THE OCCURRENCE AND DISTRIBUTION OF MERCURY AND CO-OCCURING METALS IN SELECTED NAMIBIAN AREAS AFFECTED BY INDUSTRIAL AND MINING ACTIVITIES

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Abstract

The occurrence and distribution of mercury (Hg) and other co-occurring heavy metals in the mining towns of Berg Aukas and Tsumeb in northern Namibia were studied Different forms of Hg and other heavy metals were characterized in soils, water and plants collected in these areas. Total metal concentration was determined using ICP–OES and total Hg was determined using the DMA 80 mercury analyser. Fractionation of Hg and other heavy metals were determined by performing a four step sequential extraction procedure that separates metals into four fractions, namely: exchangeable (F1), reducible (F2), oxidisable (F3) and residual (F4). Total metal results showed that there are high levels of heavy metals in tailings from Berg Aukas in comparison to international guidelines with, for example, Hg and Pb having concentrations as high as 2.24 mg/kg and 18 195 mg/kg, respectively. Although Berg Aukas soils generally showed Hg values beyond guidelines threshold levels (which is 1.0 mg/kg), the highest Hg concentration in soil (3.49 mg/kg) was found at Tsumeb. Total metal concentration in water samples from Berg Aukas showed Hg values higher than the maximum allowed for drinking water (up to 6 µg/L). Some plants collected at Berg Aukas also had high Hg levels reaching a maximum of 0.70 mg/kg in a sample collected from a pond. Distribution of Hg in tailings found at Berg Aukas revealed that about 90% of Hg was residual whereas the exchangeable (i.e. bioavailable) fraction accounts for about 7%. In contrast, the exchangeable Hg fraction in Berg Aukas soils was as high as 35% of the total Hg. This fraction may explain the presence of Hg measured in the surrounding plants and is a reason for concern due to the risks of Hg methylation as well as further uptake of the soluble forms of Hg by other living organisms. Other metals were also present in bioavailable fractions and correlation analysis enabled the identification of several metal compounds that were likely present in the study soils and tailings. Tailings are known to be highly contaminated with heavy metals and this study demonstrates that these metals are being dispersed into the surrounding soils that are used for agricultural purposes.

Keywords: Heavy metals, Sequential extraction, Hg, distribution, Tailings, soil, Berg Aukas, Tsumeb

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List of abbreviations/acronyms

AAS	Atomic absorption spectrometry
AMAP	Arctic monitoring and assessment programme
ANOVA	Analysis of variance
BCR	Community Bureau of Reference
CEC	Cation exchange capacity
CPGS	Centre of Postgraduate Studies
CRMs	Certified reference materials
DMA	Direct mercury analyser
DGM	Dissolved gaseous mercury
EC	Electrical conductivity
EF	Enrichment factor
EPA	Environmental Protection Agency
HgT	Total mercury
IHg	Inorganic mercury
MeHg	Methylmercury
IC	Ion chromatography

ICP-OES	Inductively coupled plasma optical emission spectrophotometer
MET	Ministry of Environment and Tourism
MFMR	Ministry of Fisheries and Marine Resources
MME	Ministry of Mines and Energy
NUST	Namibia University of Science and Technology
ORP	Oxidation-reduction potential
PEL	Probable effect level
QC	Quality control
RE	Reference element
RSD	Relative standard deviation
SE	Sequential extraction
SEP	Sequential extraction procedures
SD	Standard deviation
SOM	Soil organic matter
SPSS	Statistical Package for the Social Sciences
SSE	Selective sequential extraction
TC	Transfer coefficient

TDS	Total dissolved solids
TEL	Threshold effect level
TET	Toxic effect threshold
UNEP	United Nations Environmental Programme
UREC	University of Namibia Research Ethics Committee
USEPA	US Environmental Protection Agency
WHO	World Health Organisation
WHOGV	World Health Organisation Guideline Value
XRD	X-ray diffraction

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Dedication

To my daughter Abbygail Asino, my sister Sara Mutwa and my father John Mutwa.

Declaration

I, Mary Mulela Mutwa, hereby declare that this study is my own work and is a true reflection of my research, and that this work, or any part thereof has not been submitted for a degree at any other institution.

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Name of Student	Signature	Date

Chapter 1

Introduction

1.1 Background of study

The last few decades have seen an increase in urbanization and industrialization, which led to large amounts of toxic contaminants, such as heavy metals, being released into the environment. Besides the fact that some of these contaminants occur naturally in the environment as part of the earth's crust, some anthropogenic sources, especially mining activities, have contributed significantly to their increase [1]. Since some of these contaminants are heavy metals which cannot be destroyed and are not degradable, they persist and accumulate in the environment [2].

Heavy metal pollution is especially very prominent in areas of active and closed mining sites. Heavy metals commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), cobalt (Co) and nickel (Ni). These metals pose a chemical hazard to the environment and each of these metals will result in different behavioural and physiological changes when an individual is exposed to them [3]. Heavy metals are persistent environmental contaminants and occur as natural constituents of the earth crust, and since they cannot be degraded or destroyed [2]. Additionally, heavy metals, especially Cu, Ni, Cd, Zn, Cr and Pb, are considered to be one of the major sources of soil pollution [1].

One of the most commonly studied heavy metals is mercury (Hg). Hg is one of the most toxic and volatile elements [2]. It is a naturally occurring metal that is found as a liquid at room temperature and exists in three different forms namely, elemental (Hg^0), inorganic (Hg_2^{2+} and Hg^{2+}) and organic (RHgX) Hg species. All Hg species are highly toxic when humans are exposed to them [4]. Even though Hg has no biological function in humans, long term exposure (usually through ingestion of Hg containing food or inhalation of mine waste particles with elevated Hg levels) is a potential health hazard [5].

Hg is a widespread contaminant that affects humans and environmental health negatively (mainly by contaminating soils, surface water, groundwater and air).This is mostly due to its high toxicity, global transport, persistence and bioaccumulation in the environment [6]. It is released into the environment by both natural processes and anthropogenic activities. Moreover, Hg pollution is considered as a global problem because of its volatility and persistency, once it is released into the environment, it can travel and settle thousands of kilometers away from its original emission source. Even though the emission is local or regional, it can cause air, soil and water pollution, which can be felt globally [7]. The main sources of Hg pollution in the environment are fossil fuel burning, especially coal; mining, high temperature combustion [8] and artisanal gold processing, where Hg is used to form gold amalgam [9] that is used to scavenge fine gold particles. Once released into waterways, Hg enters the food chain through digestion by bacteria and is converted to methylmercury, a highly toxic form of Hg. Even though methylmercury is the most toxic form, all Hg forms are toxic to the environment and human health [10].

Hg pollution due to anthropogenic activities is higher in the northern hemisphere (Figure 1.2) due to greater industrial activity and population density [11]. Over the years, mining has been an ongoing source of Hg contamination to the environment [12]. Hg is released into and enters the environment as a result of various anthropogenic activities, which include fossil-fuel fired power plants, ferrous and non-ferrous metals manufacturing facilities, cement plants, chemical production facilities and mining activities [13] (Figure 1.1). In addition, anthropogenic emissions continue to add significantly to the global pool of Hg and due to the rise of industrial activities over the years, anthropogenic activities have introduced substantial amounts of Hg into the environment at an alarming rate [14]. This contributes about 30% of the total emissions to the global atmosphere, whereas re-emissions comprise about 60% of Hg emissions [15]. As shown in Figures 1.1 and 1.2, mining, ore processing and high temperature processes such as coal burning, dominate anthropogenic inputs of Hg to the atmosphere [11].

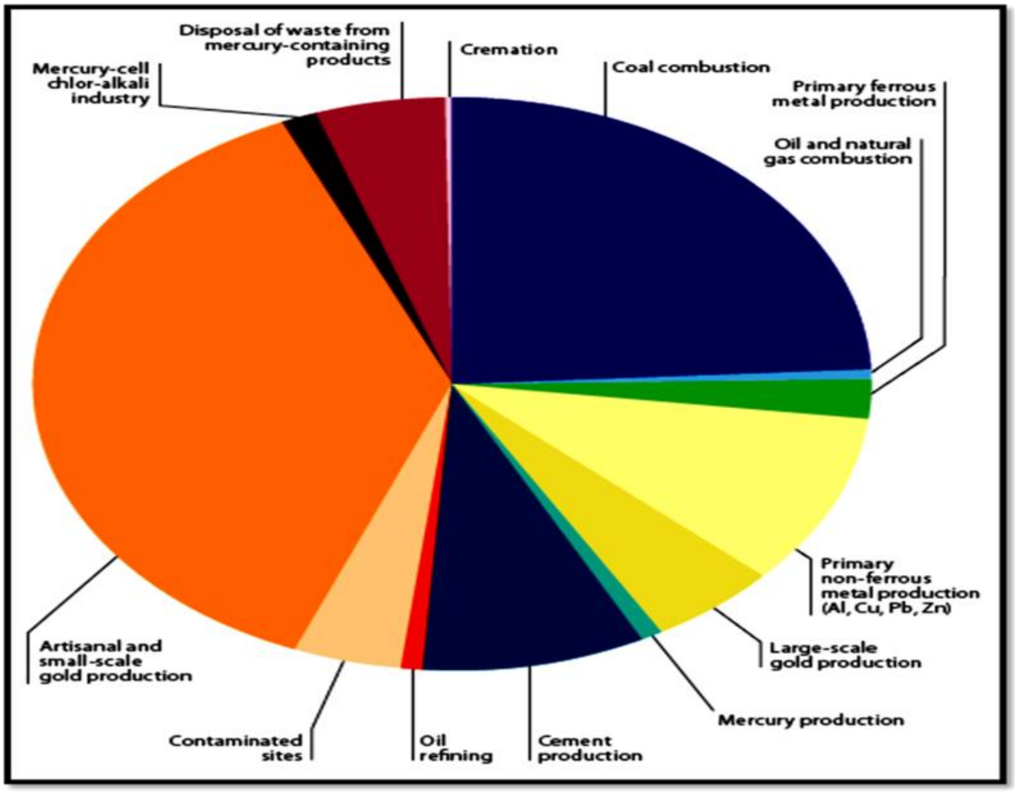

Figure 1.1: Global anthropogenic Hg emissions to air in 2010 [13]

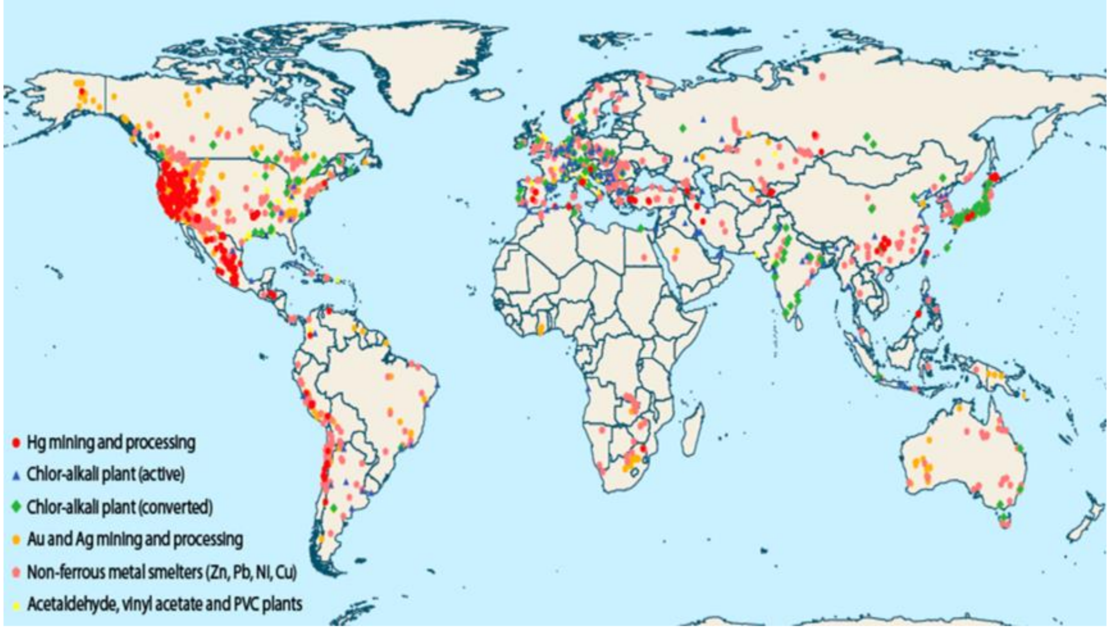

Figure 1.2: Global distribution of Hg-contaminated sites [11]

Contamination of Hg to the environment and human health has deleterious effects, especially if it occurs in highly toxic and soluble species such as mercuric chloride ($HgCl_2$) or methyl mercury (CH_3HgX). Additionally, environmental Hg levels have been on the rise since the beginning of industrialisation and have consistently progressed ever since. Highly contaminated and abandoned industrial sites as well as active mining operations continue to release Hg into the environment [16]. When released in the environment, Hg usually ends up in the atmosphere, water and soil.

Contamination of soil by heavy metals can happen in various ways and is of great concern to food production and human health. Soils may become contaminated with heavy metals through emissions from industrial and mining activities, these include but are not limited to mine tailings, disposal of metal wastes, spillage of chemicals and agricultural activities such as the application of inorganic fertilisers [3]. These activities have led to a worldwide contamination of soil by heavy metals such as Cu, Zn, Pb, Cd, Mn, Cr, As and Hg. In addition, if the concentrations of heavy metals exceed the attenuation capacity of soil, soil pollution will occur, even though soil has a natural capacity to attenuate heavy metals through various mechanisms [4]. Some of these metals, especially Hg, are mobile and readily bioavailable. Due to its bioavailability, Hg can be taken up by plants and other living organisms, a process known as bioaccumulation, subsequently causing biomagnification further up in the food chain [14]. Moreover, once Hg is deposited into soil, it can be transformed into different species by different environmental soil conditions such as pH, temperature, presence of microorganisms and humus content, which may favour the formation of some organic and inorganic species of Hg, thus displaying different mobility rates in the soil [17]. In comparison to other heavy metals, Hg is much more persistent in soils [4].

One of the negative environmental impact caused by mining and other anthropogenic activities is mining tailings, some of which can be toxic waste from mineral processing of ore after the metals have been extracted. The impacts caused by mine tailings can go on for years after mining activities have ceased [18], adversely affecting the surrounding vegetation, leading to changes in species composition [19]. In dry areas, mine tailings are important sources of soil pollution because highly contaminated particles can be dispersed by water and wind, which aids in mobilising the tailings' metal contents into the environment [20]. This mobilisation could lead up to trace metal contamination of surface soils. Therefore, contamination from mine tailings does not only affect the tailing sites but can cover large land areas including agricultural soils, posing serious environmental soil degradation. These problems continue to increase over the years [21].

The release of Hg from anthropogenic activities into aquatic systems is of huge concern because Hg has a potential of being transformed from inorganic Hg to more toxic organic forms [22]. Once Hg is in the waterways, even at low concentrations, it is methylated by algae and bacteria. Methylmercury (MeHg) then bio-accumulates and biomagnifies to unsafe levels in the food chain, into fish and eventually in humans. Hg is released into water through industrial pollution from natural sources and anthropogenic activities as well as through a natural process of off-gassing from the earth's crust [23]. One of the largest contributors to high levels of Hg in fresh water may be the direct release of Hg into water [24].

Agriculture is one of the sectors that are crucial for human sustainability worldwide. However, with the increase of industrial activities over the years, there is a risk of continuous pollution of heavy metals to plants, which if consumed by humans or animals, can have detrimental effects [25].

Hg is introduced to agricultural land through sludge, fertilizers, lime and manure. Once this organic form of Hg is taken up by the plant, the Hg concentration will increase [26]. However, the amount of Hg that is taken up by the roots from the soil depends on factors such as pH, type of soil, soil aeration, plant species and cation-exchange capacity [25]. In addition to plants taking up Hg from water and soil via roots, plants are also able to absorb Hg that is deposited on leaf surfaces. Accumulation of most of the Hg in plants is done so with minimal mobility, meaning only a small percentage is released into the atmosphere or is transported to other parts of the plant. Once accumulated in plants, Hg can be found in different forms, namely Hg (0), Hg (II) and organic Hg, with aquatic plants usually containing more methyl mercury (organic Hg) than terrestrial plants [27].

1.2 Statement of the Problem

Industrial activities such as mining generate waste that may contain high concentrations of metals which can be mobilised. Most of the heavy metals are highly toxic and are not biodegradable [28]. Unlike other pollutants like petroleum hydrocarbons and domestic and municipal waste which may visibly build up in the environment, trace metals such as Hg may accumulate in the environment to toxic levels unnoticed. In addition, Hg has been directly mobilised by humans for thousands of years into aquatic and terrestrial ecosystems through mining and metallurgical processes [29]. Unfortunately, there are limited data concerning the extent of Hg pollution in the southern hemisphere, especially on the African continent (Figure 1.2). For instance, the contribution of Hg pollution from milling, smelting and refining of sulphide ores, which are known potential sources of heavy metals, releases heavy metals into the environment, and thus cause pollution on various scales. This pollution, especially from Hg, is not adequately quantified in the Namibian context. There is, therefore, an urgent need of providing reliable data on the occurrence and release of heavy metals such as Hg in local environmental compartments affected by the above-mentioned mining activities to partly fill the currently existing gap concerning Hg emission data on the continent.

A study conducted by Podolsky *et al* [20] in the central-northern region of Namibia and Zambia found that there were high concentrations of total elemental Hg in soils from mining/smelting in northern Namibia than in the Zambian Copperbelt. Another study conducted by Kamona *et al* [30] in the southern region of Namibia reported high average values of Hg and other metals in dust emanating from the crusher at the Rosh Pinah mine. These metals were Zn, Pb, Cu, As, Hg, Cr and Cd. Furthermore, this study revealed that there were high concentrations of total S as well as high values of As, Hg, Pb and Zn in soils that are close to the tailing dams.

Some characteristics of Hg such as absorption, mobility, bioavailability and toxicity depend on its chemical forms [31]. Though these studies reported total Hg concentration, no information on Hg forms (i.e. speciation) was provided. Total elemental analysis is not enough to provide such information; therefore Hg speciation is needed [32]. This further highlights the necessity of speciation studies in the Namibian context to better understand the distribution and ecosystem fate of Hg and co-occurring metals found in areas impacted by mining activities.

1.3 Objectives of the study

a) To study the occurrence of Hg and other co-occurring metals in tailings, soils, slags, plants and waters from local areas situated near abandoned and active mining operations at Berg Aukas and Tsumeb.

b) To characterise the different forms (species) of Hg and other heavy metals occurring in the affected study sites.

c) To compare these findings with those reported worldwide, especially in areas with similar environmental and climatic conditions (i.e. semi-arid areas) and to infer from these results the likely mechanism of Hg and co-occurring metals dispersal in the study areas as well as the ecosystem risks associated with the occurrence of the observed Hg species.

1.4 Significance of the study

Hg occurrence in Namibia was reported at the Tsumeb mine, in Berg Aukas, at the Rosh Pinah Pb and Zn mine and at the Kombat mine. The highest Hg concentration was observed in soil samples from Tsumeb [20] as well at the Rosh Pinah lead and zinc mine in southern Namibia where the dust originating from the crusher was found to have Hg levels of 1.05 mg/kg, a value that is of great environmental concern [30]. Hg release leads to an increase in the amount of the metal in the atmosphere, where it enters the atmospheric-soil-water distribution cycles and it can remain in circulation for years, thus posing a high risk of Hg exposure, depending on the chemical form and route of exposure [28]. Therefore, this study, through speciation data, provides relevant information for toxicological studies and mitigation purposes, making it possible to develop the right approach in eliminating or reducing the occurrence of Hg in the affected areas.

1.5 Limitation of the study

Permission to access some of the active and abandoned sites was a limitation to this study.

1.6 Delimitation of the study

The study focused on areas affected by industrial activities, where permission to access the sites was given.

