

**ASSESSMENT OF POTENTIALLY HARMFUL ARSENIC, CADMIUM, COBALT
AND LEAD IN SOILS AND PLANTS IN NOMTSOUB SUBURB, TSUMEB TOWN.**

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ABSTRACT

A number of environmental studies previously conducted in the Tsumeb Mining district analysed total metal concentrations in soils and vegetation; with results showing high concentrations of heavy metals such as arsenic, cadmium, copper, lead and zinc which exceed international guidelines for different land uses. However, the actual concentrations of only potentially harmful species for each element were not ascertained. This study aimed at determining the concentrations of potentially harmful As^{3+} , Cd^{2+} , Co^{2+} , and Pb^{2+} in soil in the Nomtsoub suburb of the Tsumeb Town as well as determining the uptake of the potentially harmful heavy metals from soil to vegetation. The research project involved sampling of soils and vegetation in residential complexes and school grounds in the Nomtsoub suburb and surroundings which has a population of approximately 2000 people. Thirty (30) surface soil samples (0-5 cm depth) were sampled. Twenty (20) vegetation samples consisting of: Mango leaves, lemon leaves, sunflower leaves, fresh and dried papaya leaves, marula fruit, marula tree bark, fig leaves and fig fruit were collected due to their availability at the time of sampling as well as their prevalent local use. Control samples were collected from Lake Otjikoto and Farm Manheim some 15 km and 25 km from Tsumeb respectively. Sequential extraction and *Aqua regia* were used in extraction of the following targeted species: As^{3+} , Cd^{2+} , Co^{2+} , and Pb^{2+} . The samples were analysed using ICP-MS and ICP-OES at the Bureau Veritas laboratory in Vancouver, Canada. Analytical results of harmful heavy metals of soils in this study revealed moderate to high concentrations in mg/kg as follows: As^{3+} , (7 to 421), Cd^{2+} (0.5 to 35.6), Co^{2+} (2 to 6.3) and Pb^{2+} (25.9 to 3786.9). These results exceeded levels found naturally in the geosphere. When compared to Canadian Soil Quality Guidelines for agricultural and residential land use, results of soil samples in this study exceeded As, Cd and Pb guideline values for both land uses.

None of the soil samples in the study exceeded guideline values for cobalt for both residential and agricultural land uses. The minimum and maximum concentrations of bioavailable, potentially harmful heavy metals in soils in the current study are lower than those obtained in the previous studies which assessed total element concentrations. Bioaccumulations of harmful heavy metals in vegetation were as follows: (in mg/kg): As³⁺ (5.4 to 247), Cd²⁺ (0.3 to 23.77), Co²⁺ (0.2 to 2.6) and Pb²⁺ (8.43 to 801.67). WHO and EU limits of heavy metals in vegetation were exceeded for As, Cd and Pb. Co exceeded concentrations naturally found in vegetation. When uptake ratios were calculated for the various potentially harmful elements, arsenic uptake from soil to vegetation was the highest at 96%. Uptake of cadmium and cobalt was moderate to high (12.4 to 66.8% and 3.6% to 53.8% respectively). Lead had the lowest uptake (3.9 and 41.8%). The presence of potentially harmful heavy metals in the soil and vegetation/ plants in the study area poses a considerable health threat to the Tsumeb Community including threats to the gastrointestinal, musculoskeletal, immune, and reproductive and central nervous systems of human beings. The study recommended in-depth research on harmful element transfer from soils to vegetation, translocation mechanisms in vegetation as well as biomonitoring of heavy metals in people living in Tsumeb to ascertain risk levels and facilitate development of appropriate risk reduction and consequence mitigation measures if necessary.

Table of Contents

ABSTRACT.....	i
ACKNOWLEDGEMENTS.....	xi
DECLARATIONS.....	xii
Chapter 1 INTRODUCTION	1
1.1.1 Statement of the problem.....	3
1.1.2 Objectives of the study.....	4
1.1.3 Hypothesis of the study.....	4
1.2 Locality.....	5
1.3 Climate.....	6
1.3.1 Soils.....	6
1.4 Economic activities of the Tsumeb town.....	7
1.5 Geological Setting.....	7
1.5.1 Overview of the Geology of Tsumeb.....	7
Chapter 2 LITERATURE REVIEW	11
2.1 Previous studies.....	11
2.2 Heavy Metals in the environment.....	21
2.2.1 Arsenic- Occurrence, use and toxicity.....	21
2.2.2 Cadmium - Occurrence, use and toxicity.....	24
2.2.3 Cobalt - Occurrence, use and toxicity.....	26
2.2.4 Lead - Occurrence, use and toxicity.....	29
Chapter 3 METHODOLOGY	31
3.1 Sampling.....	31
3.1.1 Soil Sampling.....	31
3.1.2 Vegetation sampling.....	34
3.2 Analytical Methods.....	38
3.3 ArcGIS Spatial data Analysis.....	40
3.3.1 Natural Neighbour Method.....	40
3.3.2 Inverse Distance Weighted (IDW).....	41
3.4 Ethical considerations.....	41

Chapter 4 RESULTS	42
4.1 Analytical results of soil samples.....	42
4.2 Analytical results of vegetation samples	48
Chapter 5 DISCUSSION	54
5.1 Analysis of soil samples	55
5.1.2 Comparison of metal concentrations in the earth’s crust and concentration in Tsumeb soils	56
5.1.3 Contaminant distribution maps	57
5.1.5 Transfer Coefficients of heavy metals	70
5.2 Analysis of vegetation samples	82
5.2.1 Comparison of heavy elements occurring naturally in biota to concentrations in vegetation sampled during the current study.....	82
5.2.2 Comparison of Vegetation samples to International guidelines	84
5.2.2.1 Concentration of potentially harmful arsenic in Tsumeb vegetation samples compared to International guidelines	86
5.2.2.2 Concentration of potentially harmful cadmium in Tsumeb vegetation samples compared to EU guidelines.....	87
5.2.2.3 Concentration of potentially harmful cobalt in Tsumeb vegetation samples compared to concentration in natural biota.	88
5.2.2.4 Concentration of potentially harmful lead in Tsumeb vegetation samples compared to International guidelines	89
5.3 Comparison of current study to previous environmental studies in Tsumeb.....	90
5.3.1 Comparison of soil analysis results	90
5.3.2 Comparison of vegetation analysis results of current study to previous studies	96
Chapter 6 CONCLUSION	103
Chapter 7 RECOMMENDATIONS AND PROPOSED FUTURE RESEARCH	107
7.1 Recommendations	107
7.2 Proposed future research	108
References	109
APPENDIX 1: COORDINATES OF SAMPLING SITES	119
APPENDIX 2: CONCENTRATION OF POTENTIALLY HARMFUL ELEMENTS IN SOIL SAMPLES	122

APPENDIX 3: CONCENTRATION OF POTENTIALLY HARMFUL ELEMENTS IN VEGETATION SAMPLES	123
APPENDIX 4: SEQUENTIAL EXTRACTION PROCEDURES (SEP).....	124
APPENDIX 5: AQUA REGIA.....	125
APPENDIX 6: HUMAN HEALTH SOIL QUALITY GUIDELINES	126

LIST OF TABLES

Table 1.1: Stratigraphy of the Otavi Mountainland. Adopted from Kamona & Günzel (2007); modified after Lombaard (1986).....	9
Table 2.1: Example of cobalt species with their physical and chemical properties. The table was obtained from Kim et al (2006).	27
Table 4.1: Statistical data for potential harmful elements: arsenic, cadmium, cobalt and lead in top soils of Nomtsoub, Tsumeb area... ..	42
Table 4.2: Statistical data for potential harmful elements: arsenic, cadmium, cobalt and lead in vegetation of Nomtsoub, Tsumeb area.. ..	49
Table 5.1: Average heavy metal concentrations in different constituents of Earth's crust and some surficial deposits compared to average concentrations in Tsumeb.	56
Table 5.2: Uptake of heavy metals in vegetation compared to adjacent soils	68
Table 5.3: Coefficient for heavy metals in vegetation compared to adjacent soils.. ..	71
Table 5.4: Concentration of potentially harmful elements in Nomtsoub suburb versus Canadian soil quality guidelines for residential and agricultural land use.. ..	74
Table 5.5: Heavy metal concentrations found naturally in biota compared to average concentration in vegetation sampled during this current study.	83
Table 5.6: WHO (2001) Codex Alimentarius and EU (2006) guideline values for Agricultural plants	85
Table 5.7: Concentration of potentially harmful elements in Tsumeb vegetation compared to guidelines.	86
Table 5.8: Comparison of results of previous studies (total heavy metals in soils) versus results of the current study (potentially harmful bioavailable elements).....	92

LIST OF FIGURES

Figure 1.1: Location of study area	6
Figure 1.2: Geological map of Tsumeb and surrounding areas.	10
Figure 3.1: A sampling site just outside school grounds in the Nomtsoub Suburb.....	32
Figure 3.2: School children playing in the schoolyard in Nomtsoub suburb.....	33
Figure 3.3: Children playing on contaminated soil outside the TCL compound.....	33
Figure 3.4: Lake Otjikoto where control soil and vegetation samples were collected	34
Figure 3.5: The TCL compound from where a number of samples were collected	35
Figure 3.6: Sampling of fig leaves inside the TCL Compound	36
Figure 3.7: Soil and vegetation sample locations in and outside Tsumeb.....	37
Figure 3.8: Sampling sites outside the Nomtsoub suburb where construction is currently underway.....	38
Figure 4.1: Concentration of potentially harmful arsenic (As^{3+}) in Tsumeb top soil samples.	44
Figure 4.2: Concentration of potential harmful cadmium (Cd^{2+}) in Tsumeb top soil samples	45
Figure 4.3: Concentration of potential harmful cobalt (Co^{2+}) in Tsumeb top soil samples	46
Figure 4.4: Concentration of potential harmful lead (Pb^{2+}) in Tsumeb top soil samples	47
Figure 4.5: Concentration of potentially harmful arsenic (As^{3+}) in Tsumeb vegetation.	50
Figure 4.6: Concentration of potential harmful (Cd^{2+}) in Tsumeb vegetation.....	51
Figure 4.7: Concentration of potential harmful cobalt (Co^{2+}) in Tsumeb vegetation.....	52
Figure 4.8: Concentration of potential harmful lead (Pb^{2+}) in Tsumeb vegetation	53
Figure 5.1: Distribution of arsenic in Tsumeb soils. The map was generated using the Inverse Distance Weighted Method.....	58
Figure 5.2: Distribution of harmful arsenic in Tsumeb soils. The map was generated using the NN Method.	59
Figure 5.3: Distribution of harmful cadmium in Tsumeb soils. The map was generated using the IDW method.....	60
Figure 5.4: Distribution of harmful cadmium in Tsumeb soils. The map was generated using the NN method.....	62
Figure 5.5: Distribution of harmful cobalt in Tsumeb soils. The map was generated using IDW method.....	63
Figure 5.6: Distribution of harmful cobalt in Tsumeb soils. The map was generated using the NN method.....	64

Figure 5.7: Distribution of lead in Tsumeb soils. The map was generated using the IDW Method.....	65
Figure 5.8: Distribution of lead in Tsumeb soils. The map was generated using the NN method.....	66
Figure 5.9: Uptake of potentially harmful elements from soil to vegetation.....	70
Figure 5.10: Proportions of soil samples exceeding Canadian guideline values of arsenic for residential land use.....	75
Figure 5.11: Proportions of soil samples exceeding Canadian guideline values of arsenic for agricultural land use.....	76
Figure 5.12: Proportions of soil samples exceeding Canadian guideline values of cadmium for residential land use.	77
Figure 5.13: Proportions of soil samples exceeding Canadian guideline values of cadmium for agricultural land use.	78
Figure 5.14: Proportions of soil samples exceeding Canadian guideline values of cobalt for residential land use.....	79
Figure 5.15: Proportions of soil samples exceeding Canadian guideline values of cobalt for agricultural land use.....	80
Figure 5.16: Proportions of soil samples exceeding Canadian guideline values of lead for residential land use.....	81
Figure 5.17: Proportions of soil samples exceeding Canadian guideline values of lead for agricultural land use.....	82
Figure 5.18: Heavy metal concentrations found naturally in biota compared to average concentration in vegetation sampled during the current study.	84
Figure 5.19: Proportion of Tsumeb vegetation samples exceeding WHO guidelines for arsenic in plants.....	87
Figure 5.20: Proportion of Tsumeb vegetation samples exceeding EU guidelines for cadmium in vegetation.....	88
Figure 5.21: Proportions of Tsumeb vegetation samples exceeding cobalt levels found naturally in biota.	89
Figure 5.22: Proportions of Tsumeb vegetation samples exceeding WHO (2001) and EU (2006) guidelines for lead in plants.	90

LIST OF ABBREVIATIONS AND/OR ACRONYMS

As:	Arsenic
ATSDR:	Agency for Toxic Substances and Disease Registry
BCR:	European Unions' Bureau of Community Reference
CBD:	Central Business District
Cd:	Cadmium
Co:	Cobalt
DNA	Deoxyribonucleic acid
EU:	European Union
GSN:	Geological Survey of Namibia
IDW:	Inverse Distance Weighted
OML:	Otavi Mountainland
Pb:	Lead
MME:	Ministry of Mines and Energy
NN:	Natural Neighbour
NRC:	National Research Council (of America)
ROS:	Reactive Oxygen species

RNS: Reactive Nitrogen species

SEP: Sequential extraction procedure

TCL: Tsumeb Corporation Limited

TCLP: Toxicity characteristic leaching procedure

TE: Trace Elements

USEPA: United States Environmental Protection Agency

WHO: World Health Organization

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DECLARATIONS

I, Phrisco Minsozi Sibeso, declare hereby that this study is a true reflection of my own research, and that this work, or part thereof has not been submitted for a degree in any other institution of higher education.

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PM SIBESO

Date

Chapter 1 INTRODUCTION

This chapter gives a description of the study area in terms of location, historical and current mining activities, the studies conducted in the area, the existing knowledge gaps as well as the significance of the current study which focused on assessing potential harmful species of selected contaminant elements.

The town of Tsumeb and surrounding areas is of interest to many environmental researchers due to its long mining history and potential environmental effects that resulted from it. Tsumeb has over 100 years of mining history, mostly of copper and zinc. According to Křibek and Kamona (2005), it was once the foremost producer of lead in Africa and, over its life, has produced in excess of 2 million tons of lead, some 500,000 tons of zinc, and over 1 million tons of copper (Křibek and Kamona, 2005). The deposit was mined by open pit mining and by several shafts.

According to Křibek and Kamona (2005), the Tsumeb deposit contained around 11% lead, 5% copper and 4.3 % zinc with economic concentrations of silver, cadmium, germanium and arsenic. Ores were processed by flotation and smelted in a local smelter, which is still currently in operation (Křibek and Kamona, 2005). Whereas mining operations ceased in the year 1999, the smelter continues to process copper ores from other mines including those from outside the country notably Bulgaria, Chile, Democratic Republic of Congo and Zambia. However, in the recent past, the smelting technology at Tsumeb has been upgraded to significantly reduce environmental effects.

The long history of mining, processing and smelting activities in Tsumeb has produced environmental problems as discovered in studies conducted by various researchers over the years. Results of the study by Křibek and Kamona (2005) showed that large tracts of residential, industrial and commercial land in and around Tsumeb were heavily contaminated by heavy metals. These metals were observed in elevated concentrations of; Pb, Zn, Cu, Cd, As and Co in soils, grasses and vegetables around the town (Křibek, 2011; Mapani et al., 2014; Křibek et al., 2014). Furthermore, studies involving screening of residents of Tsumeb Town found that, a number of residents screened had anomalously high concentrations of heavy metals in their urine and blood. More than a fifth of the investigated residents showed lead concentrations in blood exceeding the WHO guideline value of 10 µg/dL. The highest value for lead in blood (55µg/dL) exceeded the WHO limit by more than five times. Statistics showed that every sixth surveyed person exceeded the WHO guideline value for arsenic concentration in urine. The highest detected arsenic concentration of 443 µg/L in urine exceeds the WHO limit of 50 µg/L by almost nine times. The study also revealed that there is a direct link between Pb, As, Cd contaminated soils and the levels of these heavy elements in the two selected media (GSN, 2006; GSN, 2008; Mapani, 2011).

To assess the bioaccumulation of heavy metals in plants, Mapani et al. (2014) investigated the agricultural products in the surroundings of the Tsumeb Smelter Complex. A variety of crops were studied comprising of field crops (pumpkin and maize), fruit crops (marula, papaya, chilli pepper), vegetables (tomato, parsley, beans and carrot) from commercial farms situated 1 to 1.5 km to the west of the smelter complex as well as private farms in the Nomtsoub suburb of the Tsumeb town. Bioaccumulation of the toxic elements lead, cadmium and arsenic was evident in all plant samples.

The coefficients for arsenic revealed a generally low degree of contaminant uptake by the plants. Stem crops (maize, chilli, tomato, beans) and fruit trees (marula, pawpaw) showed the lowest values. In contrast, arsenic uptake by root vegetables like carrots and leafy vegetables like parsley was found to be high (Mapani et al. (2014). Křibek et al. (2014) studied the impact of ore processing on the environment in the Tsumeb area to determine the extent of the past industrial pollution, on soils and grasses. All previous studies such as those done by Křibek and Kamona (2005); Mapani et al. (2014); Ellmies et al. (2015) analysed for total metal concentrations of the heavy elements. However, “In order to evaluate the risk of potential exposure to heavy metals, total metal concentration is a poor indicator because reactivity, bioavailability and toxicity depend on the distribution of the different metal species in a particular environment. Therefore, an understanding of metal speciation is required” (Vullo et al., 2008).

1.1 Basis of the study

1.1.1 Statement of the problem

Since previous studies such as those done by Křibek and Kamona (2005); Mapani et al. (2014); Ellmies et al. (2015) only analysed total metal concentrations for the heavy elements, the concentrations of only potentially harmful species for each element are unknown. In this study, the concentrations of potentially harmful species: As^{3+} , Cd^{2+} , Co^{2+} and Pb^{2+} were determined so as to bridge this knowledge gap and determine the potentially harmful concentrations since toxicity is not directly correlated to total metal content, because it is the chemical form of the metal in the soil that determines its mobilization capacity and behaviour in the environment and hence its toxicity (Krishnamurti et al., 1997; Vullo et al., 2008); Keil et al., 2011; Shivakumar et al., 2012).

1.1.2 Objectives of the study

The objectives of the study are to;

- a) Determine the concentrations of potential harmful species of As^{3+} , Cd^{2+} , Co^{2+} and Pb^{2+} in soil and vegetation of the Nomtsoub suburb, Tsumeb.
- b) Determine the transfer ratios of the potential harmful elements (specifically; As^{3+} , Cd^{2+} , Co^{2+} and Pb^{2+}) from soil to vegetation in Nomtsoub suburb in order to estimate the potential risk to human beings as a result of contamination of the food chain.

1.1.3 Hypothesis of the study

The concentrations of actual harmful species of As, Cd, Co and Pb in soils and vegetation in Tsumeb are less than those recorded during previous studies which focused on total element analysis. According to Krishnamurti et al. (1997), the heavy metals in soils are generally present in five relatively distinct categories:

- 1.) Adsorptive and exchangeable fractions
- 2.) Bound to carbonates
- 3.) Bound to reducible phases (iron and manganese oxides)
- 4.) Bound to organics and sulphides
- 5.) Detrital or bound to mineral lattices.

The heavy metals in these categories have each a different behaviour with respect to remobilization under changing environmental conditions (Krishnamurti et al., 1997; Keil et al., 2011). Keil et al. (2011) report that most elements exist in several forms and valence states, also known as “species” with different toxic potentials.

Some species are less toxic or harmful than others. However, most analytical methods generate a “total” element concentration which includes both the harmful and harmless species. In this study, *sequential extraction procedures* and *aqua regia* were used to assess only the potentially harmful species. It is therefore expected that the concentration of potentially harmful species in the Tsumeb soils and plants is less than the total heavy metal concentration reported in previous studies.

1.2 Locality

Tsumeb is located in north central Namibia approximately 430 km north of Windhoek in the central northern part of Namibia (Figure 1.1) at Latitude 19° 15' 10'' S and Longitude 017° 42' 45'' E. It lies approximately 1 310 metres above mean sea level. The population of the Tsumeb Town is 19 275 inhabitants according to the 2011 national census (NSA, 2011).

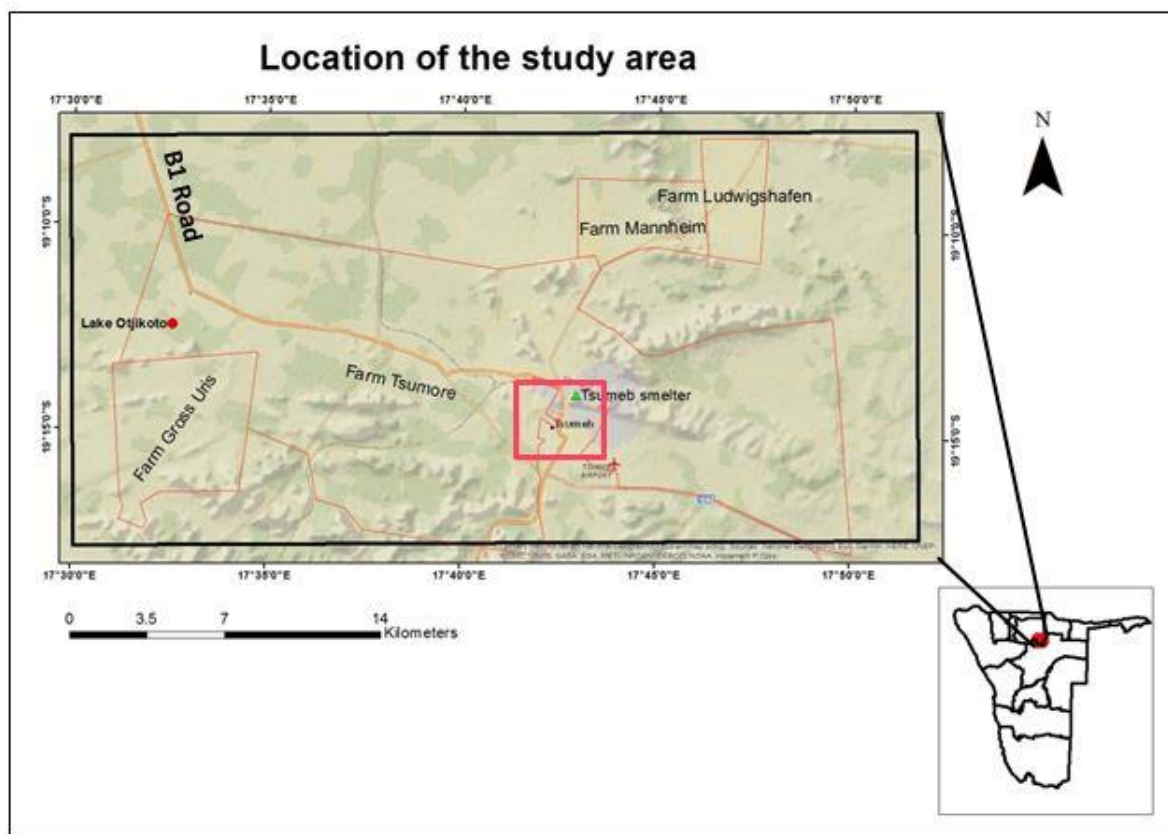


Figure 1.1: Location of study area

1.3 Climate

Tsumeb has a subtropical climate, with very short summers and mild winters. The annual mean temperature is 25° C and an annual average rainfall of 470 mm. Most of the rainfall occurs during summer, mostly between December and February. Křibek & Kamona (2005) report that easterly winds are the prevailing wind direction causing airborne pollution mainly to the west of Tsumeb. The annual rainfall in Tsumeb is 580 mm.

1.3.1 Soils

According to Křibek & Kamona (2005), soils of the Tsumeb area have been classified into four types: calcic regosols, calcic cambisols, pelitic vertisols and arenosols.

Calcic regosols mostly cover steep slopes and carbonate platforms, while foothills and slightly inclined carbonate plains are dominated by calcic cambisols. Flatlands are covered by pelitic vertisols, and in some places by arenosols derived from large sand dunes.

1.4 Economic activities of the Tsumeb town

Tsumeb has over 100 years of mining history mostly of copper and zinc. According to Křibek and Kamona (2005), it is estimated that millions of tons of mining and processing waste are stored within the area: 200 000 tonnes of slag dumps and 10 million tonnes of material in tailing ponds. Tsumeb used to be the capital of the Oshikoto Region before the proclamation of Omuthiya as a town and the region's capital in the year 2007. However, the town still remains important due to the many job opportunities available in the mining and metallurgy industries. The Tschudi Copper Mine which came into production in 2015 is located approximately 20 km west of the Tsumeb town and employs over 700 people. Agriculture remains relevant to the town and the region at large. Even though the region's agriculture is mostly focused on livestock production, there is significant production of potatoes, vegetables and sub-tropical fruits at private farms located north of the town (Křibek and Kamona, 2005).

1.5 Geological Setting

1.5.1 Overview of the Geology of Tsumeb

The major part of the current urban area of Tsumeb is developed on deeply weathered arkosic sandstone and shale of the Tschudi Formation (Mulden Group) (Table 1.1) and carbonate rocks of the Hüttenberg Formation of the Tsumeb Subgroup. The carbonate rocks of the Hüttenberg Formation are part of the Precambrian platform sedimentation close to the Congo Craton in the northern zones of the Damara Sequence (Schneider, 2004).

The famous Tsumeb deposit lies in the upper part of the Otavi Group, a late Precambrian, predominantly carbonate succession within the Damara Sequence (Table 1.1). The Otavi Group is subdivided into two sub-groups. These are: the Abenab sub-group which consists mostly of laminated dolomites in the lower part and of intercalating bedded limestone and shale with massive dolomites followed by the Tsumeb sub-group that is comprised mostly of limestones and dolomites (Table 1.1). There are however some horizons of remarkable diagenetic chert in the uppermost part of the unit, the Huttenberg Formation (Table 1.1). The closure of the Khomas Sea during the Neo-Proterozoic was responsible for the folding in the Northern platform, which acted as a northern foreland during the development of the Damara orogenic belt (Kříbek and Kamona, 2005).

Table 1.1: Stratigraphy of the Otavi Mountainland. Adopted from Kamona & Günzel (2007); modified after Lombaard (1986).

SEQUENCE	GROUP	SUBGROUP	FORMATION	
DAMARA	MULDEN		Kombat	
			Tschudi	
	OTAVI	TSUMEB SUBGROUP		Huttenberg
				Elandshoek
				Maieberg
				Ghaub
		ABENAB SUBGROUP		Auros
				Gauss
				Berg Aukas
				Varianto
		NOSIB		Askevold
				Nabis

Sedimentary rocks of the Tschudi and Hüttenberg Formations are the hosts of copper mineralization in the Tsumeb area. Mineralization is characterized by a large-scale alteration (calcification and silicification) of host rocks. Hydrothermal carbonate veins are also common in the Tsumeb region (Křibek and Kamona, 2005). The origin of the mineralization is explained by a tectonic mobilization of formation waters from the central part of the Damara Supergroup towards a tectonically less affected carbonate platform to the north during the Neoproterozoic Damaran Orogeny (Chetty and Frimmel, 2000). The ore mineralogy and rock alteration are similar to the Mississippi valley type ore deposits.

The hypogene ores are of the epigenetic, hydrothermal, replacement, and fracture filling type (Lombaard et al., 1986). The deposit contains a variety of ore minerals of lead, copper, zinc, silver, arsenic, antimony, cadmium, cobalt, germanium, gallium, gold, iron, mercury, molybdenum, nickel, tin and tungsten as well as vanadium. With such a great diversity of minerals, Tsumeb is known around the world as a mineral paradise and it is a dream location for mineral specimen collectors.

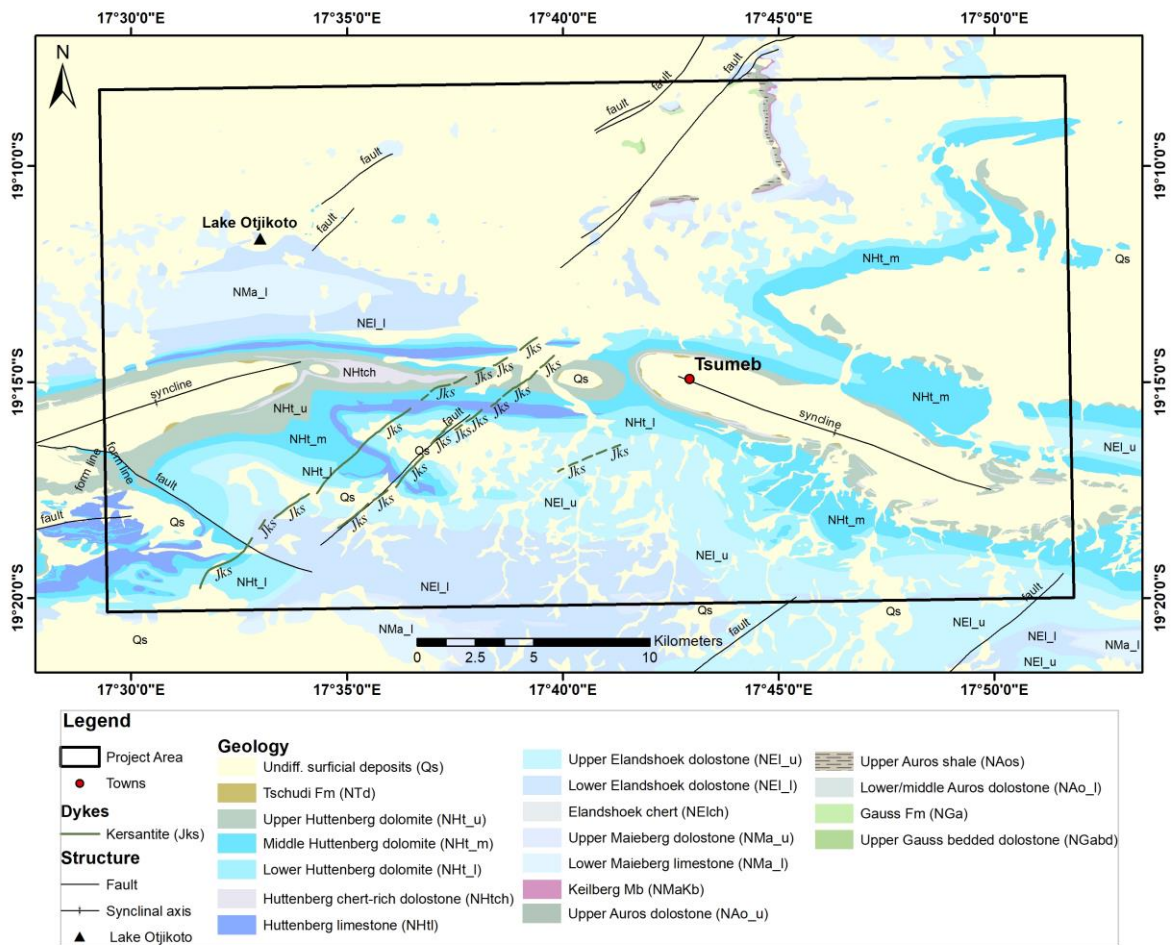


Figure 1.2: Geological map of Tsumeb and surrounding areas.

Chapter 2 LITERATURE REVIEW

2.1 Previous studies

Results of the study by Křibek and Kamona (2005) showed that large tracts of residential, industrial and commercial land in and around Tsumeb were heavily contaminated by heavy metals. These metals were observed in elevated concentrations of; Pb, Zn, Cu, Cd, As and Co in soils, grasses and vegetable around the town (Křibek, 2011; Mapani et al., 2014; Křibek et al., 2014). A study of urine and blood samples in 154 and 148 individuals respectively from the Tsumeb area revealed that there is a direct link between Pb, As, Cd contaminated soils and the levels of these heavy elements in the two selected media (GSN, 2006; GSN, 2008; Křibek, 2011). A number of research studies have been conducted in the Tsumeb area by the Geological Survey of Namibia in partnership with institutions such as University of Namibia and other international partners following the town council's request in 2005 for input into the town's proposed extension plan (Křibek and Kamona, 2005; GSN, 2006; GSN, 2007; GSN, 2008; Ettler et al., 2009; Mapani et al., 2014; Ellmies et al. 2015; Křibek, 2016).

