/g) and (0.150 µg/g). There is a relatively constant concentration of Zn from month to month. Soil acidity influences the availability of Zn more than any factor, with lower Zinc solubility as the pH increases (Page and Chaug, 1990). The study reveals that Zn is a lowest metal among others studied in the Musina soil; this might be because it was also a target by-product when Cu was being mined.

The mean concentration of Zn followed an increasing trend: S13 and S15 (Great North Mall and Mine dumps) < S7 (Gravel road) < S8 (Vegetable garden) < S9 and S18 (Shrubs and Stream sediment) < S16 (Brick yard) < S62 (Tailing dam) < S1 (Industrial site).

The lowest recordable (0.022 µg/g) was at S15 (Mine dump) and (0.158 µg/g) at S14 (Great North Mall). Zn is fairly constant from all sites. The highest recorded at Great North Mall was not surprising as the trucks loaded with Cu-Zn metals uses the site as parking for resting and shopping at the mall. Zn guideline in soil is (0.046 µg/g). Concentration recorded is above the guideline and therefore result in gastrointestinal irritation (DWAF, 1996). Zn exposure could cause decreased absorption of Cu and Fe which results in anaemia and leucopenia (WHO, 1998 & WRC, 2002).

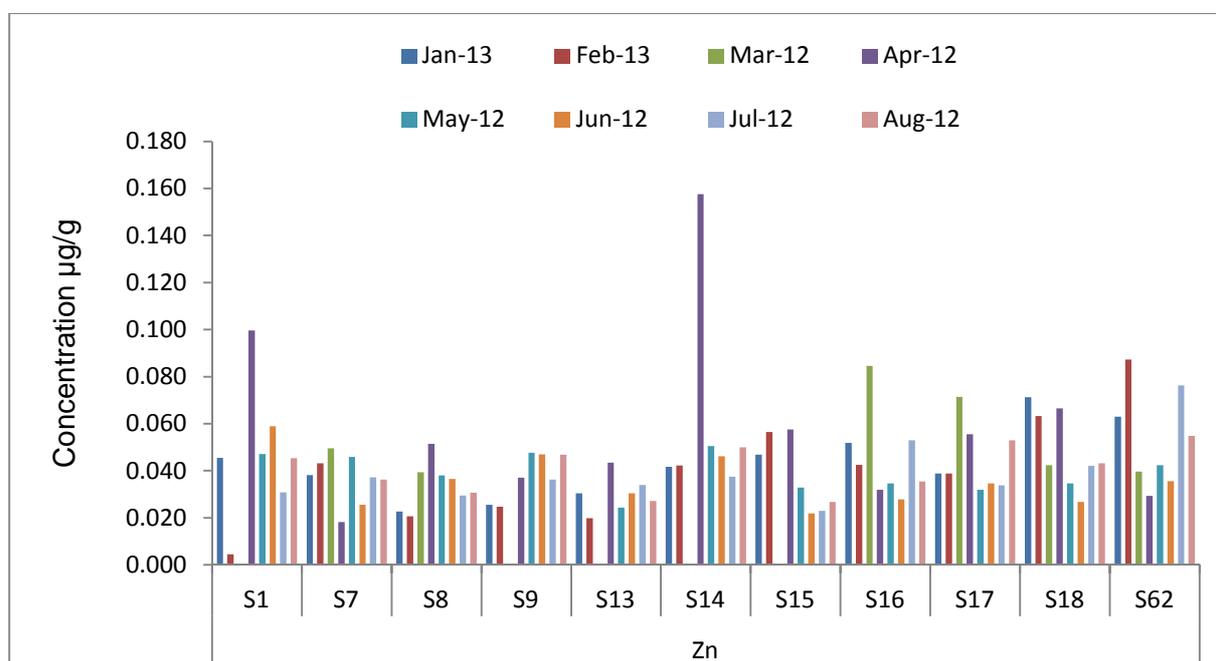


Figure 4.18 (e): Total Zn distribution per site.