Chapter 2

Literature review

Heavy metal pollution has been a severe problem in many parts of the world, due to rapid social and economic development over the past few decades. Even though trace amounts of heavy metals like Cu, Zn, Co, Ng, Ni, and Fe are needed for growth of living organisms, these heavy metals can be harmful when their concentrations go beyond the permissible limits**.** Other heavy metals such as cadmium, lead and mercury do not have any beneficial effects on living organisms [3]. In comparison to other heavy metals, Hg has two unique properties: 1) it is highly soluble in water and 2) in its pure form, elemental Hg, exists as liquid at room temperature, resulting in it slowly forming a vapour in the air [25]. In addition, Hg is a unique metal because it occurs in the environment in three different chemical forms that have different properties, usage and toxicity [33]. These forms are elemental Hg, inorganic Hg and organic Hg. The inorganic and organic Hg are more commonly Hg forms found in nature [34]. These forms enter human bodies in distinct ways, including, but not limited to, eating fish or wild game near the top of the food-chain that have high levels of Hg in their tissues and playing on or in contaminated surfaces and soils [35]. Exposure from polluted air and drinking water is usually minor. Of these forms, methylmercury is the most dangerous [36]. Properties of Hg and behaviour (e.g. bioavailability, transport, toxicity, etc.) will mostly depend on the chemical forms of occurrence (speciation), rather than on its concentration level in a given environmental compartment [34]. Thus, characterizing the Hg distribution (i.e. its speciation) provides important data when predicting metal bioavailability that appears to be site, media and matrix specific and will be of relevance, not only within the context of application to health risk assessments but also for mitigation purposes [31].

2.1 Mercury speciation

Hg is a toxic and hazardous pollutant that occurs in the environment in three different chemical forms that have different properties, usage and toxicity. The pure form, elemental Hg, is liquid at room temperature and slowly forms a vapour in the air at about 70°C [37]. Of the organic forms, methylmercury is the most dangerous because it inhibits many neurobiological processes in infants, children and adults [31]. Figure 2.1 shows how the different species of Hg occur in sediments, water and air [38]. In aquatic environments, the speciation of Hg is dependent on factors such as the pH of the water, the pE and the composition of the water matrix. Additionally, once Hg is deposited in natural waters, it undergoes an aquatic redox cycling between oxidized Hg (Hg^{2+}), dissolved gaseous Hg^0 (DGM), and MeHg [34]. In aquatic food webs, the bio-concentration of MeHg is the reason global health advisories caution against the consumption of fish that might contain elevated levels of MeHg [39].

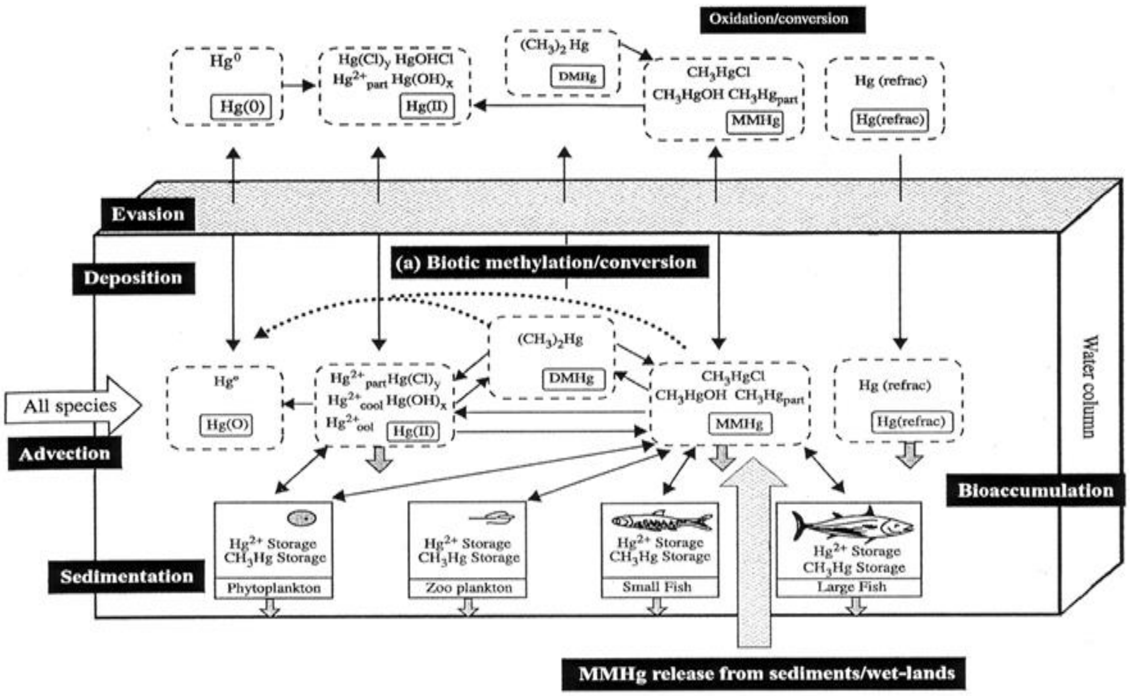

Figure 2.1: Biogeochemistry of mercury[38]

The different forms (elemental, inorganic or organic) of Hg are dominant in different environmental media. In the atmosphere, Hg occurs as elemental Hg vapour (Hg^0), which can circulate in the atmosphere for a long time, making it easy to disperse and transport for thousands of kilometers from the point of emission [37]. The inorganic forms, Hg_2^{2+} and Hg^{2+}, are mostly dominant in sediments, soil and water, whereas the organic forms (which have caused loss of life in the past) like MeHg are mostly found in biota [34]. In soils, the greater percentage of Hg present is inorganic, usually originating from atmospheric deposition or from geological sources [37]. The analysis of Hg speciation in soil is done for a better understanding of process that lead to the accumulation of Hg in organisms [21].

Speciation of Hg has not been studied in the Namibian context. However, a study on contaminated soils in Switzerland was conducted and found that exchangeable Hg was found in low amounts (1.5%) of the total mercury (HgT) [17]. Furthermore, the study reported that most of the Hg was found in the oxidisable fraction [17]. Additionally, Hg speciation was also studied in soils from Randfontein in South Africa [18]. In the Randfontein study, the authors found that soils from Randfontein mostly had oxidisable Hg, measuring up to a maximum of 52% [18].

2.1.1 Methylmercury

All forms of Hg are considered toxic but the organic forms such as MeHg are the most toxic. This form of Hg is widely studied because it affects large populations, and its toxicity is better characterised than that of other organic Hg compounds [29]. Inorganic forms of Hg are potentially converted to MeHg once they enter aquatic environments, usually by the action of microorganisms [40]. Due to its bioaccumulation and nature, MeHg spreads to the food where animals at the top of the food chain are likely to accumulate higher concentrations of MeHg, consequently getting MeHg poisoning (Figure 2.1). The primary signs and symptoms of MeHg poisoning are loss of sensation around the mouth, in the hands and feet, slurred speech, blindness or reduced vision and loss of hearing [34].

Two MeHg poisonings occurred in Japan (in the city of Minamata) and in Iraq [39]. Minamata is a small coastal town in the southern parts of Japan and it has abundant fishing resources. In 1956, Hg-containing waste was released in the industrial wastewater from the Chisso Corporation's chemical factory, which produced fertilizers, acetylene, acetaldehyde, acetic acid and vinyl chloride [39]. Moreover, the production of acetaldehyde used mercury sulfate as a catalyst [39]. Once in water, Hg was converted to MeHg by aquatic biota [34]**.** MeHg then bio-accumulated in fish and shellfish in Minamata Bay and the Shiranui Sea, which when eaten by the local population, resulted in MeHg poisoning [41].

In late 1971 and early 1972, the largest global outbreak of Hg poisoning occurred in Iraq [42]. This poisoning involved the ingestion of homemade wheat bread, whose seed grain was treated with MeHg fungicide to protect it from fungi infestation before planting [42]. MeHg is used in fungicides because it is known to have antifungal properties when applied to seed grain [42]. Moreover, the seed was not meant for consumption but rather for planting, but due to unforeseen circumstances, a farmer used it to make bread and fed it to domestic animals and humans. After the first human developed severe symptoms of Hg poisoning, the people were informed of the toxicity of the wheat [42]. This led to many farmers disposing the wheat all over the country, with some of it reaching the waterbodies, causing contamination of fish and birds and ultimately leading to an environmental disaster [43].

2.2 Sequential extraction

The concentration of total metals in soil is usually used as a soil pollution indicator. However, it is not enough in evaluating heavy metal contamination and does not provide information about toxicity, distribution, chemical interactions, mobility and/or bioavailability of metals [44].

Fractionation methods are amongst some of the many separation techniques that have been widely applied over the years to characterise the environmental reactivity of potentially toxic elements in liquid and solid phases [44]. For solid phases, sequential extraction (SE) is one of the methods used to characterise different fractions comprising of phases that are associated with potentially toxic elements [45]. Sequential extraction is a technique whereby a series of chemical reagents are applied to a solid sample in succession and elements are separated into specific fractions by selective extraction [44]. In addition, it provides information about the origin, mode of occurrence, bioavailability and mobility of trace metals in solid samples, which depends on the composition of the leaching solution, the characteristics of the solid, as well as the strength of the bond between the heavy metal and the solid matrix [37].

All sequential extraction procedures are enabled by fractionation. These fractions are named exchangeable, weakly absorbed, hydrous oxide bound, organic bound and lattice material components [44]. In addition, sequential extraction procedures are based on the theory that the most mobile metals are removed in the first fraction. The removal of metals continues in order of decreasing mobility [46].

Hg is one of the few elements that has an in-depth study of its form of occurrence (speciation) or fractional products as well as distribution [47]. In addition, the accumulation of trace metals such as Hg in soil is a serious environmental concern that creates a hazard when metals are transferred to water or plants. Due to the mobility and bioavailability of trace metals, there exists potential toxicity of trace metals in soil, thus trace metals can cause detrimental damage to the nervous system when the water or plants are consumed by humans and animals [48].

Although there exist several available sequential extraction methods developed over the last three decades, the debate continues as to which technique is preferable over the others

[37]. This is largely because the wide variety of techniques developed and used makes comparison of the different techniques difficult, a fact attributed to the optimisation of sequential extraction processes for solids and trace metals [37].

The first sequential extraction method was a seven-step method developed by Tessier *et al.* [49] who classified potentially toxic elements according to their solubility and binding forms of metallic species. Due to the time demand of seven-step (7–10 days), a three-step sequential extraction method known as the Community Bureau of Reference (BCR) was introduced by the European Community Bureau of Reference[50]. This procedure is largely similar to that produced by Tessier et al. [49], with the chief difference in the first fraction of the procedure. Instead of evaluating the exchangeable and carbonate bound separately, the BCR procedure combines both in the first fraction [50].

In Namibia, sequential extraction has been applied in several studies, using the BCR procedure. One such study was conducted by Sracek *et al* [51] who looked at the geochemistry and mineralogy of vanadium and iron in mine tailings at Berg Aukas. This study found low solubility and water leached concentrations of V as well as low Fe content. In addition, this study also looked at the formation of secondary hematite by performing sequential extraction for Fe and As in Kombat and that most of the As found in the mine tailings is residual. Moreover, sequential extraction was employed in another study that looked at the agricultural soil contamination by potentially toxic metals (Cu and Pb) dispersed from improperly disposed tailings at the Kombat mine [52]. This study by Mileusnic *et al* [52] found that the dominant fraction of Pb in mine tailings is the reducible fraction Pb, which constituted about 60% of the total Pb. This was followed by the carbonate fraction with about 30% of the total Pb while the exchangeable and oxidisable fraction had about 10 and 1%, respectively. The study further found that the distribution of Cu in the tailings varied. The reducible fraction of Cu contained about 30-60% of total Cu, oxidisable fraction about 10-40%, carbonates 10-20% and exchangeable fraction about 20%.

2.2.1 BCR extraction

Over the years, the use of sequential extraction procedures has increased. This is because these procedures may provide comparative information on mobility of trace metals in soil with varying environmental conditions. The BCR is a stepwise sequential extraction method that analyses different fractions of metals in soil. These fractions are acid extractable, reducible, oxidisable and residual [48]. The three steps involved in the BCR extraction [53] are shown in Table 2.1.

Table 2.1: The BCR three-step sequential extraction

Extraction step	Reactive /concentration/ pH	Solid phase/Fraction
1	Acetic acid (CH_3COOH, 0.11 $molL^{-1}$), pH 2.85	Exchangeable, water and acid soluble (e.g. carbonates)
2	Hydroxylammonium chloride ($NH_2OH \cdot HCl$, 0.1 $molL^{-1}$) , pH 2	Reducible (e.g. iron/manganese oxides)
3	Hydrogen peroxide (H_2O_2, 8.8 $molL^{-1}$), followed by ammonium acetate (CH_3COONH_4, 1.0 $molL^{-1}$) , pH 2	Oxidisable (e.g. organic substance and sulphides)

Residual[a]	Aqua regia ($3HCl + HNO_3$)	Remaining, silicate bound metals

[a] *Digestion of the residual material is not a speciation of the BCR protocol.*

This method aims at minimising errors during the treatment and analysis of samples. In addition, it seeks to identify the most appropriate analytical procedure as well as to supply reference materials for comparison of results. Moreover, this method appears to be, in comparison to others proposed previously, such as that of Tessier *et al* [49], more operationally effective [54].

When introduced in 1993 by the European Community Bureau of Reference, the BCR was just a three-step method but it has since been modified by Rauret *et al* [50] where a fourth step was added. Trace metals accumulate in soil, causing a serious environmental problem that creates a hazard when metals are transferred to water or plants. In order to understand the mobility and bioavailability of trace metals for different physicochemical phases of the soil, the concentrations and distributions of trace metals must be established [48].

There are three main ways that can be used to identify Hg species during fractionation methodologies, namely: chemical, thermo-desorption and X-ray absorption techniques [55]. However, applicability with the X-ray techniques in environmental samples is very limited because these techniques are expensive and require samples with mercury concentration greater than 100 mg/kg. In the few last decades, several researchers have developed and published sequential extraction methods that are more specific to Hg [55]. While some of the methods evaluate Hg availability and can be applied to a wide range of solid samples [56], other researchers proposed solutions that evaluate Hg mobility by applying methods that determine limited number of fractions, like those associated with sulfides [57].

Furthermore, selective extraction methods use extractants to release different fractions of Hg and assess the amounts of mobile Hg. This information can be used to correlate the plant-available contents under certain environmental or agricultural conditions**.** Even though these methods are capable of quantifying Hg at low levels (< 0.005 mg/kg), they are not suitable for Hg because of its diverse species [58].

Among the existing methods that are used for Hg fractionation in environmental samples, a 5 step selective sequential extraction (SSE) developed by Bloom *et al* [56] and the EPA method that is known as EPA method 3200 are procedures that can provide information on the distribution of Hg and consequently help determine what remediation steps to take [59].

2.3 Study sites

Berg Aukas, which is located at 19° 34' 12" S, 18° 15' 36" E, was a mining town discovered in 1913, where they used to mine and roast ores of Pb, V and Zn until its closure in 1979 [33]. In the early 90’s, the government of Namibia turned the abandoned mine buildings located at the town of Berg Aukas into a National Youth Training centre, where activities such as livestock farming, horticulture as well as seasonal crop farming are taking place. This abandoned mine is known to be polluted with heavy metals such Pb, Zn, Cu, Cd, As, Hg and Mo [60].

Due to the mine tailings located north of the mining area (as seen in Figure 2.1) that have been left unattended since the closure of the mine and slag deposits that are centrally located with an eroded sealing, these conditions presents a huge source of dust that is dispersed across large distances. In addition, environmental factors such as wind and rainfall have resulted in heavy metal contamination of areas that are further away from the abandoned mining site [33]. These mine tailings are not fenced off, thus, posing a health hazard to the local population.

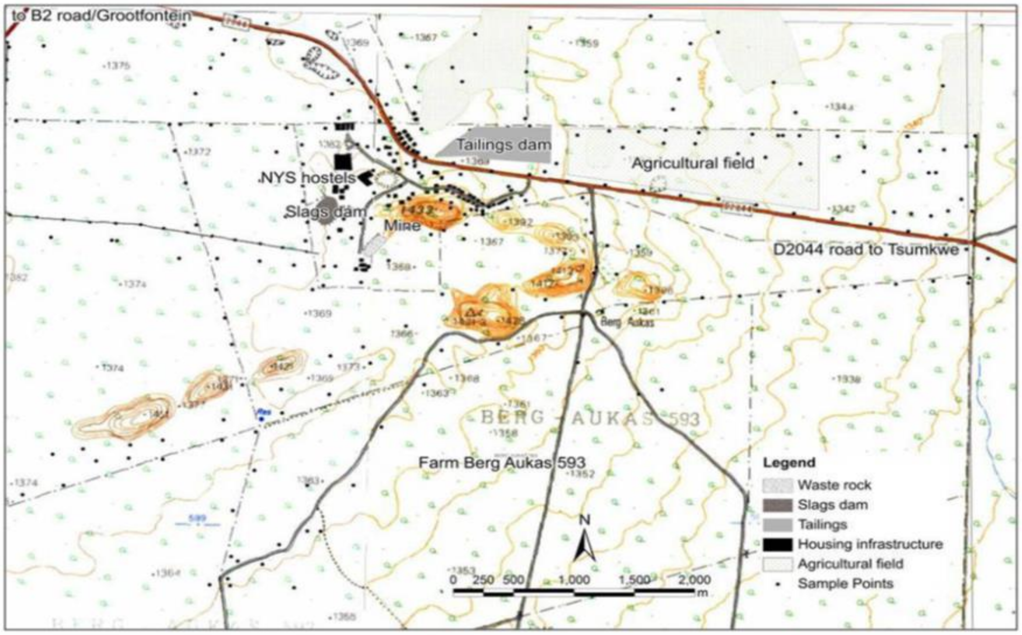

Figure 2.2: Berg Aukas map (Mapani *et al* [33])

A study conducted by Mapani *et al* [33] between 2005 and 2007 that aimed at assessing potential human health risks that might arise from consumption of crops and water in and around Berg Aukas found that there were parts of the soil, tailings and vegetation (Table 2.2) in the Berg Aukas area that were severely contaminated with heavy metals, with Hg being one of the heavy metals. In addition, this study showed that all water samples from Berg Aukas were of excellent quality in terms of conductivity. Moreover, the study also concluded that the groundwater in Berg Aukas and surrounding areas did not show any significant signs of heavy metal contamination from past mining activities. It was found that some metals such as As, Cd and Pb had values far below the limits of excellent drinking water quality (Namibian Guideline Values).

Table 2.2: Heavy metal composition of tailings and slags at Berg Aukas (2005-2007) Mapani *et al* [33]

	tailings	slags
Ctot (wt. %)	10.5	5.1
Stot (wt. %)	0.034	0.110
CO (wt. %)	37.16	6.04
Corg (wt. %)	0.42	0.00
V (ppm)	704	832
Fe (wt. %)	1.68	3.98
Cu (ppm)	184	640
Zn (ppm)	52,100	22,400
Mo (ppm)	< 5	13
Cd (ppm)	352	< 0.8
Pb (ppm)	< 10	11,600
As (ppm)	109.1	383.7
Hg (ppm)	2.228	0.028

*Ctot = total content of carbon

*Stot = total content of sulfur

*Corg = amount of organic carbon

The mining town of Tsumeb is situated in the north central part of Namibia, in Oshikoto region, and is located at 19.2443° S, 17.7281° E. The town was founded over 100 years ago (in 1899) and is famous for its rich mineral ore deposits, with the main ones being Cu, Pb, Zn, Ag and S [32]. It has a sub-tropical climate with an average rainfall of 55 mm per annum [61]. In addition, with the mining and smelting activities in Tsumeb, the town is known to be affected by prolonged exposure to multisource contamination [62]. Tailing dumps, slag deposits as well as solid and gaseous emissions from past and recent mining activities are sources of heavy metal contamination in Tsumeb [63].

A study done in 2015 by Hange *et al* [14] on soils in Tsumeb showed elevated levels of Cu, Zn, Pb and Cd at selected sampling points with concentrations of 39.0-2532.8 mg/kg, 59.5-1994.8 mg/kg, 1.2-141 mg/kg and 1.7-21.3 mg/kg respectively [14]. In addition, the overall mean concentration of the selected metals was found to be higher than the international threshold limits of 100 mg/kg for Cu, 200 mg/kg for Zn, 60 mg/kg for and 1 mg/kg for Cd. The study concluded that anthropogenic activities have an influence on heavy metal levels in soil [14].

Furthermore, another study conducted by Podolsky *et al* [20] on mercury in soils in Zambia and Namibia (Berg Aukas and Tsumeb) found high levels of Hg in soils and slimes from Tsumeb. The study also concluded that heavy metal distribution (mercury in this case) is dominated by anthropogenic activities [20].

Finally, contamination of Hg in soil, water and plants have been studied in Berg Aukas and Tsumeb over the years [20,33]. However, no Hg distribution and speciation studies have been conducted.