The series of studies conducted revealed a wealth of information on the effects on the environment of the over hundred years of mining history in Tsumeb. Mapani et al. (2014) reported heavy metal contamination of vegetables (marula fruits, pumpkins, chilli, and tomato) that correlates with the heavy metal values of the underlying contaminated top soils. Grasses on farm Tsumore 761 and Dannenberg 478 is reportedly affected by contamination especially of Pb, and to a certain extent of As and Mo (Křibek et al., 2014). Křibek and Kamona (2005) also recorded heavy anthropogenic contamination by metals over an area of approximately 20 km² stretching west of the Tsumeb smelter.

The tailings impoundment is a significant contributor to dust emissions within the area. According to Ellmies et al. (2015), over 500 soil samples have been collected in Tsumeb by various researchers and analyzed for major, minor and trace elements. Results from the analyses shows high concentrations of arsenic, cadmium, copper, lead and zinc which exceed international guidelines (i.e., Canadian, European and WHO) for residential purposes in most of the northern and partially the western parts of Tsumeb area. This led to some areas surrounding the smelter being declared as no-go areas for any kind of land use (Iipinge, 2009). When discussing contamination and pollution studies, it is common practice to refer to standards. The Canadian Council of Ministries of Environment (2007) is now taken as a major benchmark for such studies, followed by World Health Organization (WHO) and European Union (EU) guidelines which are revised from time to time to incorporate knowledge from newer research.

Studies conducted by previous researchers include; mapping of pollution using different media such as soil, as well as bioaccumulation of contaminant elements in plants, vegetables, urine and blood (GSN, 2008). Whereas previous studies focused on total metal concentrations in different media, the actual concentration of only harmful species for each element is unknown. Many metals can be both essential and toxic, and their effects on organisms depend on concentration, speciation, and bioavailability. Some metals essential to plants or animals include Co, Cr, Cu, Fe, Mn, Mo, Ni, and Zn (Smith, 2007). Smith (2007) reports some biological roles of metals that may be vital to human health. For instance, cobalt is a constituent in Vitamin B₁₂ and a factor in formation of red blood cells, Li may be essential for slow respiration on intracellular level.

Ni is important in critical enzymes, Si is important in metabolism and maintaining bone tissue, sulphur promotes enzyme reactions and aids in detoxification of the body and vanadium may play a role in metabolism of bones and teeth. Essential metals can exert adverse effects by being either too high in concentration or too low in concentration. Metals that are nonessential to biological functioning (e.g. Cd, Hg, and Pb) can be toxic at relatively low concentrations (Smith, 2007). The species and forms of metals define the toxicity profile and target organs. For instance, inorganic forms of mercury target the kidney while methylated (organic) mercury is a neurotoxin (Keil et al., 2011).

Another example is arsenic which is a metalloid whose environmental fate, toxicity and mitigation strategies vary according to its complex chemical speciation. Arsenate (As^{5+}) sorbs more strongly to common minerals and is therefore less mobile than uncharged As^{3+} . Arsenite is generally more toxic to humans than arsenate and is retained in tissues to a greater extent than arsenate (NRC, 1999). Since mobility, toxicity and mitigation varies with the speciation of As, it is always important to identify the specific dominant species in an environment. Křibek and Kamona (2005) report that heavy metal contents in the topsoil layer of the contaminated area reach 170 mg/kg for As, 35 mg/kg for Cd, 650 mg/kg for Cu, and 450 mg/kg for Pb. Gallium, germanium and thallium which accompany lead, zinc and copper were also found in the Tsumeb ore. Thallium > 0.5 ppm is restricted to the Smelter Complex Area. Contamination haloes formed by gallium (> 6.0 ppm Ga) and germanium (> 0.4 ppm) are located northwest of the Smelter Complex (Křibek and Kamona, 2005). Solid emissions from the smelter contain high amounts of sulphur dioxide, copper, lead and other metals such as Zn, As, Cd and Hg. The dust contains more than 85 wt. % of fine-grained particles of less than 10 μm (PM_{10}) that are hazardous to the human respiratory system (Křibek and Kamona, 2005).

Křibek & Kamona's study was the first of many studies to analyse the degree of metal and sulphur contamination of soils and agricultural plants in the Tsumeb region. Their study laid a foundation for many other studies which followed. Modelling of sulphur dioxide & dust fallout revealed contamination of the Tsumeb Town area by SO₂ emissions. It was also discovered that 25.8 % of grass samples exceed the threshold of the As concentration in dry feedstock according to the Czech limits, 54.8 % exceed the threshold for Mo and 12.9 % the threshold for Pb (Křibek and Kamona, 2005). Ettler et al. (2009) conducted a study on mineralogy and environmental stability of slags from the Tsumeb Smelter. The study comprised of detailed mineralogical investigations of three different slags from three different smelting technologies. Bulk chemical analysis was done, and speciation/solubility modelling with the software PHREEQC as well as batch leaching tests. Results showed that the slags are enriched in metals and metalloids and that the toxicity limits defined by United States Environmental Protection Agency (USEPA) for the toxicity characteristic leaching procedure (TCLP) test were exceeded for Cd, Pb and As. The authors also discovered that there were complex arsenates dissolving and flushing significant amounts of As, Pb, and Cu in the environment. Mapani et al. (2014) investigated the contamination of agricultural products in the surroundings of the Tsumeb Smelter Complex. A variety of crops were studied comprising of field crops (pumpkin and maize), fruit crops (marula, papaya, chilli pepper, vegetables (tomato, parsley, beans and carrot) from commercial farms situated 1 to 1.5 km to the west of the smelter complex as well as private farms in the Nomtsoub suburb of the Tsumeb town. Bioaccumulation of the toxic elements lead, cadmium and arsenic was evident in all plant samples. The coefficients for arsenic revealed a generally low degree of contaminant uptake by the plants.

Stem crops (maize, chilli, tomato, beans) and fruit trees (marula, pawpaw) showed the lowest values. In contrast, arsenic uptake by root vegetables like carrots and leafy vegetables like parsley was found to be high (Mapani et al., 2014). Křibek et al. (2014) studied the impact of ore processing on the environment in the Tsumeb area to determine the extent of the past industrial pollution, on soils and grasses. The study involved geochemical mapping of top soils, sediments and grass sampling. Numerical modelling of emissions from the smelter using Symos'97 program was also conducted. The main results showed that dust sampled from the baghouse of the Tsumeb smelter contained high amounts of both sulphur and metals. The sources of contamination identified included the smelter, tailings ponds and slag dumps. However, according to the modelling results, the expected concentration of SO₂ was found to be relatively low at less than 0.1 µg.m⁻³. Ellmies et al. (2015) also investigated the bioaccumulation of heavy metals and specific contaminant uptake by various crops. Sampling was also done in soil, water, vegetable material and fish. Results showed critical concentrations of arsenic, cadmium, copper and lead which partly exceed Canadian criteria (Contaminated sites clean up criteria 1999, updated 2006) and Germany (Eikmann-Kloke-values for soil contamination, 1993) for residential and agricultural land uses. The World Health Organization (WHO) Codex Alimentarius (2001) and European Union EU (2006) were applied for the interpretation of metal concentrations in vegetable materials. The various heavy metals were found to form a plume to the west of the Tsumeb Smelter and mining area. In general, it was observed that the closer the area is located to the historic and current smelter complex, the higher the contaminant concentration. The heavy metal concentrations of most of the fruits and vegetables generally correlated with the heavy metal concentrations of the underlying soil (Ellmies et al., 2015).

Root and leaf vegetables showed comparably high concentrations of the heavy metals while stem vegetables and fruits were less affected (Ellmies et al., 2015). This is consistent with Adriano (2001)'s observation that metal distribution in plants generally decreases from root to stem and leaf to edible parts. The high concentrations of metals in leaf vegetables in this case is contrary to Adriano (2001)'s observation and can be attributed to windborne dust (Mapani et al., 2014). Ellmies et al. (2015)'s study partly aimed at guiding urban and regional land use planning. Alternative future residential areas were proposed to be delineated to the south and east of the town. A recommendation was also given to cease any agricultural land use activities near the smelter especially in the area towards the west and north of the smelter where the study recommended that a buffer zone should be established due to bioaccumulation of lead, cadmium and arsenic which was evident in all plant samples (Ellmies et al., 2015).

According to Křibek et al. (2016), distribution of As, Mo, and Pb in grass on the regional scale clearly corresponds with the distribution of these metals in the topsoil. Křibek et al. (2016) modelled the dispersion of dust and SO₂ emissions from the smelter to delineate the contaminated area and to assess the health risks. The modelling results were verified by ground-based geochemical survey of soil and grass in the area. A good correlation between the modelling of dust fallout and the ground geochemical survey was observed. In both cases, the strongest contamination is tied to the immediate vicinity of the Tsumeb smelter, and the aureole of contamination extends along the prevailing wind direction, i.e. WNW and to a lesser extent to the south (Křibek et al., 2016). The modelling results, as well as the results of ground geochemical survey show that dust fallout strongly affected the Pasadena 477 Farm west of the smelter (Křibek et al., 2016). In a move that was applauded by political leadership and environmentalists alike, Dundee Precious Metals opened a sulphuric acid plant at the old Tsumeb Smelter in early 2016.

The plant captures sulphur dioxide emissions that result from the mineral smelting process and uses these gases to produce sulphuric acid, a critical component in mining and smelting operations. This exercise is said to be able to eliminate about 95 percent of toxic emissions which are normally pumped into the air by the smelter. This new development will go a long way in reducing the negative environmental effects of smelting. <https://www.newera.com.na/2016/04/07/geingob-opens-n3-billion-sulphuric-plant-tsumeb/> .

Apart from the Tsumeb area, environmental studies have also been conducted elsewhere in Namibia including in the Roshpinah and Kombat areas. The Rosh Pinah study which was conducted in 2007 involved geochemical characterization of groundwater and soil contamination in the surroundings of Rosh Pinah Zinc and lead Mine (Amkongo & Kawali, 2007). The study area is located approximately 20 km north of the Orange River on the eastern fringe. The main objectives of the study was to identify the extent of groundwater and soil contamination by heavy metals and anions derived from the Rosh Pinah mining area as well as to test the controls of contamination. Groundwater samples were analysed for trace metals and major cations using ICP-MS and ICP-AES at the University of Stellenbosch in South Africa. Soil samples were analysed for trace elements using ICP-MS at the council of Geoscience in Pretoria, South Africa. XRF analysis was conducted at Rhodes University in South Africa (Amkongo & Kawali, 2007). Results showed that the mining area particularly the tailings dam was the main source of soil and groundwater contamination at Rosh Pinah. The contamination was not critical as metal contaminations were still below the Germany and Netherlands soil guideline values. Topography and wind were found to be the major controls of heavy metal contamination of soil and stream sediments at Rosh Pinah (Amkongo & Kawali, 2007).

A similar study on the geochemistry of mine tailings and behaviour of arsenic was conducted at Kombat in northeastern Namibia in 2014 with the goal to determine the processes governing the mobility of contaminants especially arsenic in mine tailings and determine which contaminants could present serious risks for the surrounding environment (Sracek et al., 2014). Sequential extraction for selected bulk sediment samples were performed using the BCR procedure. Speciation modelling was performed using the program PHREEQC. Among seven analysed elements, copper and lead showed significantly high concentrations in tailings (up to 9086 mg/kg and 5589 mg/kg). As a result of improper tailing protection from erosion, adjacent arable soil west of the tailings dam had high Cu and Pb concentrations (up to 150 mg/kg and 164 mg/kg respectively) exceeding Canadian guideline values for agricultural land use (63 mg/kg and 70 mg/kg respectively) (Sracek et al., 2014). The combined pollution index showed high contamination. Given the fact that carbonate minerals dominated the tailings, the drainage was neutralized and lead and copper are rendered immobile (Sracek et al., 2014). The sequential extraction fractions showed that the first two soluble sequential fractions of soil do not have significant amounts of copper and lead. The study recommended rehabilitation of tailings dams. It also recommended limiting the use of certain crops that accumulate lead and copper in the edible parts of the plant e.g. root vegetables as well as leafy vegetables in order to reduce potential risks (Sracek et al., 2014).

Metals associated with urban soil are of environmental concern because of their direct and indirect effects on human health. Soil is a major reservoir for contaminants as it possesses an ability to bind to various chemicals. These chemicals can exist in various forms in soil and different forces keep them bound to soil particles. Shivakumar et al. (2012) emphasizes that it is essential to study these interactions because the toxicity of chemicals may strongly depend on the form in which they exist in the environment. Environmental factors may change and cause leaching of heavy metals bound to the soil particles (Shivakumar et al., 2012).

In line with the aforementioned background, Shivakumar et al. (2012) conducted research on speciation and geochemical behavior of heavy metals in soils of an industrial area in Mysore City, India. The purpose of the study was to identify heavy metals with dangerous environmental load and to find out the environmental impact of the elements: Fe, Cr, Cu, Zn and Ni. Soil samples were analyzed for pH, organic matter and electrical conductivity.

Total and available heavy metal concentrations were determined by Atomic Absorption Spectrometry (AAS). Heavy metal speciation carried out in soil samples showed that all metals were mainly associated with the oxidisable and residual fraction which allowed prediction of their mobility in the soil samples (Shivakumar et al., 2012). Shivakumar et al. (2012)'s research work indicated that application of sequential procedures for determination of speciation of heavy metals in soil of industrial areas provides an assessment of the real mobility of heavy elements.

Similarly, Myung and Thornton (1996) researched on heavy metal contamination of soils and plants around a mine. In that study, soils were sampled in and around a Pb-Zn mine in Korea from sites including the mine dump, nearby household gardens and uncultivated areas. Various plants were also collected in the household gardens including corn grain, red peppers, soybean leaves, spring onions and tobacco leaves. Similar materials were taken from a nearby control area. Analysis by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) included the metals Cd, Cu, Pb and Zn. Results show that concentration of heavy metals in soils decreased exponentially with distance from the mine source mainly due to dispersion by water and topography (Myung and Thornton, 1996). Heavy metal bioaccumulation was evident in the plants. Concentration in the plant species sampled generally decreased in the order: tobacco leaves>spring onions>soybean leaves>red pepper>corn even though this order varied for specific elements (Myung and Thornton, 1996).

The ratios of metal concentrations in plants to those in soils decreased in the order Zn>Cd>Cu>Pb. Myung and Thornton (1996) also investigated factors influencing the bioavailability of metals in soils and uptake into food crops. These were found to include total metal concentration in soil, soil pH, cation exchange capacity, organic matter content, soil texture and interaction among the elements determined. It concluded that the total metal concentrations in soil and pH were the main factors influencing metal content in plants. Olatunde and Onisoya (2017) assessed heavy metal concentrations in pawpaw (*Carica papaya* Linn) grown around seven Automobile Workshops in Port Harcourt Metropolis in Nigeria. 20mX20 m quadrats were laid out for soil and *C. Papaya* tissue sampling. One composite soil sample was collected from the topsoil (0-15cm depth) around each of the automobile workshops. Tissues (root, stem, leaf and fruit) of *C. papaya* were collected. Standard laboratory techniques were used to determine the pH, electrical conductivity and heavy metals; Pb, Hg, Cd, Cu and Zn in the soil samples and *C. papaya* tissues.

Correlation statistics were used to determine the relationship of heavy metal concentrations between soil and *C. papaya* tissues. Results showed that *C. papaya* tissues and supporting soil had significantly higher levels of pH, EC and heavy metals in the sampled plots than the control plot. The heavy metal concentrations in *C. papaya* and soil occurred in the decreasing order of Pb>Cu>Hg>Zn>Cd. Bioaccumulation of heavy metals in *C. papaya* is evident around automobile workshops and Pb, Hg, Cd concentrations were found to be above the permissible limits for human consumption according to World Health Organization (WHO) standards. Consumption of food materials grown around automobile workshops could therefore pose health risks. According to Vullo et al. (2008), anthropogenic activities are responsible for the introduction of increasing amounts of heavy metals in the environment.

Metal production, leather and tanning processes, gas and electricity production, sewage and waste disposal and related activities, contribute to the presence of copper, cadmium, zinc, lead, chromium and nickel in soil and surface and ground waters if waste products are not properly treated before discharged. Exposition to heavy metals causes irreversible damage to living organisms; their presence above certain limits is a potential risk to the environment and human health (Vullo et al. 2008).

“In order to evaluate this risk, total metal concentration is a poor indicator because reactivity, bioavailability and toxicity depend on the distribution of the different metal species in that particular environment. An understanding of metal speciation is required” (Vullo et al., 2008). Heavy-metal-contamination of foods may lead to serious depletion of nutritional components like Fe and Vitamins and this may cause physiological and pathological disorders (Tchounwou et al., 2012). Soil contamination by heavy metals is a problem that has significant financial implications both directly and indirectly. Khan et al. (2015) identified the following implications; reduction in crop production, financial loss in terms of health costs, loss of jobs due to ill-health, poverty associated with health effects and low crop yields, foods are rendered nutrient deficient due to heavy metal contamination.

2.2 Heavy Metals in the environment

2.2.1 Arsenic- Occurrence, use and toxicity

Arsenic has an atomic number of 33 and an atomic mass number of 74.9. Arsenic's toxicity is dependent largely on the valence state, solubility, rate of absorption and elimination. The three major groups for arsenic are arsine gas (-3 oxidation state), inorganic and organic forms. Arsine gas is the most toxic arsenic radicle. Some inorganic arsenic compounds such as arsenite (trivalent), arsenate (pentavalent), arsenic oxide and gallium arsenide also have a high toxic potential (Keil et al. 2011).

The highly poisonous arsenic is distributed widely in nature. It is ranked as twentieth in abundance among the elements in the Earth's crust. Arsenic exists in four valence states: -3, 0, +3, and +5 (Naja and Volesky, 2012). According to Naja and Volesky (2012), Arsenite As^{3+} , is the dominant form under reducing conditions. Arsenate, As^{5+} , is generally the stable form in oxygenated environments. Elemental arsenic is not soluble in water. Arsenic salts exhibit a wide range of solubilities, depending on pH and ionic environment. The water-soluble arsenite (As^{3+}) is considered to be the most toxic form, and arsenate (As^{5+}), the less toxic form (Naja and Volesky, 2012). Organic arsenic species which are abundant in seafood are much less harmful to health, and are readily eliminated by the body (Naja and Volesky, 2012).

The release of arsenic into the environment occurs in a number of ways including through industrial effluents, pesticides, insecticides, wood preservative agents, combustion of fossil fuels and mining activity (Naja and Volesky, 2012; USGS, 2015). Arsenic may be obtained from copper, gold, and lead smelter dust as well as from roasting arsenopyrite, the most abundant ore mineral of arsenic. Global resources of copper and lead contain approximately 11 million tons of arsenic (USGS, 2015). Tchounwou et al. (2012) report that the toxicity of arsenic in humans, is depended on several factors including the exposure dose, frequency and duration, the biological species, age, and gender, as well as on individual susceptibilities, genetic and nutritional factors. Majority of human toxicity from arsenic cases have been associated with exposure to inorganic arsenic. Inorganic trivalent arsenite (As^{3+}) is 2 to 10 times more toxic than pentavalent arsenate (As^{5+}). Arsenic (As^{3+}) can affect different organ systems by inactivating over 200 enzymes through binding to thiol or sulfhydryl groups on proteins countries (Naja and Volesky, 2012).

The organic arsenic compounds have been used as feed additives to control diseases and increase body weight in pigs and poultry since the mid 1940's and are still used today in various countries (Naja and Volesky, 2012). High-purity (99.9999%) arsenic metal was used to produce semiconductors that were used in biomedical, communications, computer, electronics, and photovoltaic applications (USGS, 2015). Arsenic toxicity has been associated with many health problems such as skin lesions, keratosis (skin hardening), lung, kidney and bladder cancer (Naja and Volesky, 2012; ATSDR, 1990). Increased infant mortality and neurological problems are also reported in connection with arsenic toxicity (ATSDR, 1990).

Arsenic is also reported to cause DNA modifications such as aneuploidy, micronuclei formation, chromosome abnormality, deletion mutations, sister chromatid exchange and cross linking of DNA with proteins (Faita et al., 2013). Mäki-Paakkanen et al. (1998) report that; inorganic arsenic can cause DNA strand break even at low concentrations. According to Pierce & Kibriya (2012), arsenic does not directly interact with DNA. It is considered a poor mutagen. It however helps the mutagenicity of other carcinogens. It has been observed experimentally that arsenic genotoxicity is primarily linked to the generation of reactive oxygen species (ROS) during its biotransformation (Lee & Oshimura, 1985; Kessel & Liu, 2002; Nesnow & Roop, 2002). Arsenic leads to cell death through a process of formation of reactive oxygen species (ROS) and reactive nitrogen species (RNS). The presence of reactive oxygen species eventually leads to inflammation, cell proliferation, and eventually to cell death through a number of processes including cytoskeleton rearrangement (Hunt et al., 2014). The enzyme responsible for synthesis of nitric oxide (NO) is inhibited by monomethylated As^{3+} compounds (Hunt et al., 2014). Nitric oxide (NO) is a part of cell regulation, including cellular metabolism, growth, division and death.

Health effects of a permanent exposure to arsenic are among others; skin damages like keratosis and Blackfoot disease, skin, lung, bladder, kidney cancer, increased infant mortality and neurological problems (ATSDR, 1990).

2.2.2 Cadmium - Occurrence, use and toxicity

Cadmium has an atomic number of 48 and an atomic mass number of 112.41. Cadmium is a relatively rare element. It is uniformly distributed in the Earth's crust, where it is generally estimated to be present at an average concentration of between 0.15 and 0.2 mg kg⁻¹. Cadmium occurs in nature in the form of various inorganic compounds and as complexes with naturally occurring chelating agents ((Naja and Volesky, 2012).

Cadmium is generally recovered from zinc ores and concentrates. Sphalerite, the most economically significant zinc mineral, commonly contains minor amounts of cadmium, which shares certain similar chemical properties with zinc and often substitutes for zinc in the sphalerite crystal lattice. The cadmium mineral greenockite is frequently associated with weathered sphalerite and wurtzite (USGS, 2015). According to Bampidis et al. (2013), more than 80% of global cadmium consumption is used in NiCd battery production whereas the rest is used in pigments, coatings and plating, stabilizers for plastics, nonferrous alloys, and other specialized uses (including photovoltaic devices). The use in coatings, pigments, and stabilizers is gradually decreasing in use in recent time due to environmental and health concerns (USGS, 2015). Cadmium has no known biological function in animals and humans but mimics other divalent metals that are essential to diverse biological functions (Bampidis et al., 2013). Cadmium is a heavy metal of considerable environmental and occupational concern. It is widely distributed in the earth's crust at an average concentration of about 0.1 mg/kg (Tchounwou et al., 2012). Once ingested, 0.5 to 7 % (depending on the animal species) of the ingested amount is absorbed into the body.

Ingested cadmium is eliminated very slowly from the body. Cadmium has an estimated biological half-life of 10-30 years (Bampidis et al., 2013). It is generally acknowledged that dietary intake of Cd is the major source of Cd exposure for the general population, excluding smokers (Smolders, 2001).

The tolerable daily intake of Cd is $1 \mu\text{g Cd kg}^{-1}$ /body weight, an equivalent to a daily intake of $70 \mu\text{g Cd}$ for an adult of 70 kg (Smolders, 2001). The following food groups have a significant contribution to dietary Cd intake: cereals, potato, vegetables and fruit. Levels of Cd in food items such as: offal, organs, equine products, shellfish, crustacean, cocoa, mushrooms and some seeds are high (Smolders, 2001). The food chain contamination by Cd normally starts with soil-plant transfer of Cd. Cadmium are easily absorbed by plant roots and transferred to the above-ground parts (Smolders, 2001). Increases in cadmium levels in soil result in an increase in the uptake of cadmium by plants, although the extent to which this happens depends on factors such as: soil pH, plant species and the part of the plant, as well as other soil characteristics (Bampidis et al., 2013; Smolders, 2001). According to Smolders (2001), the uptake of Cd by plant is proportional to increasing soil Cd when soil contains substantial concentration of Cd^{2+} salts. The Cd^{2+} salt linear increase has been observed in different field trials Smolders (2001). This linear trend is maintained within the environmentally relevant range (up to approximately 20 mg kg^{-1}) above which curvilinear trends are observed (Smolders, 2001). The following symptoms of cadmium toxicity in animals have been recorded: kidney and liver damage, anaemia, retarded testicular development or degeneration, enlarged joints, scaly skin, and reduced growth and increased mortality. Cadmium toxicity also causes a disease which is known as ‘itai-itai which means ouch-ouch in Japanese (Bampidis et al., 2013; ATSDR, 1990). Its victims suffer from pain in the joints, pseudo-fracturing of bones, skeletal deformation and renal dysfunction (ATSDR, 1990).

Data from experimental animals and humans show that pulmonary absorption is higher than gastrointestinal absorption. The gastrointestinal absorption of cadmium is influenced by the type of diet and nutritional status. Although cadmium accumulates in the placenta, transfer to the foetus is low (WHO, 2011).

2.2.3 Cobalt - Occurrence, use and toxicity

Cobalt which has an atomic number of 27 and a molecular mass of 58.93 is a naturally occurring element with one stable isotope (Co^{59}) and 26 known radioactive isotopes (Kim et al., 2006). Anthropogenic sources include the burning of fossil fuels, sewage sludge, phosphate fertilizers, mining and smelting of cobalt ores, processing of cobalt ores, processing of cobalt alloys, and industries that use or process cobalt compounds.

Table 2.1 shows some cobalt species that exist in nature. There are three valence states of Cobalt (0, +2 and +3). Cobalt (II) is more stable than Cobalt (III). Cobalt is soluble in dilute acids and even in water at 1.1mg/l (Kim et al., 2006). Cobalt in the form of Vitamin B (hydroxocyanocobalamin) is essential for humans. Vitamin B₁₂ is essential for the production of red blood cells (Kim et al., 2006). The metabolism of Vitamin B₁₂ and the daily ingestion of cobalt-containing foodstuffs provide the most significant source of cobalt in the human body (Kim et al., 2006).

Table 2.1: Example of cobalt species with their physical and chemical properties. The table was obtained from Kim et al (2006).

Species	CAS No.	Relative Molecular mass	Molecular Formula	Melting point	Solubility
Cobalt	7440-48-4	58.93	Co	1493°C	Insoluble in water
Cobalt (II) acetate	71-48-7	177.03	Co(C ₂ H ₄ O ₂) ₂	No data	Soluble in water, 2.1 g/100g methanol
Cobalt (II) acetate tetra hydrate	6147-53-1	249.1	Co(C ₂ H ₄ O ₂) ₂ .4H ₂ O	140°C	Very soluble in water
Cobalt (III) acetate	917-69-1	236.07	Co(C ₂ H ₄ O ₂) ₃	Decomposes at 100°C	Soluble in water, alcohol, acetic acid
Cobalt(II) carbonate	513-79-1	118.94	CoCO ₃	Decomposes	0.18 g/100g water
Cobalt carbonyl	10210-68-1	341.9	CO ₂ (CO) ₃	51°C	Insoluble in water, soluble in Ether
Cobalt(II) chloride	7646-79-9	129.84	CoCl ₂	724°C	450 g/l water, 544g/l ethanol, 86 g/l acetone
Cobalt(II) hydroxide	21041-93-0	92.95	Co(OH) ₂	No data	0.0032 g/l water
Cobalt(II) mesoporphyrin	21158-51-0	621.2	C ₃₄ H ₃₄ CoN ₄ O ₄	No data	No data
Cobalt(II) naphthenate	61789-51-3	407.0	Co(C ₁₁ H ₁₀ O ₂) ₂	140°C	Insoluble in water
Cobalt(II) nitrate	10141-05-6	182.96	Co(NO ₃) ₂	Decomposes at 100-105°C	Soluble in water (133.8 g/l) ethanol, acetone
Cobalt(II) nitrate hexahydrate	10026-22-9	291.03	Co(NO ₃) ₂ .6H ₂ O	55°C	133.8 g/100ml water at 0°C
Cobalt(II) oxide	1307-96-6	74.93	CoO	1935°C	Insoluble in water
Cobalt(III) oxide	1308-04-9	165.86	Co ₂ O ₃	Decomposes at 895°C	Insoluble
Cobalt(II,III) oxide	1308-06-1	250.80	Co ₃ O ₄	O ₂ at 900-950°C	Insoluble
Cobalt (II) sulfate	10124-43-3	154.99	CoSO ₄	Decomposes at 735°C	36.2 g/100 ml water at 20°C
Cobalt (II) sulfate heptahydrate	10026-24-1	281.1	CoSO ₄ .7H ₂ O	96.8°C	60.4 g/100 ml water at 3°C
Cobalt sulfide	1317-42-6	91.0	CoS	>1116°C	Insoluble in water

Background levels of cobalt are not known to be associated with adverse health effects in humans. Several milligrams of cobalt can be consumed by humans per day in their diet without causing any adverse effects (Kim et al., 2006). During clinical treatment for anaemia, higher daily doses of cobalt are normally administered without adverse effects to the heart. Historically, small amounts of cobalt (1-2 parts per million) in the form of cobalt chloride were added to a brand of beer as a foam stabiliser (Kim et al., 2006). Due to this practice, there was a reported increase in incidents of fatalities due to cardiomyopathy in those who consumed this particular beer in large quantities of more than 8 pints per day (Kim et al., 2006). Cobalt exposures leading to death ranged from 0.04 to 1.14 mg/kg body weight per day for several years (approximately 8-30 pints per day). Cardiomyopathy induced by beer cobalt bearing beer was similar to alcohol myopathy except that the onset was abrupt (Kim et al., 2006). Cobalt is typically associated with copper or nickel. The elemental cobalt in mined ores tends to be at 0.1%. Approximately 44% of the entire world's cobalt production comes from nickel ores (Kim et al., 2006). Identified world terrestrial cobalt resources are approximately 25 million tons (USGS, 2015). "The majority of these resources are in sediment-hosted stratiform copper deposits in Congo (Kinshasa) and Zambia; nickel-bearing laterite deposits in Australia and Cuba; and magmatic nickel-copper sulphide deposits hosted in mafic and ultramafic rocks in Australia, Canada, Russia, and the United States" (USGS, 2015). Cobalt resources have been identified in manganese nodules and crusts on the floor of the Atlantic, Indian, and Pacific Oceans and are estimated at more than 120 million tons (USGS, 2015).

2.2.4 Lead - Occurrence, use and toxicity

Lead has an atomic number of 82 and a molecular mass of 207.2. Lead (Pb) occurs naturally in the environment, but its industrial use e.g., in mining, smelting, processing, plumbing, alloys, pigments, batteries and ceramics, etc. has resulted in increased levels in the soil, water and air (Tchounwou et al., 2012). In the mining industry, the following lead ores are found: galena (lead sulphide), anglesite (lead sulfate), cerussite (lead carbonate), mimetite (lead chloroarsenate) and pyromorphite (lead chlorophosphate) (Tchounwou et al., 2012). Channels through which one can be exposed to lead are through food, water, soil, dust and air. Lead exists both in organic and inorganic forms (Vahter & Concha, 2001). In the environment, inorganic lead predominates over organic lead (Bampidis et al., 2013). According to Bampidis et al. (2013), lead is one of the most common poisonings in farm animals. All forms of lead are toxic. It affects almost every system in the animal body, including the blood, the cardiovascular, renal, endocrine, gastrointestinal, musculoskeletal, immune and reproductive systems. The most critical target for lead appears to be the central nervous system (CNS). The developing brain is more at risk, because lead has the potential to cause impaired cognitive development and intellectual performance in children even at low exposure levels. Inorganic lead is classified as a carcinogen (Bampidis et al., 2013). According to Keil et al. (2011), children absorb a greater proportion of lead compared to adults. The potential for adverse effects of lead exposure in children is heightened because of the following reasons: intake of lead per unit body weight is higher for children than for adults, an increased intake of lead through injection due to their tendency to put things in their mouths; physiological uptake rates of lead in children are higher than those in adults (Tong et al., 2000).

Young children are more vulnerable to the effects of lead than adults due to the fact that their systems are still developing (Keil et al., 2011). According to Keil, et al. (2011), lead exposure is also a bigger concern due to the fact that lead readily passes the placental barrier. Exposure during pregnancy poses a risk of impaired foetal and infant development. The bioavailability of lead is dependent on the form of lead whether it's inorganic, organic or metallic. It is also dependent on the quantity ingested, the age of the individual and their current dietary status (Keil et al., 2011).