4.4.8 Mean metal, standard deviation and coefficient of variation concentrations of field samples

The mean, standard deviation and coefficient of variation of As, Cu, Ni, Zn and Pb in surface soils and ground water are shown in Table 4.11 and Table 4.12 below.

4.4.81 Water sample

For water samples, the mean concentration of the metals increased in the order Pb<Cu<As<Ni. Ni is the most abundant in the water samples determined with a value of (4.60 to 6.59 µg/g). The observations have confirmed that most water contains an appreciable quantity of Ni. The mean value of As in water taken is (4.60 to 5.58) µg/g, Pb and Cu have (2.33 to 2.98 µg/g) and (1.85 to 2.66 µg/g) respectively.

Table 4.6 Mean metal concentration in water samples in both winter and summer period

Sample Sites	Metal	Total Value	Number of Samples	Mean	Standard Deviation	Coefficient of Variation
	As					
W1		39.12	8.00	4.89	1.56	0.32
W2		36.82	8.00	4.60	1.70	0.37
W3		44.60	8.00	5.58	1.21	0.22
W4		38.63	8.00	4.83	1.59	0.33
W5		36.42	8.00	4.55	1.72	0.38
	Cu					
W1		17.99	8.00	2.25	2.88	1.28
W2		14.78	8.00	1.85	3.08	1.67
W3		20.40	8.00	2.55	2.73	1.07
W4		21.30	8.00	2.66	2.67	1.00
W5		18.55	8.00	2.32	2.84	1.23
	Ni					
W1		42.53	8.00	5.32	1.34	0.25
W2		36.96	8.00	4.62	1.69	0.37
W3		52.75	8.00	6.59	0.70	0.11
W4		50.98	8.00	6.37	0.81	0.13
W5		45.09	8.00	5.64	1.18	0.21
	Pb					
W1		18.63	8.00	2.33	2.84	1.22
W2		21.24	8.00	2.66	2.67	1.01
W3		20.28	8.00	2.54	2.73	1.08
W4		22.54	8.00	2.82	2.59	0.92
W5		23.80	8.00	2.98	2.51	0.84

4.4.8.2 Soil samples

For soil samples, the mean concentration of the metals increased in the following order: Pb< Cu<Zn<As<Ni. Pb with 0.023 to 0.036 µg/g followed by Cu ranged from 0.028 to 0.045 µg/g then Zn 0.026 to 0.053 µg/g, the mean range of As in soil ranged from 0.054 to 0.086 µg/g. However, some studies show much higher contamination of As from the natural sources, followed by Ni with 0.057 to 0.144 µg/g.

Table 4.7 The mean concentration for selected metals over the entire span of the sampling sites.

Sample Sites	Metal	Total	Number of Samples	Mean	Standard Deviation	Coefficient of Variation
S1	As	431	8	54	25	0
S7		602	8	75	36	0
S8		543	8	68	52	1
S9		674	8	84	50	1
S13		618	8	77	60	1
S14		674	8	84	40	0
S15		666	8	83	44	1
S16		684	8	86	40	0
S17		599	8	75	50	1
S18		670	8	84	51	1
S62		586	8	73	53	1
S1		Cu	222	8	28	19
S7	306		8	38	18	0
S8	289		8	36	25	1
S9	289		8	36	29	1
S13	240		8	30	25	1
S14	244		8	31	20	1
S15	236		8	30	33	1
S16	308		8	39	21	1
S17	221		8	28	29	1
S18	359		8	45	21	0
S62	222		8	28	19	1