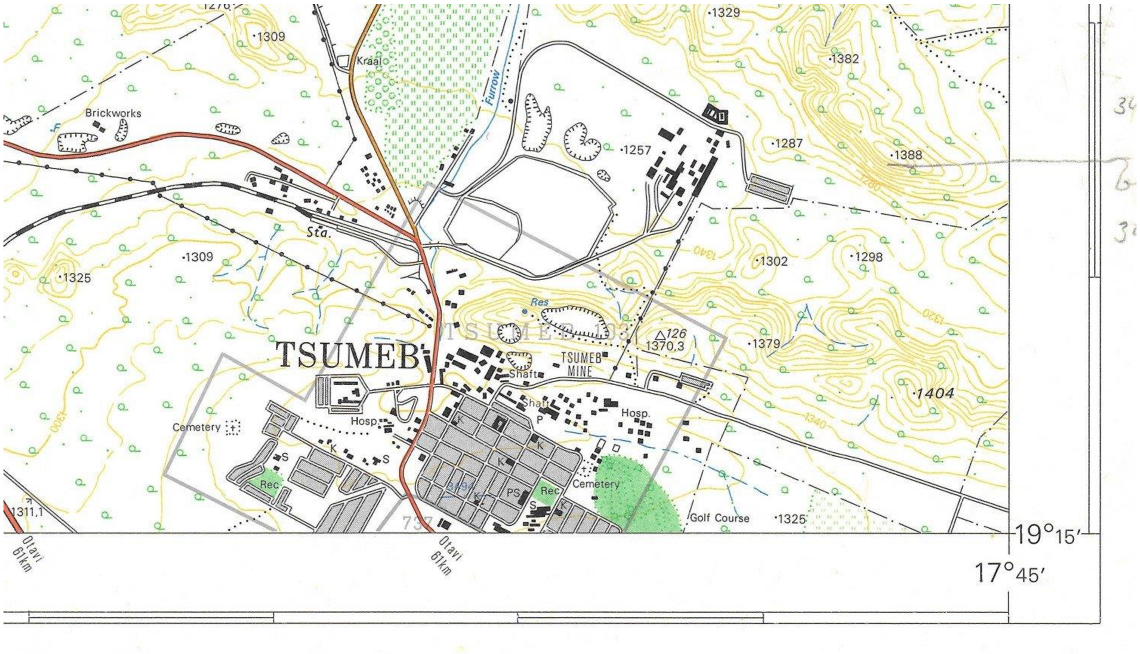

Figure 2.3: A map of Tsumeb (Dundee Precious Metal, 2019)

Chapter 3

Research Methods

3.1 Research design

Samples of soil, tailings, water and plants were collected at the study sites. These samples were then prepared accordingly using internationally accepted procedures [14] and later tested for levels of Hg and other co-occurring heavy metals. Total amounts of Hg and co-occurring heavy metals in the collected samples were quantified. The different forms of Hg association (speciation) were determined by means of sequential extraction procedures (SEP) using appropriate solvents [15]. Ancillary data (on site parameters) such as pH, electrical conductivity (EC), oxidation-reduction potential (ORP), turbidity and temperature were measured on site for water and were used together with data from elemental analyses for correlation and prediction purposes, using computer modelling. The forms of Hg that could not be determined experimentally were modelled using Microsoft excel to characterize factors controlling the Hg distribution at the study areas. Analysis of samples was performed at the Namibia University of Science and Technology (NUST) and at the Ministry of Fisheries and Marine Resources (MFMR) in Swakopmund laboratories.

3.2 Sampling

3.2.1 Tailings

Two sites were identified as tailings storage sites in the Berg Aukas area. Figure 3.1 shows mine tailing at Berg Aukas. The first site is located to the northeastern direction (n

= 12, T1-T12) and the second tailing site is located in the southern direction of the tailing site (n = 5, TT13-TT17). The samples were randomly collected with shovels from all around and at the centre of the tailings dam area. The GPS coordinates of the sampling sites are shown in Table 3.1. The collected samples were then placed in ziploc bags until further analysis. Most tailing samples were composite samples, consisting mostly of fine grains and silt-clay (Table 3.1). Once in the laboratory, the tailings samples were homogenized, and an aliquot was dried in the oven at 50℃ for 24 hours and stored in sealed polypropylene containers at room temperature until analysis.

Figure 3.1: Mine tailings at Berg Aukas

Table 3.1: Description of tailing samples collected at Berg Aukas

Sample ID	GPS Coordinates (South)	GPS Coordinates (East)	Description
T 1	19°30'43.10"	18°15'39.30"	Fine grain
T 2	19°30'43.10"	18°15'39.30"	Fine grain
T 3	19°30'43.10"	18°15'39.30"	Fine grain
T 4	19°30'42.80"	18°15'37.00"	Fine grain
T 5	19°30'42.10"	18°15'36.00"	Silt-clay
T 6	19°30'40.70"	18°15'36.10"	Silt-clay
T 7	19°30'39.20"	18°15'36.30"	Gravel_silt_clay
T 8	19°30'38.80"	18°15'37.80"	Gravel_silt_clay
T 9	19°30'39.40"	18°15'38.60"	Silt-clay
T 10	19°30'39.40"	18°15'38.60"	Silt-clay
T 11	19°30'40.10"	18°15'40.00"	Silt-clay
T 12	19°30'41.50"	18°15'37.70"	Silt-clay
TT 13	19°30'41.40"	18°15'32.10"	Sandy
TT 14	19°30'43.70"	18°15'29.00"	Sandy
TT 15	19°30'40.20"	18°15'25.40"	Sandy
TT 16	19°30'39.90"	18°15'27.80"	Silt-clay
TT 17	19°30'37.70"	18°15'29.70"	Sandy

3.2.2 Soil

A total of seven soil, sediment and slag samples were collected from an agricultural area as well as other random points around Berg Aukas. The GPS coordinates of the soil collection sites are shown in Table 3.2. These samples were silt-clay, composite, loamy as well as gravel samples (Table 3.2). Additionally, a total of eleven soil samples were collected at Tsumeb. Most of these samples were sandy/loamy as seen in Table 3.3. Since anthropogenic contamination is usually restricted to the surface layer of the soil [14], only surface samples (i.e. top 10 -15 cm of soil/sediment) were collected. Figure 3.2 shows how composite soil samples were collected in Tsumeb. In the laboratory, the soil samples were subjected to the same preliminary treatment as for the tailings and were stored at room temperature in acid washed polypropylene containers.

Table 3.2: Description of soil, sediment and slag samples collected at Berg Aukas

Sample ID	GPS Coordinates (South)	GPS Coordinates (East)	Description
S 1	19°30'43.00"	18°16'03.40"	Silt-clay
S 2	19°30'50.50"	18°15'04.90"	Silt
S 3	19°30'58.40"	18°15'02.30"	Pond sediment
S 4	19°30'54.00"	18°14'52.80"	Composite sample
S 5	19°30'48.90"	18°14'54.20"	Loamy & gravel
S L1	19°31'02.50"	18°14'51.30"	Sludge
S L2	19°31'03.00"	18°14'50.60"	Sludge

Table 3.3: Description of soil samples collected at Tsumeb

Sample ID	GPS Coordinates (South)	GPS Coordinates (East)	Description
S 6	19°14'14.00"	17°42'38.00"	Sand
S 7	19°14'18.00"	17°42'37.00"	Clay
S 8	19°14'29.00"	17°42'13.00"	Sandy/loamy
S 9	19°14'29.00"	17°42'13.00"	Sandy
S 10	19°14'31.00"	17°42'13.00"	Sandy
S 11	19°14'30.00"	17°42'13.00"	Sandy/loamy
S 12	19°14'34.00"	17°42'60.00"	Sandy/loamy
S 13	19°14'32.00"	17°42'60.00"	Sandy/loamy
S 14	19°14'29.00"	17°42'60.00"	Sandy/loamy
S 15	19°14'41.00"	17°42'14.00"	Sandy/loamy
S 16	19°14'35.00"	17°42'45.00"	Pisolitic soil

Figure 3.2: A soil sampling area in Tsumeb

3.2.3 Water

As the sampling was done during the dry months (April), no water samples were collected from Tsumeb and only a total of three water samples were collected around Berg Aukas. These samples were collected from the borehole, rainwater that had collected in an abandoned swimming pool as well as from a pond near the old mine (Table 3.4). Sampling bottles (acid washed borosilicate bottles) were first conditioned by rinsing with the site water before sampling. In addition, the sampling bottles were opened under water to avoid oxidation of the water sample. Ancillary data such as pH, Ec, ORP, temperature and turbidity (Figure 3.3) were measured on sites. The samples were processed immediately at the sampling site by the addition of a small volume of ultra-pure concentrated HNO_3 (Merck) (0.1 to 1% v/v) to one bottle for cations and the other bottle for anions was not acidified, then both bottles were placed in cooler bags. Adding acid to water samples maintains the $pH < 2$ in order to minimize any kinds of precipitation, adsorption and microbial activities[14]. In the laboratory, the water bottles were stored in the fridge at 4°C until analysis.

Table 3.4: Description of water samples collected at Berg Aukas

Sample ID	GPS Coordinates (South)	GPS Coordinates (East)	Description
W 1	19°30'43.00''	18°16'03.40''	Borehole water
W 4	19°30'50.50''	18°15'04.90''	Rainwater
W 5	19°30'58.40''	18°15'02.30''	Pond water

Figure 3.3: *In situ* measurement of ancillary data.

3.2.4 Plants

Samples of plants (leaves and fruits) were collected randomly from wetlands and from plants growing on the tailings and soils at both sampling sites (i.e. Tsumeb and Berg Aukas). Species of plants collected in this study were identified by a botanist and included *Ricinus communis* (common name castor bean), *Combretum imberbe* (common name lead wood), *Jacaranda mimosifolia*, *Dodonea viscosa*, *Sclerocarya birrea* (common name marula) and *Eucalyptus globulus* (blue gume tree). Figure 3.4 shows some of the plant species collected. The collected samples were stored in Ziploc bags until analysis.

Figure 3.4: Some of the plant species that were collected. (a) *Ricinus communis* and (b) *Combretum imberbe*

All sampling GPS coordinates were recorded and mapped with a QGIS software (Figures 3.5 and 3.6).

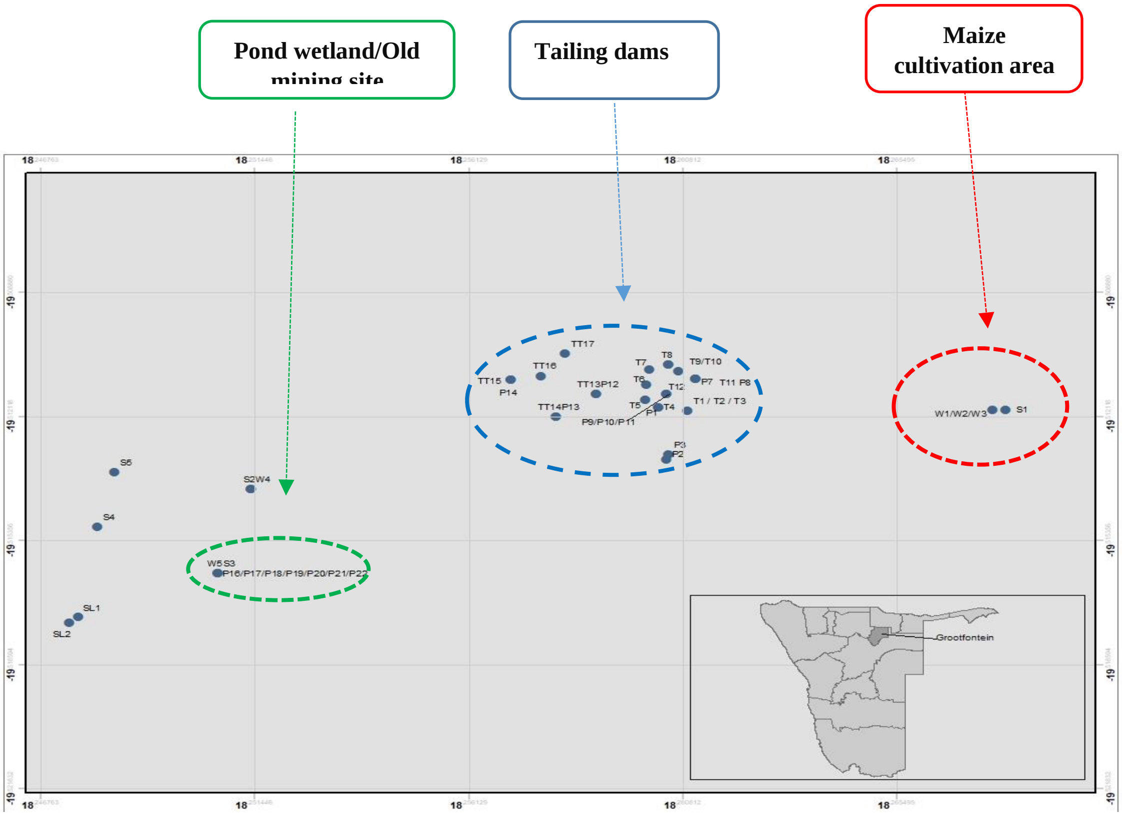

Figure 3.5: The sampling site at Berg Aukas (the blue dots are the sampling points)

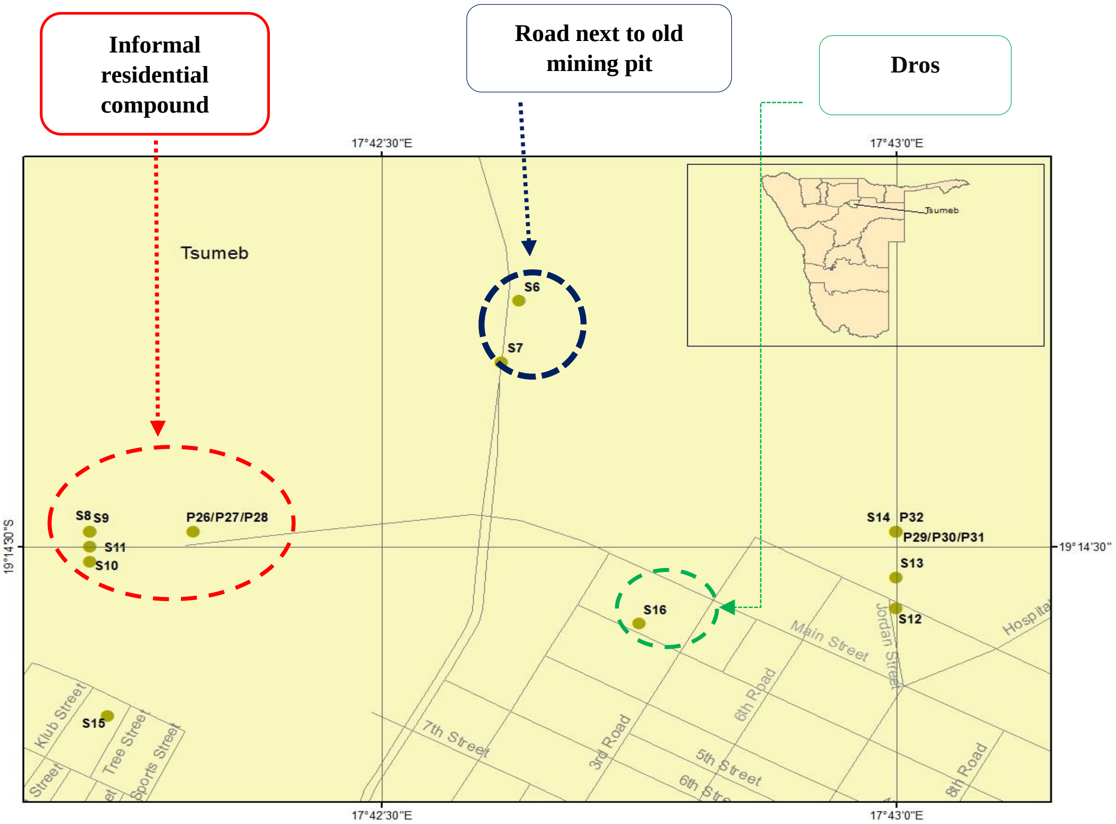

Figure 3.6: The Tsumeb sampling site and sampling points (in green dots)

3.3 Sample preparation for total metal analysis

3.3.1 Soil and tailing

Prior to analysis, the soil and tailing samples were sieved to eliminate stones and other gross particles in order to have a homogenous sample. The pH, conductivity and total dissolved solids (TDS) of the soils and tailings were determined in a water suspension of all the original samples using a Hanna HI 9911-5 meter.

Representative sample aliquots were transferred into 50 mL open vials and placed in an oven to dry at 50°C for 24 hours. Once dried, about 250 mg of each sample as well as a

Certified Reference Material (CRM), namely BCR 320R Channel Sediment, was weighed and placed in digestion vessels. To this, analytical grade acid mixture consisting of 3 ml concentrated HNO_3 (Merck), 1 mL concentrated HF (ProMark) as well as 9 mL concentrated HCl (ProMark) was added. The samples underwent acid digestion in a closed microwave digestion system (Titan MPS, Perkin Elmer). The parameters of the digestion method are shown in Table 3.5. Digestion solubilizes particulate matter in the sample and aids in the removal of potential interferences within the sample matrix [64]. After digestion, the vessels were removed and cooled to room temperature. The digested samples were placed in glass vials and 6 mL of 4% (v/v) H_3BO_3 (Merck) was added to each vial to digest and neutralize the damaging effect of HF to glass. All samples were stored in the fridge until the day of metal analysis.

Table 3.5: Microwave digestion parameters

T (°C)	**P (bar)**	**Ramp(min)**	**Hold**	**P (%)**
200	30	3	5	90
175	30	2	2	90
50	60	1	2	0
50	60	0	0	0
50	60	0	0	0

3.3.2 Plant sample preparation

Plant samples were washed well with tap water, followed by distilled water. This was to ensure that all the plant samples were free of any dirt and dust. The plant samples were then left to air dry at room temperature for several days. Once dried, they pruned into fruits and leaves and were crushed using a mortar and pestle. Between 250 and 300 mg of each sample and the Certified Reference Material (CRM), namely BCR 482 Trace Elements in lichens, was weighed and placed in digestion vessels. A mixture of concentrated HNO_3 and HCl in the volume ratio of 3:9 mL was added to the ground plant samples. The digested samples were stored in the fridge until metal analysis. For total Hg (HgT), no digestion of the solid samples was required as the instrument and method used allowed for direct solid measurement.

3.3.3 The characterization of Hg and other metals distribution in affected study sites

An approved sequential extraction procedure from the Community Bureau of Reference (BCR) was used to identify the exchangeable, reducible, oxidisable and residue fractions of Hg as well as other co-occurring heavy metals in soils and tailings. The procedure was done in the following 4 steps:

Step 1: F1 (Exchangeable): This step aimed at extracting the mobile fraction of Hg as well as other metals in soil and tailing samples [16]. About 0.1 g of soil, tailing sample as well as CRM was weighed into 50 mL vials. The weighed solids were mixed with 20 mL of 0.1 M acetic acid (Merck). The mixture was shaken, using a mechanical shaker, for ± 16 hours at 90 rpm. After shaking, the mixtures were filtered with filter paper (pore size 125 mm). The supernatant was collected and stored in the fridge at 4°C until analysis with the ICP–OES. The residue was washed with 10 mL distilled water, dried and used for the next step.

Step 2: F2 (Reducible): This step aims at extracting the contents of each metal that is bound to oxides of iron and manganese [65]. About 20 mL hydroxylamine hydrochloride (Sigma-Aldrich) solution was added to the residue from step 1. The mixture was shaken for about 16 hours using a mechanical shaker. The rest of this step followed the procedure stated in step 1 above.

Step 3: F3 (Oxidisable): The oxidisable fractions show metals that are bound to sulphur and organic matter and if conditions become oxidative, these metals will be released into the environment [65]. About 5 mL of 30% hydrogen peroxide (Merck) was added to the residue from step 2. The mixture was heated on a hotplate at 65 ± 5°C for 1 hour. Another 5 mL of hydrogen peroxide (Merck) was added and the mixture was heated for an additional 1 hour at 70 ± 5°C to reduce the volume to less than 1 mL. The residue was then extracted with 25 mL ammonium acetate (Merck) (adjusted to pH 2). As with step 1 and 2, the mixture was shaken for ±16 hours using a mechanical shaker and then filtered and stored in the fridge.