Chapter 3 METHODOLOGY

This chapter discusses the samples collected, the sample collection procedures and the analytical methods that were employed to obtain results.

3.1 Sampling

The sampling was designed to cover areas that are inhabited by people and deemed to be contaminated from the effects of mining and processing. Figures 3.1, 3.2 and 3.3 shows soil sampling sites just outside the school grounds in Nomtsoub suburb. The materials sampled were soils, vegetation and fruits. The sampling took into account the plants available at the time of sampling as well as food sources used by people so as to establish their level of contamination and risk to the population in that area. The sampling campaign took approximately one week.

3.1.1 Soil Sampling

Surface soil samples (0-5 cm depth) were sampled by hand auger from the Nomtsoub suburb of the Tsumeb town according to the Milseunic (2014) procedure. The soil samples were later composited so that at least 4 subsamples were collected from an area of 10x10 metre square within the area of study and composited to one sample. Samples of plants were taken from sites where soil samples have been obtained. Soils were dried in an oven at 25 °C and sieved to 10 mesh (< 2 mm, quartered and ground to 80 mesh (< 180 µm) in a mortar. All soil samples in this current study were top soils. Earlier studies mapped both top soils and lower soil horizons and information on the natural enrichment is available (Křibek & Kamona, 2005).

Soils were collected at various locations (Figure 3.1-3.8) such as schools, houses, vegetable gardens, sports grounds and near the Tsumeb Corporation Limited (TCL) compound where approximately 2000 former TCL workers reside. These sampling sites were chosen on the basis of resident's potential exposure to possibly contaminated soil. Nomtsoub suburb is also one of the suburbs that were sufficiently investigated by previous researchers. This makes it a good site for comparing results of previous research which involved total metal concentrations to the current study which assessed specific potentially harmful elements.

Control samples were collected at Lake Otjikoto which is located some 15 km northwest of the town of Tsumeb (Figure 3.4). Other control soil samples were collected from Farm Manheim which is approximately 25 km northeast of Tsumeb. The control sites were chosen on the basis of distance away from the smelter which is considered to be the main source of contamination. Figure 3.1-3.8 show the various sites at which samples were taken.



Figure 3.1: A sampling site just outside school grounds in the Nomtsoub Suburb



Figure 3.2: School children playing in the schoolyard in Nomtsoub suburb



Figure 3.3: Children playing on contaminated soil outside the TCL compound



Figure 3.4: Lake Otjikoto where control soil and vegetation samples were collected

3.1.2 Vegetation sampling

Twenty (20) Vegetation samples were collected from the same areas or in the vicinity where soil samples were taken. The following samples were collected: Mango leaves, lemon leaves, sunflower leaves, dried and fresh papaya leaves, marula fruit, marula tree bark, fig leaves and fig fruit. These particular vegetation samples were chosen due to their availability in the area and the fact that they are normally used by the surrounding population and therefore their contamination status has implications on the health of the residents. Sunflower leaves are believed by the locals to have diuretic properties. They are also used as fodder for animals. Lemon leaves are locally believed to be useful for de-worming. They are also used to wrap meat for roasting as well as for garnishing desserts. Mango leaves are believed to be useful in management and treatment of hypertension and respiratory problems. The Papaya leaves drink is believed to boost the immune system.

Control fruit samples were obtained from Farm Manheim some 25 km northeast of the town of Tsumeb. The control site was chosen on the basis of distance away from the smelter which is considered to be the main source of contamination.



Figure 3.5: The TCL compound from where a number of samples were collected



Figure 3.6: Sampling of fig leaves inside the TCL Compound

Sample preparation and analysis

In terms of sample preparation, the vegetation samples were first dried in a controlled environment before sending them to the Bureau Veritas laboratory in Vancouver, Canada. At the Bureau Veritas laboratory, the vegetation samples were ashed at 475 degrees Celsius ($^{\circ}\text{C}$). Bioavailable fractions were extracted using Sequential extraction procedures (SEP) and *aqua regia* (Appendix 4 and 5 respectively). The step by step SEP procedure used is the Tessier et al. (1979) method which is a standard reproducible method used across the globe. Analysis was done using ultratrace Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

A total of 50 samples were obtained comprising 30 soil samples and 20 vegetation samples. Figure 3.7 shows all the sampling locations. Coordinates of sampling locations are attached as Appendix 1.

These samples were analysed using ICP-OES and ICP-MS at the Bureau Veritas Laboratories in Canada with the financial assistance of the UNESCO-SIDA project. Results are attached as Appendix 2 and 3 and also presented in Chapter 4.

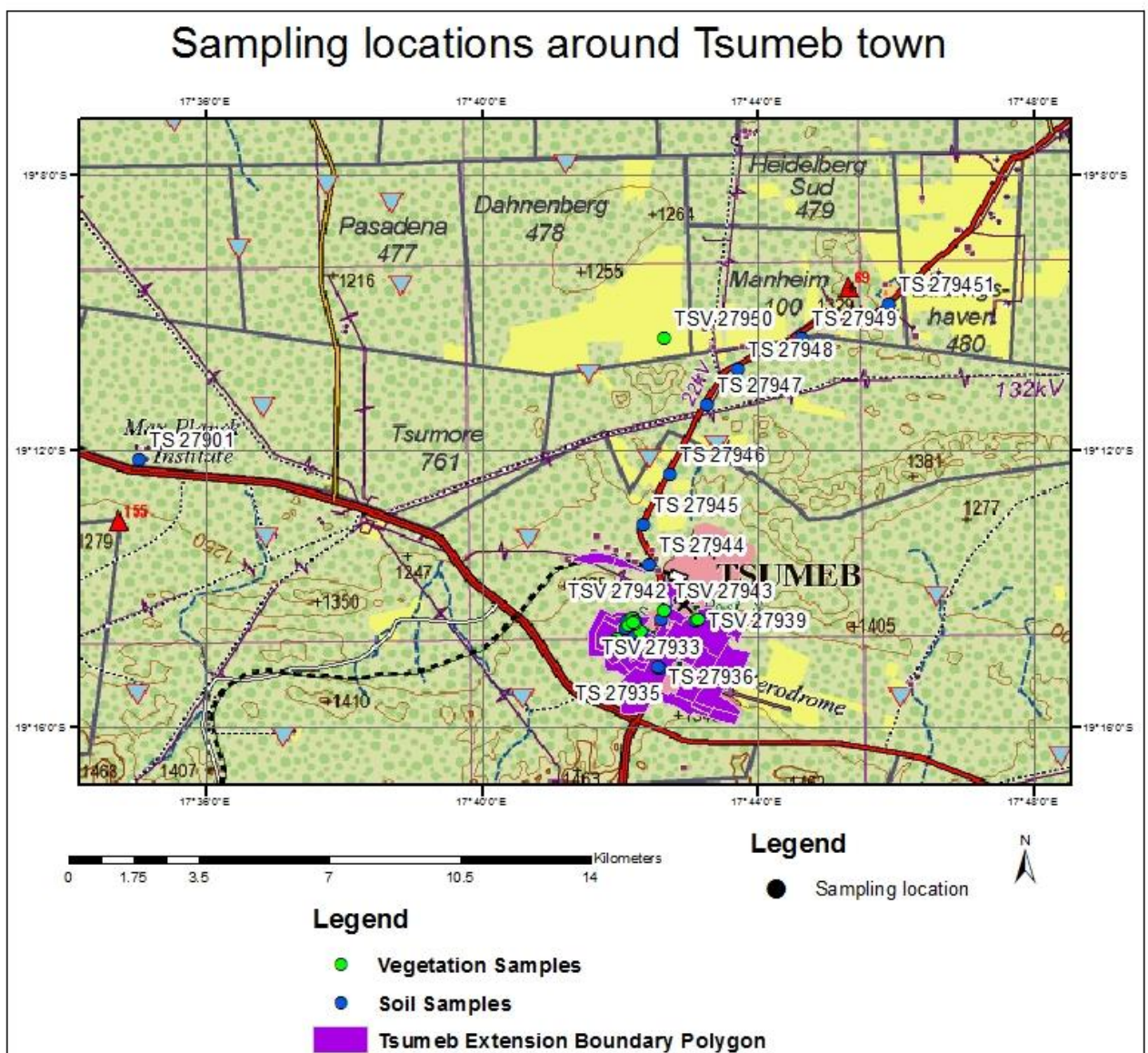


Figure 3.7: Soil and vegetation sample locations in and outside Tsumeb



Figure 3.8: Sampling sites outside the Nomtsoub suburb where construction is currently underway

3.2 Analytical Methods

All vegetation and soil samples were subjected to analysis by ICP-OES and ICP-MS at the Bureau Veritas Laboratories in Canada. Appendices 4 and 5 spell out the procedures that were used. The use of total metal concentration as a criterion to assess the potential effects of heavy metal contamination in soils and other media has limitations. The key limitation is that it implies that all chemical forms of metals negatively impact the environment.

Most elements exist in several forms and valence states, also known as “species”. “Identifying the species of an element that is involved in an exposure can be clinically relevant because different elemental species exhibit unique toxicokinetics and toxic potential” (Keil et al., 2011). Keil et al., (2011) observed that most analytical methods do not differentiate between elemental forms. Most methods generate a “total” element concentration which is not problematic if results are low or as expected. However, if results are high, further tests are needed to evaluate the significance of such results. Arsenic is a good example of this concept because it has 30 known forms of arsenic, with different toxic potentials. To distinguish between the species responsible for an elevated total arsenic result or any other element, a separation step is needed either during sample preparation (e.g. extraction) or analysis (chromatography) (Keil et al., 2011). In this study, separation took place during sample preparation whereby; sequential extraction procedures and aqua regia were used in the extraction of the following targeted species: As^{3+} , Cd^{2+} , Co^{2+} and Pb^{2+} .

Sequential extraction procedures (SEP) offers the potential to gain understanding of the composition of solid wastes. SEP attempts to classify potentially harmful elements by their associations with phases or fractions in soils with the aim of understanding the behaviour of heavy metals in soils. A better understanding of the chemical composition of the soils and plants can enhance environmental management in particular land use planning (Chen & Ma, 2001). The SEP procedure is based on the successive use of aqueous solutions or reagents of increasing aggressiveness, for sequential release of trace elements (TE) associated with the targeted phases (Okoro et al., 2012). According to Okoro et al. (2012), digestion in strong acids such as nitric acid, hydrochloric acid or a mixture such as aqua regia have been commonly used to leach out the recalcitrant metals that are bound to soils in the residual phase. This residual phase has been used to give an estimate of the maximum amount of elements that are potentially mobilizable with changes in the environment.

The amounts of associated metals are also used by some authors as the difference between the total concentration and the sum of the fractions of the metals extracted during the previous steps (Okoro et al., 2012). Appendix 4 provides further information on SEP and its benefits in environmental studies.

3.3 ArcGIS Spatial data Analysis

ArcGIS spatial analyst was used to create contaminant distribution maps (discussed under Chapter 5 of this thesis). ArcGIS spatial analyst is an extension to ArcGIS for desktop that provides tools for comprehensive, raster-based spatial modelling and analysis. Through ArcGIS spatial analyst, users can derive and analyse new information via existing data and build spatial models. Each of the interpolation methods available in the ArcGIS Spatial Analyst extension uses a different approach for determining output cells. In this project, two different interpolation methods were used to come up with the contaminant distribution maps. Below are brief descriptions of how each method works.

3.3.1 Natural Neighbour Method

According to Sibson (1981), the algorithm used by the Natural Neighbour Interpolation tool finds the closest subset of input samples to a query point and applies weights to them based on proportionate areas to interpolate a value. Natural Neighbour can be used for both interpolation and extrapolation. It does not infer trends and therefore, will not produce peaks, pits, ridges or valleys that are not already represented by the input samples. The surface passes through the input samples and is smooth everywhere except at locations of the input samples (Sibson, 1981). Its advantage is that it generally works well with clustered scatter points and can efficiently handle large input data sets.

3.3.2 Inverse Distance Weighted (IDW)

IDW determines cell values using a linear-weighted combination set of sample points. In this method, the weight assigned is a function of the distance of an input point from the output cell location. The greater the distance, the less influence the cell has on the output value. This method should be used when the set of points is dense enough to capture the extent of local surface variation needed for analysis (Sibson, 1981).

3.4 Ethical considerations

The Bureau Veritas Laboratory's safety and waste disposal regulations were followed in disposing of samples. No direct measurements were done on the residents of Tsumeb during field observation and sampling process, therefore no special permissions were required from them.

Chapter 4 RESULTS

4.1 Analytical results of soil samples

This chapter reports on the results obtained from the laboratory analysis of soil and vegetation samples using ICP-MS and ICP-OES.

Thirty (30) soil samples and twenty (20) vegetation samples were analyzed for their heavy metal concentration at the Bureau Veritas Laboratory in Vancouver, Canada. The study analyzed the speciation of heavy elements that are prone to be absorbed in the human digestive system and by plant tissue (bioavailable fractions). The analytical results of potentially harmful heavy elements in soil are attached in Appendix2. Table 4.1 shows statistical data for the potential harmful elements.

Table 4.1: Statistical data for potential harmful elements: arsenic, cadmium, cobalt and lead in top soils of Nomtsoub, Tsumeb area. Number of samples: 30. The Tsumeb Mine Pit results were treated as outliers and therefore are not included in the calculations of these statistical parameters.

		PERCENTILES						
Component	Min.	10%	25%	50% (median)	75%	90%	Max	Mean
Arsenic	7.0	11.0	16.0	38.0	68.0	148.4	195.0	55
Cadmium	0.4	0.5	1.2	2.3	5.9	10.3	28.6	4.8
Cobalt	1.9	2.4	2.6	3.2	3.6	5.3	12.0	3.6
Lead	25.9	32.3	58.8	116.6	270.7	544.8	1835.1	255

Explanation: Min: Minimal value, Max: Maximum value.

The results of the 30 soil samples analysed by ICP-OES and ICP-MS are also expressed in the form of bar graphs for better visualization. The bar graphs were generated using Microsoft Excel Windows 10 (Figure 4.1 to Figure 4.4).

Arsenic (III) in soil samples

Results indicate that the concentrations of the potentially harmful heavy element Arsenic (III) in top soil samples in this study ranged between 7 mg/kg and 421 mg/kg (Figure 4.1). The lowest arsenic concentration of 7 mg/kg is recorded in sample TS 27951 which was collected approximately 25 km northeast of Tsumeb along the Tsintsabis road. The highest content of arsenic (421 mg/kg) was detected only in one sample collected from the old Tsumeb Mine pit and is considered an outlier because it represents primary mineralization of the deposit. The next highest concentration was 195 mg/kg and it was recorded in a sample collected within 8 km of the mine along the Tsintsabis road. Ninety (90) % of the samples had values below 148.4 mg/kg (Table 4.1). The average/mean concentration of arsenic in the soil samples was 55 mg/kg and the median was 38 mg/kg.

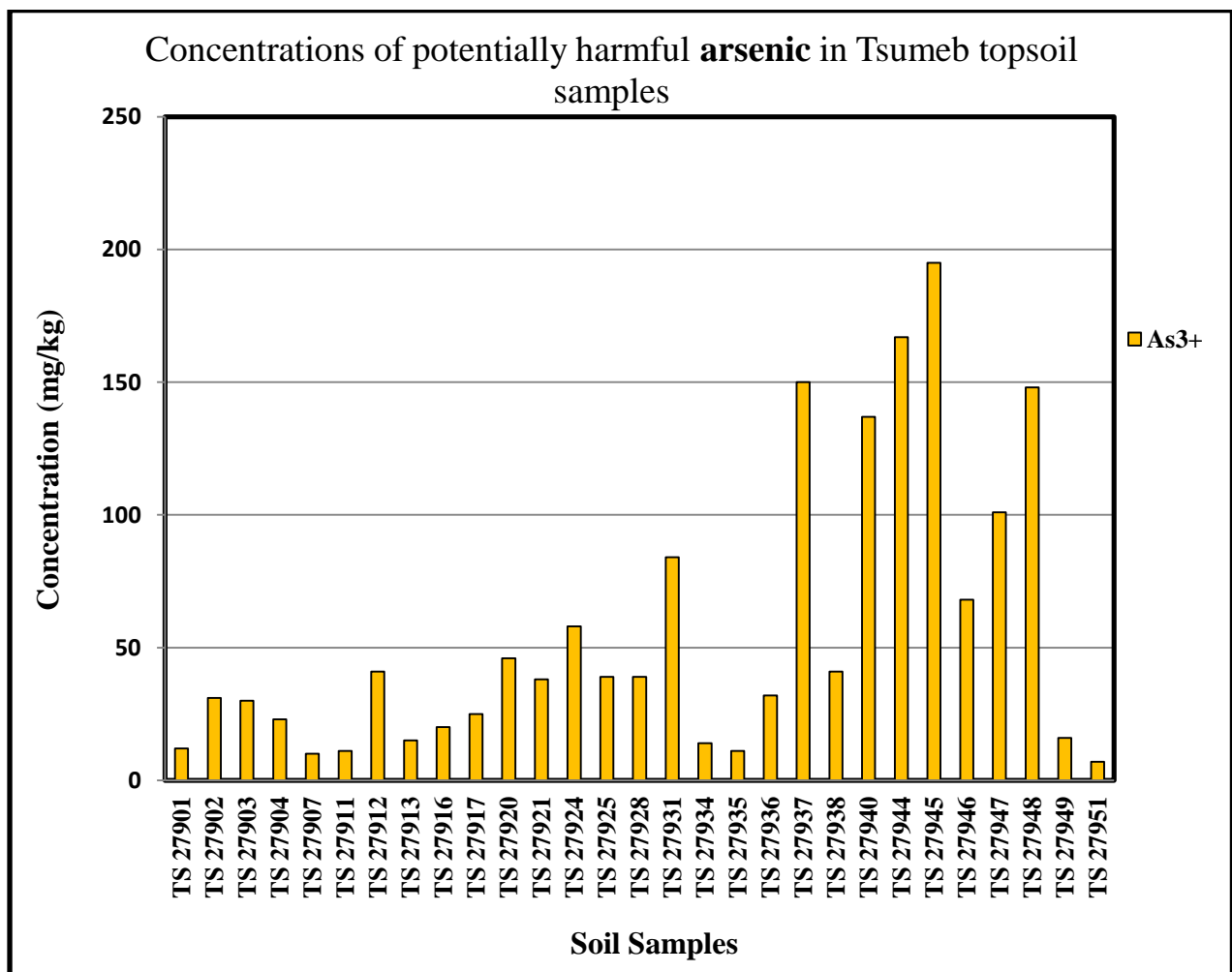


Figure 4.1: Concentration of potentially harmful arsenic (As^{3+}) in Tsumeb top soil samples

Cadmium (Cd^{2+}) in soil samples

Cd^{2+} concentrations in the soil samples in this study ranged between 0.5 mg/kg and 35.6 mg/kg. The lowest concentration of cadmium (0.5 mg/kg) was recorded at Lake Otjikoto 15 km west of Tsumeb where a control sample was taken. The highest concentration (35.6 mg/kg) was recorded in sample TS 27941 which was collected in the vicinity of the Old Tsumeb Open Pit Mine (Figure 4.2). This sample is considered an outlier. The next highest result is 28.6 mg/kg. However, more than 90% of the soil samples had Cd^{2+} concentrations below 15 mg/kg (Table 4.1).

The average concentration of Cd^{2+} is 4.8 mg/kg and a median of 2.3 mg/kg was calculated. Results of samples collected from the old Tsumeb Mine pit were considered outliers and therefore were not used in the calculation of statistical parameters.

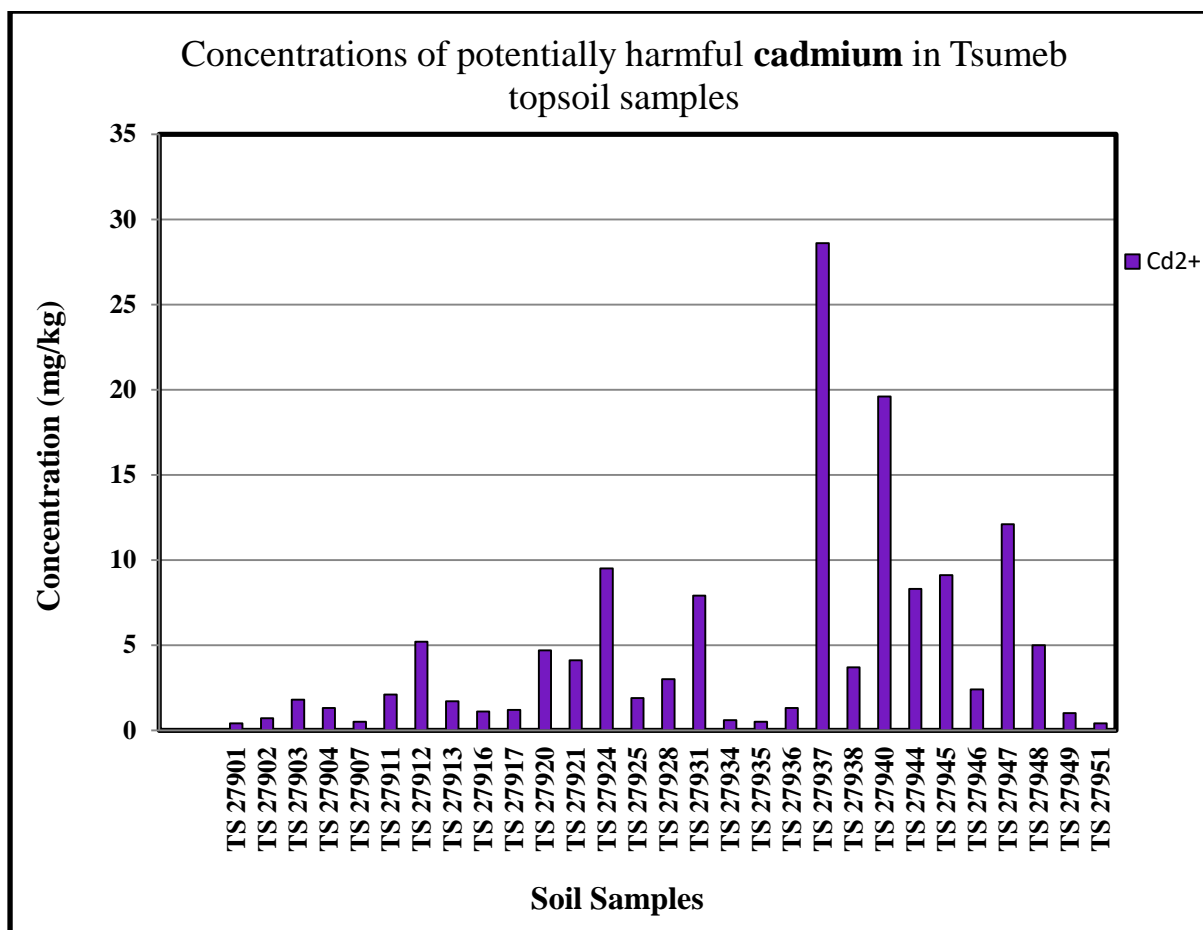


Figure 4.2: Concentration of potential harmful cadmium (Cd^{2+}) in Tsumeb top soil samples

Cobalt (Co^{2+}) in soil samples

Cobalt concentrations in the samples were generally low and ranged between 1.9 mg/kg and 12 mg/kg (Table 4.1). The lowest concentration of cobalt (1.9 mg/kg) was recorded at Lake Otjikoto 15 km west of the Tsumeb Central Business District (CBD). The highest concentration (12 mg/kg) was recorded in sample TS 27907 which was collected approximately 5km west of the Old Tsumeb Mine (Figure 4.3). More than 90% of the samples were below the Co^{2+} concentration of 10 mg/kg (90% quartile =5.5). The average concentration of Co^{2+} in the soils was 3.6 mg/kg and the median was 3.2 mg/kg.

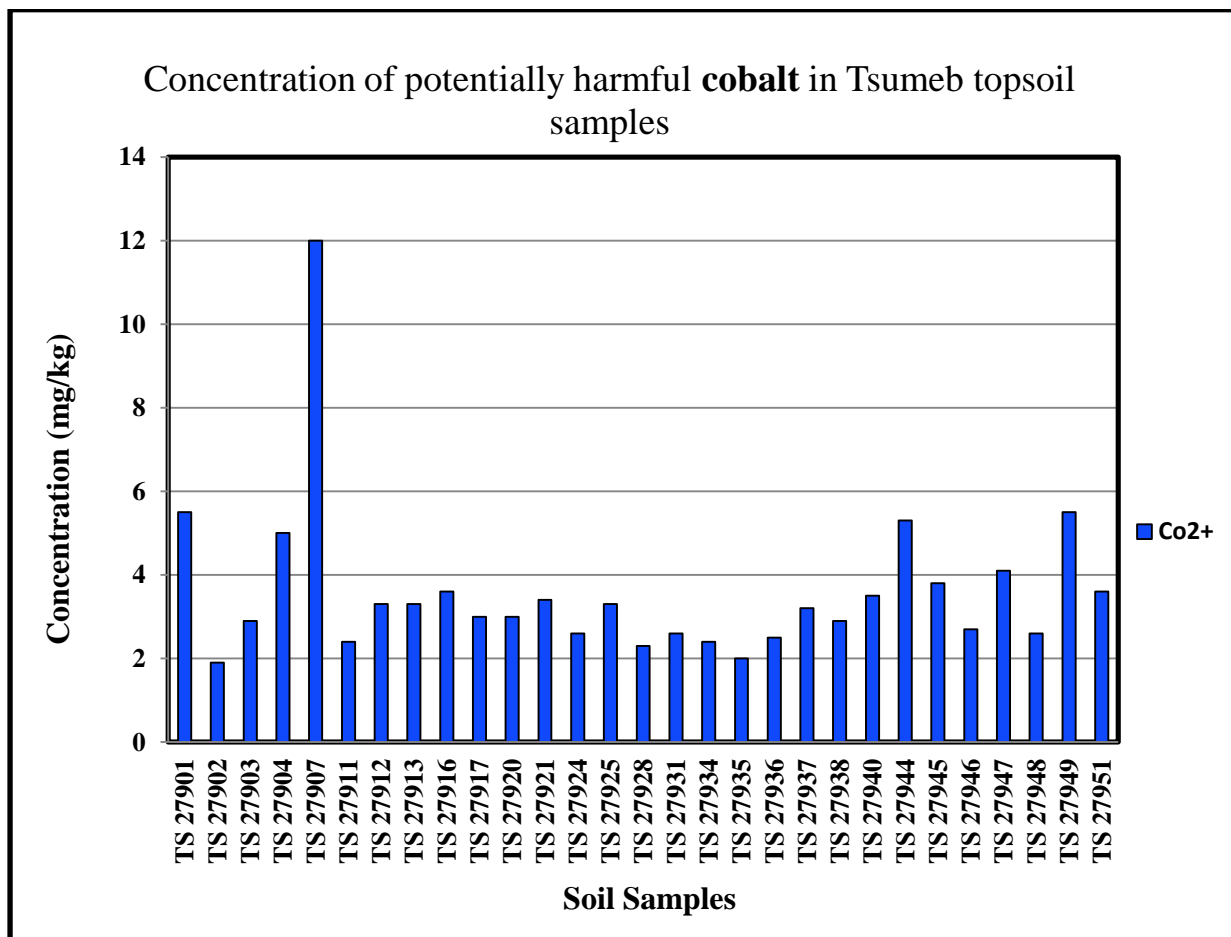


Figure 4.3: Concentration of potential harmful cobalt (Co^{2+}) in Tsumeb top soil samples

Lead (Pb^{2+}) in soil samples

Concentrations of lead in surface soils ranged from 25.9 mg/kg and 1835.1 mg/kg. A figure of 3786.9 mg/kg was recorded from a sample collected at the Old Tsumeb Mine Pit and represents primary mineralization. A mean of 255 mg/kg and a median of 116.6 were recorded (Table 4.1). The lowest Pb^{2+} value of 25.9 mg/kg was recorded in sample TS 27913 collected from Nomtsoub suburb followed by sample TS 27951 (Figure 4.4) which was collected approximately 25 km northeast of Tsumeb along the Tsintsabis road.

Though it is clear that the highest value of 3786.9 mg/kg is an outlier, 90% of the samples had a value of approximately 660, 91 mg/kg.

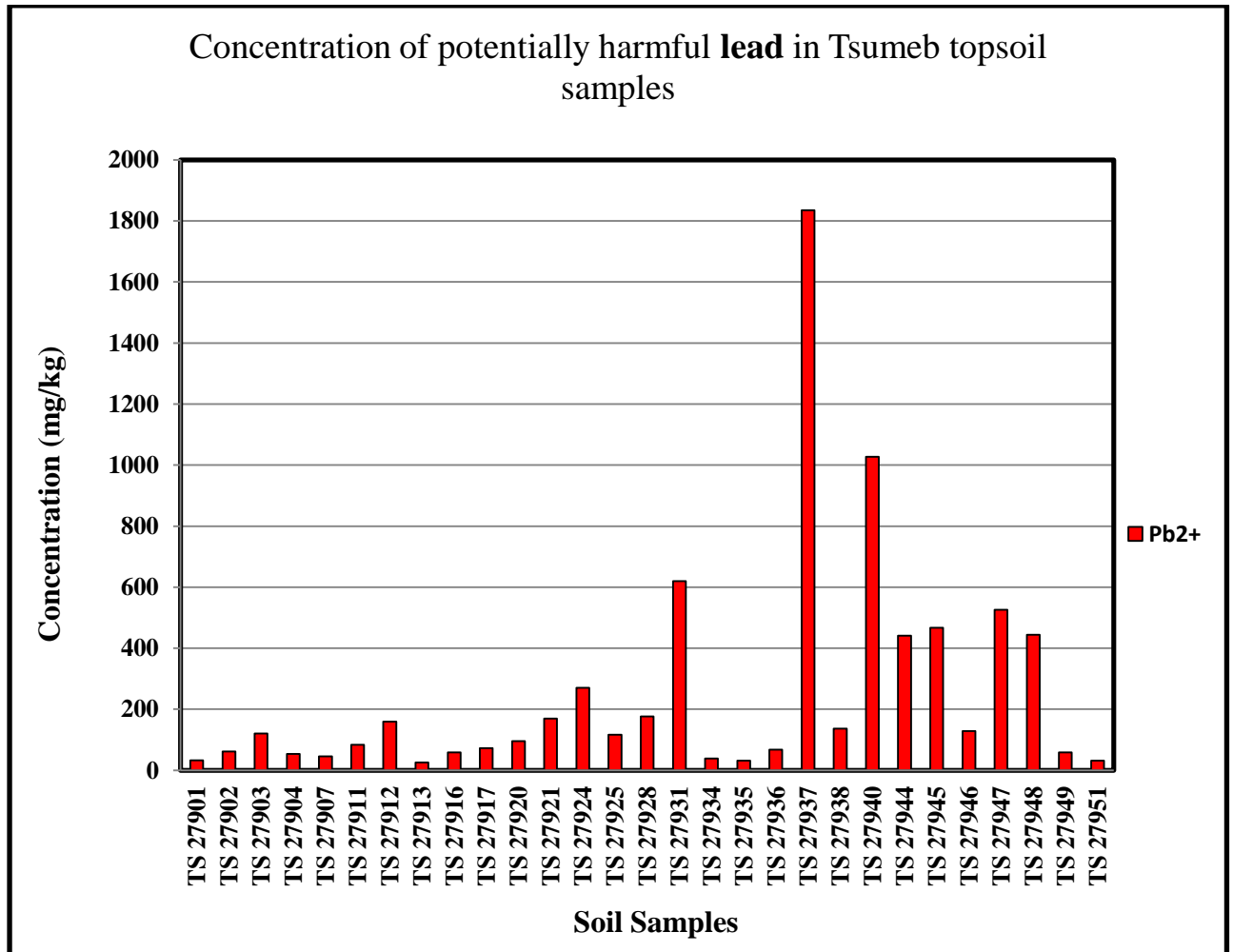


Figure 4.4: Concentration of potential harmful lead (Pb²⁺) in Tsumeb top soil samples

In summary, the highest concentrations of potentially harmful heavy metals As³⁺, Cd²⁺, Co²⁺, and Pb²⁺ in top soils were generally found in samples collected from the Old Tsumeb Open Pit Mine or areas proximal to the old Tsumeb open pit Mine. The lowest concentrations were found in the control samples collected approximately 25 km northeast of Tsumeb along the Tsintsabis road.