S1		714	8	89	43	0
S7		1152	8	144	36	0
S8		839	8	105	27	0
S9		591	8	74	24	0
S13		503	8	63	29	0
S14	Ni	473	8	59	24	0
S15		963	8	120	28	0
S16		817	8	102	21	0
S17		755	8	94	14	0
S18		694	8	87	16	0
S62		452	8	57	14	0
<hr/>						
S1		191	8	24	33	1
S7		288	8	36	12	0
S8		255	8	32	8	0
S9		200	8	25	18	1
S13		219	8	27	15	1
S14	Pb	212	8	27	53	2
S15		202	8	25	19	1
S16		230	8	29	21	1
S17		204	8	26	16	1
S18		186	8	23	13	1
S62		225	8	28	17	1
<hr/>						
S1		332	8	42	14	0
S7		294	8	37	16	0
S8		269	8	34	10	0
S9		265	8	33	16	0
S13		210	8	26	19	1
S14	Zn	426	8	53	13	0
S15		265	8	33	16	0
S16		362	8	45	14	0
S17		358	8	45	14	0
S18		390	8	49	16	0
S62		278	8	35	14	0

References

Annegarn HJ, Moja SJ, Malahlela J, Kgoshane P & De Lange B 2002: Vanderbiljpark-Golden Highway project: Dust fall out monitoring Report_AER 221785_GHP.

APHA 1989: Standards Methods for examination of water and waste water, 17th Edition. American Public Health Association, American Water Works Association. *Water Pollution Control Federation*, in Washington DC, USA.

Aucamp PJ & Vivier FS 1990: Water Quality Criteria in South Africa. *Technology S.A.*, June 1990, 21-30.

ASTM 1973: Test Methods of determination of turbidity in static mode.

AWWA 1971: *Water quality and Treatment. A Handbook of public water supplies*, 3rd Edition. The American Water Works Association, McGraw-Hill Book Company, New York.

Ayers 1985: Water quality for Agriculture, FAO Irrigation and Drainage paper No.29. FAO, Rome.

Berman E 1980: *Toxic Metals and their Analysis*. Heyden, London.

Bowman HJM 1979: *Environmental Chemistry of the Elements*. Academic's Press. London.

Brenner KP, Rankin CC & Roybal YP 1993: New medium for the simultaneous detection of total coliforms and Escherichia. *Appl Environ Micro bid.* 1993:59:334.

Dallas HF & Day 1993: The effect of Water Quality Variable on Riverine Ecosystems. Water Reservation Commission Report No: TT 61/93.

Department of Water affairs and forestry (DWAF) 1996: Analytical Methods Manual TR 151.

DISME 2013: Desertification Indicator System for Mediterranean Europe. www.dis4m3.com Hoover, JM 1971: Surface improvement and dust palliation of unpaved secondary roads and streets, Engineering Research Institute, Iowa State University Ames, Iowa.

Koranteng AEJ, Owusu AE, Boamponsem LK, Bentum JK, & Arthur S 2011: Levels of Zinc, Copper, Iron, and Manganese in soil of abandoned mine pits around Tarkwa gold mining area of Ghana. *Adv. Appl. Sci. Res.*, 2011, 2 (1): 280-288.

Michaud JP 1991: A citizen's guide to understanding and monitoring lakes and streams: Olympia, Washington state department of ecology publication 94-149, pp66.

Moja SJ 2007: Manganese fractions and distribution in street dust and roadside soils from Tshwane, South Africa. D-Tech Thesis, Department of Environmental Sciences. Tshwane University of Technology.

Nyangababo JT & Hamya JW 1986: The deposition of Lead, Cadmium, Zinc and Copper into traffic on brachiaria enimi and soil along a major Bombo road in kampala city. *Intern. J. Environ. Studies*, 27: 115-119.

Okonkwo JO, Awfolu OR, Moja SJ, Forbes PCB & Sonwo ZN 2006: Total petroleum hydrocarbons and trace metals in streets dust from Tswane Metropolitan Area, South Africa, *J. of Env. Sci and Health Part A*. 41, Pp 2789-2798.

Page AL & Chaug AC 1990: Deficiencies and Toxicities of Trace Elements. In: Agricultural salinity Assessment and management K.K. Tanjii (Ed.). ASCE Manual and Reprints on Engineering practice No. 71, ASCE New York 1990.