Step 4 F4: (Residual): Metals found in this fraction are the most difficult to separate because they have the strongest association with the crystalline structures [65]. The amount was calculated by subtracting the total of the first three fractions from the total amount of metal found in the sample ((Total metal – (F1 + F2 + F3)) = Residual.

In comparison with the selective sequential extraction (SSE) protocol developed by Bloom *et al* [56], the following Hg species can be associated to the BCR fractions:

Exchangeable (F1): water soluble and acid leachable Hg species such as $HgCl_2$, $HgSO_4$, HgO and, to a certain extent, CH_3Hg^+.

Reducible (F2): Hg bound to Fe and Mn oxides, Hg complexed to humic acid and, most likely, $Hg(OH)_2$.

Oxidisable (F3): strongly complexed Hg species such as the mineral lattice bound Hg, Hg_2Cl_2, HgS, and eventually liquid Hg^0.

Residue (F4): HgS (cinnabar), m-HgS (meta-cinnabar), HgSe, and HgAu (amalgams).

3.3.4 Leaching procedure for sulphur and anions determination

Sulphur species such as sulphide (S^{2-}), sulphate (SO_4^{2-}) and organic sulphur are, together with other anions such as carbonate, chloride and nitrate, important ligands that may affect metals properties such as mobility. For instance, it is common knowledge that all metal nitrates and most carbonates are soluble in water whereas metal sulphides have extremely low solubilities in water. Hence, to understand the distribution of Hg and other metals in soil (and tailings) it is critical to identify some of the ligands that may play a role in the behaviour of these metals in a given environment.

A simple sequential leaching process was used to determine the level of anions and total sulphur in selected soil and tailings from Berg Aukas and Tsumeb. First, about 3.0 g of the solid samples were mixed with 30 mL of distilled water and shaken for ± 16 hours with a mechanical shaker. The mixture was then filtered, and the leachate was kept in the fridge until analysis. This fraction was used to identify the water leachable ligands present in the sample (e.g. sulphate, chloride, nitrate and fluoride) and it is also likely to comprise the forms of sulphur present in F1 and F2 of the BCR SEP.

The remaining filter cake was then mixed with 30 mL of aqua regia and subjected to the same treatment as for the water leaching. This fraction was used to determine the remaining total sulphur content and it is assumed to comprise the hardly soluble forms of sulphur that are found in F3 and F4 of the BCR SEP.

3.4 Analytical techniques

This section briefly presents the different analytical techniques used in this study.

3.4.1 Mercury analysis of soil, tailings, plant and water

Total Hg (HgT) was determined by directly introducing the samples (i.e. no prior preparation was required) to an automated mercury analyzer (DMA-80 milestone) shown in Figure 3.7. This technique employs direct combustion that decomposes the sample in an oxygen-rich environment and removes any interfering elements [61].

Figure 3.7: The DMA-80 milestone instrument used for total Hg quantification

About 0.1g of sample, including CRMs, was weighed into nickel boats using an analytical balance (Kern). The boats were placed on the instrument auto sampler (Figure 3.8) and the instrument was started.

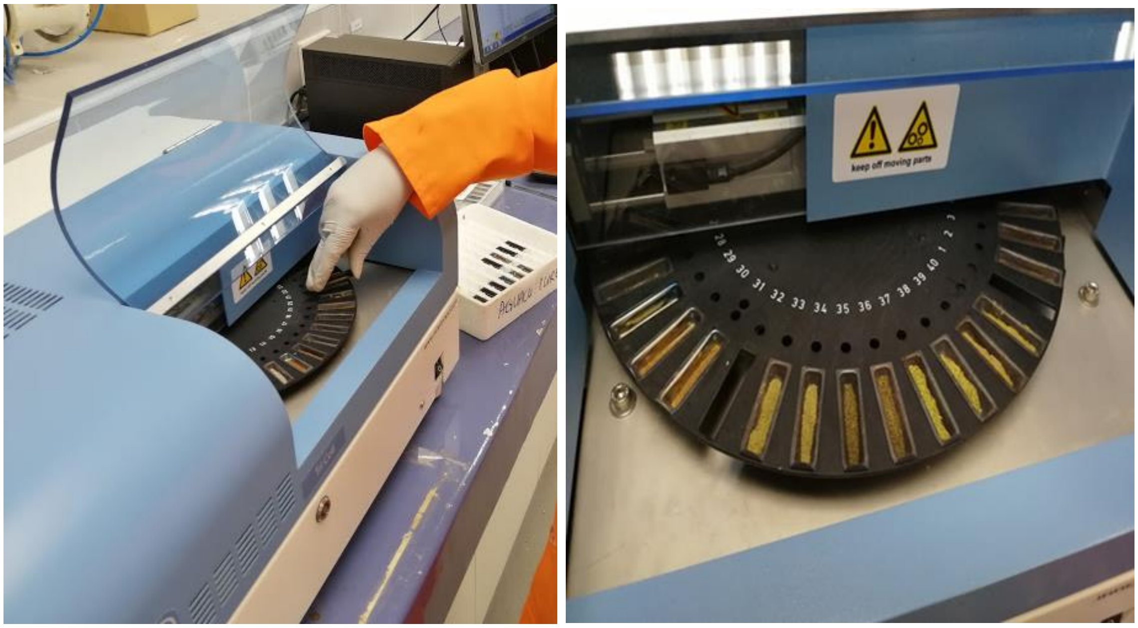

Figure 3.8: Nickel boats with samples on the DMA 80 instrument

3.4.2 Elemental analysis of soil, slag tailings, plant and water samples

This was done using an Inductively Coupled Plasma Optical Emission Spectrophotometer, ICP-OES (Optima 8000, Perkin Elmer), shown in Figure 3.9. ICP-OES is useful in quantifying the majority of the elements of the periodic table in a variety of different sample matrices with very low detection limits. Concentrations that can be detected by the ICP-OES range from trace (5 µg/kg) to very high (mg/kg) [67]. Sample solutions introduced into the ICP-OES are nebulized and then transferred into a plasma generated by the radio frequency excitation of argon (Ar) gas [68].

Once the sample mist reaches the plasma, it is quickly dried, vaporized and energized through collisional excitation at high temperature. The plasma emits the atomic emission which can be viewed in either a radial or axial configuration, collected with a lens or mirror, and imaged onto the entrance slit of a wavelength selection device. Up to 70 elements can be determined simultaneously [67]. These multi-element determinations are performed with the combination of a polychromator and an array detector. With regards to sample throughput and sensitivity, the analytical performance of such systems is competitive with most other inorganic analysis techniques such as atomic absorption spectrometry (AAS) especially for sample sensitivity [69].

To calibrate the equipment, working standard solutions in 1% (v/v) HNO_3 were prepared by diluting the stock solution (Mercury and multi-elemental standards, Perkin Elmer) with distilled water until the desired concentration was achieved. Calibration blanks were also prepared in 1% (v/v) HNO_3.

Figure 3.9: Inductively Coupled Plasma Optical Emission Spectrophotometer, ICPOES (Optima 8000, Perkin Elmer)

All analytical techniques and methods used in this study were validated using appropriate quality control (QC) standards and certified reference materials (CRMs), respectively.

3.4.3 Determination of anions

Anions such as fluoride (F^-), chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-) and sulphate (SO_4^{2-}) in water leachates from selected soil and tailings were quantified with a Metrohm (Eco) ion chromatographer (IC). The eluent was a solution of 0.2 mM $NaHCO_3$ and 5.0 mM Na_2CO_3. A 0.1 M solution of H_2SO_4 was used as a conductivity suppressor regenerant solution. Samples were loaded and injected into the IC by means of an auto-sampler. For calibration, standards of F^-, Cl^-, NO_2^-, NO_3^- and SO_4^{2-} were prepared by accurately diluting, with deionized water, stock solutions prepared from their corresponding salts, namely NaF (Merck), NaCl (Merck), $NaNO_2$ (Merck), $NaNO_3$

(Merck) and Na_2SO_4 (Merck). Analyses were performed using the parameters presented in Table 3.6 below.

Table 3.6: IC parameters for the analysis of anions

Flow (mL/min)	1.10
Pressure (MPa)	12.02
T (°C)	±20
Run time (min)	13.0

3.5 Data analysis

Basic Analysis of Variance (ANOVA) was used to statistically compare the reported mercury concentrations of the used CRMs to the concentrations obtained with the above proposed methods. These tests are critical for the quality assurance as well as for the validation of the data that was generated during the study. Correlation analyses was carried out with the collected data and field measurements, using statistical software such as the Statistical Package for the Social Sciences (SPSS) to understand the factors controlling Hg distribution in the samples.

3.6 Research Ethics

Ethical clearance for the study was obtained from the University of Namibia Research Ethics Committee (UREC) and research permission from the Centre of Postgraduate Studies (CPGS) (appendix 1).

Chapter 4

Results

4.1 Method validation

4.1.1 Total elements

In this chapter, the results of soils, tailings and water from the two sites are presented. The sites from which the samples were obtained are presented in Chapter 3, Figures 3.5 and 3.6. The different analytical methods used for the quantification of Hg and other elements were validated using appropriate CRMs. Tables 4.1 and 4.2 show the results obtained for the triplicate analysis of the CRMs used.

Table 4.1: Elemental concentrations of the CRM used for the validation of soils and tailings analysis

BCR-320R Channel Sediment	As (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	Mn (mg/kg)	Hg (mg/kg)
Certified ± U	21.7 ± 2.0	46.3 ± 2.9	25700 ± 1300	85 ± 5	59 ± 4	910 ± 50	0.85 ± 0.09
Measured ± SD$^{(*)}$	23.6 ± 5.0	47.5 ± 2.2	23133 ± 332	90 ± 8	57 ± 3	894 ± 11	0.87 ± 0.06
Recovery (%)	108.8	102.6	90.0	105.9	96.6	98.2	102.3

$^{(*)}$: Results obtained with ICP–OES except for Hg which was analysed by the DMA 80.

U = Uncertainty

SD = Standard Deviation

Table 4.2: Elemental concentrations of the CRM used for the validation of plant analysis

BCR-482 Lichen	As (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Hg (mg/kg)
Certified ± U	0.85 ± 0.07	7.03 ± 0.19	2.47 ± 0.07	40.9 ± 1.4	100.6 ± 2.2	4.12 ± 0.15	0.48 ± 0.02
Measured ± SD	0.95 ± 0.12	6.09 ± 0.04	2.24 ± 0.06	36.6 ± 0.5	97.7 ± 0.6	3.49 ± 0.27	0.49 ± 0.01
Recovery (%)	111.8	86.6	90.7	89.6	96.9	84.7	102.1

U = Uncertainty

SD = Standard Deviation

In general, the obtained results showed excellent repeatability and reproducibility with percent relative standard deviation (RSD) below 10%. Excellent recoveries were also obtained with both CRMs, ranging between 90.0 - 108.8% (mean: 100.6%) and 84.7 - 111.8% (mean: 94.6%) for BCR-320R and BCR-482, respectively. Except for Fe in BCR-320R for which the discrepancy between certified and measured values could be attributed to its extremely high concentration. This result into multiple dilutions during analysis and, thus increasing risks of inaccuracy, only one significant difference, in Cu for BCR-482, was statistically observed at 95% confidence level. Fortunately, this deviation from accuracy is not critical for environmental studies as the difference between the certified and measured values was below 1 mg/kg which is relatively insignificant for Cu in impacted soils.

4.1.2 BCR sequential extraction

The validation of the sequential extraction steps used in soils and tailings was performed with a material certified for its extractable element content and species, namely BCR-701 of lake sediment. A comparative table between the certified and obtained values is presented in Table 4.3 below.

Table 4.3: Quality control of sequential extraction data using the CRM BCR-701 (n=3,RSD)

Step	**Metal**	**BCR-701**		**% Recovery**
		Certified value mean ± U (mg/kg)	Obtained value (n=3) Mean ± SD (mg/kg)	
1	Cd	7.3 ± 0.4	8.6 ± 0.1	117.8
	Cu	49.3 ± 1.7	63.8 ± 1.3	129.4
	Pb	3.18 ± 0.21	2.98 ± 0.19	93.7
	Zn	205 ± 6	230 ± 4	112.2
2	Cd	3.77 ± 0.28	2.98 ± 0.00	79.0
	Cu	124 ± 3	140 ± 2	112.3
	Pb	126 ± 3	109 ± 3	86.5
	Zn	114 ± 5	95 ± 12	83.3
3	Cd	0.27 ± 0.06	0.075 ± 0.01	27.8
	Cu	55 ± 4	40 ± 3	72.7
	Pb	9.3 ± 2.0	9.6 ± 0.6	103.2
	Zn	46 ± 4	46 ± 1	100.0

n, number of replicates; U (half-width of 95% confidence interval); SD

Of the 12 sets of data examined, only one case (Zn step 2) showed % SD above 10% (i.e. 12.6%) whereas 10 of the 12 data sets had RSD below 5%. Although statistical differences were observed in a few cases between certified and measured values (e.g. Pb step 2 and Cd, Cu step 3), this would not affect the significance of the data in terms of environmental studies due to the closeness of both values at each step [70] and as overall extracted for each element (e.g. 11.34 mg/kg of Cd is certified to be extractable by the 3 steps and 11.65 mg/kg were actually extracted with the used method).

The obtained data from CRMs analyses for both total elements and sequential extraction, therefore, showed the reliability of the proposed methods.

4.2 Ancillary data for tailings, soils and waters

The pH, EC and TDS data obtained in the study samples are shown in Tables 4.4 to 4.6.

Table 4.4: pH, EC and TDS of Berg Aukas tailings

Sample ID	Description	pH	EC (µS/cm)	TDS (mg/L)
T1	Fine grain	8.0	300	140
T2	Fine grain	8.0	390	180
T3	Fine grain	8.2	310	150
T4	Fine grain	8.1	270	120
T5	Silt-Clay	8.2	500	230
T6	Silt-Clay	8.2	410	180
T7	Gravel_Silt_Clay	8.1	180	80
T8	Gravel_Silt_Clay	8.3	270	120
T9	Silt-Clay	8.1	320	150
T10	Silt-Clay	8.1	310	150
T11	Silt-Clay	8.1	320	140
T12	Silt-Clay	8.1	330	160
TT13	Sandy	8.2	200	80
TT14	Sandy	8.1	330	120
TT15	Sandy	8.1	160	70
TT16	Silt-Clay	8.1	390	180
TT17	Sandy	8.1	140	60

The average pH, EC and TDS of Berg Aukas tailings ranged between 8.0 – 8.3 (mean: 8.1), 140 – 500 (mean: 312) µS/cm and 60 – 230 (mean: 141) mg/L, respectively.

The pH was uniform at both tailings' sites denoting that these tailings were of the same origin. The measured EC and TDS which can be an indication of soluble (ionic) species values were relatively low and close to values measured in tap waters which could be an indication that most of the metals in the tailing material were not in their free (i.e. ionic) forms but rather as metal-ligand complexes.

Table 4.5: pH, EC and TDS values of soil from Berg Aukas (S1 to SL2) and Tsumeb (S6 to S16)

Sample ID	Description	pH	EC (µS/cm)	TDS (mg/L)
S1	Silt-Clay	8.1	380	180
S2	Silt-Clay	8.3	420	200
S3	Pond Sediment	8.0	870	420
S4	Composite Soil	8.1	360	160
S5	Loamy & Gravel	7.9	430	210
SL1	Slag	8.8	310	610
SL2	Slag	8.9	400	190
S6	Sandy	7.8	450	210
S7	Clay	8.0	880	460
S8	Sandy/Loamy	7.8	350	150
S9	Sandy	7.6	380	180
S10	Sandy	7.8	320	140
S11	Sandy/Loamy	7.7	280	140
S12	Sandy/Loamy	7.8	430	250
S13	Sandy/Loamy	7.4	390	210
S14	Sandy/Loamy	7.5	380	170
S15	Sandy/Loamy	7.8	360	160
S16	Pisolitic Soil	7.9	630	300

The pH of Berg Aukas soils were in the range of 7.9 – 8.9 (average 8.3), in general, slightly more alkaline than the ones of Tsumeb (with range of 7.4 – 8.0, average 7.7) even though both areas are underlaid by carbonate rocks. The lowest pH was observed in loamy soils whereas the most alkaline pH was obtained from sludge samples (Berg Aukas) and clayish soils (Tsumeb).

EC and TDS where slightly higher for tailings (respective averages of 453 µS/cm and 281 mg/L for Berg Aukas; 441 µS/cm and 215 mg/L for Tsumeb) and with much more variability (310 – 870 µS/cm and 160 – 610 mg/L in Berg Aukas; 280 – 880 µS/cm and 140 – 460 mg/L in Tsumeb). The highest values were observed in the pond soil (Berg

Aukas) and in clayish soil (Tsumeb). One would, therefore, expect much more soluble forms of metals in the samples from soils than in the tailings.

Table 4.6: pH, ORP and EC of Berg Aukas waters

Sample ID	Description	pH	Eh (mV)	EC (µS/cm)
W1$^{(*)}$	Borehole Water	7.4	218	800
W4	Old Pool (Rain) Water	9.0	104	945
W5	Pond Water	8.5	130	512

$^{(*)}$: W1 data, here and elsewhere, are averages of the analysis of 3 borehole samples (W1, W2 and W3)

Water samples, which were only collected in Berg Aukas, also showed considerable variability, depending on their source, from almost neutral pH (7.4) in borehole waters to alkaline values, in the rainwater accumulated in an old pool at the camp site (pH = 9.5). ORP values, on another hand, revealed the predominance of anaerobic conditions at the site (mean: 151 mV and range: 104 – 218 mV) whereas EC was still low with values below µS/cm (range: 512 – 945 µS/cm and average: 752 µS/cm).

4.3 Occurrence of total mercury (HgT) in tailings, soils and plants

Figure 4.1 shows examples of the low and high range calibration curves respectively, obtained with the DMA-80.

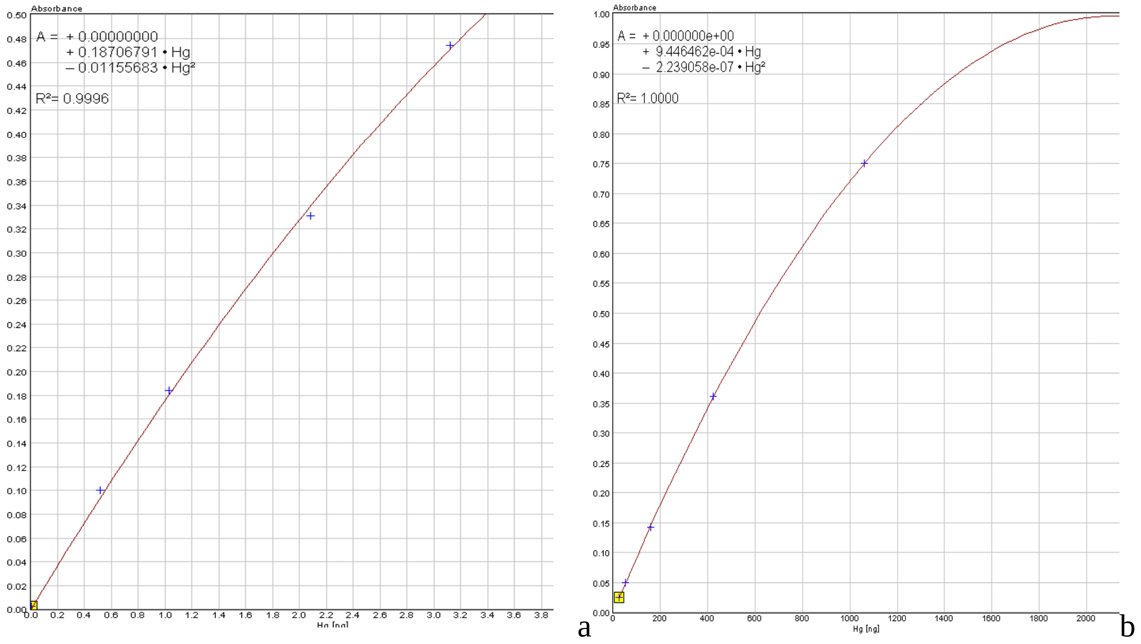

Figure 4.1: Calibration curves of low range (a) and high range (b) Hg of DMA 80

All tailing samples collected from both tailing sites had high values of HgT with concentrations ranging from 0.04 to 2.24 mg/kg (Figure 4.2) with an average value of 1.40 mg/kg. Only one tailing sample collected from the TT sampling site had a very low Hg concentration of 0.04 mg/kg (TT17).