Results from samples collected at the old Tsumeb Mine were considered outliers and therefore not included in statistical calculations. Table 4.1 indicates the statistical parameters for the potential harmful elements.

4.2 Analytical results of vegetation samples

Heavy metals have the capability to migrate from polluted soil to plant tissues and accumulate in different plant organs and pose a physiological risk for plants. In the case of edible plants, this in turn can cause serious health risks for human beings who may eat the contaminated plants (Khan et al., 2015). One of the objectives of this study was to establish the potentially harmful fractions of the heavy elements: arsenic, cadmium, cobalt and lead in the following vegetation samples: mango leaves, lemon leaves, fresh and dry papaya leaves, sunflower leaves, fig leaves and fig fruits, marula fruit and tree bark. Appendix 3 shows analytical results of 20 vegetation samples that were analysed for the potentially harmful bioavailable fractions of the following heavy elements: arsenic, cadmium, cobalt and lead. Statistical data for potential harmful elements: arsenic, cadmium, cobalt and lead in vegetation of Nomtsoub, in the Tsumeb area is presented in Table 4.2. The results of the 20 vegetation samples analysed are also expressed in the form of bar charts using Microsoft Excel Windows 10 (See Figure 4.5 to Figure 4.8).

Table 4.2: Statistical data for potential harmful elements: arsenic, cadmium, cobalt and lead in vegetation of Nomtsoub, Tsumeb area. Number of samples: 20. The Tsumeb Mine Pit results were treated as outliers and therefore are not included in the calculations of these statistical parameters.

Component	PERCENTILES						Max	Mean
	Min.	10%	25%	50% (Median)	75%	90%		
Arsenic	5.4	16.8	24.3	46.7	102	165.9	247	72
Cadmium	0.3	0.4	0.8	2.8	4.3	6.5	12.8	3.3
Cobalt	0.2	0.2	0.8	1.1	1.6	1.8	2.6	1.1
Lead	7.6	16.3	28.0	40.9	116.8	182.1	415.3	90

Arsenic (As³⁺) in vegetation samples

The results of vegetation analysis showed that the concentration in mg/kg of potentially harmful heavy element As³⁺ in vegetation ranged from 5.4 to 247 with a mean of 72 mg/kg and a median of 46.7 mg/kg (Table 4.2). The highest concentrations (247 mg/kg) were found in fig leaves sampled approximately 5km west of the Old Tsumeb Mine (Figure 4.5). A Sample collected from the Tsumeb Mine had a concentration of 421 mg/kg of As³⁺. Marula tree bark collected from the vicinity of the Old Tsumeb Mine also had high arsenic concentrations with As³⁺ levels exceeding 100 mg/kg. Ninety (90) % of the vegetation samples had arsenic values of 165.9 g/kg and below.

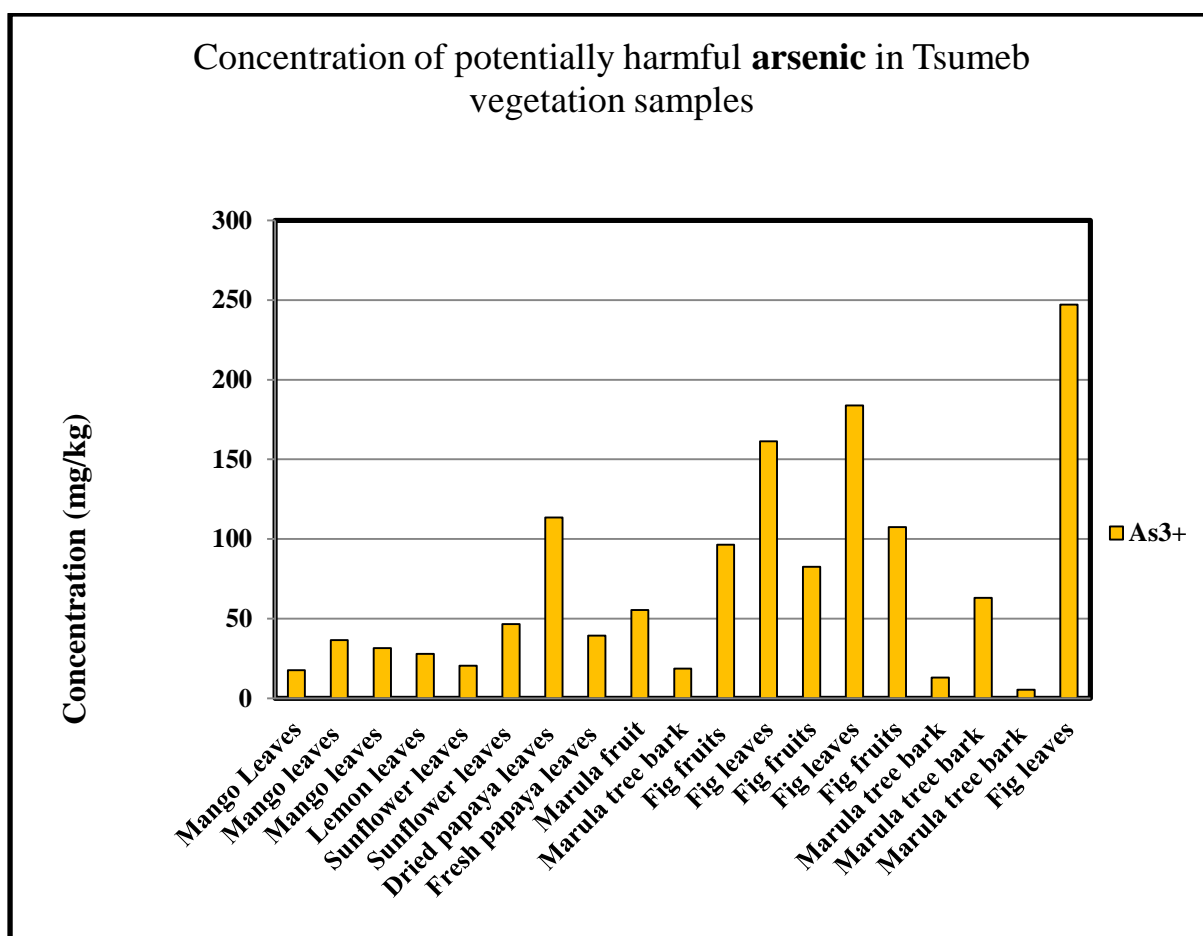


Figure 4.5: Concentration of potentially harmful arsenic (As^{3+}) in Tsumeb vegetation.

Cadmium (Cd^{2+}) in vegetation soil samples

The concentration in (mg/kg) of potentially harmful heavy element Cd^{2+} in vegetation was generally moderate ranging from 0.3 to 23.77 as seen in Figure 4.6. The highest sample result was from the old Tsumeb Mine pit and is considered an outlier. The second highest concentration was 12.8 mg/kg in marula tree bark sampled near the Tsumeb Mine. The average concentration of Cd^{2+} in the vegetation was 3.3 mg/kg and the median value was 2.8 mg/kg (Table 4.2). The lowest concentration was recorded in a marula tree bark sample (TSV 27950) which was collected approximately 25 km northeast of Tsumeb along the Tsintsabis road. An isolated sample of sunflower leaves sampled from Nomtsoub suburb showed an elevated cadmium concentration of 8.13 mg/kg.

Ninety (90) % of the vegetation samples had cadmium values of 12.8 mg/kg and below. Low concentrations of cadmium were observed in papaya and fig fruits.

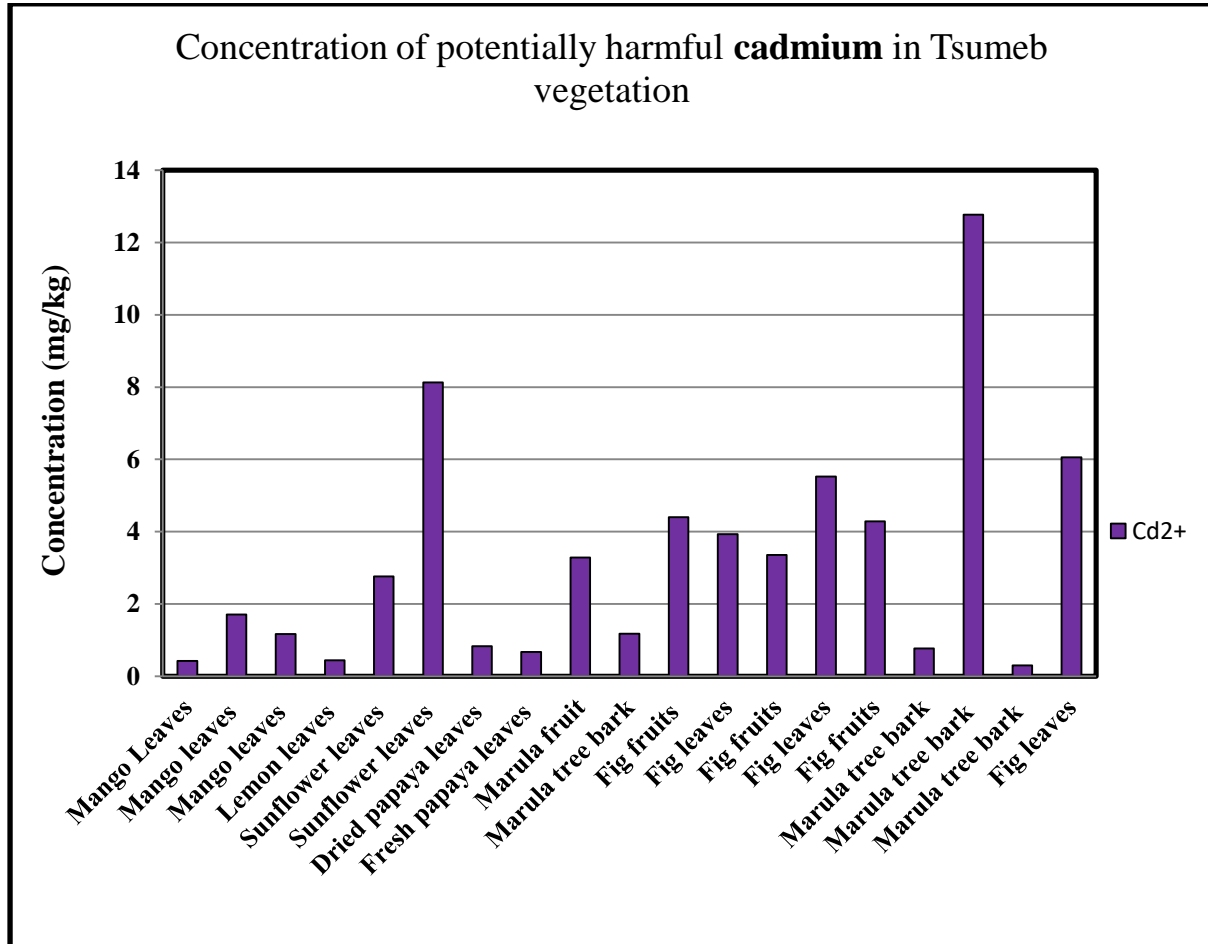


Figure 4.6: Concentration of potential harmful (Cd²⁺) in Tsumeb vegetation

Cobalt (Co²⁺) in vegetation samples

Low concentrations of potentially harmful cobalt were recorded in vegetation with values ranging between 0.2 and 2.6 mg/kg (Table 4.2). The highest concentration was recorded in fig leaves collected within 5km west of the Tsumeb Mine. The Tsumeb Mine sample had 1.3 mg/kg Co²⁺. The lowest concentration was recorded in a marula tree bark sample collected from the Nomtsoub suburb (Figure 4.7). More than 90% of the samples were below the concentration of 1.8 mg/kg Co²⁺ (90% quartile =1.8). The average concentration of Co²⁺ in the vegetation was 1.1 mg/kg and the median value was also 1.1 mg/kg (Table 4.2).

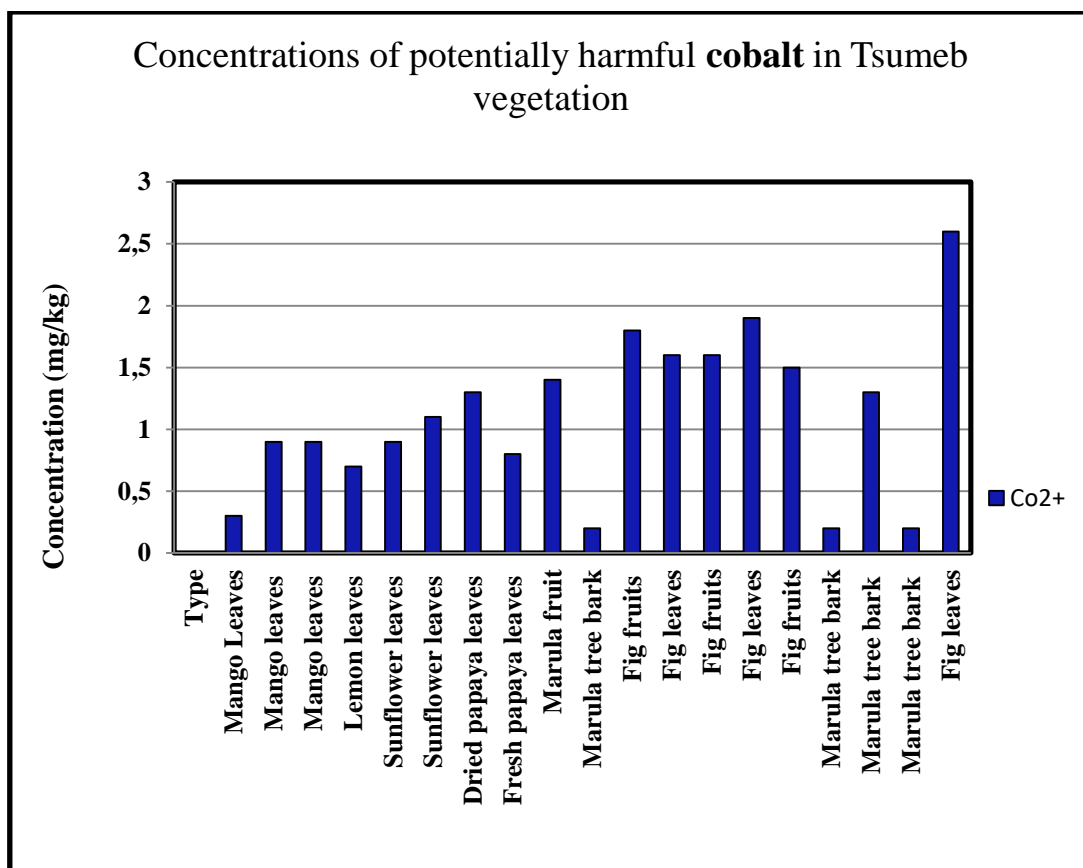


Figure 4.7: Concentration of potential harmful cobalt (Co²⁺) in Tsumeb vegetation

Lead (Pb²⁺) in vegetation samples

The concentration (mg/kg) of potentially harmful heavy metal Pb²⁺ in vegetation was generally moderate to high. Values ranged from 7.6 to 801.67 mg/kg. The highest concentration of Pb²⁺ (801.67 mg/kg) was recorded in sample TSV 27942 which was collected from the old Tsumeb Mine and is an outlier as it represents primary mineralization. The second highest result was 415.3 mg/kg and was recorded in Marula tree bark (Figure 4.8). A marula tree bark sample (TSV 27950) which was collected approximately 25 km northeast of Tsumeb along the Tsintsabis road had the lowest Pb²⁺ concentration of 7.6 mg/kg. Table 4.2 shows that more than 90% of the vegetation samples had Pb²⁺ concentration below 200 mg/kg (90% quartile=182.1). The average concentration of Pb²⁺ in the vegetation was 90 mg/kg and the median was 40.9 mg/kg (Table 4.2).

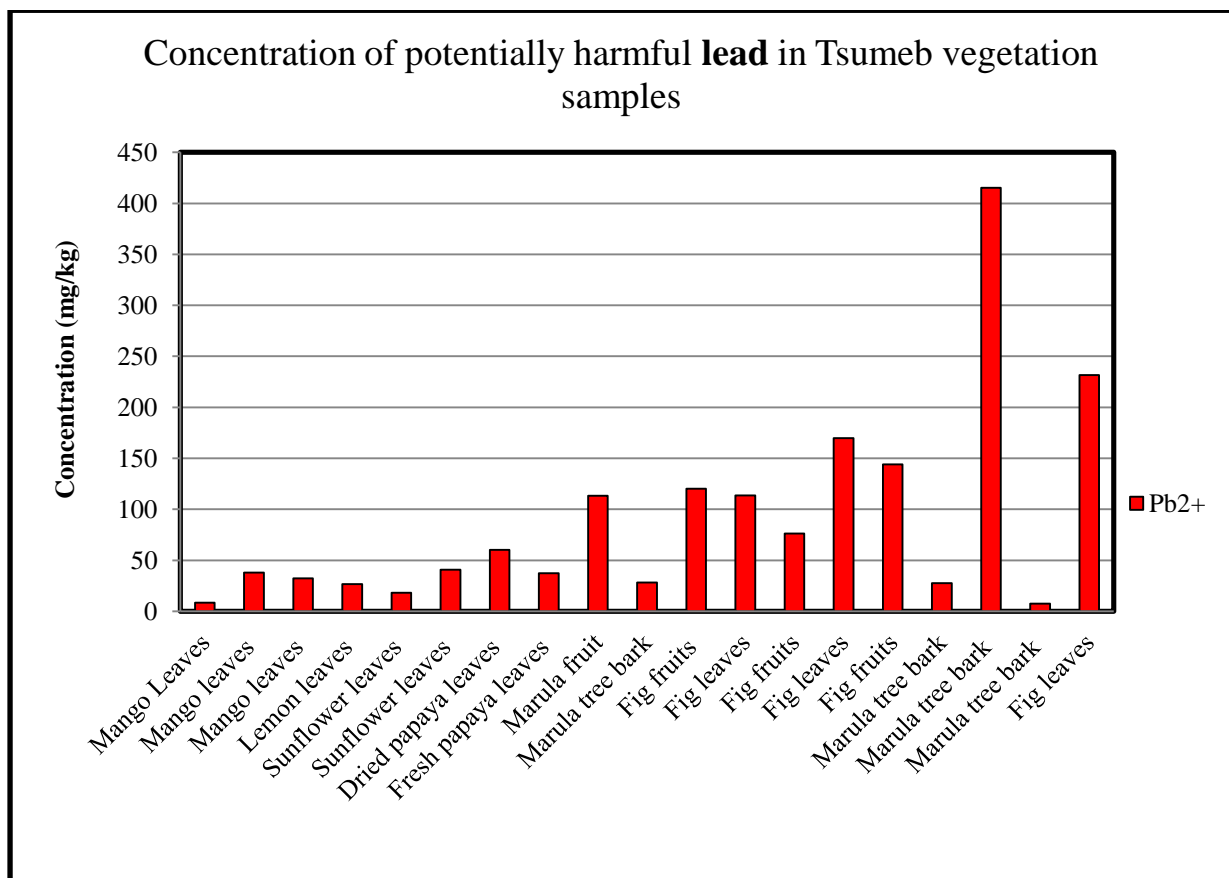


Figure 4.8: Concentration of potential harmful lead (Pb²⁺) in Tsumeb vegetation.

Chapter 5 DISCUSSION

This chapter discusses the analytical results of soil and vegetation samples from Nomtsoub suburb in Tsumeb. The chapter has six main components: firstly, the anthropogenic influence on the environment is discussed using reported background values and current results as evidence. Secondly, current results are discussed by making a comparison between the concentrations of the different elements that are under investigation in this study and the concentrations found naturally in the earth's crust. Thirdly, contaminant distribution is discussed with the aid of maps produced using ArcGIS. The transfer ratios of the different potentially harmful elements from soil to vegetation in cases where soil samples and vegetation samples were taken in the same locality are also discussed. The results of this current study considered potentially harmful species of the following elements: arsenic, cadmium, cobalt and lead are compared to the results obtained in previous studies by other researchers who analysed total element concentrations. The implications of the differences and similarities are also discussed. Finally, the results of this current study are also compared to International guideline values for different land uses. In pollution or contamination studies, it is customary to compare contaminants and toxins found in different media to standards. The standards are allowable values within which a toxin or contaminant is not considered harmful for specific uses (WHO, 2011). Different countries have adopted their own guidelines and standards. However, the World Health Organization (WHO) Codex Alimentarius and European Union (EU) guidelines as well as the Canadian Soil Quality Guidelines for the protection of Environmental and Human Health are the most widely used standards in environmental/contamination studies worldwide. Namibia does not have its own standards; therefore, the Canadian Soil Quality Guidelines for the protection of the Environment and Human Health and the Update 7.0, of 2007 for agricultural and residential land use of the Canadian Guidelines will be applied.

Appendix 6 elaborates how the soil quality guidelines are derived. Results of vegetation samples are compared to the EU (2006) and WHO (2001) guidelines.

5.1 Analysis of soil samples

5.1.1 Evidence of anthropogenic influences in the area

Křibek and Kamona (2005) report ground breaking environmental work done by a number of researchers in the Tsumeb area in the early 2000's. Before then, there had not been comprehensive environmental work done in the area. Results from those studies clearly point to anthropogenic influences on the environment. The background values for arsenic, cadmium and lead are generally low. This is evidenced by low median values for elements in the lower soil horizons in Tsumeb which are presumed to be less disturbed by mining and processing activities (Křibek and Kamona, 2005). A gradual decrease of arsenic from the surface layer of soil (median: 28.4 mg/kg) through soil rhizosphere (median: 29.0 mg/kg) toward the lower soil horizon (median: 3.43) is documented by Křibek and Kamona (2005). Křibek and Kamona (2005) further document the distribution of cadmium in surface soils which is essentially identical with that of arsenic. Compared to the surface soils, contents of cadmium in the lower soil horizon are very low (median: 0.32 mg/kg) thus indicating anthropogenic origin of the element in surface soil layer. Due to favourable landscape morphology between the smelter and Tsumeb town (there occurs prominent hills between the two locales), contamination of the town with cadmium is generally low. Similarly, lead contents decrease from surface soils (median: 181 ppm) to the soil rhizosphere (median Pb: 119 ppm) and to the lower soil horizon (median Pb: 46) (Křibek and Kamona, 2005). This is further evidence of anthropogenic origin of the elements in the surface soil layer. The current surface soil sample results: As^{3+} , (7 to 421 mg/kg), Cd^{2+} (0.5 to 35.6 mg/kg), Co^{2+} (2 to 6.3 mg/kg) and Pb^{2+} (25.9 to 3786.9 mg/kg) also indicate anthropogenic contamination.

5.1.2 Comparison of metal concentrations in the earth's crust and concentration in Tsumeb soils

All heavy elements under this study occur naturally in the earth's crust. In this section, their natural concentrations are compared to the concentrations found in this study. Table 5.1 shows Average heavy metal concentrations in different constituents of Earth's crust and surficial deposits compared to average concentrations in Nomtsoub Township in Tsumeb.

Table 5.1: Average heavy metal concentrations in different constituents of Earth's crust and some surficial deposits compared to average concentrations in Tsumeb. The table is modified from Van der Voet et al. (2013).

Metal	Lithosphere mg/kg	Soil worldwide mg/kg	Average concentration in soils in current study.
As	1.8	6	55
Cd	0.10	0.35	4.8
Co	10-23	8	3.6
Pb	12-20	12	255

The concentrations of As, Cd, Co and Pb in the lithosphere are: 1.8, 0.10, 10-23 and 12-20 mg/kg respectively. The concentrations in soils are; 6.0, 0.35, 8, 12 mg/kg for As, Cd, Co and Pb respectively. According to Table 5.1, the average concentrations of potentially harmful species of arsenic, cadmium and lead in Tsumeb soils exceed concentrations found naturally in soils. The only exception is cobalt whose average concentration in the soils of the study area is lower than that reported in natural soils. This result could be due to low levels of cobalt in the rocks found in the Tsumeb area.

5.1.3 Contaminant distribution maps

ArcGIS spatial analytical tool, an extension of ArcGIS for desktop was used to create contaminant distribution maps to visualize the distribution of the harmful heavy metal contaminants in the area of study. Two different interpolation methods were used to generate the contaminant distribution maps (Figures 5.1 to 5.8). For each heavy metal the following methods were used; Inverse Distance Weighted (IDW) and Natural Neighbour (NN). The aspects of how each method works are discussed in chapter three which deals with methods used.

Arsenic distribution in soil

Figures 5.1 and 5.2 show the distribution of arsenic as modelled using the IDW and the NN methods respectively. In both cases, the highest concentration of arsenic is shown to be linked to the old Tsumeb open pit mine. The further away from that point, arsenic concentration is reduced. The Natural Neighbour method shows the elevated concentration of arsenic to be extending for approximately 5km in a northerly direction from the Tsumeb Mine. Elevated concentrations in that direction may be due to the combined effects of the former Tsumeb open pit Mine and the old tailings storage facility which are located northerly to northeasterly respectively of the Tsumeb Mine Old pit. Elevated concentrations in that direction are also probably due to prevailing easterly winds causing airborne pollution mainly to the area northwest of Tsumeb.

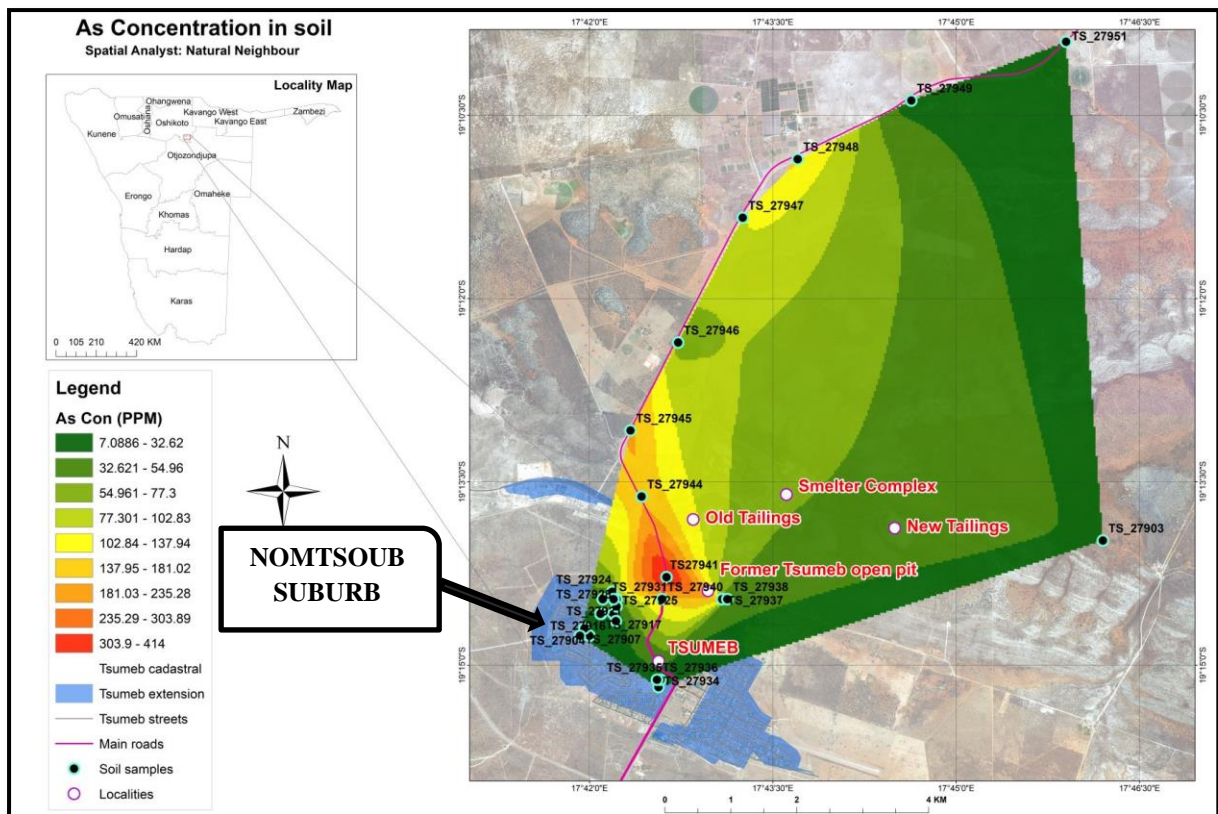


Figure 5.2: Distribution of harmful arsenic in Tsumeb soils. The map was generated using the NN Method. The black dots represent the sampling points for soils.

According to the Natural Neighbour Method, arsenic values over the entire study area range from 7-414 mg/kg. The dark green colour represents the lowest concentration and red represents the highest arsenic concentration. The method shows Nomtsoub suburb to have arsenic concentration of 77.3 mg/kg and below (light green to dark green).

Cadmium distribution in soil

Figures 5.1 and 5.2 show the distribution of cadmium as modelled using the IDW and the NN methods respectively. The IDW method shows moderate to high contamination haloes of approximately 5x5 km in a northwesterly direction.

This contamination distribution is likely to be due to the combined effects of the former Tsumeb Open pit mine, the old and new tailings storage facilities, the smelter complex as well as prevailing easterly winds causing airborne pollution mainly to the area northwest of Tsumeb. The map does not provide a picture of what happens south of the Tsumeb town due to limited samples collected in that direction because the studies concentrated on the areas north and west of the Tsumeb Town. However, cadmium concentrations are not expected to be high in that area due to the prevailing easterly wind direction.

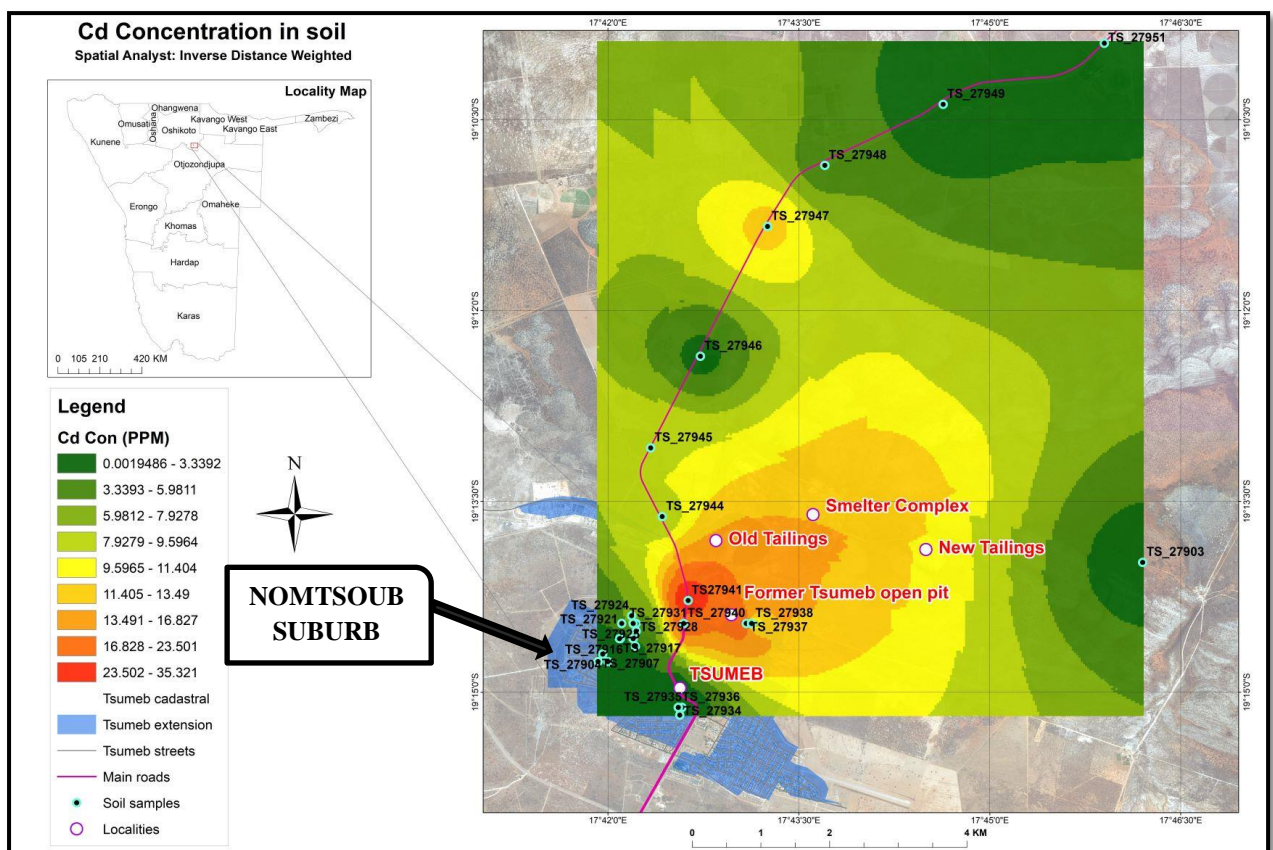


Figure 5.3: Distribution of harmful cadmium in Tsumeb soils. The map was generated using the IDW method. The black dots represent the sampling points for soils.