Pratt PF & Soares DL 1990: Irrigation water quality assessment, ASCE New York 1990.

SANS 2005: Drinking Water Quality Management Guide for Water Services Authorities, SANS 241: September 2005, Drinking water, Edition 6.

Schomolke G & Forth W 1988: Arsenic-Copper interaction in the rat kidney. Naunyn Schmiedenberg's Arch, Toxicol., 337.

Tao BN 1998: The effect of type of water supply on water quality in a developing country in South Africa, *Water Science Technology*. 1998:35 (11-12):35-40.

Thomson, E 2005 (6): Acid Mine Waters in South Africa and their amelioration. Draft Acid Rock Drainage.

USEPA 2003a: Guideline for 2004 Assessment, listing and reporting requirement of the Clean Water Act, TMDL-01-03.

Wikipedia 2013: en.wikipedia.org/wiki/vegetation

WHO 2003: Guidance for drinking water quality. Geneva, 2003 (WHO/SDE/WSH 03.04).

WRC 2002: Addendum No 1. Edition 1 (1997): Permissible utilisation and disposal of sewage sludge. TT. 150101. Water Research Commission, Pretoria.

Ziegler AC 2002: Issues related to use of turbidity measurement, Workshop of turbidity and other sediments surrogates April 30-May 2, 2002, Reno, Nevada.

CHAPTER FIVE: SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

In this chapter, the research findings are summarised, conclusions are drawn and the recommendations are made for further studies and guidance.

5.1 Summary

Generally, Pb-Zn-Cu-As-Ni levels obtained in soil studied were high and harmful even though they were slightly above the threshold. But with time, accumulation of said metals near the community may lead the area to be declared unsafe for residential use and the community might be forced to leave the town. The results presented indicated that the soil from the Musina area contained high levels of Pb-Zn-Cu-As-Ni as compared to the soil from the nearby Matswale and Nancefield township and rural area of Madimbo. Pb recorded shows an increase from the background concentration (0.035 µg/g) to (0.036 µg/g), Zn has increased from (0.036 µg/g) to a higher concentration (0.053 µg/g), Cu in background location shows a lower concentration of (0.002 µg/g) but with an influence of mining, the concentration goes up to (0.045 µg/g), As has moved from (0.061 µg/g) to (0.086 µg/g). Ni concentration in background locations was very high, recorded at (0.104 µg/g) as opposed to the (0.144 µg/g) value recorded in a disturbed area. This was a strong indication of the influence of mining activities to the concentration of the above mentioned metals. Overall, total Pb obtained was lower than the levels reported by the other sources like the Council of Geoscience, except for those obtained at the entrance of the mall where trucks from Africa north of South Africa park.

The Pb-Cu-As-Ni levels in the water studied may be low and harmless at the present moment, but with the passing of time, accumulation of the said metals in drinking water may cause severe damage to human health. The pH levels of water were within the acid range to slightly alkaline. The pH values lower than 6.5 are considered too acidic for human consumption. The pH levels of the soil were in the alkaline range. The high pH may have originated from the lime applications used during rehabilitation programme. The EC concentration values measured in ground water were within the WHO permissible limit for drinking water. Samples from all the boreholes studied were below the turbidity threshold of 5.0 NTU as per the requirements by DWAF and WHO.

It is therefore crucial that an investment be made by Musina Local Municipality into the land determination in order to derive maximum benefits from the abandoned copper mine. This entails turning the pollution challenges into opportunities. Rehabilitated land could be used for recreational or other economic activities.

Mining without protective clothing is very dangerous since miners' health is negatively affected due to exposure to toxic chemicals. The small-scale mine operations such as the one in Musina where miners work without protective clothing is a health hazard. Corrective measures and proper licensing need to be taken. Most of these mining activities are operated illegally and exposed workers to dangerous chemicals. Appropriate measures such as rehabilitating the contaminated land should be undertaken to lessen the pollution effects.