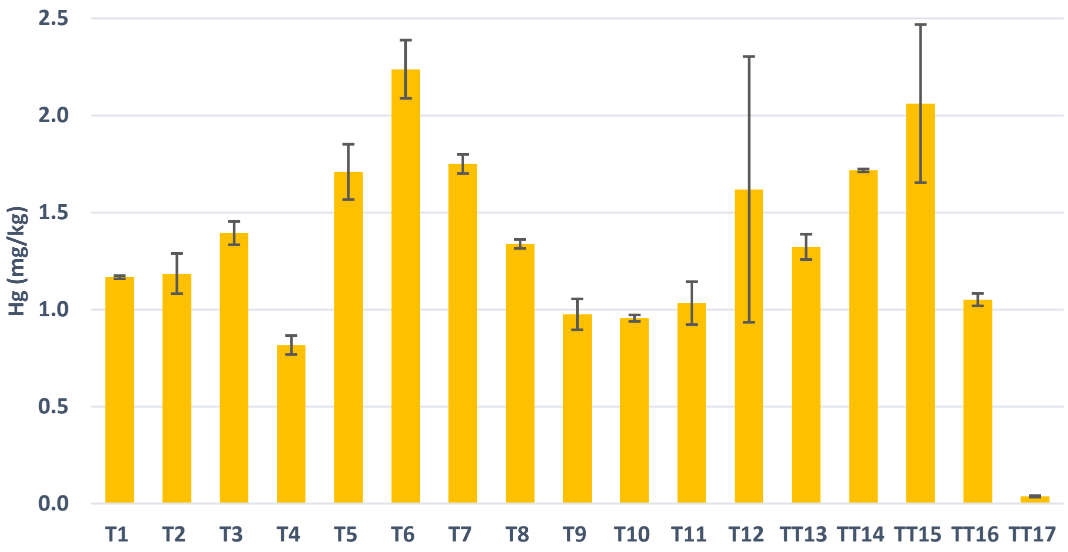

Figure 4.2: HgT in Berg Aukas tailings

Soil samples collected from both Berg Aukas and Tsumeb also showed the occurrence of HgT with concentrations ranging from 0.02 mg/kg to 3.49 mg/kg and mean concentration of 0.60 mg/kg (Figure 4.3). Although higher Hg values were generally observed in Berg Aukas soils, one soil sample that was collected around the vicinity of the Dros restaurant in Tsumeb (S16) had the highest Hg concentration of all study soils with a value of 3.49 mg/kg. A soil sample (S4), which was collected randomly in Berg Aukas around the community area, had the second highest concentration of 3.11 mg/kg.

It was also noted that another soil sample (S3) which was collected at the bottom of a pond wetland near the abandoned mine site in Berg Aukas showed the third highest HgT value of 2.49 mg/kg.

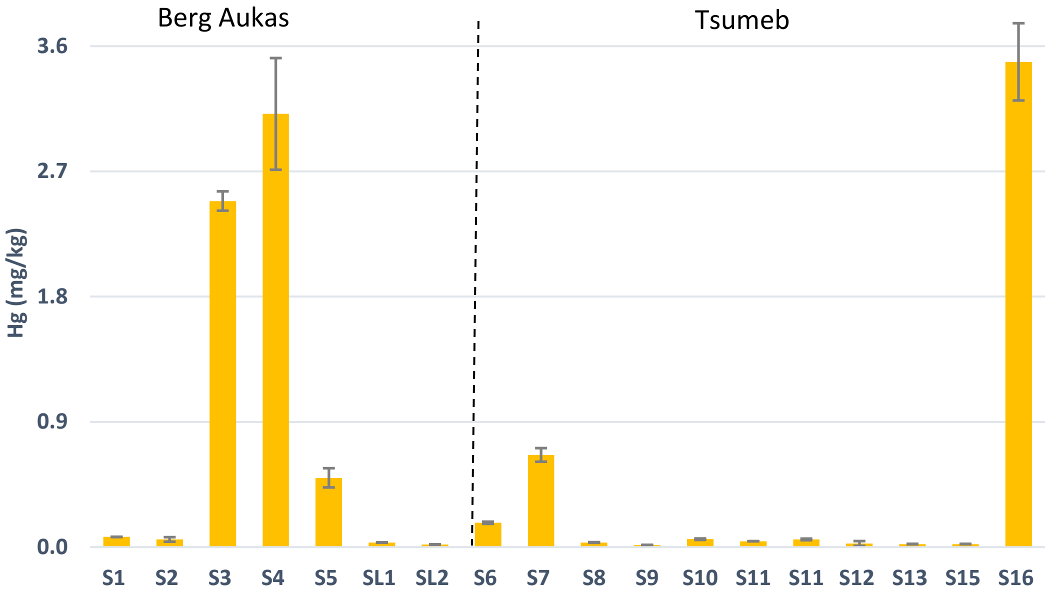

Figure 4.3: HgT in Berg Aukas and Tsumeb soils

A total of 31 plant samples (P1 - P32) were collected from Berg Aukas and Tsumeb and they all had detectable amounts of HgT with the lowest being 0.04 mg/kg while the highest was 0.07 mg/kg (Figure 4.4).

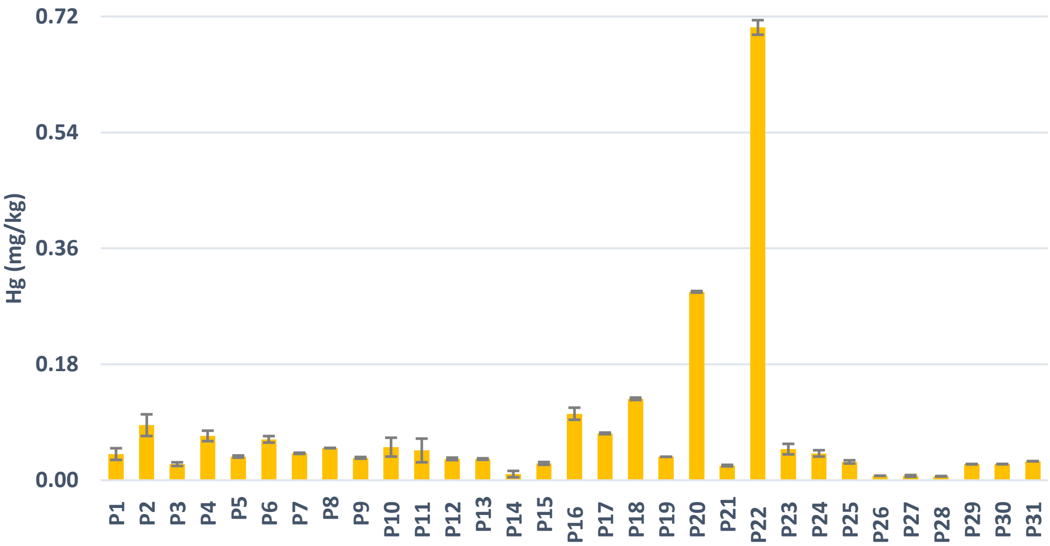

Figure 4.4: HgT in plants (only results for leaves analysis are shown)

The plant sample that showed the highest concentration of HgT (0.70 mg/kg) was collected from the same pond wetland as for S3. The mean concentration of HgT for all plant samples collected in this study was 0.06 mg/kg.

It was observed that different parts of the same plant accumulated different concentrations of Hg, with the leaves having the highest concentrations (Table 4.7)

Table 4.7: HgT in different parts of plants

Sample ID	**HgT (mg/kg)**
P8 Fruit	0.04
P8 Leaves	0.05
P10 Fruit	0.01
P10 Leaves	0.05
P12 Fruit	0.01
P12 Leaves	0.03
P13 Leaves	0.03
P13 Fruit	0.01
P24 Leaves	0.04
P24 Fruit	0.009
P25 Leaves	0.023
P25 Fruit	0.01

All water samples collected during this study had concentrations of HgT ranging between 2 to 6 µg/L (Figure 4.5) with a mean concentration of 3 µg/L. These values are all higher than the permissible Hg concentration in drinking water of 1 µg/L (ppb) as per WHO guidelines.

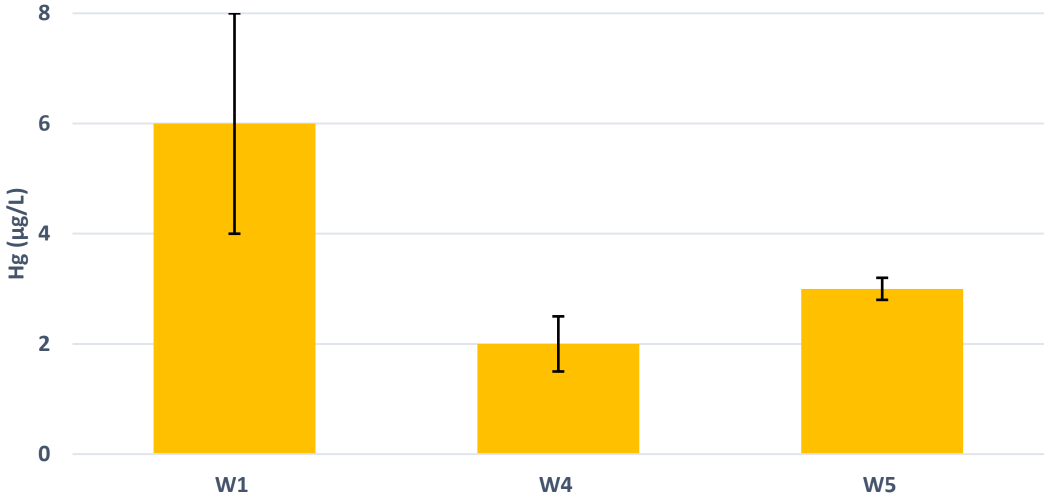

Figure 4.5: HgT in Berg Aukas waters

4.4 Occurrence of other heavy metals in Berg Aukas and Tsumeb

4.4.1 Tailings

Generally, Hg and the co-occurrent metals exhibited extremely high concentrations at both tailing dump sites in Berg Aukas (Figure 4.6). For instance, the concentration of Fe ranged from 11091 to 37605 mg/kg (mean: 21509 mg/kg), Cu concentrations were between 142 and 439 mg/kg (mean: 193 mg/kg) whereas Co and Ni were measured at relatively low amounts with the highest being 5.3 mg/kg (mean: 2.7 mg/kg) and 1.3 mg/kg (mean: 0.76 mg/kg), respectively.

Moreover, the values for Cd, Mn, Zn, Pb and As ranged from 253 to 422 mg/kg (mean: 320 mg/kg), 289 to 701 mg/kg (mean: 396 mg/kg), 18387 to 38509 mg/kg (mean: 25090 mg/kg), 6679 to 18195 mg/kg (mean: 10045 mg/kg) and 68.2 to 266 mg/kg (mean: 127 mg/kg), respectively.

Most of the tailings had Fe, Al, Zn and Pb concentrations near or greater than the percentage levels (i.e. ≥ 10,000 mg/kg) as shown in Figure 4.6.

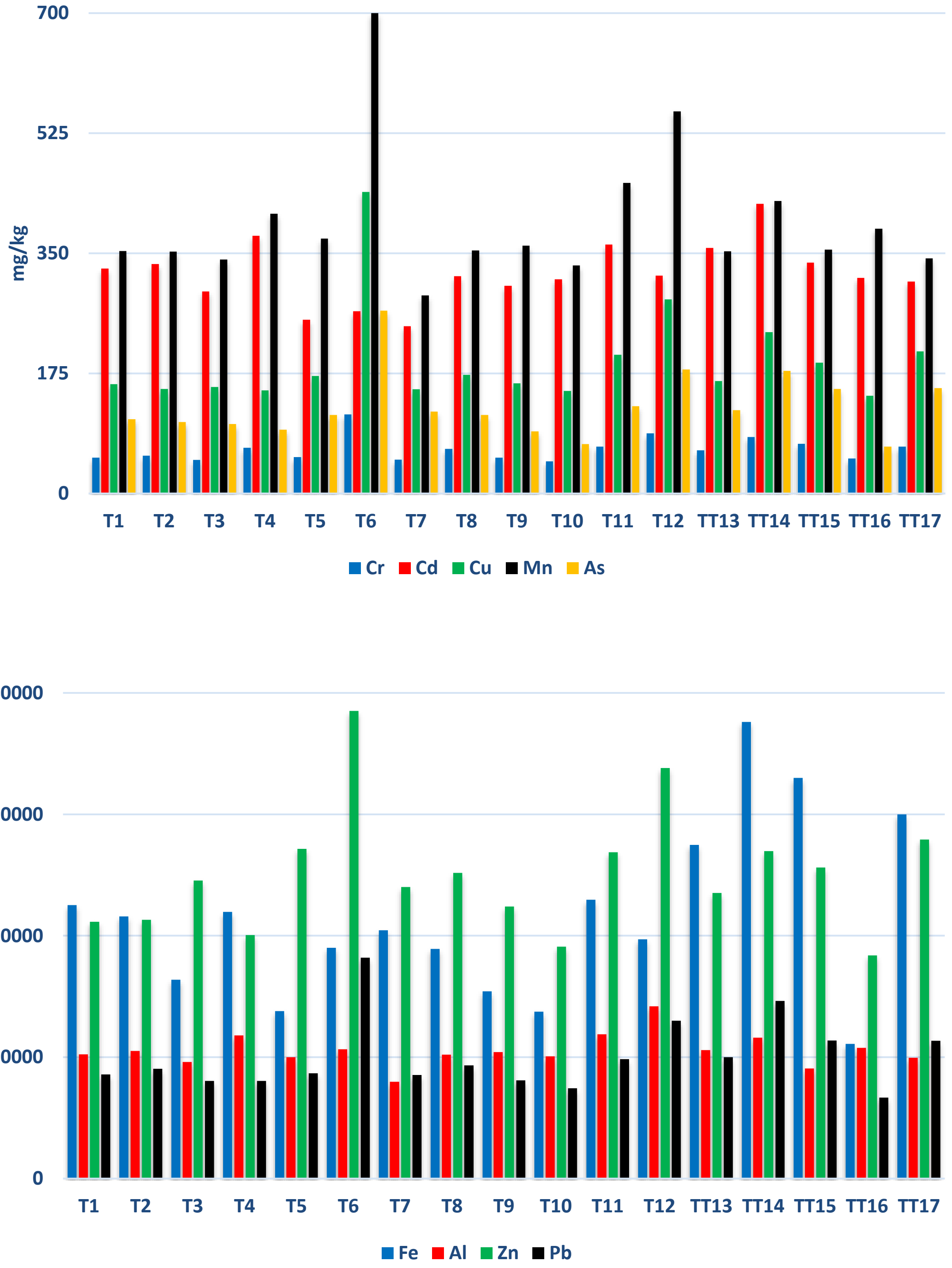

Figure 4.6: Metals and metalloids in Berg Aukas tailings

4.4.2 Soil

Table 4.8 summarises results of heavy metal concentration in soils from Berg Aukas and Tsumeb. Soil samples collected during this study showed concentrations of Fe ranging between 6614 and 26769 mg/kg (mean: 14576 mg/kg or 1.5% Fe). Two slag samples collected at Berg Aukas also showed elevated levels of Fe (mean: 39962 mg/kg or about 4.0% Fe). These two samples also showed elevated concentrations of other heavy metals. Al and Zn also occurred at or near percentage levels, especially in slag samples, with an average concentration of 31791 mg/kg (3.2%) and 6144 mg/kg (0.6%), respectively in soils, and 26630 mg/kg (2.7%) and 19676 mg/kg (2.0%), respectively in slags.

Additionally, toxic metals such as As, Cd and Pb were observed at relatively high concentrations, especially in Berg Aukas soils. The mean concentration for As was 101 mg/kg, with the highest values measured in soil S4 (298 mg/kg) and slags (mean: 334 mg/kg) from Berg Aukas. The average Cd concentration was 21 mg/kg with the highest level measured in sample S4 from Berg Aukas (204 mg/kg). Tsumeb soils generally showed low Cd level, although one sample (S7) had Cd at a concentration of 6.9 mg/kg.

Pb, on the other hand, was measured at concentrations ranging from 8.5 to 18525 mg/kg (mean: 2050 mg/kg), with the highest concentration measured in sample S4 from Berg Aukas and lower concentrations observed in soils from Tsumeb. Cr, Cu, Co and Ni also were present in the study soils though at relatively lower concentrations than the other metals. The highest concentrations of these elements were measured in Berg Aukas slags with mean values of 178, 1066, 8.8 and 13.6 mg/kg for Cr, Cu, Co and Ni, respectively. But, the soil sample with the highest concentration of Cu (S6: 1213 mg/kg) was, in contrast, collected in Tsumeb. Finally, while soils showed Mn concentrations ranging from 121 to 585 mg/kg, the highest Mn concentrations were measured in slags with an average concentration of 39962 mg/kg (i.e. about 4.0%).

Table 4.8: Metals and metalloid in soils from Berg Aukas and Tsumeb

		Concentration (mg/kg)										
	ID	Cr	Mn	Fe	Cd	Al	Ni	Cu	Zn	As	Co	Pb
Berg Aukas	S1	65	441	18760	32	44323	12.0	118	1607	26	9.3	489
	S2	31	121	8091	31	17849	1.5	16.6	1996	17	1.1	512
	S3	103	238	20077	153	16435	2.3	344	28163	224	3.9	13894
	S4	116	585	26769	204	10728	1.5	458	37551	298	3.9	18525
	S5	48	250	11593	26	16437	1.1	161	16636	97	2.3	5770
	SL1	158	732	35051	1.6	22275	10.9	881	20063	318	6.0	3293
	SL2	199	965	44874	nd(*)	30985	16.3	1252	19288	349	11.5	1907
Tsumeb	S6	29	162	7107	10	24054	nd	1213	271	95	2.0	470
	S7	37	353	8365	6.9	33264	2.0	934	516	164	2.2	1551
	S8	28	177	8171	2.0	30618	1.9	35	41	35	2.9	37
	S9	34	234	10121	nd	36909	3.4	27	40	27	3.7	19
	S10	32	185	8324	2.7	39518	1.6	69	78	38	2.3	95
	S12	35	177	9102	3.8	41804	2.4	24	41	23	3.9	8.5
	S13	43	311	11570	nd	46620	4.2	36	44	33	4.7	32
	S14	38	335	10801	2.2	36932	2.6	51	60	43	3.0	54
	S15	28	167	6614	0.24	37979	1.0	18	33	26	3.7	nd
	S16	26	248	7901	0.86	38359	1.8	43	46	28	1.6	33

(*): nd = not detected

4.4.3 Plants

Plant samples were randomly collected at both Berg Aukas and Tsumeb. Table 4.9 shows the metals concentration measured in leaves.

Table 4.9: Metals concentration (mg/kg) in leaf samples from Berg Aukas and Tsumeb

ID	Concentration (mg/kg)								
	Cr	Mn	Fe	Cd	Al	Ni	Cu	Zn	Pb
P1	1.2	207	77	0.86	32	nd	14	239	33
P2	0.98	107	188	13	76	nd	10	682	97
P3	0.83	35	103	nd	91	nd	5.0	271	36
P4	1.8	36	148	nd	151	1.9	7.1	380	86
P5	1.3	32	69	nd	82	0.64	4.7	122	22
P6	0.90	233	82	nd	70	nd	24	412	62
P7	1.3	65	118	5.4	35	nd	4.9	528	81
P8	1.2	28	78	nd	57	nd	2.3	306	76
P9	1.0	135	72	0.93	44	nd	12	734	39
P10	1.1	42	123	nd	49	0.27	4.6	379	58
P11	1.1	27	84	nd	85	nd	4.9	281	37
P12	0.86	70	115	nd	36	0.25	7.8	210	16
P13	0.97	113	103	nd	59	0.79	10	148	1.4
P14	0.52	90	106	nd	22	nd	8.2	311	11
P15	0.90	37	51	1.3	410	0.22	3.0	104	10
P16	1.2	133	77	0.39	135	nd	20	507	35
P17	1.4	45	49	14	37	nd	2.2	334	8.5
P18	1.1	27	60	nd	34	nd	4.1	224	14
P19	2.3	15	89	nd	207	0.56	3.2	59.5	11
P20	8.2	865	596	3.4	492	8.4	27	2362	747
P21	1.5	278	51	nd	18	nd	3.0	256	2.9
P22	2.2	295	192	0.50	71	nd	7.5	720	187
P23	2.0	217	144	nd	93	1.3	9.1	280	51
P24	1.3	131	76	nd	39	0.87	6.5	114	14
P25	1.7	142	72	nd	39	nd	0.6	140	15
P26	1.4	56	50	nd	32	1.4	7.8	24.9	nd
P27	1.8	36	50	nd	37	1.3	7.1	17	nd
P28	1.9	44	55	nd	34	1.5	7.9	27	nd
P29	2.3	69	123	nd	145	1.4	10	18	nd

P30	1.8	68	107	nd	138	1.2	7.7	14	nd
P31	2.7	80	205	nd	187	1.6	15	29	1.4
P32	3.2	1.5	65	nd	38	1.0	4.8	nd	nd

nd = not detected

As it was the case for Hg, metals accumulation in plants varied according to the location, the type of plant species and the part of the plant. The obtained mean values for each identified metal showed the following trend in terms of metal accumulation in leaves: Zn > Mn > Fe > Al > Pb > Cu > Cd > Cr > Ni. The highest metal levels were recorded in plants from Berg Aukas with Zn reaching concentration as high as 2362 mg/kg in sample P20 from the wetland. Sample P20 exhibited the highest values for all the identified metals.