The IDW method shows cadmium values over the entire study area to range from 0.002 -35.6 mg/kg (Figure 5.3). The dark green colour represents the lowest concentration and red represents the highest cadmium concentration. The method shows Nomtsoub suburb soils to have predominantly cadmium concentration of 5 mg/kg and below (green to dark green). The NN method (Figure 5.4) shows the concentration of cadmium to be forming a haloe for approximately 5 km in a northerly direction. In both potentially harmful element distribution maps generated by the two different methods, the highest concentration of cadmium is in the immediate vicinity of the Old Tsumeb Open pit Mine. Both methods show the area immediately surrounding sample point TS27947 to have low to moderate values. This isolated elevated value can be attributed to windborne dust from the smelter complex or possibly use of waste material for the construction of the road in the area. The area immediately surrounding sample point TS27946 shows low cadmium values due to the fact that its a pond area and while particulate matter can be retained in the pond due to sedimentation processes, the fractions in dissolved form are highly mobile and can be easily washed off with the surface runoff.

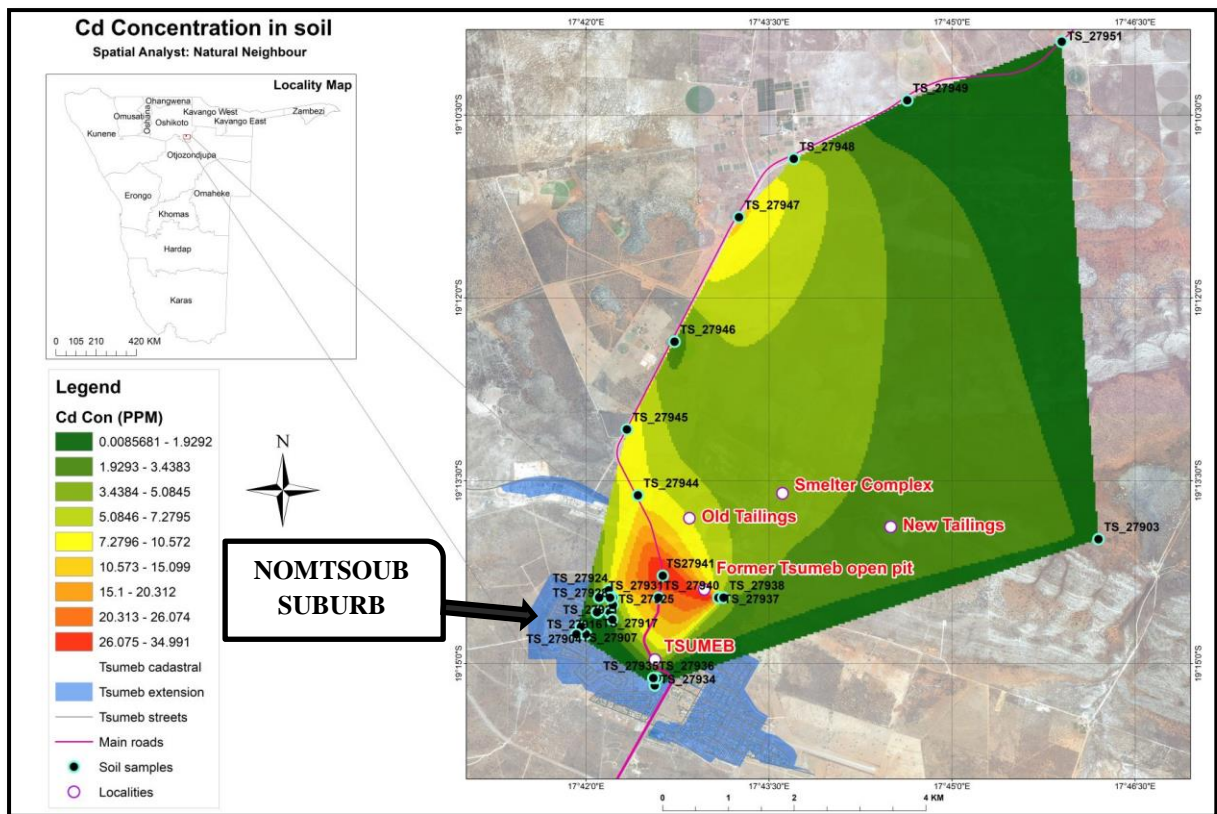


Figure 5.4: Distribution of harmful cadmium in Tsumeb soils. The map was generated using the NN method. The black dots represent the sampling points for soils.

Cadmium values over the study area range from 0.4 -35.6 mg/kg (Figure 5.4). The dark green colour represents the lowest concentration and red represents the highest cadmium concentration. According to the NN method, potentially harmful cadmium concentrations in soils of Nomtsoub suburb are in the range of 10 mg/kg and below.

Cobalt distribution in soil

Figures 5.5 and 5.6 show the distribution of cobalt as modelled using the Inverse distance weighted and the Natural Neighbour methods respectively. The Inverse Distance Weighted method shows a moderate to high contamination haloe of approximately 5x5 km in a northerly direction with the highest concentration linked to the former Tsumeb Open pit and the old tailings dump.

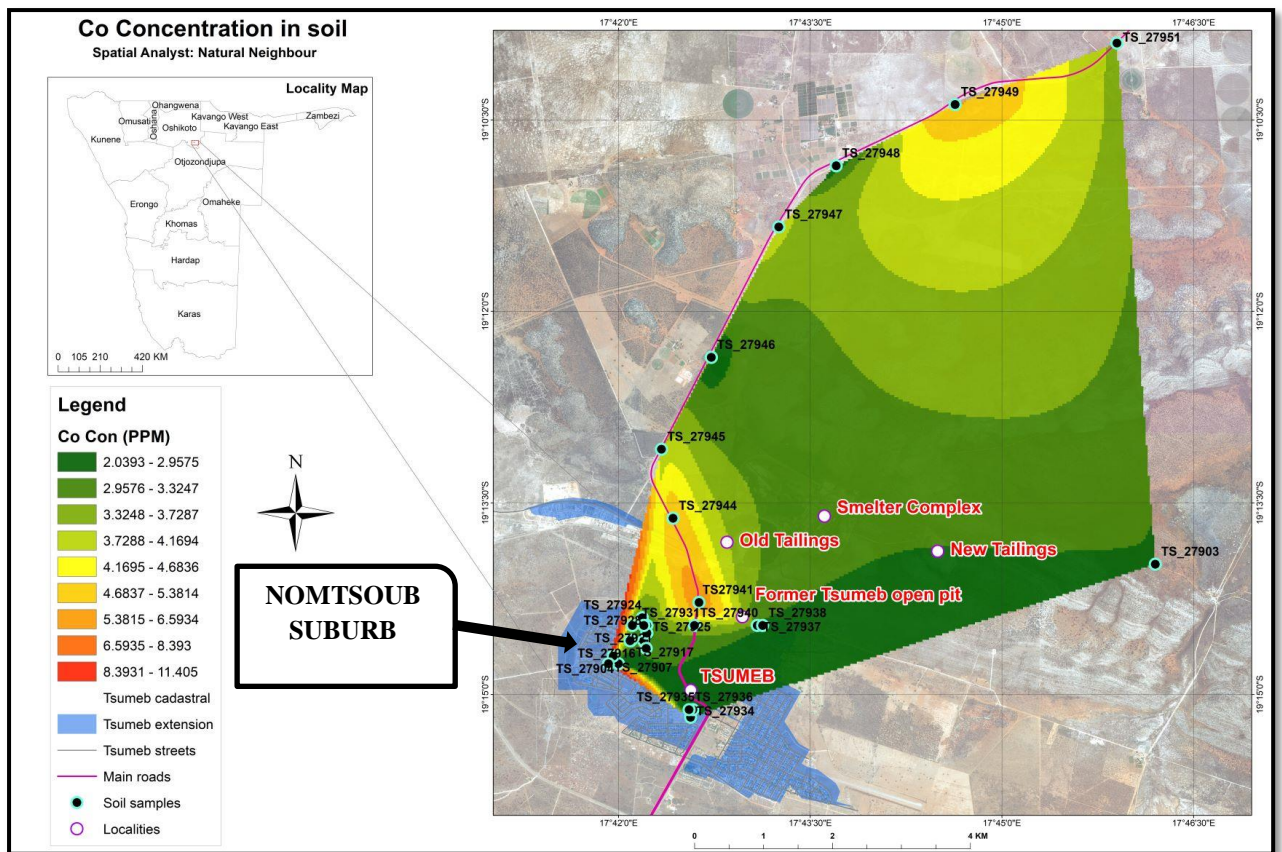


Figure 5.6: Distribution of harmful cobalt in Tsumeb soils. The map was generated using the NN method. The black dots represent the sampling points for soils.

Cobalt values in the study area range from 2 - 11 mg/kg (Figure 5.6). The dark green colour represents the lowest concentration and red represents the highest cobalt concentration. The method shows Nomtsoub suburb soils to have cobalt concentration between 3 and 5 mg/kg (yellow to orange).

Lead values in the study area map range from 31 - 3753 mg/kg (Figure 5.7). The dark green colour represents the lowest concentration and red represents the highest lead concentration. The method shows Nomtsoub suburb soils to predominantly have lead concentration below 500 mg/kg and below (green to dark green).

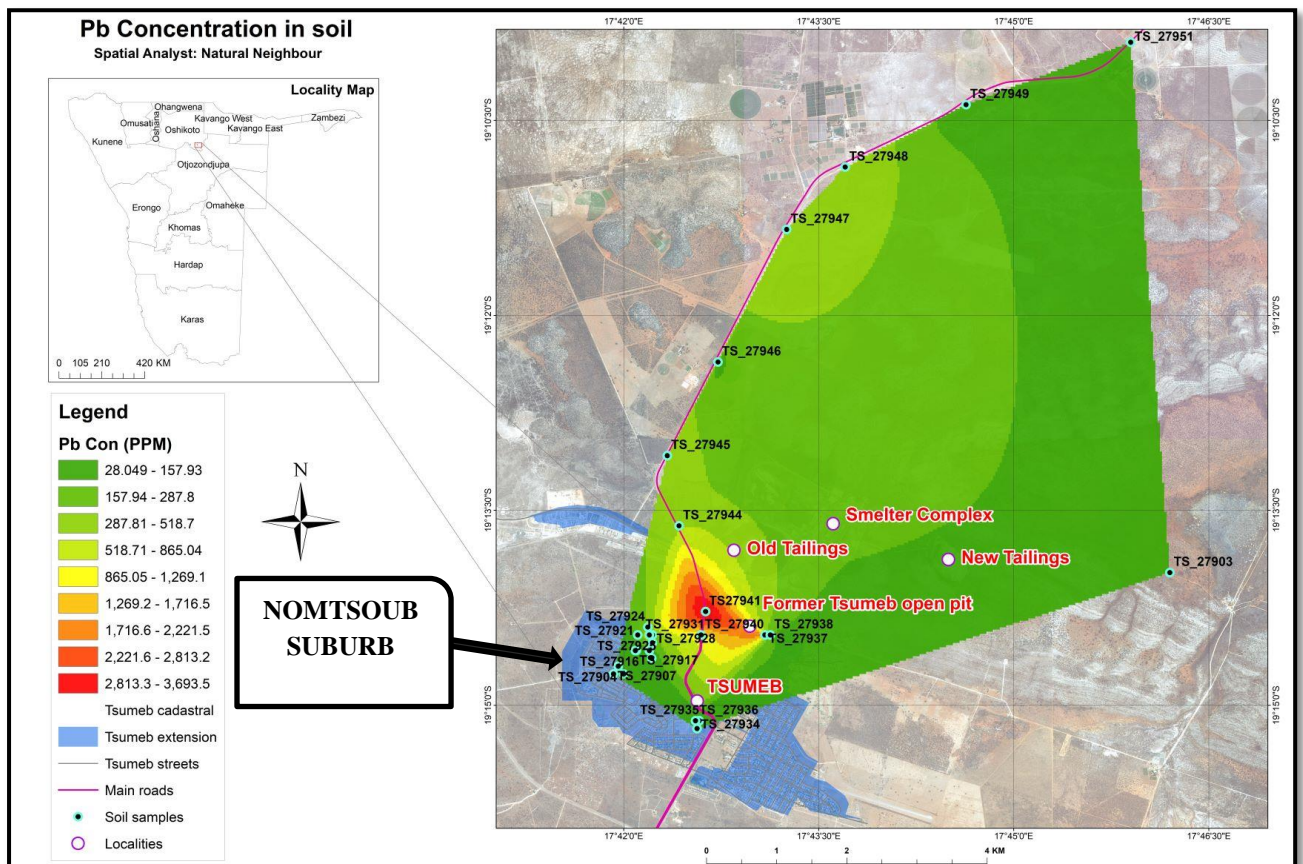


Figure 5.8: Distribution of lead in Tsumeb soils. The map was generated using the NN method. The black dots represent the sampling points for soils.

Lead values in the map range from 31 - 3753 mg/kg (Figure 5.8). The dark green colour represents the lowest concentration and red represents the highest lead concentration. The method shows Nomtsoub suburb soils to predominantly have lead concentration below 500 mg/kg and below (green). In summary, the Inverse distance weighted method was the best in modelling the contaminant distribution in the area. Its results were consistent with the reality on the ground where the highest heavy element concentrations are linked to the Old Tsumeb Open Pit Mine and the concentration reduced with distance away from that locality.

The eastern parts of Tsumeb were shown to generally have low concentrations of all elements. This is due to the fact that in this current study, sample collection did not extend to the areas around the smelter and the new tailings storage facility as these were covered in detail by researchers in previous studies although those studies focused on total metal concentrations.

5.1.4 Uptake of heavy metals from soil to vegetation

Contaminant uptake by plants and its mechanisms have been explored by several researchers over the recent years. According to Tangahu et al (2011), plants have evolved highly specific and very efficient mechanisms to obtain essential nutrients from the environment, even when present at low ppm or mg/kg levels. Plant roots aided by plant-produced chelating agents and plant induced pH changes and redox reactions are able to solubilize and take up nutrients from very low levels in the soil, even from nearly insoluble precipitates (Tangahu et al., 2011). Plants have also evolved highly specific mechanisms to translocate and store micronutrients (Tangahu et al., 2011). These same mechanisms are also involved in the uptake, translocation and storage of toxic elements whose chemical properties simulate those of essential elements (Tangahu et al., 2011). Given this ability for plants to uptake heavy metals, the current study had an objective of determining the transfer ratios of the potential harmful elements; As^{3+} , Cd^{2+} , Co^{2+} and Pb^{2+} from soil to vegetation. According to Khan et al. (2015), the accumulation rate of heavy metals varies from organ to organ and some organs accumulate more heavy metals than others. For this study, uptake ratios were calculated for all cases where the soil sample and the vegetation sample were taken at the same locality. The vegetation samples for which uptake ratios were calculated included: lemon leaves, mango leaves, fig fruits and marula tree bark (Table 5.2). Plant uptake of contamination from soil is calculated by the following equation: Concentration in plant material/Concentration in soil in % (Mapani et al., 2014).

Table 5.2: Uptake of heavy metals in vegetation compared to adjacent soils in %

Sample No.	Sample Type	As (mg/kg)	Cd (mg/kg)	Co(mg/kg)	Pb(mg/kg)
TSV 27906	Mango Leaves	17.7	0.4	0.3	8.4
TS 27904	Soil	23.0	1.3	5.0	53.3
	Uptake (%)	77.0	33.1	6.0	15.8
TSV 27914	Sunflower leaves	20.6	2.8	0.9	18.3
TS 27945	Soil	195.0	9.1	3.8	467.3
	Uptake (%)	10.6	30.3	23.7	3.9
TS 27938	Soil	41.0	3.7	2.9	136.1
TSV 27939	Fig fruits	13.2	0.8	0.2	27.7
	Uptake (%)	32.2	20.8	6.9	20.4
TSV 27922	Fresh papaya leaves	55.6	3.3	1.4	113.2
TS 27924	Soil	58.0	9.5	2.6	270.7
	Uptake (%)	95.9	34.6	53.8	41.8
TSV 27923	Marula fruit	18.8	1.2	0.2	28.2
TS 27924	Soil	58.0	9.5	2.6	270.7
	Uptake (%)	32.4	12.4	7.7	10.4
TSV 27943	Marula tree bark	63.2	12.8	1.3	415.3
2727941	Soil	421.0	35.6	6.3	3786.9
	Uptake (%)	15.0	35.9	20.6	11.0
TSV 27942	Marula tree bark	116.5	23.8	2.4	801.7
2727941	Soil	421.0	35.6	6.3	3786.9
	Uptake (%)	27.7	66.8	38.1	21.2
TSV 27950	Marula tree bark	5.4	0.3	0.2	7.6
TS 27949	Soil	16.0	1.0	5.5	58.8
	Uptake (%)	33.8	30.0	3.6	12.9

Arsenic– uptake of arsenic ranged from 15% to 95.6% for the different plants/vegetation. Generally, the uptake of arsenic from the soil to vegetation was high. The highest uptake ratio being that of fresh papaya leaves (95%) followed by mango leaves (77%). Sunflower leaves and marula tree bark generally showed lower uptake ratios of arsenic at 10% and 15% respectively (Table 5.2). The two plants seem to have a mechanism of excluding arsenic from soil into their tissues.

Cadmium- Most of the plants sampled in this study seem to have mechanisms against accumulation of cadmium in their tissues. The cadmium uptake from the soil to vegetation was generally moderate (below 36%). However, marula tree bark had a high uptake of 66.8%. (Table 5.2). Similar to their uptake behaviour with arsenic, sunflower leaves and mango leaves generally showed comparatively lower uptake ratios of cadmium at 30% and 33% respectively. The lowest uptake of cadmium was observed in marula fruit at 12.4%.

Cobalt- Cobalt uptake from the soil to vegetation/plants ranged between 3.6% and 53.8% (Table 5.2). Fresh papaya leaves had the highest uptake ratio of cobalt. Mango leaves and fig fruits had low uptake ratios of 6 and 6.9% respectively. This behaviour is consistent with Kim et al. (2006)'s observation that although plants may take up cobalt from the soil, the translocation of cobalt from the roots to other parts of the plants is not normally significant.

Lead- The lead uptake ratio from the soil to vegetation ranged between 3.9% in sunflower leaves and 41.8% in fresh papaya leaves (Table 5.2). The fig fruit seemingly has a mechanism to exclude lead; a very low lead uptake ratio of 20.4% was recorded. Marula tree bark had an even lower uptake ratio of 12.9%. Lead uptake across all vegetation was generally low to moderate. From the findings in this study, the plants investigated seem to have developed mechanisms to considerably exclude toxins from their tissues except fresh papaya. Fresh papaya leaves showed the highest uptake of three of the four potentially harmful elements with uptake ratios of 95.9%, 53.8% and 41.8% of arsenic, cobalt and lead respectively (Figure 5.9). The potentially harmful element uptake in papaya occurred in the decreasing order of As>Co>Pb. The translocation of arsenic in plants seems to be good as evidenced in the high arsenic uptake by leaves and fruit. The fresh papaya leaves had the highest arsenic uptake of 95.9%.

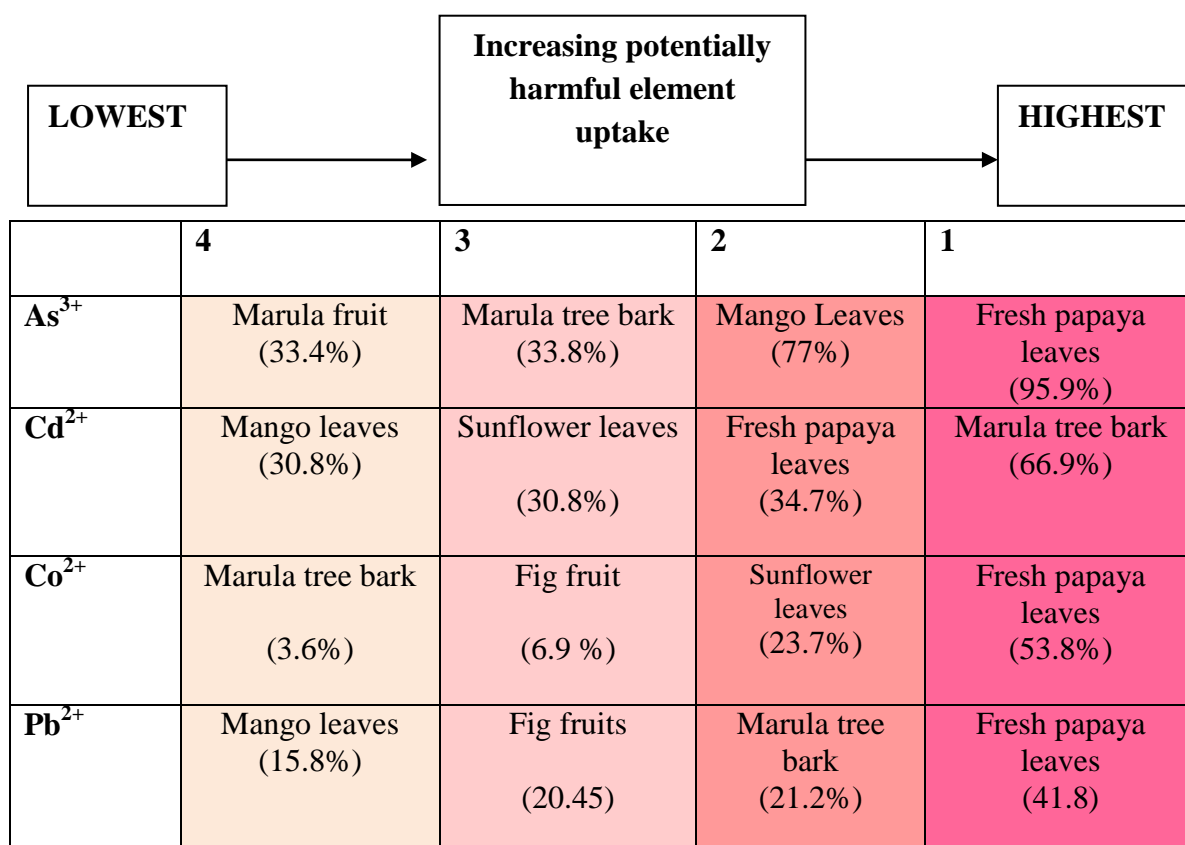


Figure 5.9: Uptake of potentially harmful elements from soil to vegetation

5.1.5 Transfer Coefficients of heavy metals

The bioaccumulation factor of heavy metals is measured by the ratio of metal concentrations in plants to metal concentrations in that soil (Khan et al., 2015). Bioaccumulation Factor = $C_{\text{plant}}/C_{\text{soil}}$ where C_{plant} and C_{soil} are the concentrations of potentially harmful elements in plants and in soils respectively. In this study, the term transfer coefficient is preferred to bioaccumulation factor.

Table 5.3: Coefficient for heavy metals in vegetation compared to adjacent soils. The shaded results exceed a transfer coefficient of 0.50 meaning that half of the metals in the soils are transferred to the plant.

Sample No.	Sample Type	As (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Pb (mg/kg)
TSV 27906	Mango Leaves	0.77	0.31	0.06	0.16
TSV 27914	Sunflower leaves	0.11	0.31	0.24	0.04
TSV 27939	Fig fruits	0.32	0.22	0.07	0.20
TSV 27922	Fresh papaya leaves	0.96	0.35	0.54	0.42
TSV 27923	Marula fruit	0.32	0.13	0.08	0.10
TSV 27943	Marula tree bark	0.15	0.36	0.21	0.11
TSV 27942	Marula tree bark	0.28	0.67	0.38	0.21
TSV 27950	Marula tree bark	0.34	0.30	0.04	0.13

Table 5.3 shows that most of the plants sampled in this study have mechanisms against the transfer of toxins as evident in their generally low to moderate transfer coefficients.

However, the papaya has a very efficient mechanism in transferring toxins from the soil to its plant tissues; for instance, papaya almost uptakes all the arsenic in the soil (0.96). Papaya has the highest transfer coefficients for arsenic and cobalt. The significantly high concentrations of heavy metals in papaya show the tendency of papaya to absorb and retain heavy metals in its tissues. This high tendency to transfer toxins is consistent with Olatunde and Onisoya (2017)'s observations in their assessment of heavy metal concentrations in pawpaw (*Carica papaya Linn*) around automobile workshops in Port Harcourt Metropolis in Nigeria. In that study, heavy metals in soil positively correlated with heavy metals in the tissues of *C. papaya*.

This correlation suggests that the absorption of heavy metals in the tissues of *C. papaya* was greatly controlled by the content of the heavy metals and bioavailability of metals in soil. This makes *C. papaya* a potentially good biomonitoring tool of environmental contamination of heavy metals (Olatunde and Onisoya, 2017). The papaya's ability to take up toxins can be attributed to its morphology which is mostly made up of phloem and xylem.

The Marula tree bark had significant heavy metal transfer coefficients ranging from 0.1 in lead to 0.669 in cadmium. The high coefficient of cadmium is of concern because of Marula tree bark's popular use locally. The marula bark is locally used for medicinal purposes. Marula whose scientific name is *Sclerocarya birrea* is a widespread species throughout the semi-arid deciduous savannas of much of sub-Saharan Africa (Prinsloo & Street, 2013). According to Prinsloo & Street (2013), all parts of the tree have been utilized since ancient times. The fruits are utilized for food, juice, jelly and beer, the bark has been used for medicinal purposes, the kernels have been used for food and oil and the wood for fuel. Hypoglaecemic activity, anti-inflammatory and antibacterial properties have been revealed by recent studies (Prinsloo & Street, 2013). The coefficients for arsenic reveal a generally moderate to high tendency of contaminant uptake by the plants: 0.28 to 0.96 (Table 5.3). The coefficients for cadmium were also moderate to high. The transfer coefficients for cadmium ranged from 0.126 to 0.669 (Table 5.3). The coefficients for cobalt reveal a generally low to moderate degree of uptake by the plants: 0.036 to 0.538 (Table 5.3). Typically, cobalt is more mobile than other metals such as lead, but less mobile than cadmium (Smith, 2007). All the plants in this study in exception of fresh papaya seem to have a mechanism to exclude lead from their plant tissues.

5.1.6 Comparison of soil sample results to International guideline values

In the absence of guideline values for soil contamination in Namibia, the evaluation of the hazardous potential of the top soils with respect to potentially harmful elements: As^{3+} , Cd^{2+} , Co^{2+} and Pb^{2+} was based on Canadian Soil Quality Guidelines for the protection of Environmental and Human Health, Update 7.0, 2007 for agricultural land use and residential areas as presented in Canadian Council of Ministers of the Environment (2007). The guideline values refer to acceptable concentration for which adverse effects are not expected for the intended use of a particular site. It is assumed that the concentration of the potentially harmful elements analysed in this study is less than the total heavy metal concentration. This is because there is a relationship between total metal content in an earth material and potential toxicity. Not all the total metal content in an earth material is usually geoavailable, bioavailable or toxic (Smith, 2007). According to Smith (2007), availability and toxicity are a function of the total metal content's access and susceptibility to weathering and other environmental conditions. Therefore, within the total content of a particular metal, there will be a fraction that is bioavailable and potentially toxic. It is this fraction that was the subject of this study. The use of the Canadian soil quality guideline values (though based on total heavy metal concentration) is valid.

Analysis of soil's suitability for residential and agricultural land use.

Potentially harmful element concentrations in Nomtsoub were compared to Canadian soil quality guideline values; the shaded results exceed Canadian soil quality guideline values for residential and agricultural use (Table 5.4). The results are also expressed in the form of pie charts using Microsoft Excel 2010 (Figure 5.10 to 5.17).

This was done in order to provide a better visual comparison of the proportions of samples that exceeded the Canadian soil quality guideline values for residential and agricultural land use and the proportions of samples that were within the recommended guideline values.

Table 5.4: Concentration of potentially harmful elements in Nomtsoub suburb versus Canadian soil quality guidelines for residential and agricultural land use. Statistical data excludes the outlying results/data of the old Tsumeb Mine pit.

Potentially harmful Element	Minimum Conc. Mg/kg	Average Conc. Mg/kg)	Maximum Conc. Mg/kg	Canadian soil quality guideline values
				Residential use
As ³⁺	7.0	55	195	12
Cd ²⁺	0.4	4.8	28.6	1.2
Co ²⁺	1.9	3.6	12	50
Pb ²⁺	25.9	255	1835	140
Potentially harmful Element	Minimum Conc. Mg/kg	Average Conc. Mg/kg)	Maximum Conc. mg/kg	Canadian soil quality guideline values
				Agricultural use
As ³⁺	7.0	55	195	12
Cd ²⁺	0.4	4.8	28.6	1.2
Co ²⁺	1.9	3.6	12	40
Pb ²⁺	25.9	255	1835	70

5.1.6.1 Soil's suitability for residential and agricultural land use with respect to arsenic levels.

Concentrations of potentially harmful arsenic in the soil samples in this study ranged between 7 mg/kg and 195 mg/kg (See Table 5.4). The Old Tsumeb Mine pit had a value of 421 mg/kg which is an outlier. The lowest concentration (7 mg/kg) is lower than the Canadian Guideline value for both residential areas and agricultural land use. The highest value obtained (195 mg/kg) is greater than the Canadian soil quality guideline value for As for residential areas and agricultural land use. At 55 mg/kg, the average concentration of arsenic in the soil samples was also above the soil quality guideline values for both residential areas and agricultural land use.

Of the 30 soil samples which were collected in this study, 83% of those samples had As^{3+} values exceeding the Canadian soil quality guidelines for residential land use versus 17% that were within the guideline values (Figure 5.10). Equally, 83% of the samples had As^{3+} values exceeding the Canadian soil quality guidelines for agricultural land use. Seventeen (17) % of the soil samples fall in the range within which it is safe for agricultural activities to take place (Figures 5.11).