5.1.1 Rehabilitation strategies to be developed

5.1.1.1 Re-vegetation strategy

Covering surface soil will help to minimise the spread of the contaminated soil by wind or contaminated water by rain. The re-vegetation strategy ensures rapid vegetation of the disturbed areas prior to the onset of heavy wet season rain. Appropriate preparation of the affected soil is required for successful plant establishment. The surface should be ripped or loosened and shaped so that the surface retains a rough or cloddy texture.

5.1.1.2 Minimisation of risks to the public safety

An abandoned Cu mine in Musina is a serious health hazard and a cause of concern since some shafts and holes were left open or were not properly covered. These sites are easily accessed and together with uncovered mine tailing; they threaten the safety of members of the community and animals.

5.1.1.3 Stabilisation of the high walls of the tailing and ensuring resistance to erosion

Soil erosion can also be reduced by the use of benches in the high walls of the tailing. The other useful strategy for reducing soil erosion can be reducing the angle of the slope to a much lesser slope.

5.1.1.4 Encouragement of small-scale miner to practice rehabilitation

This can be done by organising workshops that teach practitioners about environmental rehabilitation during small-scale mining. Through these workshops, small-scale miners can be encouraged to begin practicing rehabilitation where they are operating.

5.2 Conclusions

This study has satisfied the aims and objectives by analysing the metals concentration of soil and water. The results and concentrations have been unexpected and the patterns of those concentrations have been surprising and unanticipated. From the results it can be concluded that the Musina defunct mine and its surroundings is not a pristine, but a less contaminated area.

The quality of ground water supplied by the five boreholes studied was satisfactory with turbidity (T), electrical conductivity (EC) and Heavy metals (HMs) below the WHO limit. The water therefore may, according to the WHO Standards be safely used for drinking purposes. The concern lies on pH which has been shown to be slightly (0.5) below the standards. There is a serious need to monitor the ground water which is now used for drinking purposes.

This study revealed that heavy metal pollution in soil from Musina's abandoned copper mine is a threat to the health of the community. Although the pollution is medium to low, it is important for the Musina Municipality or mine owner of Musina (TVL) Development Co Ltd copper mine to advocate possible actions which will safeguard the environment.

The studied metals show the possibility of detrimental effects on the local environment in lesser concentration as compared to the background levels. These metals, however, must be monitored to ensure that their concentration doesn't reach a critical point where the community might need to be uprooted and located outside the town. The other metals, namely As and Pb, are not known for any benefit to human and environmental system, therefore any level of their concentration is considered harmful to the system. The concentrations exhibited may presently result in lesser deleterious or harmful effects. However, further discharge of said metals from the source, in any of the areas examined may have major effects on the surrounding environment.

The tailing at Musina's old copper mine have high pH and they lack normal soil stabilisation processes. As a result the tailings do not develop a good plant cover. Pollution of the ground water resources is also evident in the study area where there is seepage or ingress of polluted water to the underground aquifers. Small-scale mining in Musina, although is causing further degradation to the environment, supports the South African Waste Hierarchy by promoting the reuse and recycling of the tailing. Mine workers are exposed to heavy metals on a daily basis. Prevention is better than cure; hence it is advisable that precaution measures be taken to prevent exposure to heavy metals.