The majority of the Tsumeb samples had undetected to low metal content in the leaves. As mentioned above, it also was observed at both sites (Figure 4.7), as for HgT, that different parts of the same plants accumulated different metals concentrations with the leaves having the highest concentrations and the lowest in the seeds, indicating an eventual translocation of the uptaken metals from the roots to the upper part of the plants.

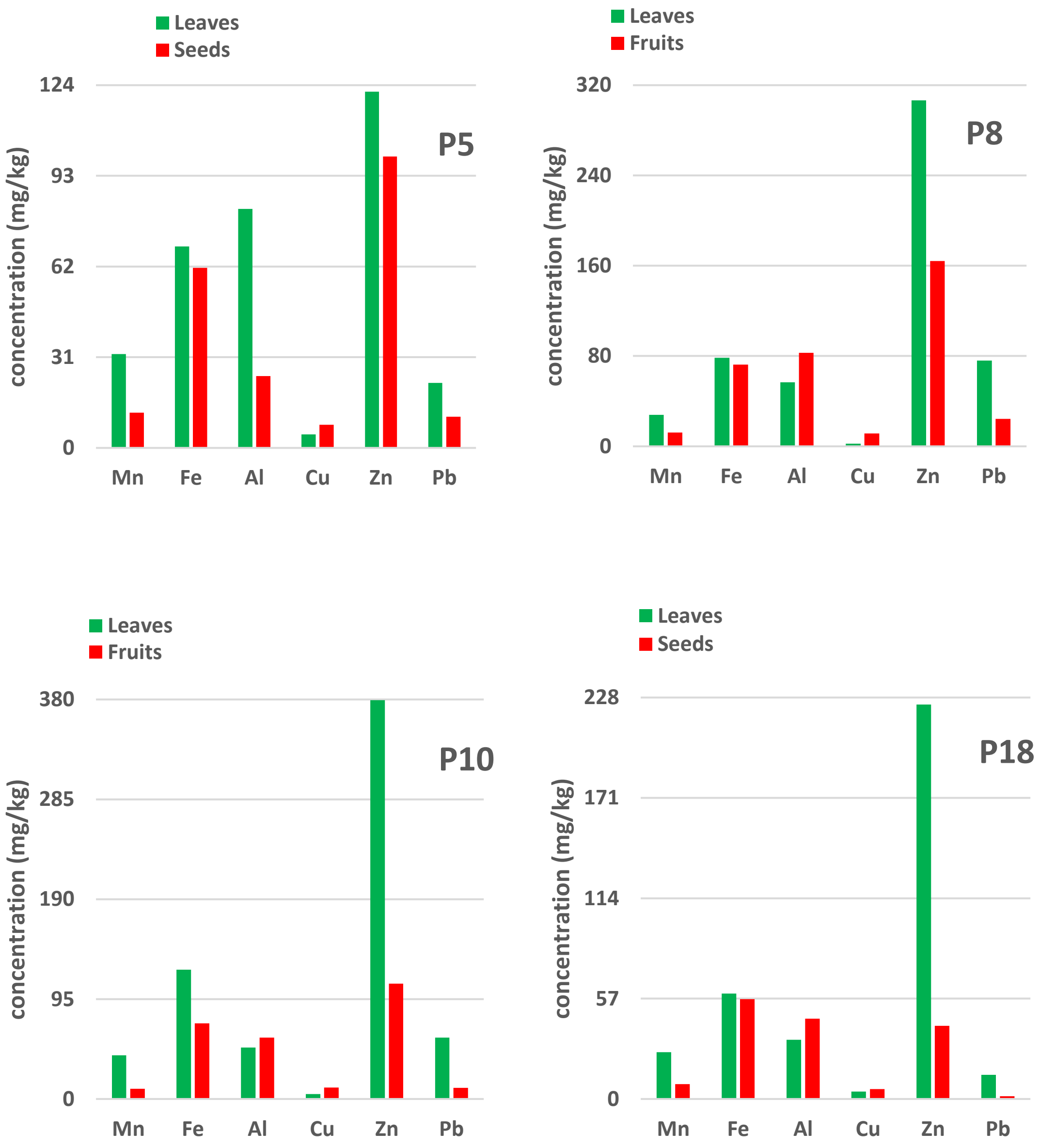

Figure 4.7: Metal concentrations in samples of different plant parts

4.4.4 Water

The results in Table 4.10 show that water samples collected at Berg Aukas showed no detectable amounts of the heavy metals except for Pb which had concentrations ranging from 0.132 to 0.824 mg/L, and Mn which was between nd and 0.014 mg/L. The sample collected from a pond near the abandoned mine (W5) had presence of Fe, Zn and Pb with concentrations of 0.281, 1.29 and 0.518 mg/L, respectively.

Table 4.10: Metal concentrations (mg/L) in Berg Aukas waters

	Concentration (mg/L)			
ID	**Mn**	**Fe**	**Pb**	**Zn**
W1	nd	nd	0.132	0.857
W4	0.003	nd	0.435	nd
W5	0.014	0.281	0.824	1.29

nd = not detected

4.5 Fractionation of mercury in tailings and soils

4.5.1 Mercury fractions in tailings materials

The BCR sequential extraction procedure was used in the study to estimate the amounts of Hg and other heavy metals in tailing and soil samples, which can be mobilized with changing environmental conditions [65]. Figure 4.8 shows the extractable fractions of Hg from the tailing material collected at both tailing sites (i.e. T and TT) in Berg Aukas. The results obtained showed the occurrence of mainly three fractions: exchangeable (range: 0 - 12.6% and mean: 7.6%), reducible (range: 0 - 4.1% and mean: 0.4%), and residue (range: 88.0 - 100% and mean: 91.9%. None of the samples had any (or measurable) oxidisable Hg present whereas the reducible fraction was only observed at site TT in two samples, namely TT14 and TT15.

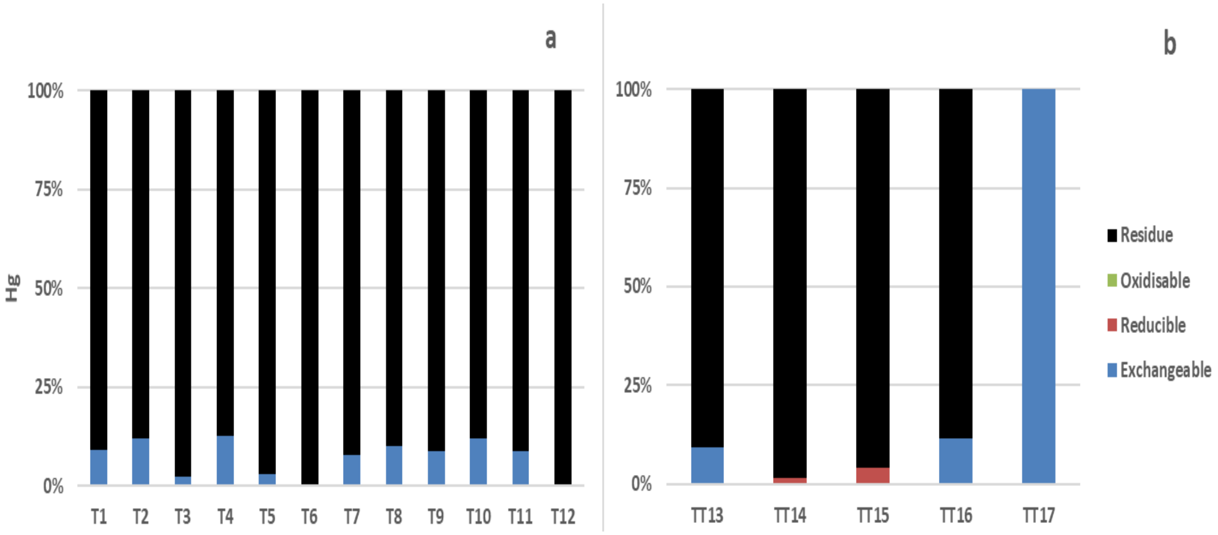

Figure 4.8: Speciation of Hg in Berg Aukas tailings, (a)T sampling site and (b)TT sampling site

4.5.2 Hg fractions in soils

Although Hg was found in all four fractions (F1,F2,F3 and F4) of the BCR protocol (Figure 4.9), only sample S16 from Tsumeb had all the fractions present in it. About 12% of the Hg in the soil samples from Berg Aukas was exchangeable Hg. Three soil samples (S2, S4 and S5) showed the presence of the reducible fraction while S1 and S2 showed 37 and 49%, of the oxidisable fraction, respectively. This fraction indicated the amount of Hg that is bound to sulphur. Should conditions become oxidative, this Hg fraction could be released to the environment.

While all the analysed soils had a residual fraction averaging at 37 and 41% in Berg Aukas and Tsumeb, respectively, Hg in sample S3 from a Berg Aukas wetland only occurred as residual (i.e. 100%).

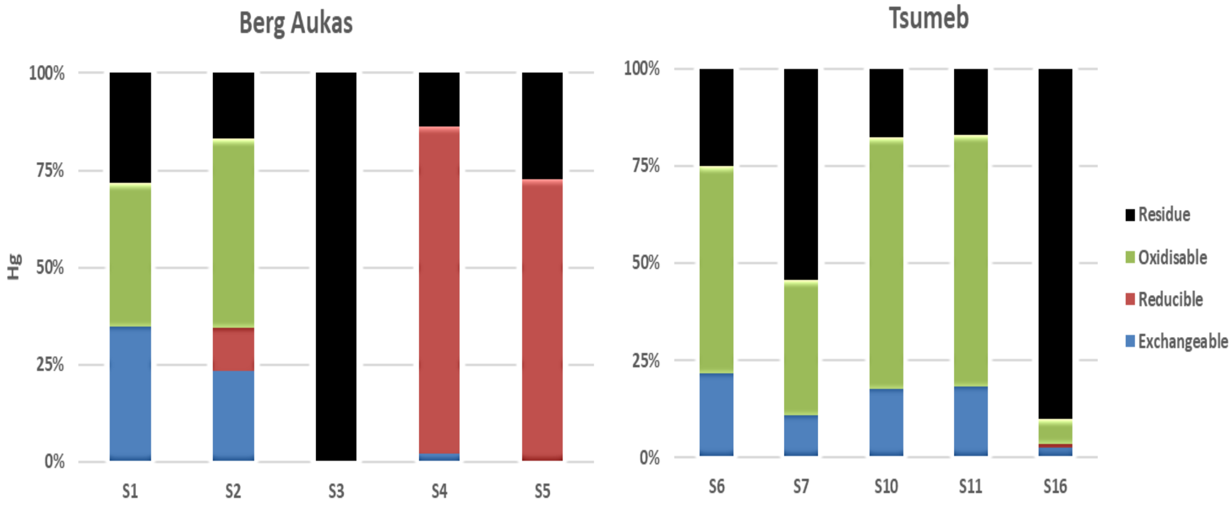

Figure 4.9: Speciation of Hg in soil samples from Berg Aukas and Tsumeb

All 11 samples collected around the town of Tsumeb showed presence of exchangeable Hg, ranging from approximately 2 to 22% (Figure 4.9). They also showed relatively high occurrence of oxidisable Hg forms ranging from 6 to 65% (Mean: 45%) and only one sample (S16) had the reducible Hg fraction at 1%. Hence, as mentioned above, the sample collected in the vicinity of the Dros restaurant (i.e. S16) was the most polluted and had all four fractions of Hg present, 90% of it being in the residual form. There is generally low occurrence of Hg in Tsumeb soils and some of the samples did not show reliable fractionation data.

4.6 Fractionation of co-occurring metals

4.6.1 Arsenic (As)

The distribution of As was studied and compared in selected soil and tailing samples from Berg Aukas (Figure 4.10). Tailing materials had less of the exchangeable fraction (mean: 0.6%) in comparison to the soil samples (mean: 1.6%). Although the reducible fraction was also present in all samples (mean: 5.3% in soil and 3.3% in tailings), the most predominant fractions were the oxidisable (mean: 12% in soil and 21% in tailings) and residual (mean: 81% in soil and 75% in tailings) forms. This indicated that more than 90% of the As found in Berg Aukas soils and tailings occurred in strongly bound forms in the sample matrices.

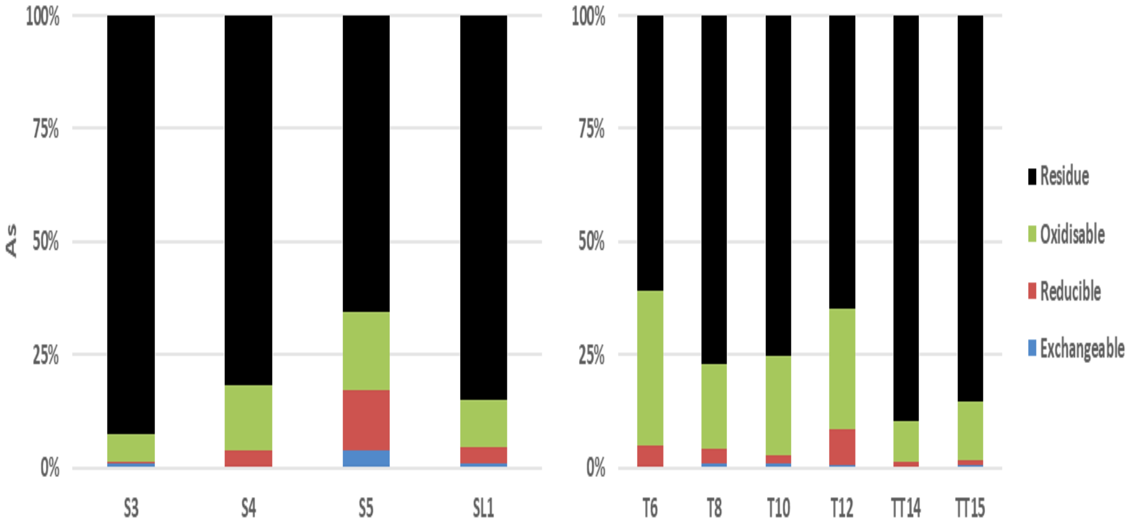

Figure 4.10: Speciation of As in Berg Aukas soils and tailings

4.6.2 Cobalt (Co)

The distribution of Co showed that, on average, about 31% (range: 0 to 61%) of the Co from Berg Aukas was exchangeable and the corresponding amount was 20% (range: 9 to 52%) in Tsumeb soils (Figure 4.11). Here again, the residual fraction was the most predominant with averages of 53% (range: 3.4 to 99.6%) and 55% (range: 11 to 82%) for

Berg Aukas and Tsumeb, respectively. In addition, the majority of Tsumeb soils exhibited a considerable occurrence of the reducible fraction with a mean of 25% (range: 0 to 44%).

Hg in Berg Aukas soils and Co in sample S3 from the wetland occurred essentially in the residual fraction (99.6%) with a tiny portion (0.4%) of the exchangeable fraction.

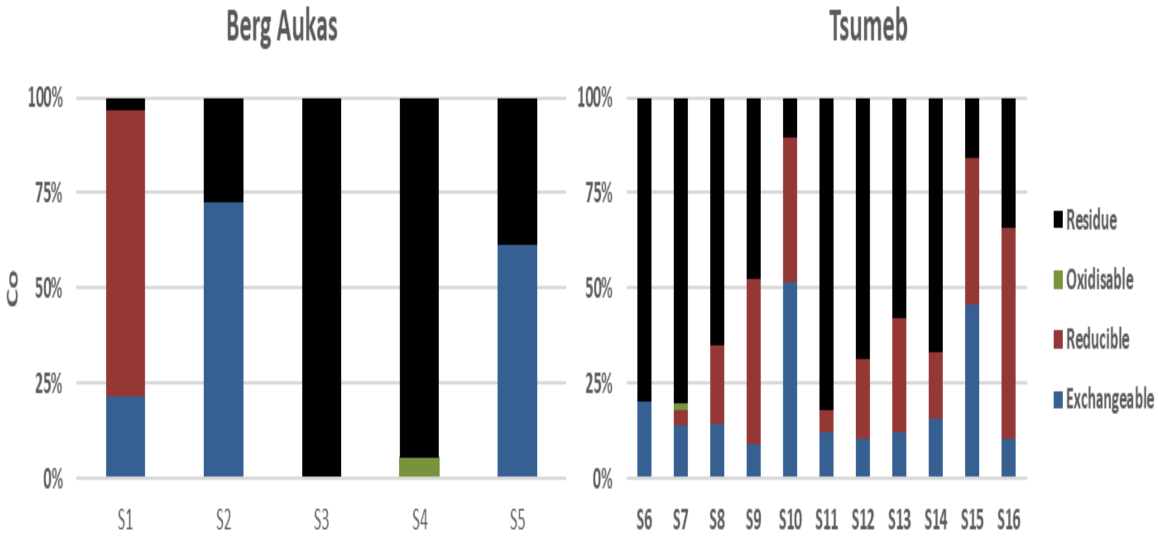

Figure 4.11: Speciation of Co in Berg Aukas and Tsumeb soils

The two tailing collection sites were studied and compared for the distribution of Co. The results show that both tailing sites had varying amounts of the different fractions of Co (Figure 4.12). Approximately, 22% of Co in tailings was found in the exchangeable fraction whereas the Co in the reducible fraction almost counted for 40% of the total Co. The reducible fraction of Co was present in all the samples collected from both sites at an average of approximately 38%.

Although Co in the oxidisable fraction was quite low (about 1.5%) in the study tailings, it still reached some considerable values in a few samples such as T6 and T12 which counted about 9 and 14%, respectively.

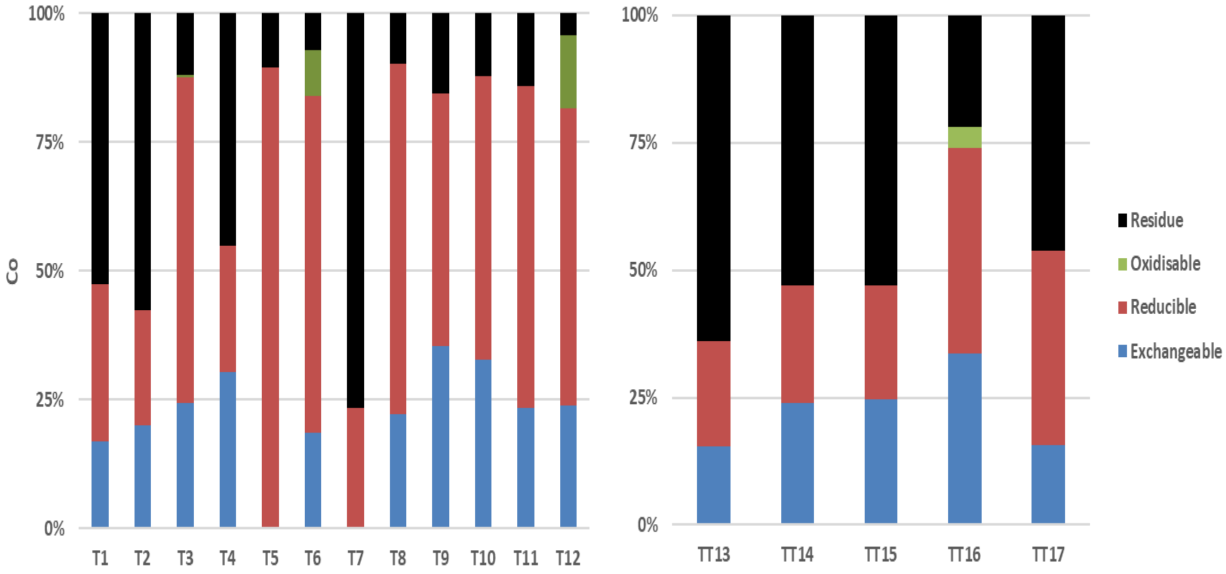

Figure 4.12: Speciation of Co in Berg Aukas tailings

4.6.3 Cadmium (Cd)

The fractionation of Cd in soils and tailings revealed the occurrence of relatively elevated exchangeable forms, with averages of about 22 and 59% in soils from Berg Aukas and Tsumeb, respectively (Figure 4.13).