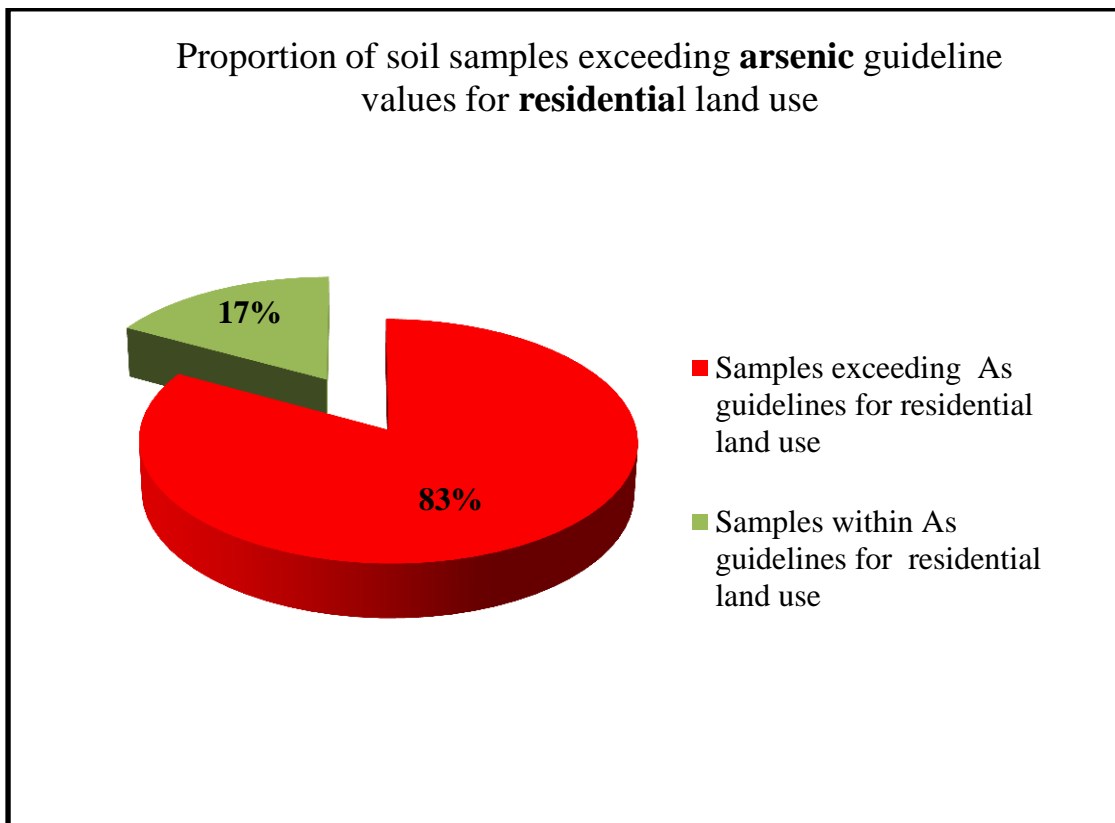


Figure 5.10: Proportions of soil samples exceeding Canadian guideline values of arsenic for residential land use

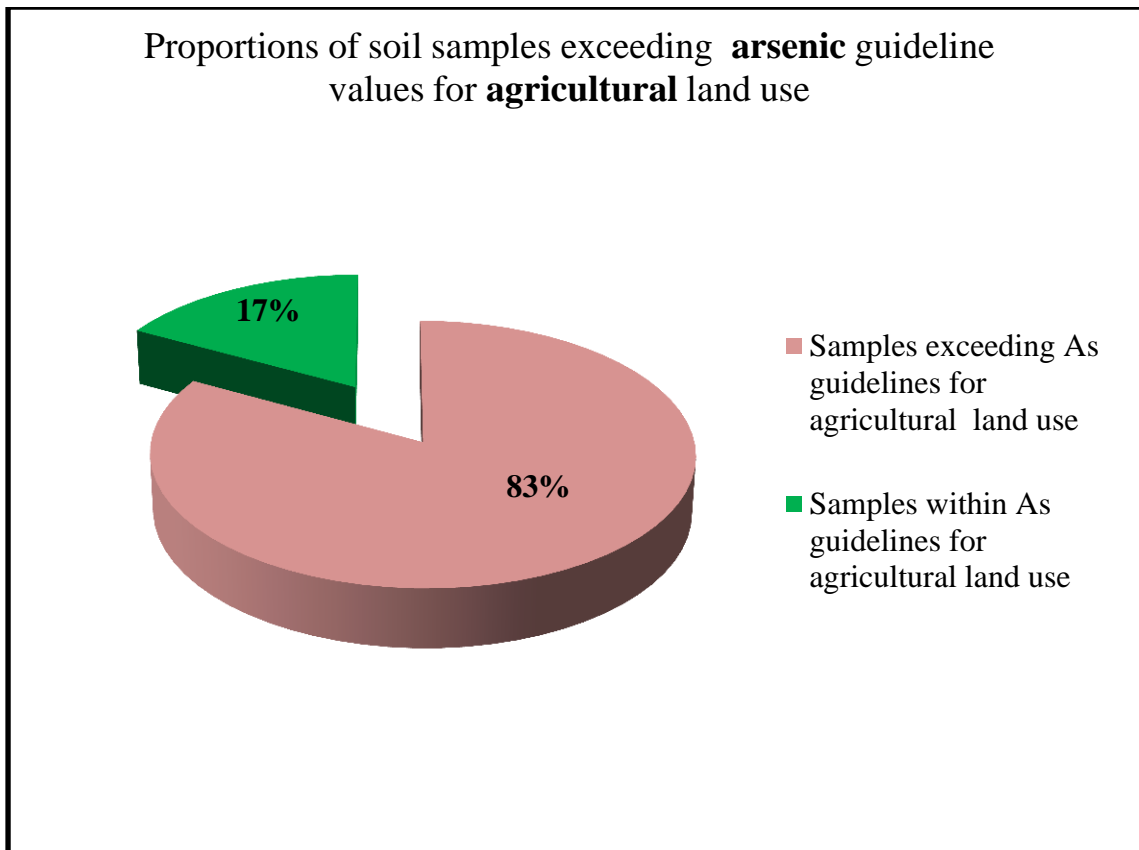


Figure 5.11: Proportions of soil samples exceeding Canadian guideline values of arsenic for agricultural land use

5.1.6.2 Soil's suitability for residential and agricultural land use with respect to cadmium levels.

Concentrations of harmful cadmium in the soil samples in this study ranged between 0.4 mg/kg and 35.6 mg/kg (See Table 5.4). The maximum value obtained for Cadmium (35.6 mg/kg) represents primary mineralization as the sample was collected from the Tsumeb Mine and is considered an outlier. The next highest value obtained is 28.6 mg/kg which exceeds the Canadian soil quality guideline values of 1.2 mg/kg for both residential and agricultural areas. At 4.8 mg/kg, the average values obtained for Cd^{2+} also exceeds Canadian soil quality guideline values for residential and agricultural areas.

Sixty seven (67) % of all the soil samples had Cd values above the Canadian soil quality guideline value for residential and agricultural land use (Figure 5.12 and Figure 5.13 respectively).

Thirty three (33) % of the samples were within the cadmium guideline values for residential and agricultural land use.

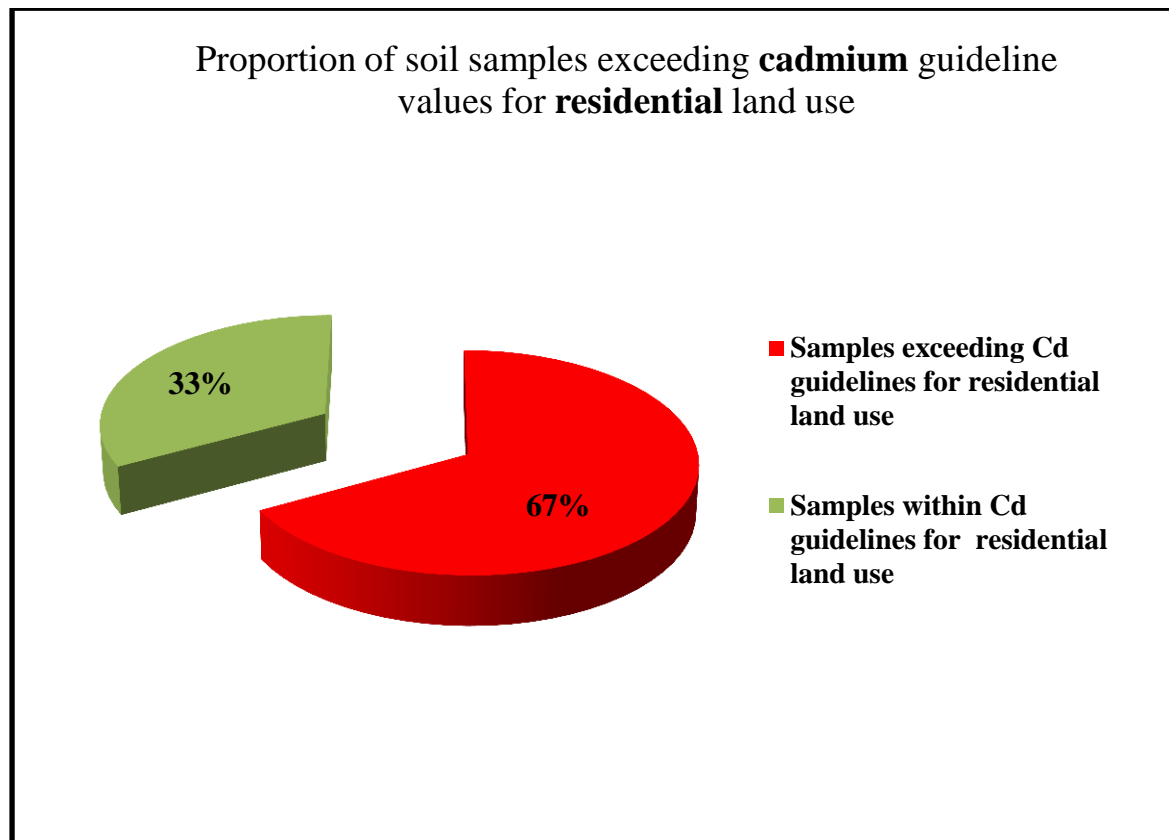


Figure 5.12: Proportions of soil samples exceeding Canadian guideline values of cadmium for residential land use.

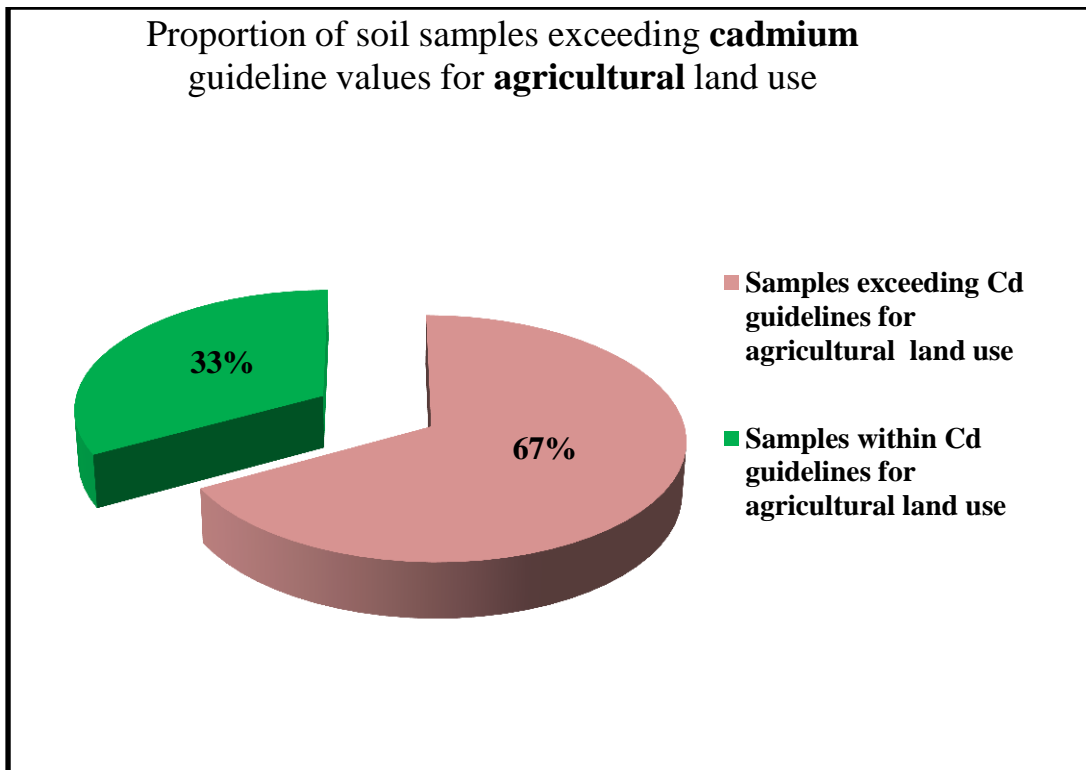


Figure 5.13: Proportions of soil samples exceeding Canadian guideline values of cadmium for agricultural land use.

5.1.6.3 Soil's suitability for residential and agricultural land use with respect to cobalt levels.

None of the soil samples analyzed in this study had Co^{2+} values exceeding the Canadian soil quality guideline values of 50 mg/kg and 40 mg/kg for residential and agricultural land use respectively (See Figure 5.14 and 5.15). The highest value obtained is 12 mg/kg. The average values obtained for Co^{2+} in soils is 3.6 mg/kg. All current values were below the guideline values for both land uses.

Proportion of soil samples exceeding **cobalt** guideline values for **residential** land use.

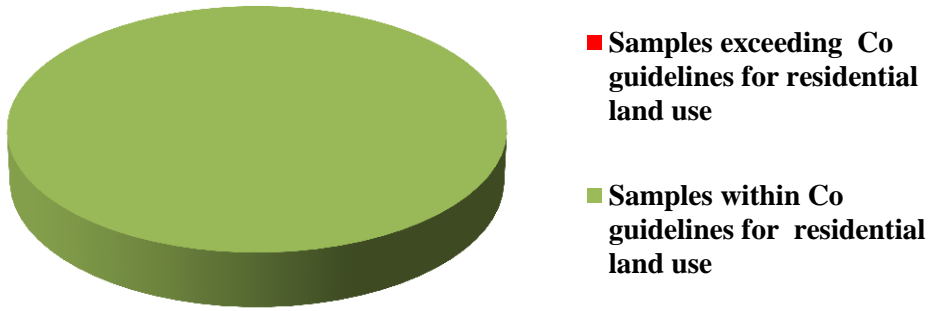


Figure 5.14: Proportions of soil samples exceeding Canadian guideline values of cobalt for residential land use.

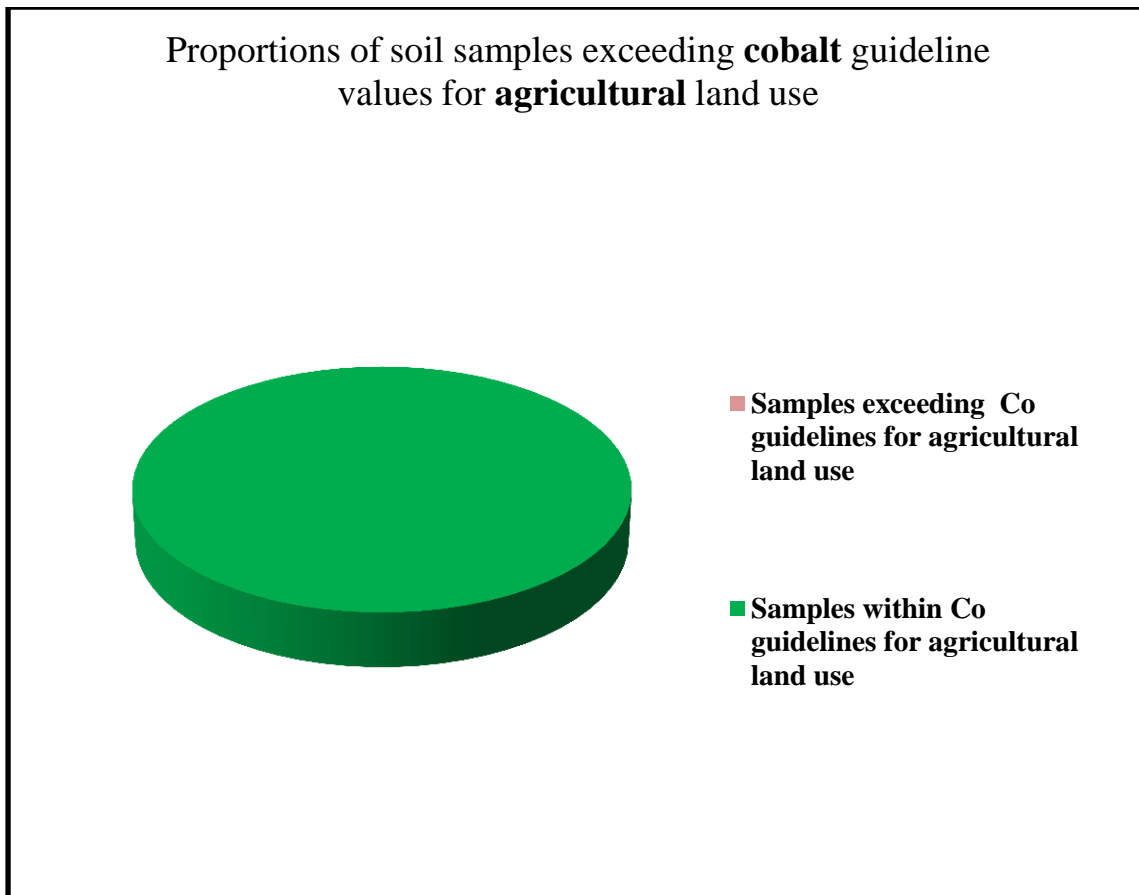


Figure 5.15: Proportions of soil samples exceeding Canadian guideline values of cobalt for agricultural land use.

5.1.6.4 Soil's suitability for residential and agricultural land use with respect to lead levels.

The concentrations of lead in the soil samples in this study ranged between 25.9 mg/kg and 3786, 9 mg/kg (see Table 5.4). The lowest value for Pb^{2+} is within the Canadian soil quality guideline value for Pb for residential areas. The maximum value (3786, 9 mg/kg) is an outlier sampled at the Old Tsumeb Mine pit. Excluding the outlier, the next highest result was 1835 mg/kg from a sample collected near the old Tsumeb Mine. At 255 mg/kg, the average value obtained for Pb^{2+} in soils is above the Canadian soil quality guideline values for residential areas (Table 5.4). Figure 5.8 shows that 40% of the soil samples in this study had Pb values above the Canadian soil quality guideline value for residential areas whereas 60% were within the guideline values for residential land use.

Sixty three (63) % of the soil samples analysed in this study exceeded the Canadian soil quality guideline values of lead for agricultural land use. Thirty seven (37) % of the soil samples fell within the guideline values for agricultural land use (Figures 5.17). At 255 mg/kg, the average values obtained for Pb in soils also exceeded the Canadian guideline value of soils for agricultural use (Table 5.4).

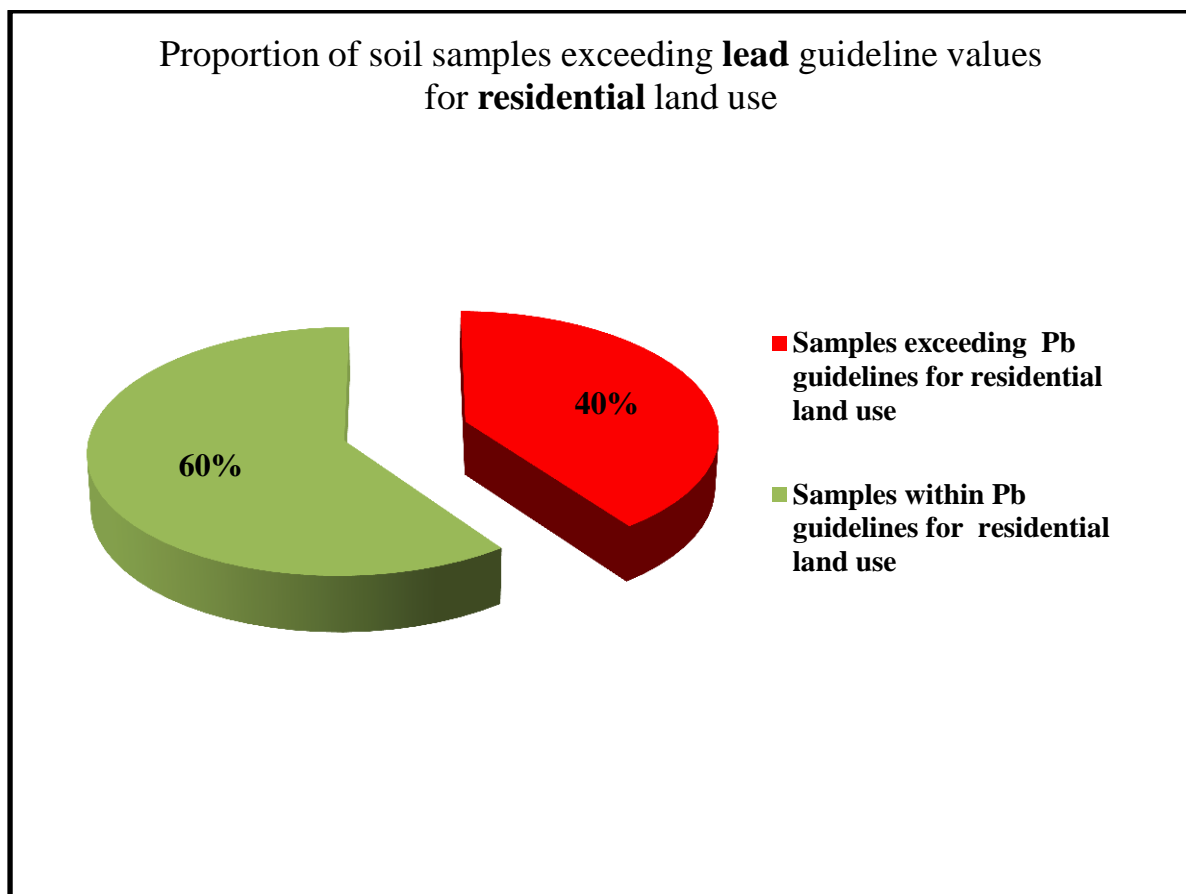


Figure 5.16: Proportions of soil samples exceeding Canadian guideline values of lead for residential land use.

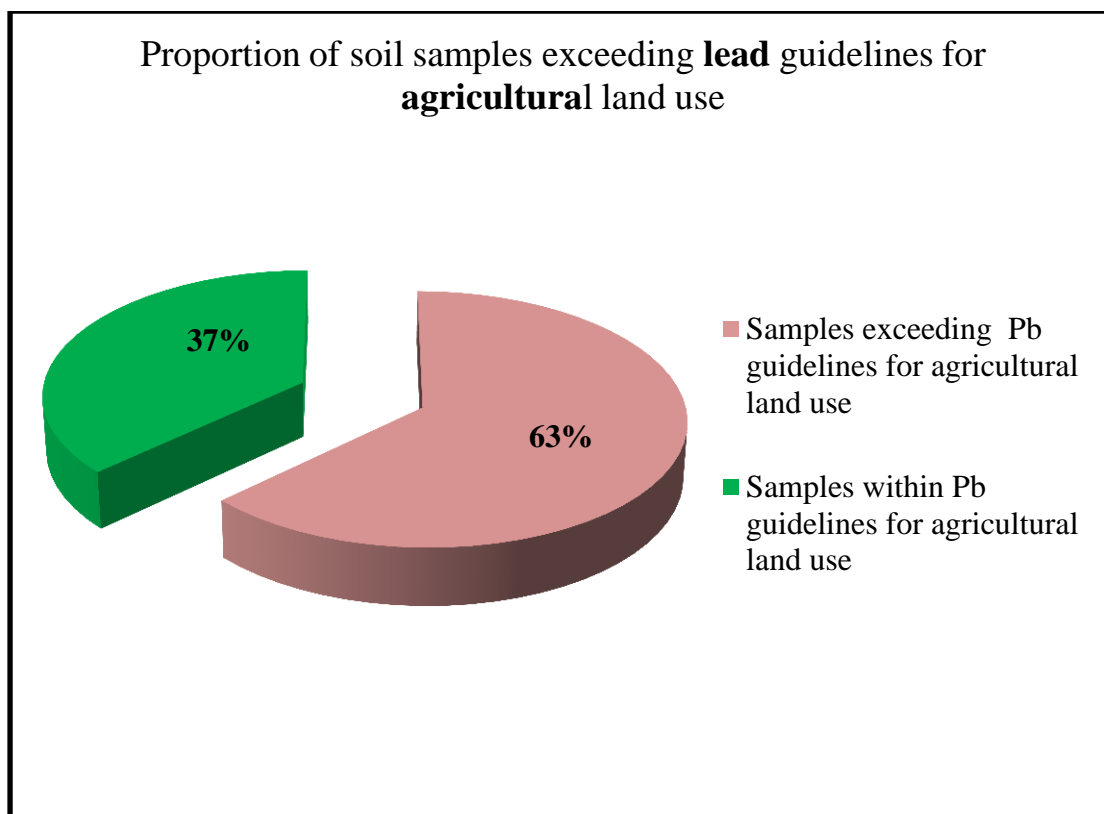


Figure 5.17: Proportions of soil samples exceeding Canadian guideline values of lead for agricultural land use

5.2 Analysis of vegetation samples

Heavy metals have the capability to migrate from polluted soil to plant tissues. Toxic metals accumulate in different plant organs at a rate that varies from organ to organ. Some organs accumulate more heavy metals than others (Khan et al., 2015). This study therefore also analysed potential harmful element concentration in vegetation.

5.2.1 Comparison of heavy elements occurring naturally in biota to concentrations in vegetation sampled during the current study

The concentration of heavy elements occurring naturally in biota was compared to the concentration in vegetation sampled in this study (Table 5.5). The average concentration of arsenic and lead in the vegetation in this study was found to be higher than the concentrations found naturally in biota.

There is hardly any lead occurring naturally in vegetation (Table 5.5). Significant amount of lead in plants in this study points to anthropogenic influence (Figure 5.18). The average concentration of Cd^{2+} and Co^{2+} in this study is lower than concentrations reported to be found naturally in biota. This result could be due to a number of factors such as; low Cd^{2+} and Co^{2+} in the rocks and soils, low bioavailable fractions of Cd^{2+} and Co^{2+} in the soil, type of soil in which the heavy metals are concentrated. A number of other factors may have influenced the bioavailability of Cd^{2+} and Co^{2+} .

Table 5.5: Heavy metal concentrations found naturally in biota compared to average concentration in vegetation sampled during this current study. Statistics on elements in lithosphere and Biota adapted from Van der Voet et al. (2013).

Metal	Lithosphere mg/kg	Biota mg/kg	Average potentially harmful element concentration in vegetation in current study (mg/kg)
As	1.8	3	72.1
Cd	0.10	16	3.3
Co	10-23	22	1.1
Pb	12-20	0.008	90

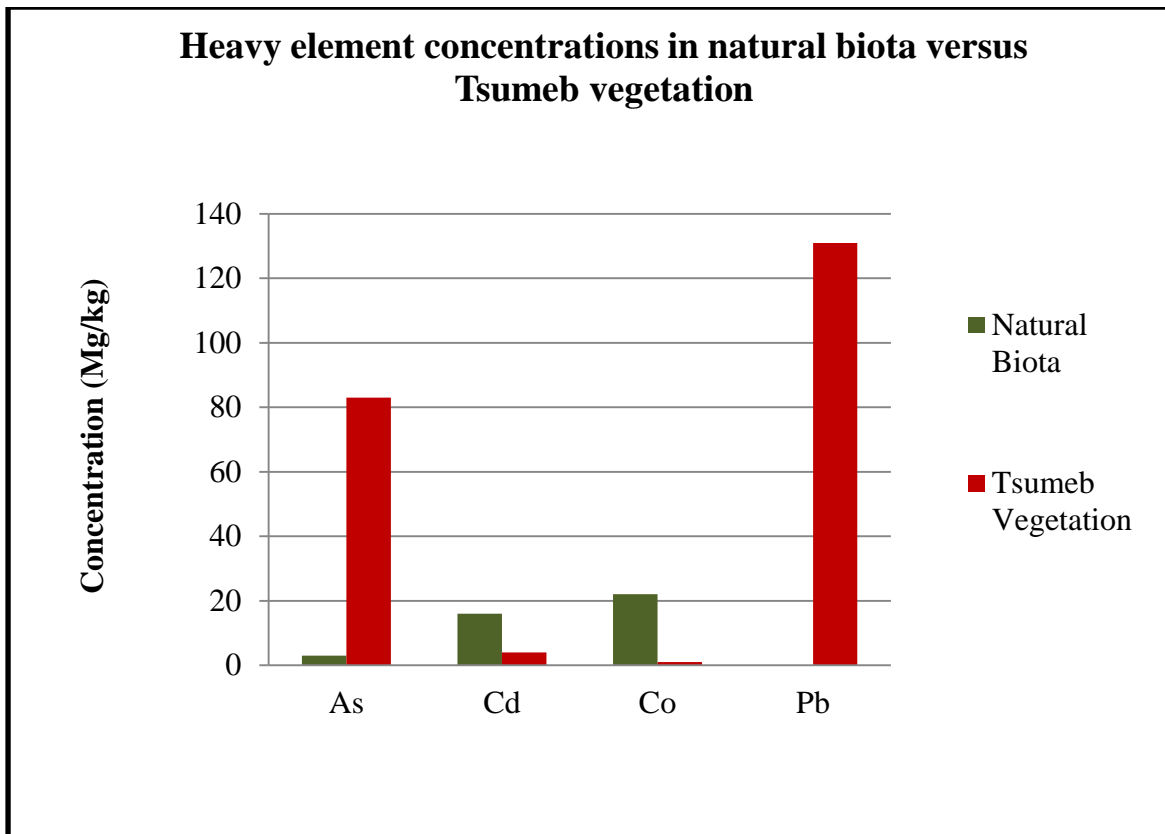


Figure 5.18: Heavy metal concentrations found naturally in biota compared to average concentration in vegetation sampled during the current study.

5.2.2 Comparison of Vegetation samples to International guidelines

For interpretation of results, the guideline values of the WHO (2001) Codex Alimentarius and EU (2006) were applied in this study in the absence of Namibian guidelines. Both guidelines are indicated in Table 5.6.

Table 5.6: WHO (2001) Codex Alimentarius and EU (2006) guideline values for Agricultural plants

Element	WHO (2001) guidelines	EU (2006) guidelines
As (mg/kg)	0.5	N/A
Cd (mg/kg)	N/A	0.2
Co (mg/kg)	N/A	N/A
Pb (mg/kg)	0.4	0.3

N/A =guideline values are not available.

Potentially harmful elements in Tsumeb vegetation were compared to the aforementioned guidelines. All shaded results exceeded the WHO (2001) and EU (2006) guideline values (Table 5.7).

Table 5.7: Concentration of potentially harmful elements in Tsumeb vegetation compared to guidelines. All shaded results exceeded the WHO (2001) and EU (2006) guideline values.

Sample No	Vegetation type	Concentration (mg/kg)			
		As ³⁺	Cd ²⁺	Co ²⁺	Pb ²⁺
TSV 27906	Mango leaves	17.7	0.43	0.3	8.43
TSV 27908	Mango leaves	36.6	1.71	0.9	37.86
TSV 27909	Mango leaves	31.6	1.17	0.9	32.19
TSV 27910	Lemon leaves	28	0.44	0.7	26.78
TSV 27914	Sunflower leaves	20.6	2.76	0.9	18.25
TSV 27915	Sunflower leaves	46.7	8.13	1.1	40.93
TSV 27918	Dried papaya leaves	113.6	0.83	1.3	60.43
TSV 27919	Fresh papaya leaves	39.4	0.67	0.8	37.36
TSV 27922	Marula fruit	55.6	3.29	1.4	113.18
TSV 27923	Marula tree bark	18.8	1.18	0.2	28.23
TSV 27926	Fig leaves	247	6.06	2.6	231.74
TSV 27927	Fig fruits	96.5	4.4	1.8	120.08
TSV 27929	Fig leaves	161.4	3.93	1.6	113.59
TSV 27930	Fig fruits	82.6	3.36	1.6	76.38
TSV 27932	Fig leaves	183.9	5.53	1.9	169.69
TSV 27933	Fig fruits	107.5	4.29	1.5	144.17
TSV 27939	Marula tree bark	13.2	0.77	0.2	27.7
TSV 27942	Marula tree bark	116.5	23.77	2.4	801.67
TSV 27943	Marula tree bark	63.2	12.77	1.3	415.26
TSV 27950	Marula tree bark	5.4	0.3	0.2	7.58
Arsenic WHO(2001) Guideline		0.5	N/A		0.3
Arsenic EU(2006) Guideline		N/A	0.2		0.4
Natural levels in biota (Figure obtained from Kim et al. (2006))				0.35	

5.2.2.1 Concentration of potentially harmful arsenic in Tsumeb vegetation samples compared to International guidelines

All plant samples investigated in this study showed arsenic concentrations exceeding the WHO (2001)'s limit of 0.5 mg/kg for plants (Figure 5.19). The highest concentrations were found in fig leaves and fruits, marula tree barks and papaya leaves. Concentrations exceeded the limit over 200 times (Table 5.7). Sunflower leaves also had high arsenic concentrations.