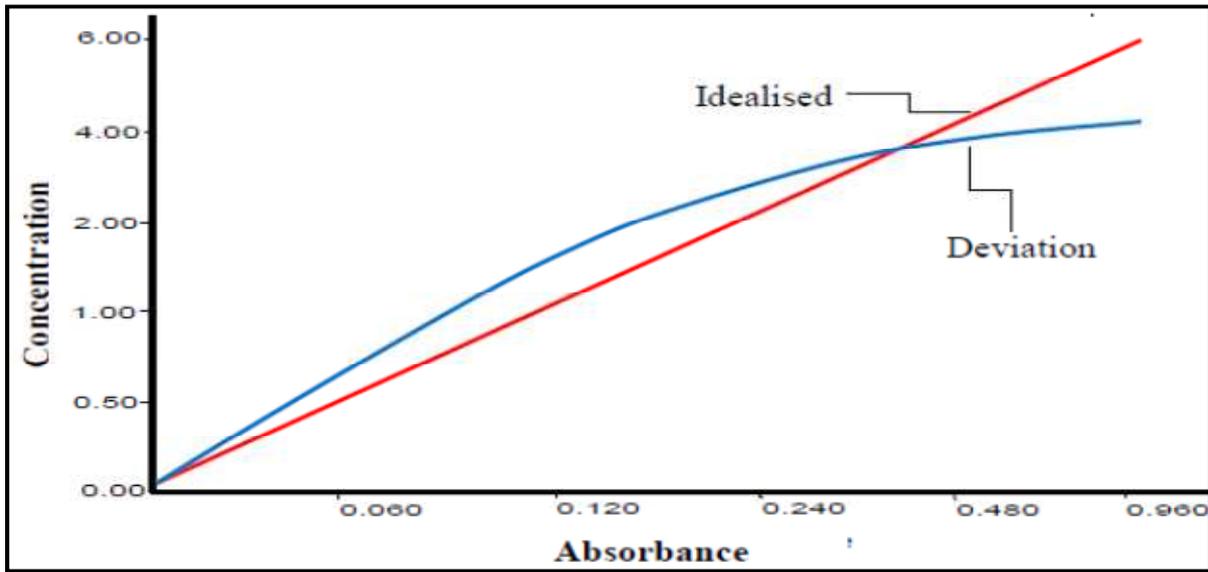
5.3 Recommendations

Based on the findings of this study, the following recommendations for further action and studies are suggested:

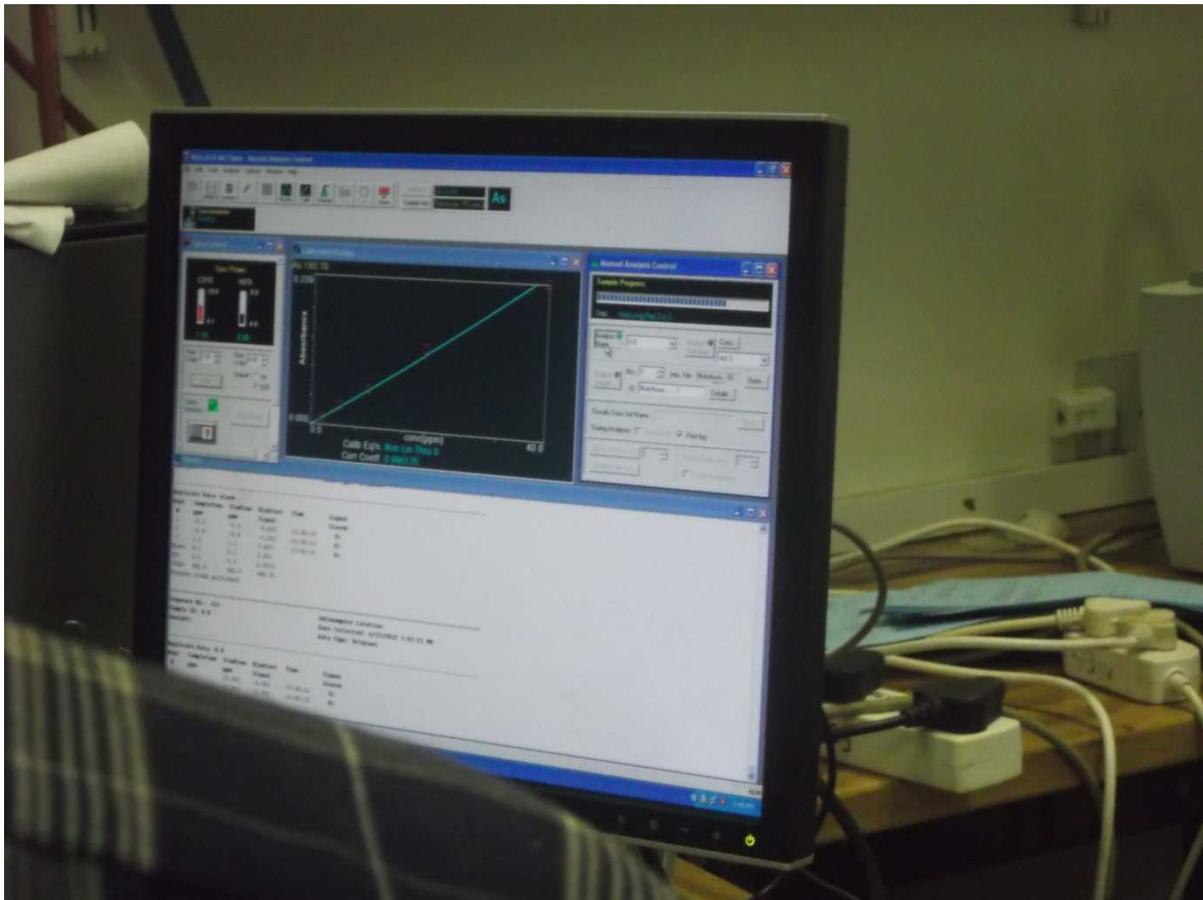
- ✓ Vegetation consisting of tree and shrubs should be applied on the tailing to act as a windbreak. Additional grasses cover to complete surface wind and water erosion protection should be planted.
- ✓ There is a need to study the health-related parameters that include fluorides, nitrate and pesticides pollution.
- ✓ Sewage sampling should be done to determine how much of the heavy metals pollution in the ground water comes from the sewage system.
- ✓ Small-scale mine workers must use PPE to prevent lung irritations or related diseases.
- ✓ Salinity, temperature and redox potential all affect uptake and retention of metals in the soil. This aspect should be investigated further in order to fully comprehend metals in the study area.