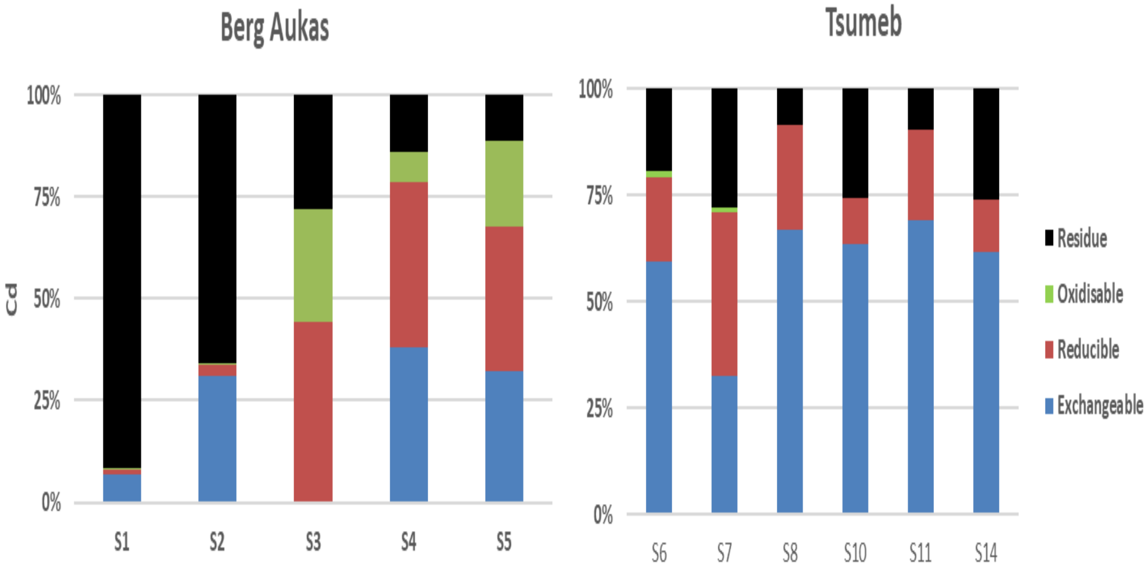

Figure 4.13: Speciation of Cd in Berg Aukas and Tsumeb soils

While the Cd distribution in Tsumeb soils appeared to have a similar trend with also the occurrence of the reducible and residual fractions at an average of 21% and 20%, respectively, there was a slight presence of the oxidisable form in S6 and S7 at 2% and 1%, respectively. Berg Aukas soils showed more variability in its Cd distribution. For instance, the residual fraction of Berg Aukas soils varied from 11 to 92% from S1 to S5 whereas the exchangeable fraction showed a change between 0.4% (S3) to 38% (S4). Moreover, while S3, S4 and S5 showed relatively similar amounts of the reducible (44, 41 and 36%, respectively) and oxidisable (28, 8, 21, respectively) forms of Cd, S1 and S2 showed very little occurrence of these fractions (mean: 2 and 0.5% of reducible and oxidisable fractions, respectively).

Tailings materials also exhibited a relatively uniform trend with the predominance of the reducible fraction (45 and 43% on average at T and TT, respectively), followed by the residual fraction (mean: 15% for T and 34% for TT), the exchangeable fraction (mean: 28% for T and 12% for TT) and finally, the oxidisable fraction (mean: 12% at both sites).

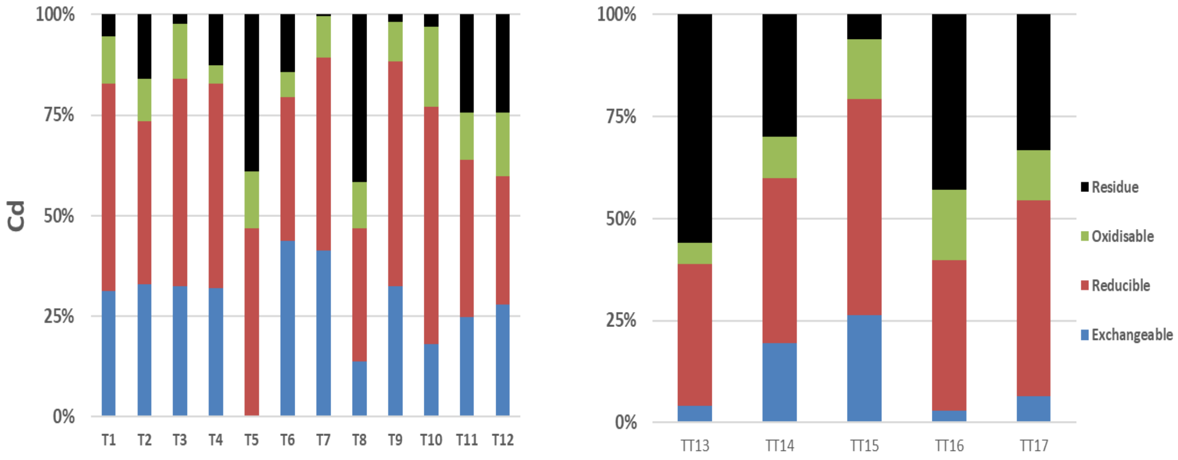

Figure 4.14: Speciation of Cd in Berg Aukas tailings

4.6.4 Copper (Cu)

The distribution of Cu in soils from Berg Aukas and Tsumeb (Figure 4.15) illustrates that exchangeable Cu is present at low amounts in soils from both study sites (average of about 4%), with the highest amount of 9.4% measured in a sample collected at Tsumeb (S6; 1213 mg/kg). The most abundant fractions were the residual (mean: 51% in Berg Aukas and 66% in Tsumeb) and the reducible ones (mean: 33% Berg Aukas and 25% Tsumeb). Furthermore, as it was observed for many other metals, S3 from the Berg Aukas wetland did not show any occurrence for the exchangeable and reducible fractions and had about 80% of its Cu in the residual form.

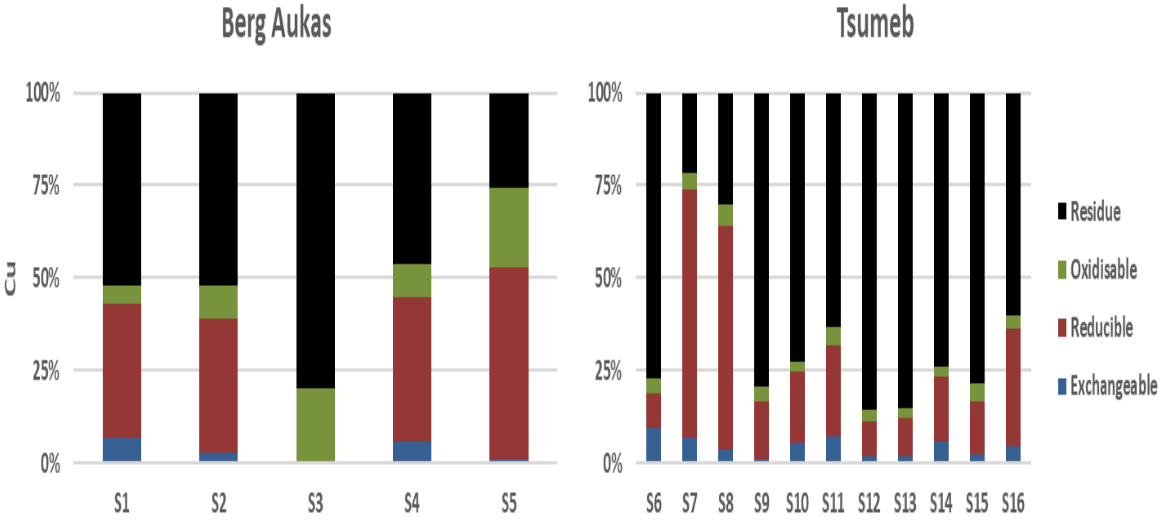

Figure 4.15: Speciation of Cu in Berg Aukas and Tsumeb soils

When the distribution of Cu was studied and compared between the two tailing sites, the results showed (Figure 4.16) that the majority of the exchangeable Cu (10% on average) was in the T tailings dump site. Reducible Cu was present in varying amounts in all tailing samples (mean: 42% at T and 26% at TT), with the highest amount (67%) found in sample T5. In addition, oxidisable Cu was measured at an average of 10% at both sites whereas residual Cu, the most predominant fraction was at an average of 38% and 61% for sites T and TT, respectively. The highest fraction (73%) was recorded in sample TT13.

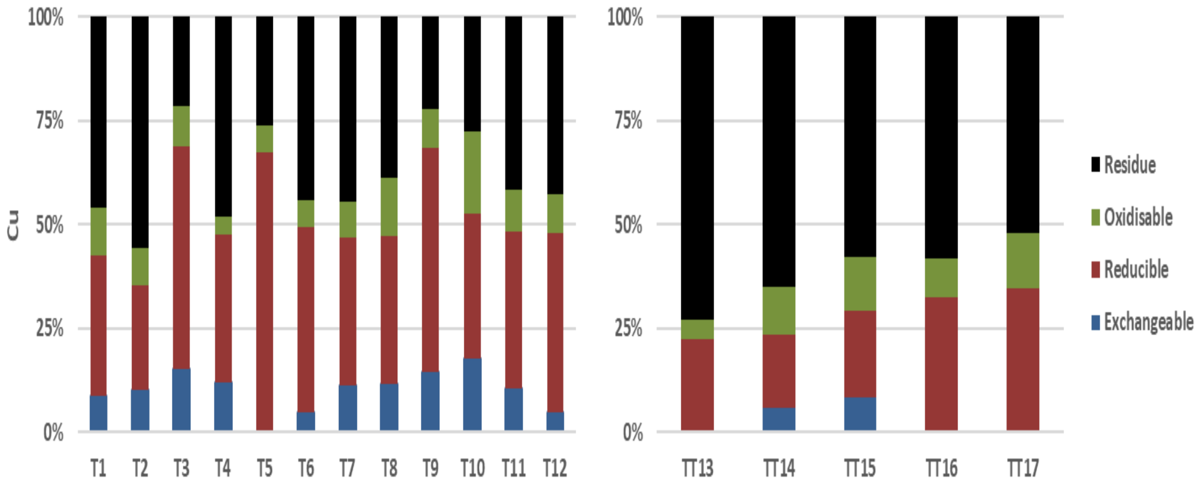

Figure 4.16: Speciation of Cu in Berg Aukas tailings

4.6.5 Lead (Pb)

The fractionation of Pb in soils from Berg Aukas and Tsumeb are shown in Figure 4.17. All defined fractions of the BCR SEP were observed for Pb in all soil samples studied. Berg Aukas soils had exchangeable Pb ranging from 4 to 18% (mean: 9%) whereas the same fraction in soils from Tsumeb ranged from 1 to 36 % (mean: 9.6%). Reducible Pb was observed in high levels in the soil samples (mean: 58% at both sites), with the highest amount (73%) found at Tsumeb (S9). Oxidisable Pb was, however, not present in high amounts. It ranged from 2 to 17% in Berg Aukas (mean: 6%) and from 2 to 27% in Tsumeb (mean: 13%).

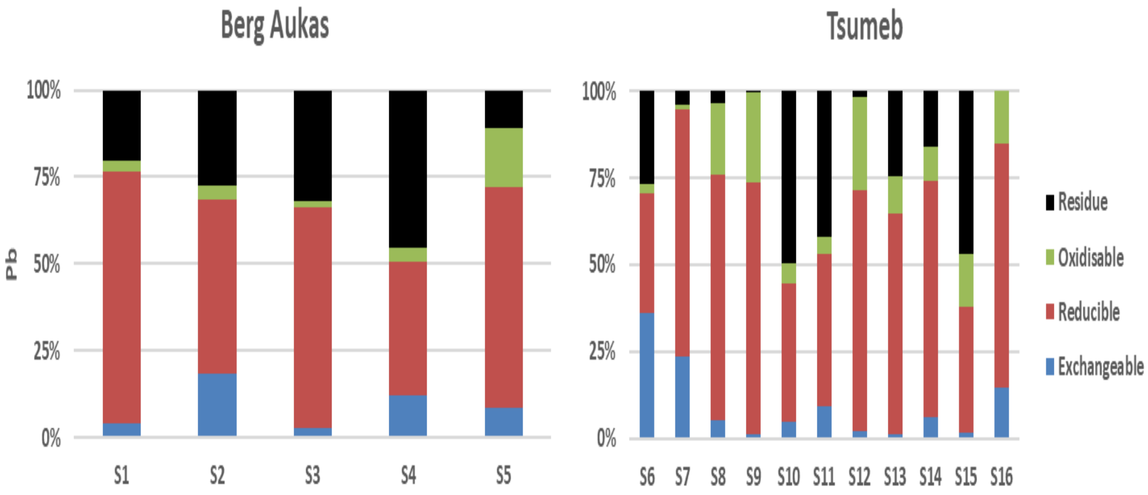

Figure 4.17: Speciation of Pb in Berg Aukas and Tsumeb soils

On another hand, all tailings samples with the exception of T5, T7, TT16 and TT17, had detectable amount of exchangeable Pb between 10 and 33% with an average of 15% (Figure 4.18). The highest amount of exchangeable Pb was found in sample T3. The reducible fraction also was present in all tailings and ranged between 15 and 67% (mean: 36%). Although oxidisable Pb was present in all samples, it did not occur in high amounts i.e. from 3 to 10% with an average of 6%. The residual fraction of Pb had the highest average (45%) of all fractions with at least six tailing samples containing more than 50% of this non-soluble fraction of Pb.

Since Pb in Berg Aukas tailings occurred at concentrations beyond the percentage level (i.e. > 10,000 mg/kg), the exchangeable (bioavailable) fraction of Pb obtained in the tailings reached values as high as 4926 mg/kg (T6).

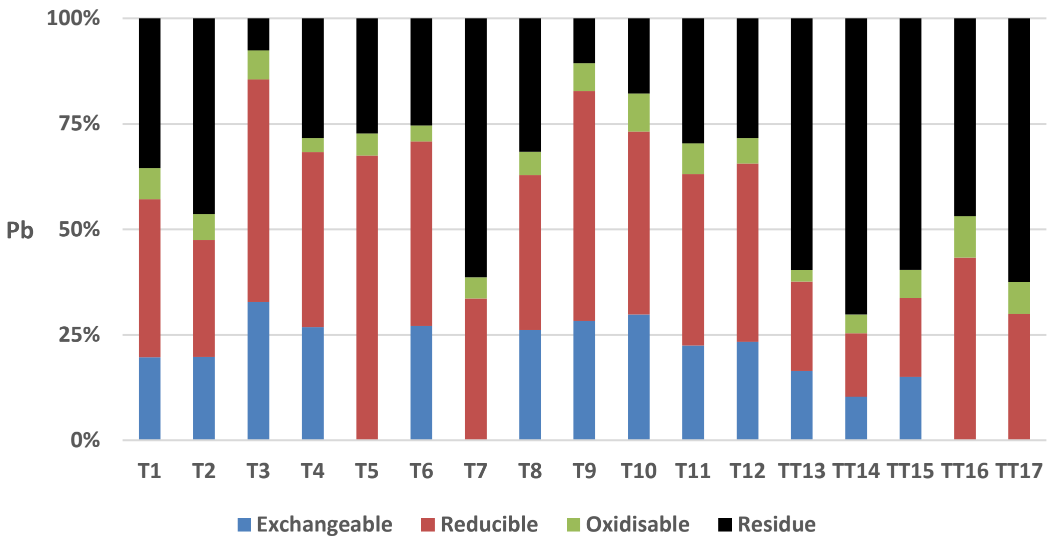

Figure 4.18: Speciation of Pb in Berg Aukas tailings

4.6.6 Manganese (Mn)

All four fractions of the BCR SEP were observed for Mn in soils from both Berg Aukas and Tsumeb. The amounts varied between the different fractions, with exchangeable being present in high amounts and oxidisable present in low fractions (Figure 4.19). Exchangeable Mn ranged from 11 to 63% in soils from Berg Aukas (mean: 43%). This fraction of Mn was measured at amounts ranging from 15 to 37% (mean: 29%) of the total Mn (MnT) in soils from Tsumeb. Furthermore, reducible Mn ranged from 15 to 51% (mean: 33%) of MnT, with the highest amount found in a sample from Tsumeb (S8). Oxidisable Mn was measured to be less than 12% in all samples studied averaging to approximately 4% of MnT.

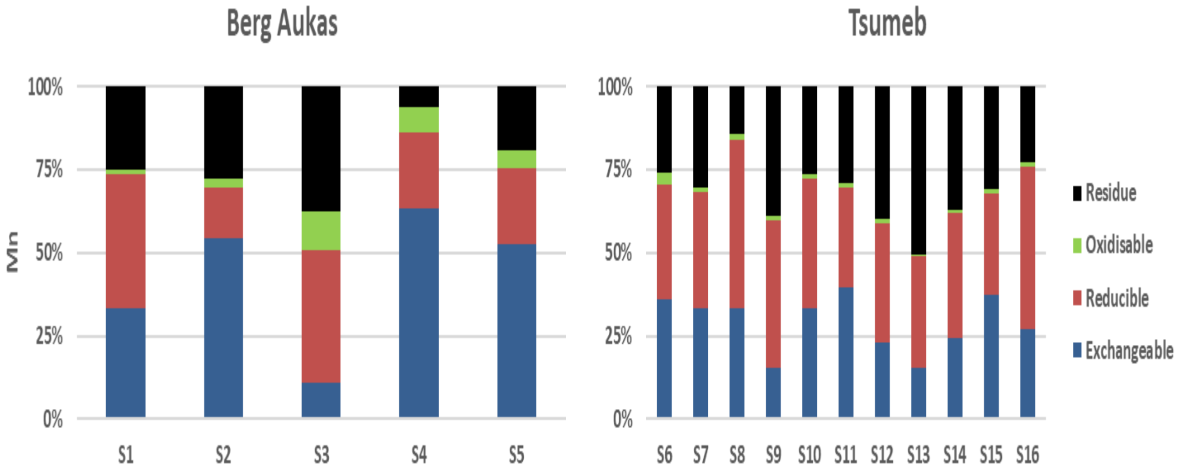

Figure 4.19: Speciation of Mn in soils from Berg Aukas and Tsumeb

The Mn fractionation in tailings from Berg Aukas is illustrated in Figure 4.20. These samples revealed the predominance of the reducible fraction (mean: 41%) with the highest measuring about 52% (from the first tailing site) of the total Mn present with the highest record (52%) obtained in T7. The exchangeable Mn (mean: 16%) had its highest fraction (33%) in TT17. Moreover, oxidisable Mn in tailings ranged between 6% and 23% (mean: 14%) while the residual Mn averaged 29% of MnT and peaked at 45% in T11.