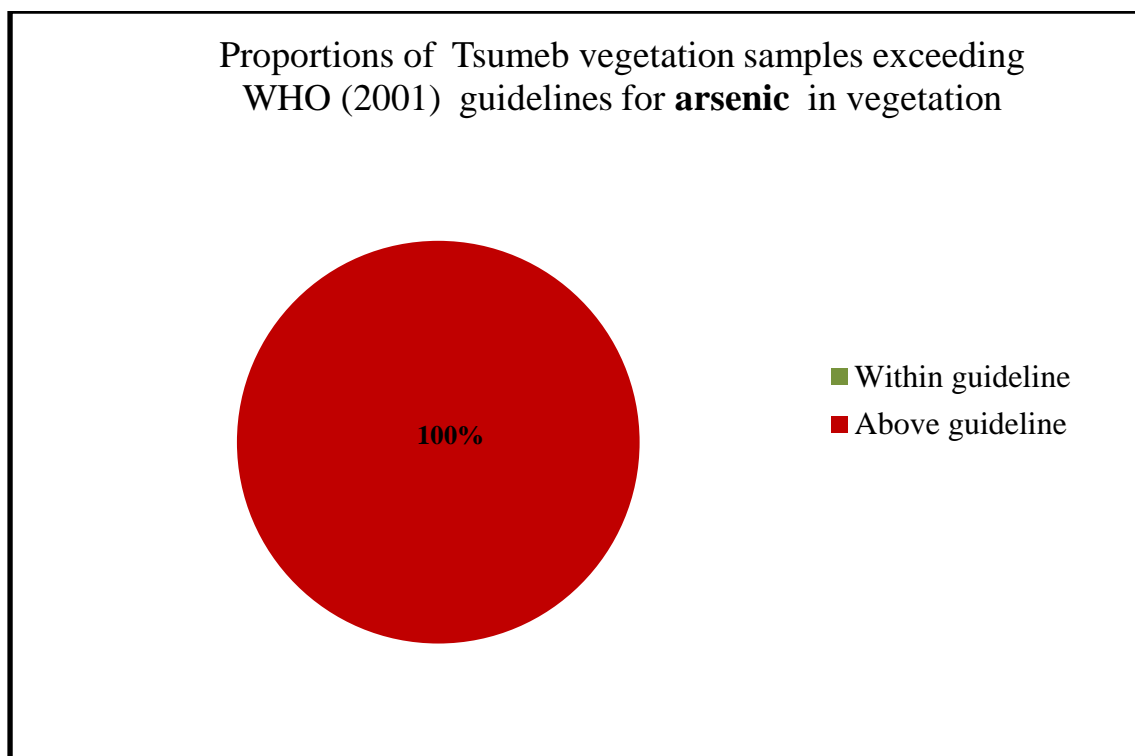


Figure 5.19: Proportion of Tsumeb vegetation samples exceeding WHO guidelines for arsenic in plants.

5.2.2.2 Concentration of potentially harmful cadmium in Tsumeb vegetation samples compared to EU guidelines.

The EU (2006) guideline value of 0.2 mg/kg for cadmium was exceeded in all vegetation samples (Figure 5.20). The highest concentrations were found in marula tree bark. An isolated sample of sunflower leaves (TSV 27915) collected from Nomtsoub suburb also showed high cadmium concentration of 8.13 mg/kg (Table 5.7). The elevated concentration in this sample could be attributed to bedrock enriched in cadmium.

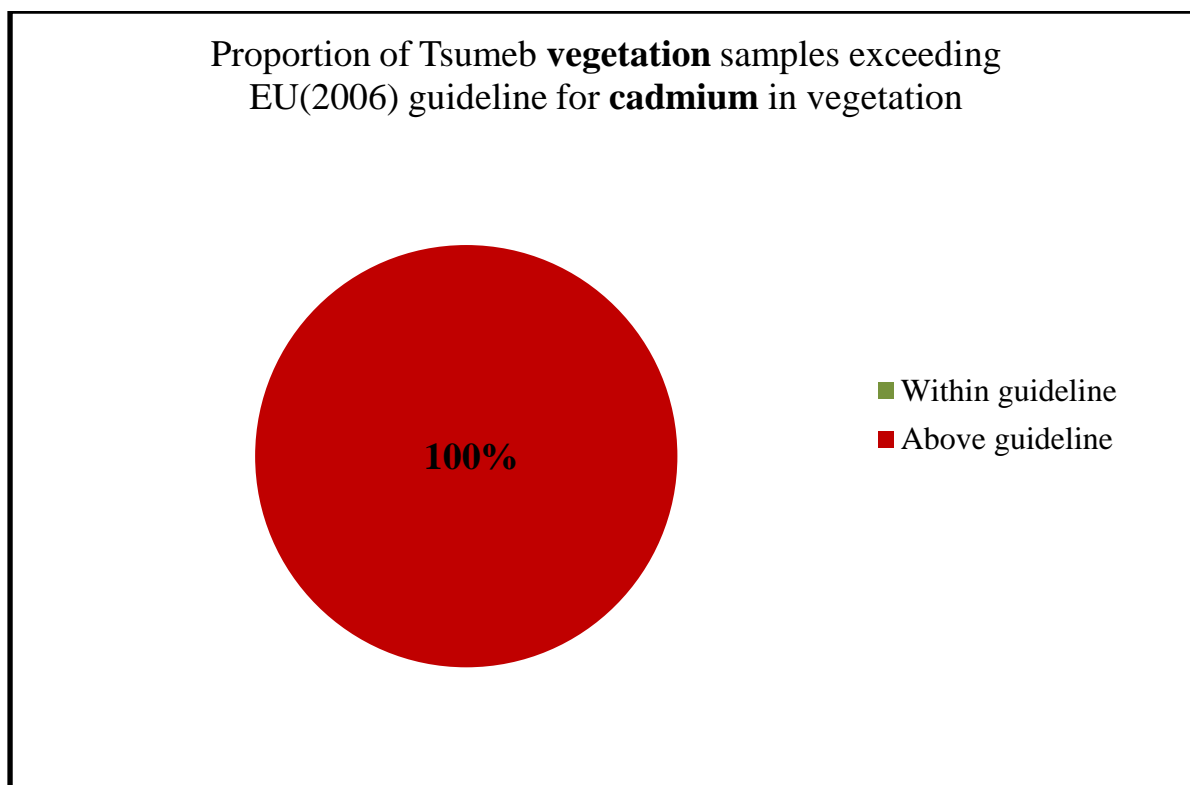


Figure 5.20: Proportion of Tsumeb vegetation samples exceeding EU guidelines for cadmium in vegetation.

5.2.2.3 Concentration of potentially harmful cobalt in Tsumeb vegetation samples compared to concentration in natural biota

In the absence of guidelines on concentration of cobalt in vegetation, the cobalt concentrations in Tsumeb vegetation sampled during this study were compared to concentrations that are found naturally in vegetation where anthropogenic pollution is not present. According to Kim et al. (2006), the cobalt content of living plants depends on the species, the cobalt content of the soil and numerous other environmental factors. Terrestrial plants normally contain cobalt concentrations of 0.2 -0.35 $\mu\text{g/g}$ (equivalent to 0.35 mg/kg) but grasses from cobalt deficient regions contain only 0.06 $\mu\text{g/g}$ or 0.06 mg/kg (Kim et al., 2006).

Kim et al. (2006) also report that some plants with cobalt tolerance called hyperaccumulators of cobalt have been found with mean concentrations of 4303 mg/kg. Cobalt concentration in Tsumeb vegetation is above what is normally found naturally in plants. Table 5.7 shows the concentration of Co^{2+} in different vegetation samples in Tsumeb. The natural concentration of cobalt in vegetation (0.35 mg/kg) is exceeded in more than 80% of the vegetation samples albeit only moderately (Figure 5.21).

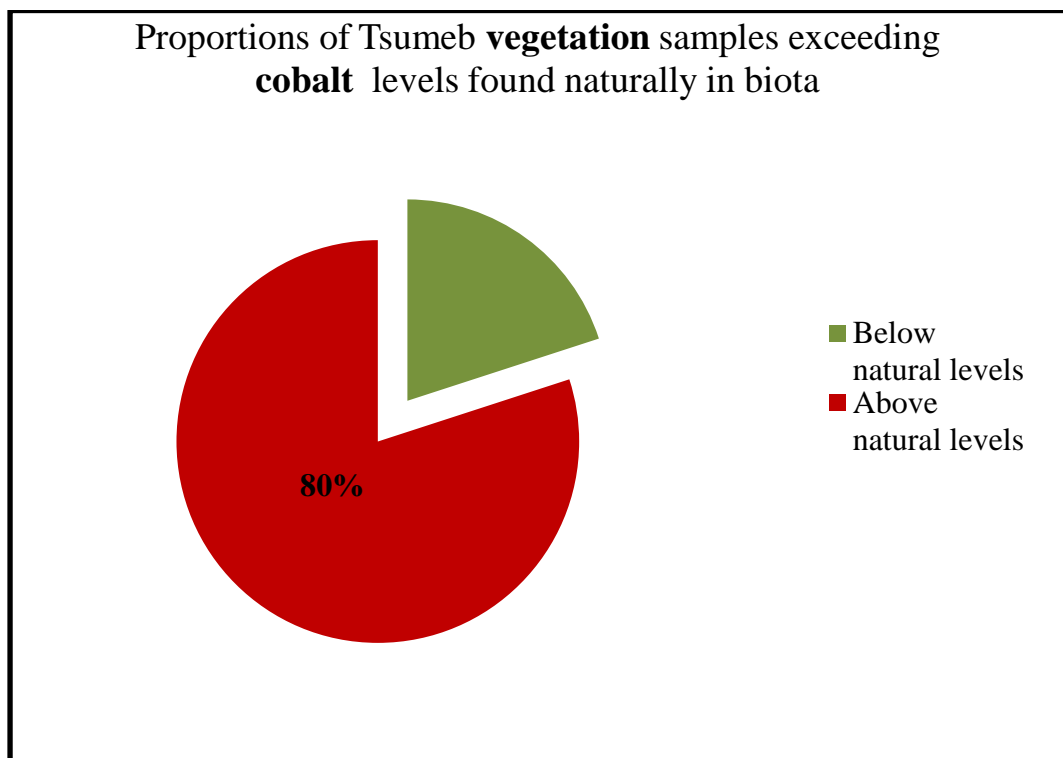


Figure 5.21: Proportions of Tsumeb vegetation samples exceeding cobalt levels found naturally in biota.

5.2.2.4 Concentration of potentially harmful lead in Tsumeb vegetation samples compared to International guidelines

Table 5.7 shows the concentration of Pb^{2+} in different vegetation samples. All vegetation samples in this study had lead concentration exceeding the WHO (2001) and EU (2006) guideline values of 0.3 and 0.4 mg/kg respectively for lead in vegetation (Figure 5.22).

The highest concentrations were found in marula tree barks (801.67 mg/kg) and fig leaves (231.74 mg/kg) sampled west of the Tsumeb Mine. Fresh papaya leaves also had high Pb²⁺ concentrations.

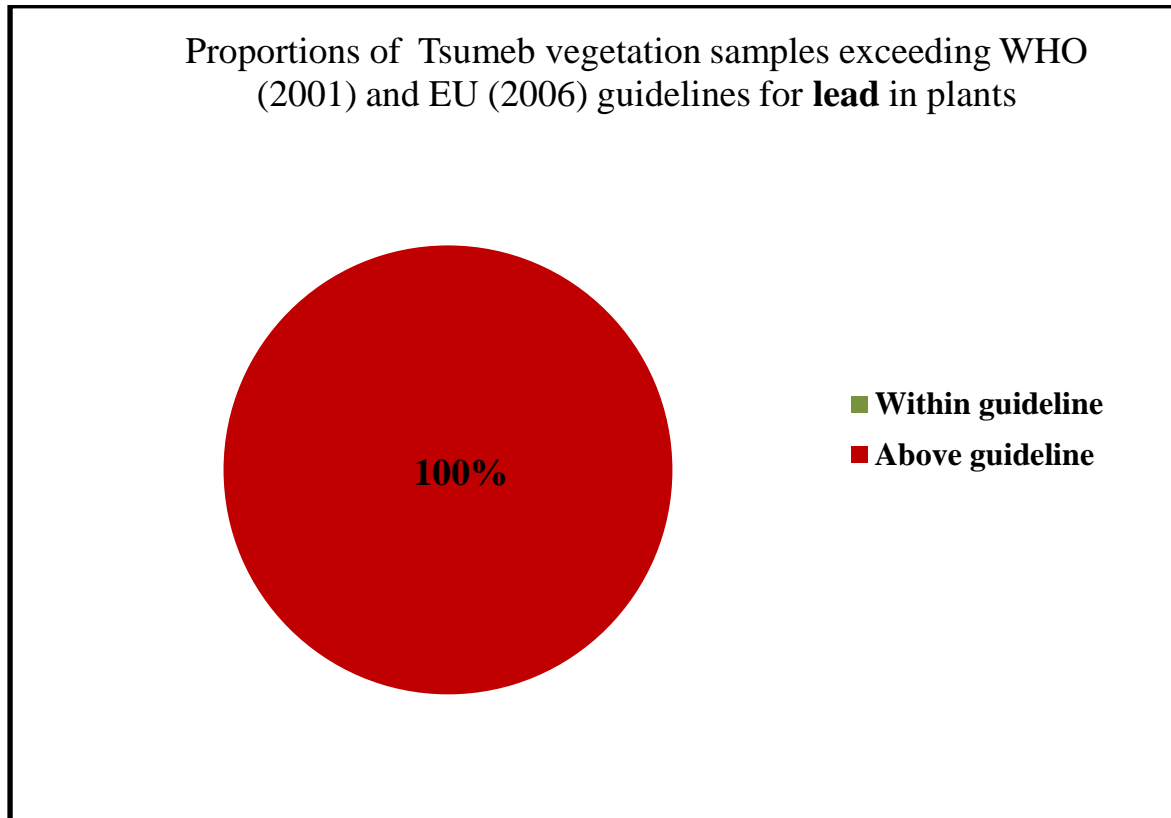


Figure 5.22: Proportions of Tsumeb vegetation samples exceeding WHO (2001) and EU (2006) guidelines for lead in plants.

5.3 Comparison of current study to previous environmental studies in Tsumeb

5.3.1 Comparison of soil analysis results

Křibek & Kamona (2005) reported on pioneering environmental work done in Tsumeb in 2005 and previous years. The sampling covered areas all around the Tsumeb town. They record the following results from analysis of surface soil samples in the Tsumeb area: maximum values of 170 mg/kg As, 35 mg/kg Cd and 450 mg/kg Pb. Results of lower soil horizon samples are taken as background.

The following median values are recorded: 3.43 mg/kg for arsenic, 0.32mg/kg for cadmium and 46 mg/kg lead (Křibek and Kamona, 2005). In 2009, Ipinge conducted a geochemical and mineralogical study of the heavy metal contaminants in soils of the Tsumeb area. The sample coverage was widespread in extent covering the smelter complex, the tailings and slag dumps as well as the former Tsumeb open pit Mine. She reported the following results for her work in the Tsumeb area: As (21 -34900 ppm), Cd (2 -171 ppm), Pb (32 -25600 ppm), Zn (21 – 2280 ppm). These values are several magnitudes higher than results obtained in the current study.

Křibek et al. (2014) mapped out the distribution of metals in pasture grass in the Tsumeb area. Sampling covered both the north western and north eastern areas surrounding Tsumeb even as far as farm Pasadena 477, Tsumore 478, Dannenberg and Manheim 100 some approximately 25km away from the Tsumeb CBD. Mapani et al.'s 2014 study concentrated on areas west and northwest of Tsumeb including the Nomtsoub suburb and areas along the road to Tsintsabis. The following results were recorded: Arsenic concentrations in the range of 19-849 ppm in soil samples; Cd ranged from 2 to 224 ppm and lead ranged from 100-3020 ppm. Ellmies et al. (2015) investigated the environmental situation of the area surrounding the smelter. The study showed that the highest soil contaminations were adjacent to the historic smelter area with maximum values of 229 mg/kg As, 38.7 mg/kg Cd, 483 mg/kg Cu and 1080 mg/kg Pb exceeding guideline values many fold. More studies followed for the same area with Křibek et al. (2016) studying the contamination of soil and grass in the Tsumeb smelter area and modelling contaminant dispersion. The study also involved ground geochemical verification. Křibek et al. (2016) reported the following results of analysis of Tsumeb soil samples: 4.4 -2477.9 mg/kg As, 0.3 -159.1 mg/kg Cd and 24 -7392 mg/kg Pb.

In this current study, analytical results of harmful species of heavy metals in soils revealed moderate to high concentrations as follows: 7 – 421 mg/kg As³⁺, 0.4 - 35.6 mg/kg Cd²⁺, 2 - 6.3 mg/kg Co²⁺ and 25.9 - 3786.9 mg/kg Pb²⁺. In previous studies, samples were analysed for total element concentrations. The current study analysed only the potentially harmful, bioavailable portions of the aforementioned heavy metals. *Results obtained in previous studies were compiled from combined data from Kamona & Křibek (2005); Iiping (2009); Mapani et al. (2014); Ellmies et al. (2015) and Křibek et al. (2016). The average minimum values were calculated from the individual minimum values of elements obtained by the aforementioned researchers. Similarly, the average maximum values were calculated from the individual maximum values of elements obtained by each of the aforementioned researchers. The average concentrations are actually averages of the average values obtained in the previous studies.

Table 5.8: Comparison of results of previous studies (total heavy metals in soils) versus results of the current study (potentially harmful bioavailable fractions).

	*Average Minimum Concentrations (mg/kg)		*Average Maximum Concentrations (mg/kg)		*Average Concentrations (mg/kg)	
	Previous Studies	Current Study	Previous Studies	Current Study	Previous Studies	Current Study
Arsenic	19	7	745	195	50	55
Cadmium	2	0.4	224	28.6	4.1	4.8
Cobalt	*N/A	1.9	*N/A	12	*N/A	3.68
Lead	100	25.9	7508	1835.1	255	255

The green colour in Table 5.8 represents the lower concentration between the studies under comparison.

The pink represents the higher concentration between the studies under comparison.*N/A: Cobalt was not part of previous studies that were conducted in the Tsumeb area and therefore could not be compared. The results of this current study are also graphically compared to results of previous studies. Figure 5.23 shows that; the average minimum and average maximum of the bioavailable fractions of the element arsenic, are lower than the minimum and maximum concentrations obtained for arsenic in previous studies which dealt with total metal concentration. The average arsenic concentration in the current study is however slightly higher than results recorded in previous studies involving total metal concentrations.

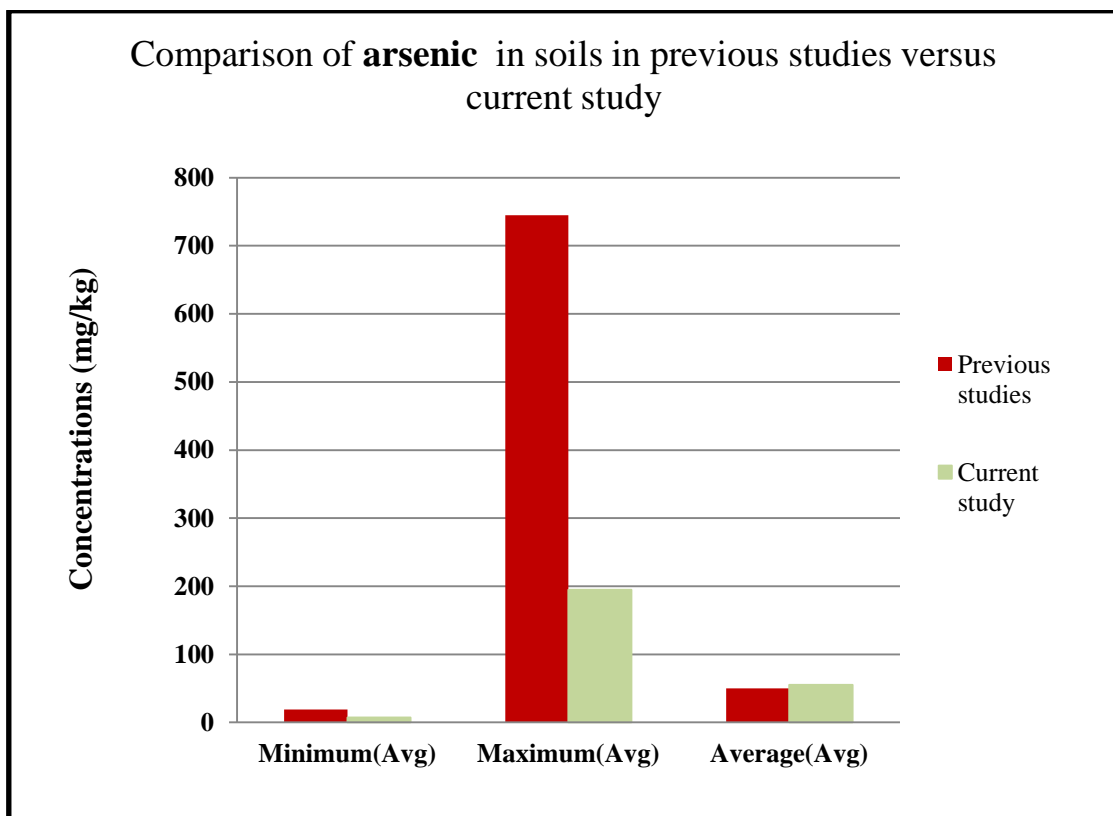


Figure 5.23: Comparison of arsenic in soils in previous studies versus current study

Figure 5.24 shows that; the average minimum and average maximum of the bioavailable fractions of cadmium is lower than the minimum and maximum concentrations obtained for cadmium in previous studies which dealt with total metal concentration.

The average cadmium concentration in the current study is however slightly higher than results recorded in previous studies involving total metal concentrations.

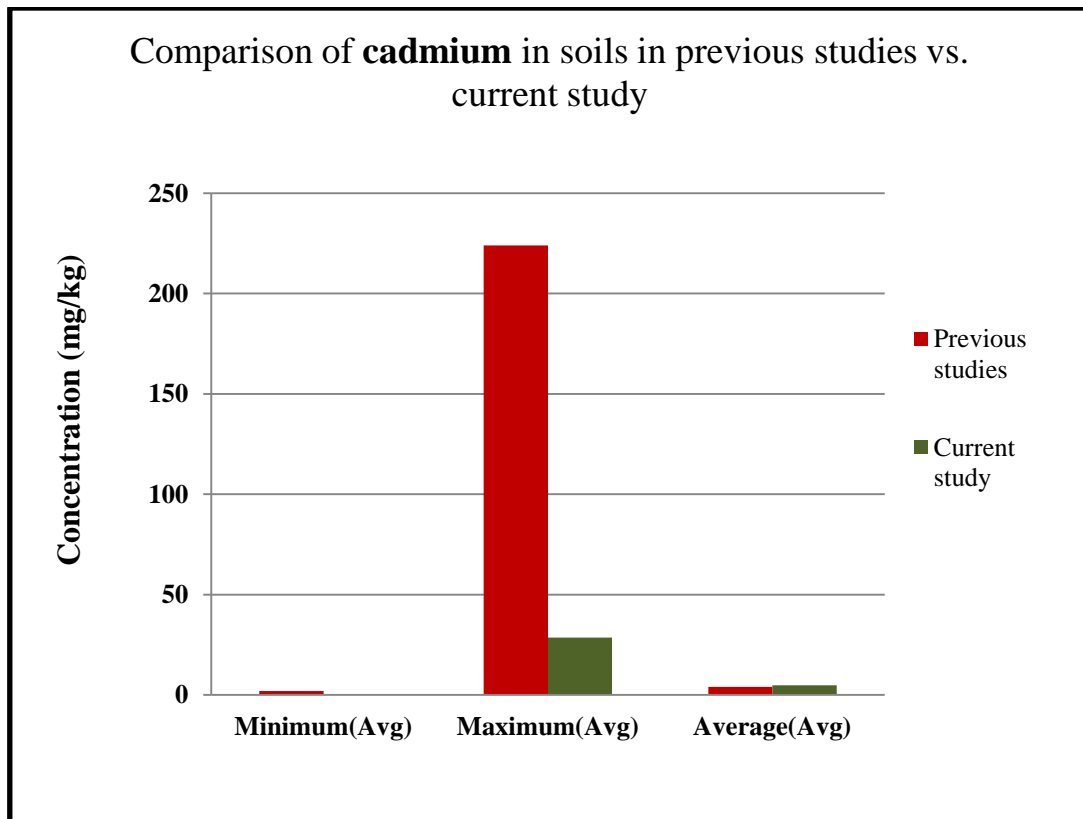


Figure 5.24: Comparison of cadmium in soils in previous studies versus current study

Figure 5.25 shows that; the average minimum and average maximum of the bioavailable fractions of lead is lower than the minimum and maximum concentrations obtained for lead in previous studies which dealt with total metal concentration. The average lead concentration in the current study is the same as the average values recorded in previous studies involving total metal concentrations.

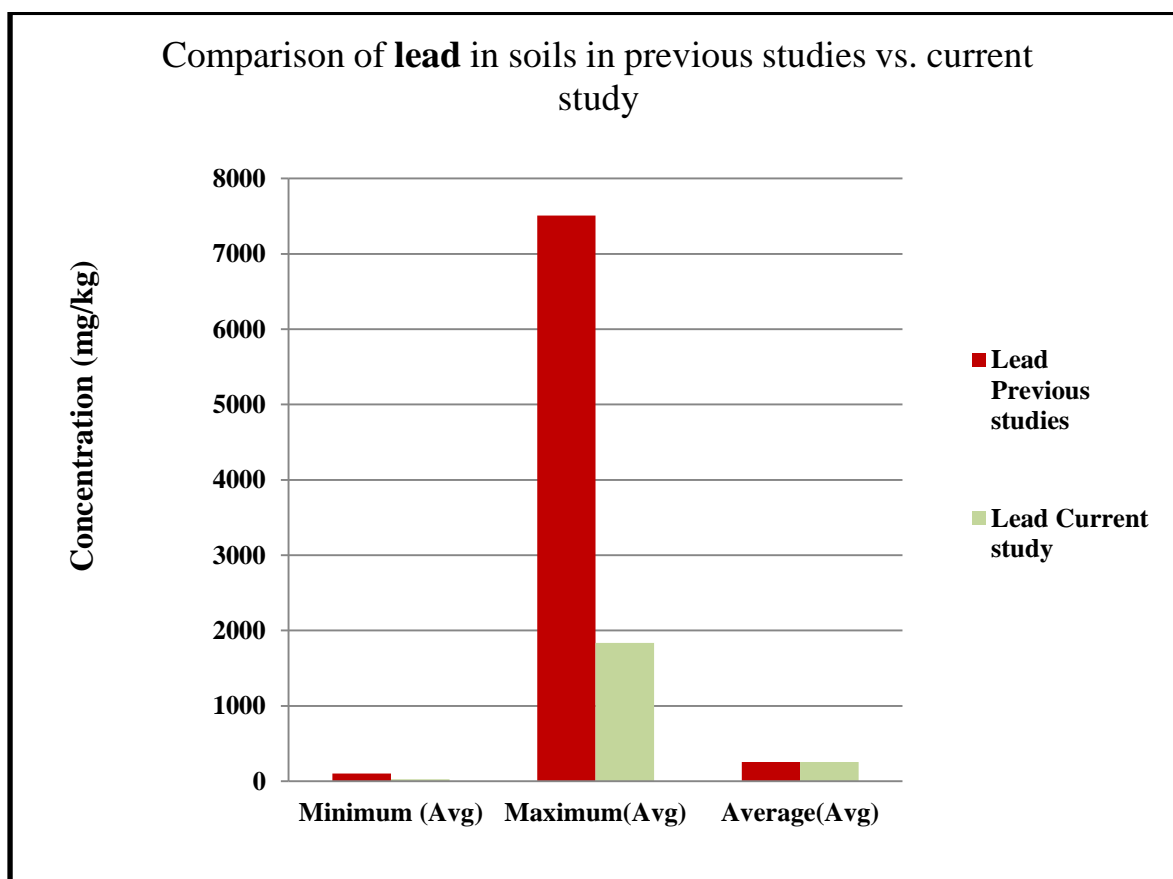


Figure 5.25: Comparison of lead in soils in previous studies versus current study

In summary, the minimum obtained values for all elements in the soil samples of the current study are lower than those obtained in the previous studies where total element concentrations were obtained. This is in exception of cobalt which was not part of the previous studies and could therefore not be compared. Without exceptions, maximum values also followed the same trend. The average concentrations of the potentially harmful elements arsenic and cadmium in current study are slightly higher than average concentrations recorded in previous studies. The average concentrations of the potentially harmful elements lead in the current study is the same as the average lead concentrations recorded in previous studies by earlier researchers.

The hypothesis that the concentrations of potentially harmful species of As, Cd, Co and Pb in soils and vegetation in Tsumeb are less than those obtained during previous studies which assessed total element concentrations was true for minimum and maximum concentrations.

5.3.2 Comparison of vegetation analysis results of current study to previous studies

Heavy metals in vegetation could not be directly compared between the previous studies and the current study as different vegetation samples were involved in the different studies. Khan et al (2015) records that the bioaccumulation of heavy metal is different for the various plant species. The same heavy metal can be accumulated at different ratios in different plant species. This is because the mechanisms of elemental uptake by plants are not the same for all plant species. Different plant species also show different toxicity to the same pollutant in the same environmental conditions. For this reason, the concentration of the potentially harmful elements in vegetation in this current study cannot be compared to previous studies because different plants were considered. However heavy metal contamination in vegetation is reported as follows from previous studies: The highest contents of metals were reported as follows from previous studies: 26.6 ppm As, 52.6 ppm Mo and 104 ppm in the grass species *Eragrostis cf. Porosa* sampled in the grassland near the Tsumeb Smelter. A large number of grasses from the Tsumore 761 Farm and 1335 Cadastre and peripheral parts of the Dannenberg 478 Farm were found to be affected by contamination. Very high Pb concentrations in grass were found in the grasses samples in the vicinity of the smelter (Křibek et al., 2014). The contamination with Mo and As could be traced over a distance of 12 km NW of the Tsumeb Smelter (Křibek et al., 2014). In a previous study done by Mapani et al. (2014), for generally the same area, the arsenic concentrations in papaya and marula varied between 0.3 and 1.1 mg/kg and thus exceeded guideline values only moderately.

In this current study, arsenic concentrations in papaya and marula fruit were as high as 113.6 mg/kg and 55.6 mg/kg respectively. The highest concentrations of metals As: 18.7 mg/kg, Cd: 3.3 mg/kg, Pb: 51.7 mg/kg were found in grass samples collected from the vicinity of the Tsumeb Smelter (Křibek et al., 2016).

In this study, analytical results of potentially harmful heavy metals in vegetation revealed moderate to high concentrations. The concentrations were as follows in mg/kg: 5.4 to 247 mg/kg As^{3+} , 0.3 to 23.77 mg/kg Cd^{2+} , 0.2 to 2.6 mg/kg Co^{2+} and 8.43 to 801.67 mg/kg Pb^{2+} . In summary, both previous studies and the current study showed significant contamination of different vegetation within a distance of 15-20 km away from the smelter.

5.4 Human health risk for Nomtsoub Suburb and Tsumeb population

Heavy metal risk assessments are normally done for the purpose of ultimately protecting environmental and human health. The process of risk assessment involves four major steps according to Dorne et al (2011) namely; hazard identification, hazard characterization, and exposure assessment as well as risk characterization. Hazard identification has been defined as identification of biological, chemical and physical agents capable of causing adverse health effects and which may be present in a particular food or food groups. The main purpose of hazard identification applied to metals is to evaluate the weight of evidence for adverse health effects, based on an assessment of all the available data regarding toxicity and mode of action of the particular metal. Hazard characterization (also known as dose-response assessment) constitutes the qualitative and/or quantitative evaluation of the nature of the adverse health effects associated with chemical agents which may be present in food (Dorne et al, 2011). Exposure assessment is the qualitative and/or quantitative evaluation of the likely intake of biological, chemical and physical agents via food as well as exposure from other sources if relevant.

Exposure assessment integrates the occurrence and the concentrations of the compound in the human diet measured using validated analytical techniques and the human consumption patterns for the different food categories available. Risk characterization is the final step and represents “the qualitative and/or quantitative estimate, including attendant uncertainties, of probability of occurrence and severity of known or potential adverse health effects in a given population based on hazard identification, hazard characterization and exposure assessment. In practice, risk characterization integrates the hazard identification and characterization leading to a health based guidance value and the human exposure estimated from either deterministic or probabilistic methods to conclude on the likelihood of adverse effects for public health (Dorne et al, 2011). The whole process of chemical risk assessment leads to health agencies setting health-based guidance values to prevent the occurrence of adverse health effects in humans. To estimate the potential risk to human beings and animals in Tsumeb, soil results were compared to Canadian Soil Quality Guidelines for the protection of Environmental and Human Health, Update 7.0, 2007 for agricultural land use and residential areas. Vegetation sample results were also compared to the guideline values of the WHO (2001) Codex Alimentarius and EU (2006). Human health soil quality and vegetation quality guidelines provide concentrations of contaminants in soil at or below which no appreciable human health risk is expected. It is therefore a health concern that in exception of cobalt, the soil quality guidelines for As, Cd and Pb for residential purposes were exceeded in the majority of samples; 83% of the soil samples exceeded As guidelines, 67% of the soil samples exceeded Cd guidelines, and 40% of the soil samples exceeded Pb guidelines. Soil quality guidelines for As, Cd and Pb for agricultural purposes were also exceeded in the majority of samples; 83% of the soil samples exceeded As guidelines, 67% of the soil samples exceeded Cd guidelines, and 63% of the soil exceeded Pb guidelines (Table 5.9).