APPENDICES

Appendix 1 Idealised/deviation response curves for FAAS



Appendix 2 Calibration curve as shown on the computer during analysis



Appendix 3 Ethics Clearance (Ref. Nr.: 2012/CAES/015)

Ref. Nr.: 2012/CAES/015

To the student:

Student nr: 49100955

Mr NK Singo
Department of Environmental Science
College of Agriculture and Environmental Sciences

Dear Mr Singo

Request for Ethical approval for the following research project:

An assessment of heavy metal pollution near an old copper mine dump in Musina, South Africa

The application for ethical clearance in respect of the above mentioned research has been reviewed by the Research Ethics Review Committee of the College of Agriculture and Environmental Sciences, Unisa. Ethics clearance for the above mentioned project (Ref. Nr.: 2012/CAES/015) is **granted** after careful consideration of all documentation submitted to the CAES Ethics committee.

Please be advised that the committee needs to be informed should any part of the research methodology as outlined in the Ethics application (Ref. Nr.: 2012/CAES/015), change in any way. Should this be the case, a memo should be submitted to the Ethics Committee in which the changes are identified and fully explained.

We trust that sampling, data gathering and processing of the relevant data will be undertaken in a manner that is respectful of the rights and integrity of all participants, as stipulated in the UNISA Research Ethics Policy.

The Ethics Committee wishes you all the best with this research undertaking.

The Ethics Committee wishes you all the best with this research undertaking.

Kind regards,



Prof E Kempen,
CAES Ethics Review Committee Chair

Appendix 4 Expected Outcomes of the Research

Title of Draft Article (s):

1) Heavy metals in drinking water and their impact on human health, Rwanda Township, Musina

2) Soil pollution by heavy metals in a residential area of Musina town, Limpopo Province, South Africa

Authors: SJ Moja*, NK Singo & KW Maphangwa

Targeted Journal: *Journal of Environmental Science and Human Health* (Toxic/Hazardous Substances and Environmental Engineering).

Year: 2013