Table 5.9: Proportions of soil and vegetation samples in current study exceeding quality guideline values.

Element	SOIL SAMPLES		VEGETATION SAMPLES
	Proportions of soil samples exceeding guidelines for land use Residential	Proportions of soil samples exceeding guidelines for land use Agricultural	Proportions of samples exceeding guidelines for heavy metals in vegetation
Arsenic	83%	83%	100%
Cadmium	67%	67%	100%
Cobalt	0%	0%	87% of samples exceeded natural levels in biosphere
Lead	40%	63%	100%

Without exception, all the vegetation samples exceeded the quality guidelines for As, Cd and Pb. This indicates that there is appreciable potential risk to the human health of the Nomtsoub suburb and entire Tsumeb Town. The results obtained in this current study are very significant due to the fact that the analyses were done on only the potentially harmful bioavailable portions as they are a better indicator when evaluating potential risk posed by harmful metal contamination on the environment and in human beings. Under certain environmental conditions, these potentially harmful elements can be very toxic and detrimental to environmental and human health (Tangahu et al, 2011). This is because environmental processes can transform metals from one species (valence state) to another. Heavy elements have soil residence times of thousands of years and pose many health dangers to higher organisms (Tangahu et al, 2011). They are also known to have an effect on plant growth and a negative impact on soil microflora. All of which are to the disadvantage and detriment of human beings who have no biological use for some of the harmful elements.

The challenge is compounded by the fact that heavy metals cannot be chemically degraded and need to be physically removed or be transformed into non-toxic compounds. The presence of potentially harmful heavy metals in the soil and vegetation/ plants in the study area poses a considerable health threat to the Tsumeb Community over the long term. Hutchinson & Meema (1987) record the following effects resulting from exposure to arsenic; the most characteristic effects following chronic arsenic exposure are hyperkeratosis of the palms and soles of the feet together with hyperpigmentation, particularly in areas not exposed to the sun. Skin tumours have also been commonly reported and these are often located on the hands and feet (Hutchinson & Meema, 1987). Haemangioendothelioma of the liver, a very rare form of cancer, has been associated with long term arsenic exposure in several instances. Lung cancer and liver dysfunction are also recorded (Natural Research Council, 1999). The cardiovascular system is also affected by exposure to arsenic in the form of peripheral vascular disturbances leading to gangrene (Natural Research Council, 1999). Neuropathy and hearing defects are recorded as effects to the nervous system caused by arsenic exposure. Arsenic exposure may also lead to an increased frequency of spontaneous abortions and disturbed erythropoiesis with anaemia. Increased infant mortality and neurological problems are also reported in connection with arsenic toxicity (ATSDR, 1990). Arsenic is also reported to cause DNA modifications such as aneuploidy, micronuclei formation, and chromosome abnormality (ATSDR, 1990). Health effects of a permanent exposure to arsenic are among others; skin damages like keratosis and Blackfoot disease, skin, lung, bladder, kidney cancer, increased infant mortality and neurological problems (ATSDR, 1990). The following symptoms of cadmium toxicity in animals have been recorded: kidney and liver damage, anaemia, retarded testicular development or degeneration, enlarged joints, scaly skin, and reduced growth and increased mortality (ATSDR, 1990).

Cadmium toxicity also causes a disease which is known as “itai-itai which means ouch-ouch in Japanese (Bampidis et al., 2013; ATSDR, 1990). Its victims suffer from pain in the joints, pseudo-fracturing of bones, skeletal deformation and renal dysfunction (ATSDR, 1990). Data from experimental animals and humans show that pulmonary absorption is higher than gastrointestinal absorption (ATSDR, 1990). The gastrointestinal absorption of cadmium is influenced by the type of diet and nutritional status (ATSDR, 1990).

Background levels of cobalt are not known to be associated with adverse health effects in humans. Several milligrams of cobalt can be consumed by humans per day in their diet without causing any adverse effects (Kim et al., 2006). Historically, small amounts of cobalt (1-2 parts per million) in the form of cobalt chloride were added to a brand of beer as a foam stabiliser (Kim et al., 2006). Due to this practice, there was a reported increase in incidents of fatalities due to cardiomyopathy in those who consumed this particular beer in large quantities of more than 8 pints per day (Kim et al., 2006). Cobalt exposures leading to death ranged from 0.04 to 1.14 mg/kg body weight per day for several years (approximately 8-30 pints per day) (Kim et al., 2006). Cardiomyopathy induced by cobalt bearing beer was similar to alcohol myopathy except that the onset was abrupt (Kim et al., 2006).

Lead affects almost every system in the animal body, including the blood, the cardiovascular, renal, endocrine, gastrointestinal, musculoskeletal, immune and reproductive systems. The most critical target for lead appears to be the central nervous system (Bampidis et al., 2013). The developing brain is more at risk, because lead has the potential to cause impaired cognitive development and intellectual performance in children even at low exposure levels (Bampidis et al., 2013). Inorganic lead is classified as a carcinogen (Bampidis et al., 2013). According to Keil et al. (2011), children absorb a greater proportion of lead compared to adults.

The potential for adverse effects of lead exposure in children is heightened because of the following reasons: intake of lead per unit body weight is higher for children than for adults, an increased intake of lead through injection due to their tendency to put things in their mouths; physiological uptake rates of lead in children are higher than those in adults (Tong et al., 2000). Young children are more vulnerable to the effects of lead than adults due to the fact that their systems are still developing (Keil et al., 2011). According to Keil, et al. (2011), lead exposure is also a bigger concern due to the fact that lead readily passes the placental barrier. Exposure during pregnancy poses a risk of impaired foetal and infant development. The bioavailability of lead is dependent on the form of lead whether it is inorganic, organic or metallic (Keil et al., 2011). It is also dependent on the quantity ingested, the age of the individual and their current dietary status (Keil et al., 2011).

Chapter 6 CONCLUSION

The objectives of the study were to determine the concentrations of potentially harmful species: As^{3+} , Cd^{2+} , Co^{2+} and Pb^{2+} in soil and vegetation of the Nomtsoub suburb in Tsumeb. Analysis of soils in the Nomtsoub suburb revealed a generally low to moderate potentially harmful element contamination. The highest value of arsenic in soils of the Nomtsoub suburb was approximately 91 mg/kg. This is more than the average value of 55 mg/kg that was calculated for the suburb. The concentration of heavy metals was highest in the areas close to the Old Tsumeb Mine and the old smelter. The control site some 25 km away had a low value of 7 mg/kg arsenic. 83% of the soil samples had As^{3+} exceeding the Canadian soil quality guideline values for residential areas and agricultural areas.

Cd^{2+} concentration in the soil samples collected from Nomtsoub suburb ranged between 1 mg/kg and 10 mg/kg. The lowest concentration of cadmium (0.5 mg/kg) was recorded for the control site at Lake Otjikoto 15 km west of Tsumeb. At 35.6 mg/kg, the Old Tsumeb Mine pit had the highest record of Cd^{2+} . The average concentration of Cd^{2+} in the entire study area was 1.2 mg/kg. Similarly to arsenic, the potentially harmful element concentrations gradually decreased downwind from the Mine and the smelter in a westerly and north-westerly direction.

The Co^{2+} concentration in soil samples was generally low for the Nomtsoub suburb. Nomtsoub samples averaged 3.27 mg/kg. Cobalt results in this study were all within Canadian soil quality guideline values of 50 mg/kg Co for residential areas and 40 mg/kg Co for agricultural areas. This implies that the risk of cobalt toxicity on the community of Tsumeb is minimal. Cobalt was not included in previous studies conducted by other researchers. This study therefore is contributing new information to the body of existing knowledge on the Tsumeb environmental situation.

The concentration of potentially harmful lead in the soil samples collected at Nomtsoub suburb was below 500 mg/kg. This is significantly less than the high concentration of lead recorded at the Tsumeb Mine Old pit (3786.9 mg/kg). The average concentration of Pb^{2+} in soil was 127 mg/kg. Forty (40) % and 63% of the soil samples had Pb^{2+} exceeding the Canadian soil quality guideline values for residential and agricultural areas respectively.

The minimum obtained values for all elements in the soil samples of the current study are lower than those obtained in the previous studies where total element concentrations were obtained. This is in exception of cobalt which was not part of the previous studies and could therefore not be compared. Without exceptions, maximum values also followed the same trend. The average concentrations of the potentially harmful elements in this current study are not significantly lower than average concentrations recorded in previous studies. The hypothesis that the concentrations of potentially harmful species of As, Cd, Co and Pb in soils and vegetation in Tsumeb are less than those obtained during previous studies which assessed total element concentrations was true for minimum and maximum concentrations.

All vegetation samples in this study showed arsenic concentrations exceeding the WHO (2001)'s limit of 0.5 mg/kg for plants. The highest concentrations were found in fig leaves and fruits as well as in marula tree barks exceeding the limit over 200 times. The EU (2006) guideline value of 0.2 mg/kg for cadmium was exceeded in all vegetation samples although none of the samples had critical concentrations of cadmium. The natural concentrations of cobalt in vegetation (0.35 mg/kg) were exceeded in more than 80% of the vegetation samples albeit only moderately. The EU (2006) and WHO (2001) guideline values of 0.3 and 0.4 mg/kg Pb^{2+} were exceeded in all vegetation samples. The highest concentrations were found in marula tree barks and fig leaves. Fresh papaya leaves also had high Pb^{2+} concentrations.

Since vegetation analysed showed evidence of bioaccumulation of the toxic elements; As^{3+} , Cd^{2+} , Co^{2+} and Pb^{2+} , transfer ratios were calculated. The highest transfer ratios were naturally recorded in the vicinity of the old Tsumeb mine influenced by high heavy element concentrations in soils due to natural mineralization. The highest uptake ratio of arsenic was observed in the following vegetation in order of magnitude: fresh papaya leaves (95%) followed by mango leaves (77%). The cadmium uptake ratio from the soil to vegetation/plants was moderate to high with values ranging from 12.4 to 66.8% in marula fruit and tree bark respectively. The cobalt uptake ratio from the soil to vegetation/plants ranged between 3.6% and 53.8% with Fresh papaya leaves having the highest cobalt uptake ratio. Mango leaves and fig fruits had low cobalt uptake ratios of 6% and 6.9% respectively, consistent with Kim et al.'s observation of low translocation of cobalt from the roots to other parts of the plants (Kim et al., 2006). The lead uptake ratio from the soil to vegetation/plants was generally low to moderate. Uptake ratios for lead ranged between 3.9% in sunflower leaves and 41.8% in fresh papaya leaves. The marula tree bark and fig fruit had low uptake ratios of 2.3% and 3% respectively. Lemon leaves and Mango leaves had even lower uptake ratios of lead at 0.1% and 0.4% respectively. The low uptake of lead from the soil is consistent with Nriagu (1984)'s observation that lead is usually quite tightly fixed in soils and therefore is not easily transferred from soils to plants. According to observations in this study, the translocation of lead to different parts of the plant is also low.

Fresh papaya leaves showed significantly high uptake of all four contaminants; As^{3+} , Cd^{2+} , Co^{2+} and Pb^{2+} . This poses a potential health risk to the community who use it for various purposes. Fresh papaya leaves are used as a skin treatment and digestive aid. There is considerable risk to the human population living in the Nomtsoub Township and Tsumeb Town at large as a result of contamination of the food chain.

This was evident in the majority of soil samples exceeding Canadian Soil Quality Guidelines for the protection of Environmental and Human Health, Update 7.0, 2007 for agricultural land use and residential areas. The risk was even more evident in all vegetation samples in the current study exceeding guideline values of the WHO (2001) Codex Alimentarius and EU (2006) for heavy metals in vegetation. Most of the vegetation is used by the Tsumeb population. Human health soil quality guidelines and vegetation quality guidelines provide concentrations of contaminants in soil at or below which no appreciable human health risk is expected. The results obtained in this current study are very significant due to the fact that the analyses were done on only the potentially harmful bioavailable fractions of heavy metals which are mobilizable with changes in the environment. Under certain environmental conditions, these potentially harmful elements can be very toxic and detrimental to environmental and human health. Higher residence times compounds the existing problem. The fact that mining has been taking place in Tsumeb for almost 100 years implies that there are members of the Tsumeb community who may have been subjected to repeated exposure to these potentially harmful heavy elements for a long period of time making them more vulnerable to possible physiological effects of these heavy metals.

Chapter 7 RECOMMENDATIONS AND PROPOSED FUTURE RESEARCH

7.1 Recommendations

In light of the foregoing conclusions, this study makes the following recommendations in order to safeguard the environmental and human health situation in Nomtsoub suburb and the rest of the Tsumeb Town.

- Monitoring of potentially harmful elements in plant tissues is essential in order to prevent excessive buildup of these elements in the human food chain.
- The use of papaya, marula tree bark as food and medicine respectively should be done with caution due to the potential risk that is associated with their use as revealed by the high contaminant uptake ratio that this study revealed.
- Fig fruits should also be used with caution even though the study revealed lower contaminant uptake ratios. This is because, other factors such as age, nutrition status and poor health conditions may aggravate the effects of exposure even to such low concentrations.
- Regular screening, monitoring, intervention and evaluation of the effects on the local population by government and concerned environmental groups are recommended.
- The Namibian government should take advantage of already existing research data for the Tsumeb area to proactively develop cost-effective and science-based public health policies aimed at protecting the residents of this mining town from the potential risk associated with heavy metals mining and processing.
- It is recommended that the interested and affected parties should engage in proactive planning by establishing a fund that will cater for targeted research on the environmental and human health situation in the historic mining town of Tsumeb.

The fund could have a social component that deals with assisting those who may already be suffering the consequences of exposure to potential harmful elements.

- A multidisciplinary approach is recommended. This would ensure the existence of programs which create awareness of risks associated with harmful element pollution and increase emphasis on adequate nutrition, health care and attention to socioeconomic conditions that may exacerbate the effects of harmful exposure.

7.2 Proposed future research

There is need to engage in interdisciplinary, empirical research in order to obtain comprehensive knowledge to ensure the health of the population living in the Tsumeb town. This study reported on the uptake ratios of heavy metals (specifically As^{2+} , Cd^{2+} , Co^{2+} , and Pb^{2+}) from soil to plants. However, future studies could focus on comprehensively studying specific heavy metals to understand the pathways of their uptake and metabolism in plants (e.g. study on the translocation of arsenic from soils to plants using different types of plants especially edible plants). Another further study opportunity is on biomonitoring of blood and urine for heavy metal contamination. In Tsumeb, only one such research study was conducted before. The research revealed heavy metal contamination in some residents of Tsumeb town (GSN, 2008). There is scope for in-depth studies concentrating on children who are at high risk of heavy metal contamination especially from lead. According to Bampidis, Nistor & Nitas, (2013), Inorganic lead has the potential to cause impaired cognitive development and intellectual performance in children even at low exposure levels.

It is imperative therefore that further studies need to be conducted to ascertain risk levels in Tsumeb and develop risk reduction or consequence mitigation measures.

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APPENDIX 1: COORDINATES OF SAMPLING SITES

TSUMEB SOILS & VEGETATION SAMPLES				
	SAMPLE NO.	SAMPLE TYPE	COORDINATES	
1	TS 27901	Soil sample	E 017 35.045'	S 19 12.134'
2	TS 27902	Soil sample	E 017 41.999'	S 19 14.772'
3	TS 27903	Soil sample	E 017 42.005'	S 19 14.005'
4	TS 27904	Soil sample	E 017 41.959'	S 19 14.717'
5	TS 27907	Soil sample	E 017 41.922'	S 19 14.761'
6	TS 27911	Soil sample	E 017 42.217'	S 19 14.628'
7	TS 27912	Soil sample	E 017 42.198'	S 19 14.619'
8	TSV 27913	Soil sample	E 017 42.216'	S 19 14.634'
9	TS 27916	Soil sample	E 017 42.093'	S 19 14.567'
10	TS 27917	Soil sample	E 017 42.090'	S 19 14.574'
11	TSV 27920	Soil sample	E 017 42.107'	S 19 14.484'
12	TS 27921	Soil sample	E 017 42.109'	S 19 14.464'
13	TS 27924	Soil sample	E 017 42.188'	S 19 14.417'
14	TS 27925	Soil sample	E 017 42.219'	S 19 14.471'
15	TS 27928	Soil sample	E 017 42.222'	S 19 14.510'
16	TS 27931	Soil sample	E 017 42.200'	S 19 14.477'
17	TS 27934	Soil sample	E 017 42.563'	S 19 15.153'
18	TS 27935	Soil sample	E 017 42.583'	S 19 15.138'
19	TS 27936	Soil sample	E 017 42.549'	S 19 15.133'
20	TS 27937	Soil sample	E 017 43.085'	S 19 14.453'

21	TS 27938	Soil sample	E 017 43.129'	S 19 14.443'
22	TS 27940	Soil sample	E 017 42.592'	S 19 14.434'
23	TS 27941	Soil sample	E 017 42.631'	S 19 14.302'
24	TS 27944	Soil sample	E 017 42.428	S 19 13.647'
25	TS 27945	Soil sample	E 017 42.333'	S 19 13.061'
26	TS 27946	Soil sample	E 017 42.727'	S 19 12.340'
27	TS 27947	Soil sample	E 017 43.255'	S 19 11.327'
28	TS 27948	Soil sample	E 017 43.706'	S 19 10.831'
29	TS 27949	Soil sample	E 017 44.635'	S 19 10.363'
30	TS 279451	Soil sample	E 017 45.899'	S 19 09.886'
31	TSV 27906	Mango leaves	E 017 41.961'	S 19 14.709'
32	TSV 27908	Mango leaves	E 017 41.915'	S 19 14.758'
33	TSV 27909	Mango leaves	E 017 41.917'	S 19 14.751'
34	TSV 27910	Lemon leaves	E 017 41.917'	S 19 14.751'
35	TSV 27914	Sunflower leaves	E 017 42.294'	S 19 14.614'
36	TSV 27915	Sunflower leaves	E 017 42.294'	S 19 14.614'
37	TSV 27918	Dried papaya leaves	E 017 42.132'	S 19 14.518'
38	TSV 27919	Fresh papaya leaves	E 017 42.132'	S 19 14.518'
39	TSV 27922	Marula fruit	E 017 42.188'	S 19 14.417'
40	TSV 27923	Marula tree bark	E 017 42.188'	S 19 14.417'
41	TSV 27926	Fig leaves	E 017 42.219'	S 19 14.471'
42	TSV 27927	Fig fruits	E 017 42.219'	S 19 14.471'
43	TSV 27929	Fig leaves	E 017 42.222'	S 19 14.510'
44	TSV 27930	Fig fruits	E 017 42.222'	S 19 14.510'
45	TSV 27932	Fig leaves	E 017 42.200'	S 19 14.477'

46	TSV 27933	Fig fruits	E 017 42.200'	S 19 14.477'
47	TSV 27939	Marula tree bark	E 017 43.129'	S 19 14.443'
48	TSV 27942	Marula tree bark	E 017 42.631'	S 19 14.302'
49	TSV 27943	Marula tree bark	E 017 42.631'	S 19 14.302'
50	TSV 27950	Marula bark tree	E 017 44.635'	S 19 10.363'

APPENDIX 2: CONCENTRATION OF POTENTIALLY HARMFUL ELEMENTS IN SOIL SAMPLES

Detection limits were as follows: As (lower limit: 0.5ppm, upper limit: 1000ppm), Cd (lower limit: 0.5ppm, upper limit: 10 000ppm), Co (lower limit: 0.5ppm, upper limit: 10 000ppm), Pb (lower limit: 0.5ppm, upper limit: 40 000ppm).

X	Y	Sample No.	Sample Type	As ³⁺	Cd ²⁺	Co ²⁺	Pb ²⁺
				PPM	PPM	PPM	PPM
17,5841	-19,202	TS 27901	Soil	12	0.5	5.5	32.4
17,7	-19,246	TS 27902	Soil	31	0.7	1.9	61.7
17,7001	-19,233	TS 27903	Soil	30	1.8	2.9	120.8
17,6993	-19,245	TS 27904	Soil	23	1.3	5	53.3
17,6987	19,246	TS 27907	Soil	10	0.5	12	45.7
17,7036	-19,244	TS 27911	Soil	11	2.1	2.4	83.7
17,7033	19,2437	TS 27912	Soil	41	5.2	3.3	159.6
17,7036	-19,244	TS 27913	Soil	15	1.7	3.3	25.9
17,7016	-19,243	TS 27916	Soil	20	1.1	3.6	59.1
17,7015	-19,243	TS 27917	Soil	25	1.2	3.0	72.5
17,7018	-19,241	TS 27920	Soil	46	4.7	3.0	95.4
17,7018	-19,241	TS 27921	Soil	38	4.1	3.4	169.1
17,7031	-19,24	TS 27924	Soil	58	9.5	2.6	270.7
17,7037	-19,241	TS 27925	Soil	39	1.9	3.3	116.6
17,7037	-19,242	TS 27928	Soil	39	3.0	2.3	176.4
17,7033	-19,241	TS 27931	Soil	84	7.9	2.6	620.2
17,7094	-19,253	TS 27934	Soil	14	0.6	2.4	38.2
17,7097	-19,252	TS 27935	Soil	11	0.5	2.0	32.1
17,7092	-19,252	TS 27936	Soil	32	1.3	2.5	67.7
17,7181	-19,241	TS 27937	Soil	150	28.6	3.2	1835.1
17,7188	-19,241	TS 27938	Soil	41	3.7	2.9	136.1
17,7099	-19,241	TS 27940	Soil	137	19.6	3.5	1027.3
17,7105	-19,238	TS27941	Soil	421	35.6	6.3	3786.9
17,7071	-19,227	TS 27944	Soil	167	8.3	5.3	440.7
17,7056	-19,218	TS 27945	Soil	195	9.1	3.8	467.3
17,7121	-19,206	TS 27946	Soil	68	2.4	2.7	128.5
17,7209	-19,189	TS 27947	Soil	101	12.1	4.1	526
17,7284	-19,181	TS 27948	Soil	148	5.0	2.6	443.8
17,7439	-19,173	TS 27949	Soil	16	1.0	5.5	58.8
17,765	-19,165	TS 27951	Soil	7	0.5	3.6	31.7
	Pulp duplicates	TS 27924	Soil	58	9.5	2.6	270.7
		TS 27924	REP	56	9.2	2.5	276.4

APPENDIX 3: CONCENTRATION OF POTENTIALLY HARMFUL ELEMENTS IN VEGETATION SAMPLES

Detection limits in vegetation were as follows: As (lower limit: 0.1ppm, upper limit: 10 000ppm), Cd (lower limit: 0.01ppm, upper limit: 2 000ppm), Co (lower limit: 0.01ppm, upper limit: 2 000ppm), Pb (lower limit: 0.01ppm, upper limit: 10 000ppm).

X	Y	Sample No.	Sample Type	As ³⁺	Cd ²⁺	Co ²⁺	Pb ²⁺
17,69935	-19,2452	TSV 27906	Mango Leaves	17.7	0.43	0.3	8.43
17,69858	-19,246	TSV 27908	Mango leaves	36.6	1.71	0.9	37.86
17,69862	-19,2459	TSV 27909	Mango leaves	31.6	1.17	0.9	32.19
17,69862	-19,2459	TSV 27910	Lemon leaves	28	0.44	0.7	26.78
17,7049	-19,2436	TSV 27914	Sunflower leaves	20.6	2.76	0.9	18.25
17,7049	-19,2436	TSV 27915	Sunflower leaves	46.7	8.13	1.1	40.93
17,7022	-19,242	TSV 27918	Dried papaya leaves	113.6	0.83	1.3	60.43
17,7022	-19,242	TSV 27919	Fresh papaya leaves	39.4	0.67	0.8	37.36
17,70313	-19,2403	TSV 27922	Marula fruit	55.6	3.29	1.4	113.18
17,70313	-19,2403	TSV 27923	Marula tree bark	18.8	1.18	0.2	28.23
17,70365	-19,2412	TSV 27927	Fig fruits	96.5	4.4	1.8	120.08
17,7037	-19,2418	TSV 27929	Fig leaves	161.4	3.93	1.6	113.59
17,7037	-19,2418	TSV 27930	Fig fruits	82.6	3.36	1.6	76.38
17,70333	-19,2413	TSV 27932	Fig leaves	183.9	5.53	1.9	169.69
17,70333	-19,2413	TSV 27933	Fig fruits	107.5	4.29	1.5	144.17
17,71882	-19,2407	TSV 27939	Marula tree bark	13.2	0.77	0.2	27.7
17,71052	-19,2384	TSV 27942	Marula tree bark	116.5	23.77	2.4	801.67
17,71052	-19,2384	TSV 27943	Marula tree bark	63.2	12.77	1.3	415.26
17,71058	-19,1727	TSV 27950	Marula tree bark	5.4	0.3	0.2	7.58
17,70365	-19,2412	TSV 27926	Fig leaves	247	6.06	2.6	231.74

APPENDIX 4: SEQUENTIAL EXTRACTION PROCEDURES (SEP)

It is widely known that the application of strong acid leaching can be used to determine the total content of potentially harmful elements in solid phases but results in an overestimation for environmental exposure. Varying acid or other reagents sequentially by increasing strength or type (*i.e.*, acidity or dissolution ability), can result in the successive solubilisation phases and release of associated elements from operationally defined fractions in the samples (Chen et al., 2015). For solid phases, sequential extraction can be used to characterize different material fractions, each of which consists of phases with which potentially harmful elements are associated. Knowledge concerning bioavailability of the elements of interest provides better understanding on minimization of environmental impact. To accurately determine potentially harmful/toxic elements in soils and vegetation in Tsumeb, Sequential Extraction Procedures (SEP) and aqua regia were employed to analyse total-recoverable heavy metals in soils. This was done in order to estimate the maximum element availability to plants and human beings (Chen & Ma (2001). Selective or sequential extractions can target elements held in specific soil phase or a range of phases thus allowing better interpretation of ion mobility and geochemical processes. Used sequentially, the leaches can determine whether elements in soils are present as salts, adsorbed to clay minerals, adsorbed/complexed with organics or associated with amorphous Mn and Fe hydroxides.

The advantage that SEP offers is that it simulates to a certain extent various environmental conditions to which the sediment may be subjected; deductions can then be made about the trace metal levels likely to be observed under these conditions in the environment (Tessier et al., 1979). In this study, the analysis involved 30 samples of 100g each. The samples were dried at 60° C and sieved to -80 mesh. The Bureau Veritas laboratory, Canada used Tessier et al (1979)'s SEP method which is the standard reproducible method used across the globe.

APPENDIX 5: AQUA REGIA

To accurately determine potentially harmful/toxic elements in soils and plants, Sequential Extraction Procedures (SEP) and *aqua regia* were employed to analyse total-recoverable heavy metals in soils. These procedures are used to estimate the maximum element availability to plants and human beings (Chen & Ma , 2001). Residual elements that are not released by aqua regia digestion are mostly bound to silicate minerals and are considered unimportant for estimating the mobility and behaviour of elements. The conventional aqua regia digestion procedure consists of digestion soil samples on a hotplate with a 3:1 mixture of HCL and HNO₃. The nitric acid reacts with the concentrated HCL to form aqua regia: $3\text{HCL} + \text{HNO}_3 \rightarrow \text{NOCL} + \text{Cl}_2$. In this tsudy, both ICP-OES and MS were used to expand the detection limits and increase the number of elements analysed. The elements under discussion have the following Detection limits:

As	Detection limit (0.5ppm)	upper limit (1000ppm)
Cd	Detection limit (0.5ppm)	upper limit (10 000ppm)
Co	Detection limit (0.5ppm)	upper limit (10 000ppm)
Pb	Detection limit (0.5ppm)	upper limit (40 000ppm)

APPENDIX 6: HUMAN HEALTH SOIL QUALITY GUIDELINES

Evidence (epidemiological, toxicological as well as molecular evidence) from all around the world has shown a variety of health risks to human populations associated with environmental, occupational and dietary exposure to such metals. As a consequence, health agencies have been setting health-based guidance values to prevent the occurrence of adverse health effects in humans (Dorne et al, 2011). According to Dorne et al (2011), four steps are normally taken during chemical risk assessment namely; hazard identification, hazard characterization, and exposure assessment as well as risk characterization.

Hazard identification has been defined as identification of biological, chemical and physical agents capable of causing adverse health effects and which may be present in a particular food or food groups. The main purpose of hazard identification applied to metals is to evaluate the weight of evidence for adverse health effects, based on an assessment of all the available data regarding toxicity and mode of action of the particular metal.

Hazard characterization (also known as dose-response assessment) constitutes the qualitative and/or quantitative evaluation of the nature of the adverse health effects associated with chemical agents which may be present in food. One approach is to use the dose-response data from studies in the most sensitive species to estimate the shape of the overall dose response relationship for a particular endpoint. In practice, the identification of the reference point such as the No Observed Adverse Effects Limit (NOAEL) constitutes a basis for characterization of a particular chemical (Dorne et al, 2011).

Exposure assessment is the qualitative and/or quantitative evaluation of the likely intake of biological, chemical and physical agents via food as well as exposure from other sources if relevant.

Exposure assessment integrates the occurrence and the concentrations of the compound in the human diet measured using validated analytical techniques and the human consumption patterns for the different food categories available. Additionally, a range of intake/exposure scenarios are taken into account so that special subgroups of the population that may be at either high dietary exposure or high consumers are taken into account.

Risk characterization is the final step and represents “the qualitative and/or quantitative estimate, including attendant uncertainties, of probability of occurrence and severity of known or potential adverse health effects in a given population based on hazard identification, hazard characterization and exposure assessment. In practice, risk characterization integrates the hazard identification and characterization leading to a health based guidance value and the human exposure estimated from either deterministic or probabilistic methods to conclude on the likelihood of adverse effects for public health (Dorne et al, 2011).

There are guiding principles in the derivation of soil quality guidelines for human health in Canadian Council of Ministers of the Environment, 2007 highlight the following:

- i) There should be no appreciable risk to humans from a contaminated site. For each specified land use, there should be no restrictions as to the extent or nature of the interaction with the site. All activities normally associated with the intended land use should be free of any health risk.

- ii) Guidelines are based on defined, representative situations. Deriving numerical guidelines necessitates defining specific scenarios within which the exposure likely to arise on the site can be predicted with some degree of certainty.
- iii) Guidelines are derived by considering exposure through all relevant pathways. The total exposure from soil, air, water and food is considered in the development of guidelines.
- iv) A critical human receptor is identified for each land use. To ensure that the guidelines do not limit the application of a site within the intended land use category, the defined exposure scenarios are usually based on the most sensitive receptor to the chemical and the most critical health effect.
- v) Guidelines are developed by applying scientifically derived information, backed by professional judgement where data gaps occur.

Classifications of toxic effects to environmental contaminants

(Canadian Council of Ministers of the Environment, 2007) classifies toxic effects from exposure to environmental contaminants as organ-specific, neurological, behavioural, reproductive/developmental, immunological, carcinogenic and mutagenic.

These effects can be manifested at the biochemical, cellular, histopathological, carcinogenic and morphological levels. Effects vary depending on the dosage, route of exposure (e.g. ingestion, inhalation, or dermal contact), frequency and/or duration of exposure, species, physiological state, sex and age of the exposed population. (Canadian Council of Ministers of the Environment, 2007) further highlights that: toxicological effects from exposure to chemical substances may be brief or prolonged, reversible or irreversible, immediate or delayed. Exposure less than the reference dose should pose a zero probability of incidence of an adverse effect in the population.

Derivation of the final Human health soil quality guidelines

For Agricultural land use, the direct human health soil quality guideline is calculated taking into consideration, infiltration of volatile compounds into indoor air, protection of potable groundwater and ingestion of produce, meat and milk produced on-site.

The final guideline is set at the lowest value of the applicable soil quality guidelines. This ensures that the final soil quality guideline is protective of all these potential contaminant media transfer pathways (Canadian Council of Ministers of the Environment, 2007). In the case of residential land use, the direct human health soil quality guideline is calculated, soil quality guideline for infiltration of volatile compounds into indoor air and soil quality guideline for protection of potable groundwater are calculated. The final human health soil quality guideline is set at the lowest of the values generated (Canadian Council of Ministers of the Environment, 2007).