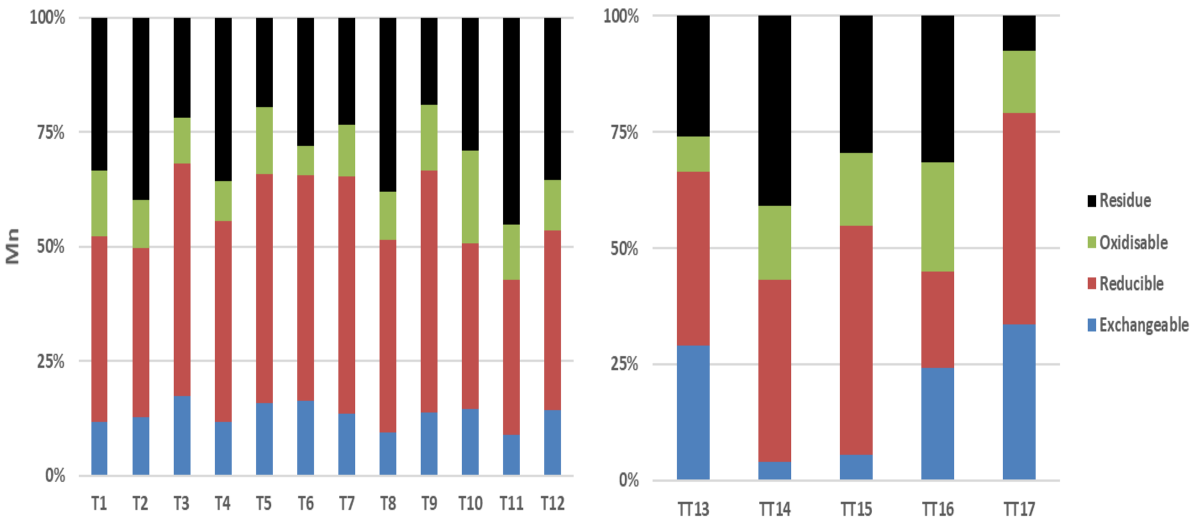

Figure 4.20: Speciation of Mn in tailings from Berg Aukas

4.6.7 Nickel (Ni)

Ni, which occurred at very low concentrations, exhibited an average of 12 and 24% of its total value as exchangeable in soils from Berg Aukas and Tsumeb, respectively (Figure 4.21). The highest fraction of Ni was in the reducible form (mean: 50% in Berg Aukas and 32% in Tsumeb) whereas the oxidisable Ni averaged at 10% (Berg Aukas) and 23% (Tsumeb) and the residual at 28 and 21% for Berg Aukas and Tsumeb, respectively.

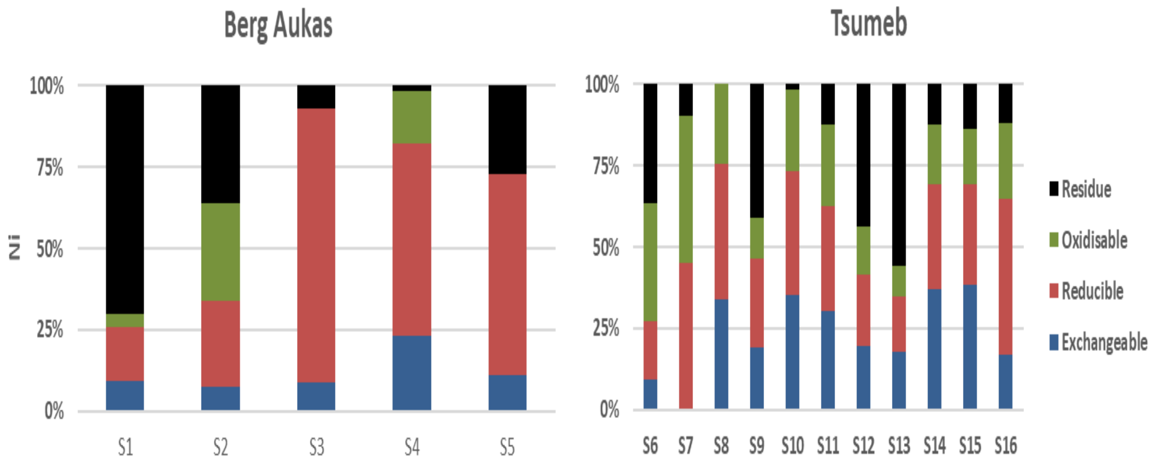

Figure 4.21: Speciation of Ni in soils Berg Aukas and Tsumeb

Ni was not detected at any of the study tailings implying a natural occurrence of this metal in soils at both sites. This could explain the low values measured in soils.

4.6.8 Zinc (Zn)

Zn occurred at extremely high concentration in Berg Aukas (soils and tailings) as compared to Tsumeb. As an illustration, the highest concentration of Zn in Berg Aukas soils in the exchangeable, reducible and oxidisable fractions were 3406 mg/kg (S4), 5883 mg/kg (S4) and 3396 mg/kg (S3), respectively in soil and 3426 mg/kg (T6), 7405 mg/kg (T6), and 2839 mg/kg (TT17), respectively in tailings. It was observed that all soil samples in this study had all four fractions present. Two samples from Berg Aukas (S1 and S2) had more than 50% of the exchangeable fraction which averaged at 28% in Berg Aukas and 18% in Tsumeb (Figure 4.22). The lowest amount of exchangeable Zn in Berg Aukas (2%) was in S3 from the wetland. Soil samples from Berg Aukas had less reducible Zn (mean: 17%) in comparison to soil samples from Tsumeb (mean: 30%). The highest amount (53%) of reducible Zn was found in S7 from Tsumeb. Oxidisable Zn ranged between 4 and 14% (mean: 8%) in Berg Aukas soils, and between 8 and 25% (mean: 16%) in soils from Tsumeb. The residual fraction of Zn had the highest proportions in soil from both sites, averaging at 47% in Berg Aukas and 36% in Tsumeb.

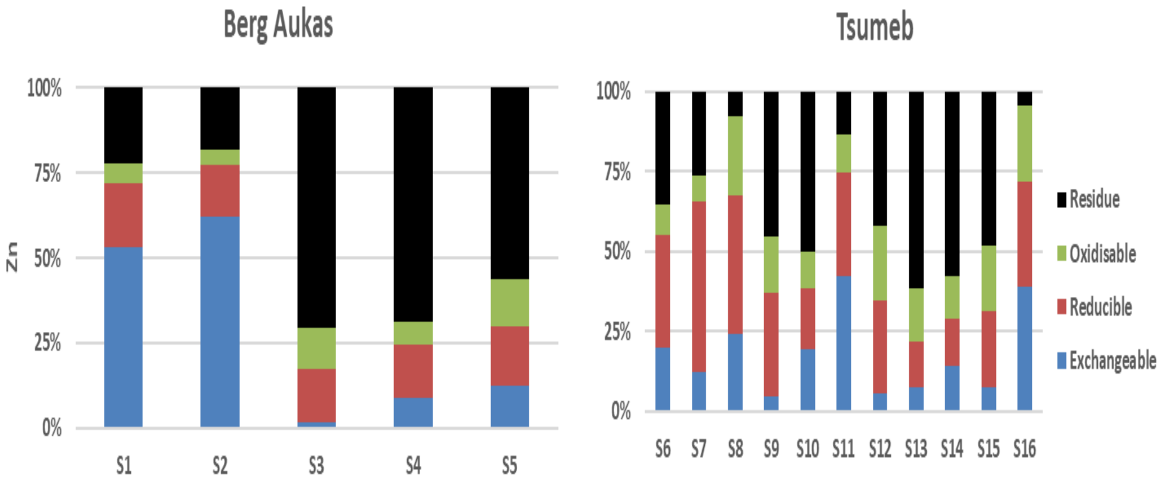

Figure 4.22: Speciation of Zn in Berg Aukas and Tsumeb soils

As shown in Figure 4.23, it was revealed that all fractions were present in almost all the analysed tailings, except for sample T5 that had no detectable amount of exchangeable Zn. The exchangeable Zn fraction ranged between 6.5 and 13% (mean: 9%). Reducible and oxidisable Zn were present in low proportions (mean: 13% of reducible and 8% of oxidisable). Finally, residual Zn was observed in all samples in very high amounts averaging 70% of the total Zn.

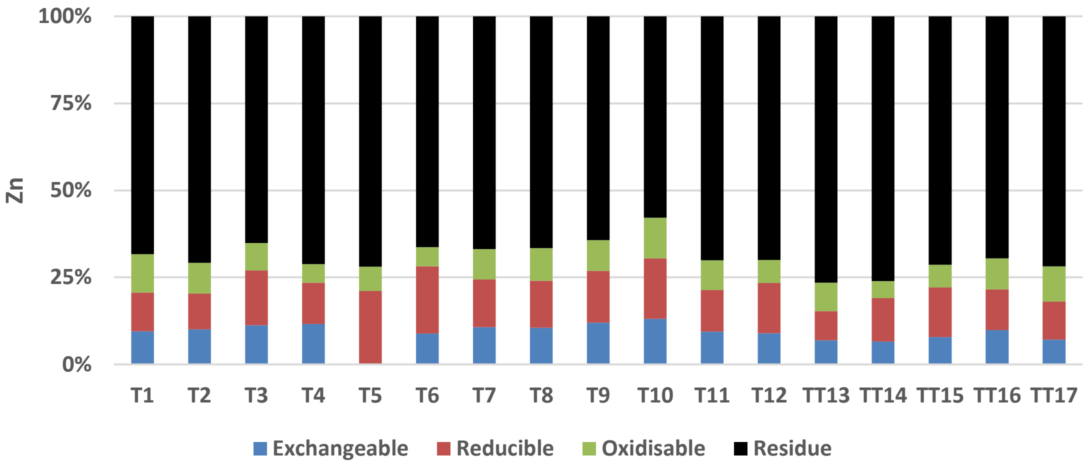

Figure 4.23: Speciation of Zn in Berg Aukas tailings

Overall, the trends observed in the mobile and bioavailable fractions of Berg Aukas and Tsumeb soils were Mn > Cd > Zn > Pb > Cu > As and Cd > Mn > Zn > Pb > Cu > As, respectively. Ni did not appear in these sequences due to its extremely low occurrence in the study soils as mentioned earlier.

4.7 Occurrence of sulphur and anions in soils and tailings materials

Figure 4.24 shows examples of standard chromatogram and calibration lines obtained during IC analysis.

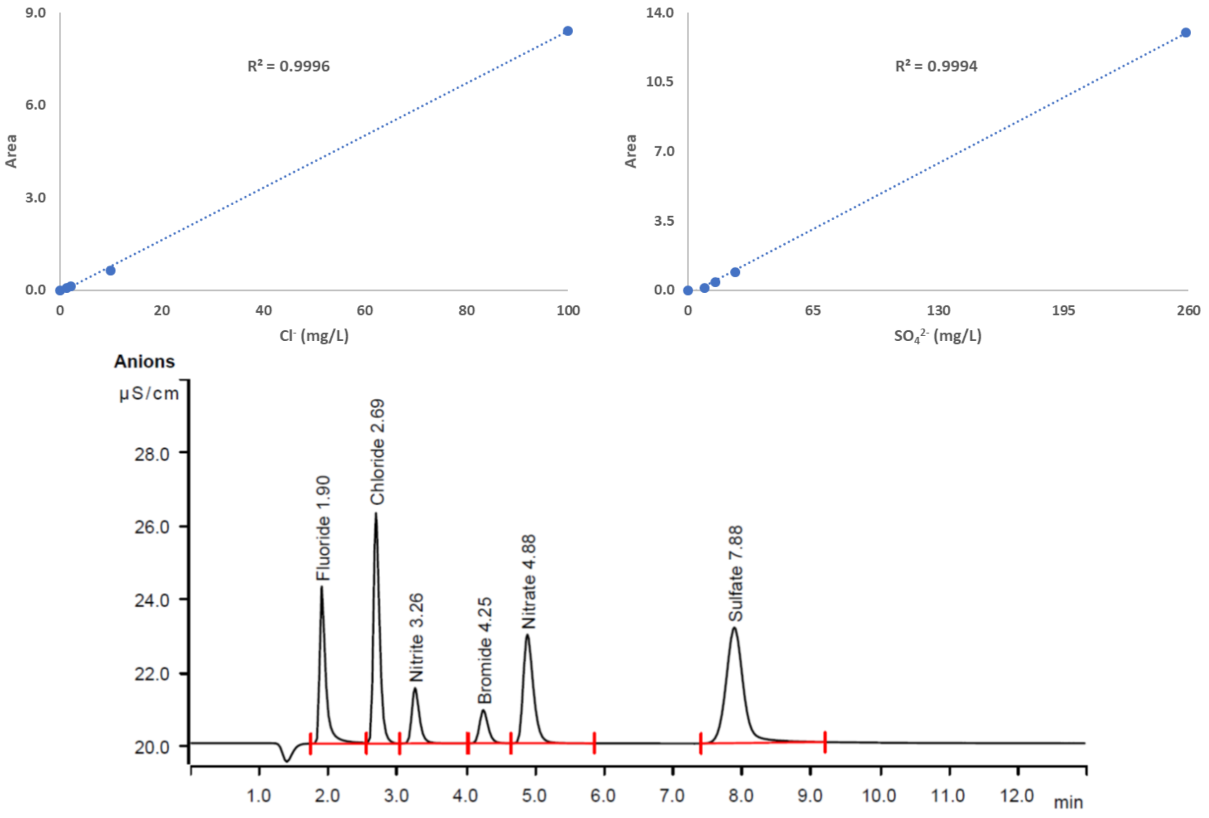

Figure 4.24: IC chromatogram of a multi-anion standard and calibration lines for chloride and sulphate standards

Results of ICP-OES determination of total sulphur and IC analysis of anions in selected soils (Berg Aukas/Tsumeb) and tailings (Berg Aukas) are shown in Figure 4.25 and Table 4.11, respectively.

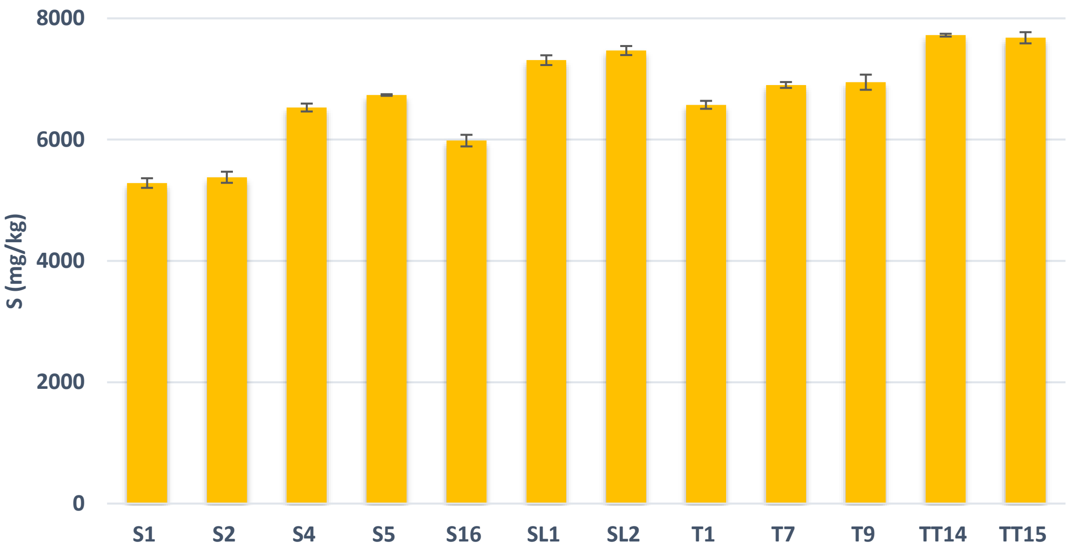

Figure 4.25: Total sulphur in soils, slags and tailings

The concentrations of sulphur in soil and tailings samples were relatively uniform and averaged at 6385 mg/kg in soils (range: 5285 to 6736 mg/kg) and 7165 mg/kg in tailings (range: 6574 to 7723 mg/kg). Additionally, Berg Aukas slags had similar total sulphur levels as for the tailings with SL1 and SL2 showing sulphur concentrations as high as 7310 and 7469 mg/kg, respectively.

The IC data, on another hand, revealed that sulphate was the most predominant anion in both soils (mean: 1305 mg/kg) and tailings (mean: 1426 mg/kg), followed by chloride (mean: 769 mg/kg in soil and 760 mg/kg in tailings), nitrate (mean: 139 mg/kg in soil and 61 mg/kg in tailings), fluoride (mean: 6.5 mg/kg in soil and 8.3 mg/kg in tailings) and nitrite (Table 4.11).

Table 4.11: Anions in soil and tailings

ID	concentration (mg/kg)				
	F^-	**Cl^-**	**NO_2^-**	**NO_3^-**	**SO_4^{2-}**
S1	7.7	791	nd	217	1328
S2	6.6	766	6.9	206	1302
S4	7.3	751	nd	117	1308
S5	5.5	771	nd	171	1306
S16	6.7	781	3.0	143	1312
SL1	5.4	765	nd	62	1299
SL2	6.4	756	nd	58	1281
T1	12	757	nd	59	1286
T7	7.4	758	nd	56	1275
T9	7.3	742	nd	66	1253
TT14	7.5	779	nd	58	2023
TT15	6.9	762	nd	66	1293

nd = not detected

Nitrite was only detected in two soil samples, namely S2 from Berg Aukas (6.9 mg/kg) and S16 from Tsumeb (3.0 mg/kg).

From the above results, it could be deduced that sulphate counted for an average of about 21% of the total sulphur in soil (i.e. 1305 mg/kg of 6385 mg/kg) and 20% of the total sulphur in tailings (i.e. 1426 mg/kg of 7165 mg/kg) as shown in Figure 4.26. Thus, the average sulphate in soils and tailings was about 20% of the total sulphur, the remaining 80% is understood to comprise other species of sulphur that are here labelled as “sulphide” forms, meaning all organic and inorganic sulphur forms other than SO_4^{2-} (e.g. S^{2-}, HS^-, RSH, etc.).

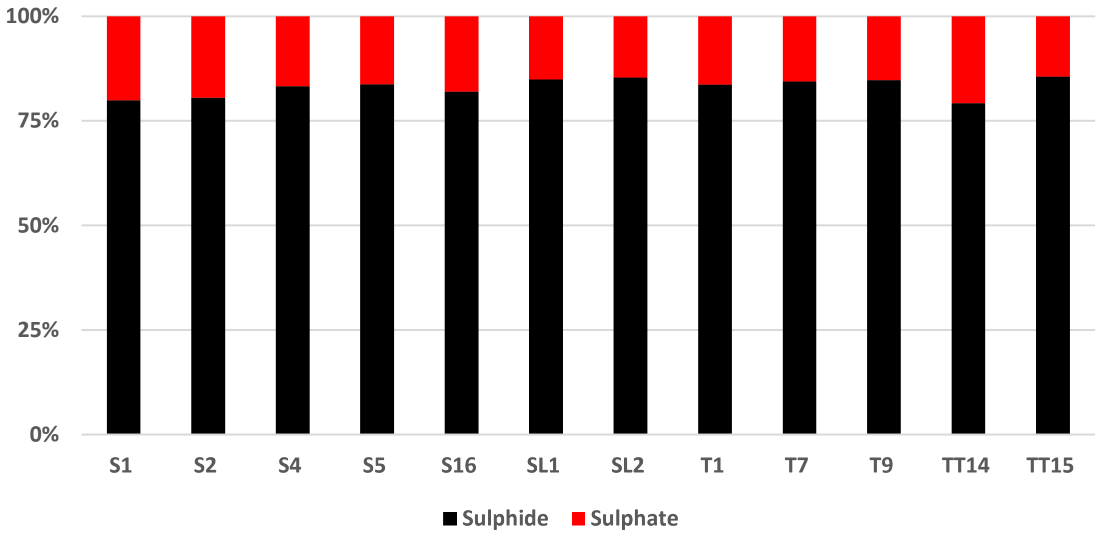

Figure 4.26: Sulphate versus sulphide in soils and tailings from Berg Aukas and Tsumeb

Chapter 5

Discussion

5.1 Occurrence of total mercury

HgT was found at high levels in Berg Aukas tailings with a mean concentration of 1.40 mg/kg which was lower than the one of 2.23 mg/kg reported by Mapani *et al* [33] for the same site. The observed difference can be attributed mainly to the number of samples analysed, 17 in this study and 6 in the study conducted by Mapani *et al* [33], and to a certain extent, to the season when the different sampling campaigns were carried out. Higher Hg values are expected to be observed during dry season as leaching processes would normally reduce metals load at the surface of tailings during rainy seasons. Furthermore, a study done in South Africa on tailings reported HgT ranging between 0.89 to 6.75 mg/kg [47]. These concentrations, although higher, are still in line with the range of 0.82 to 2.24 mg/kg measured for Berg Aukas tailings. However, the range reported here does not include sample TT17 (HgT: 0.04 mg/kg) which was statistically excluded as an outlier.

On another hand, although both Berg Aukas and Tsumeb soils showed some cases of extremely high Hg contents, concentrations in Berg Aukas (surface) soils were more variable than in Tsumeb (Figure 5.1).

This variability could be an indication of either different point sources of pollution or Hg mobility causing its dispersion in the study area. The expected Hg mobility could be caused by wind dispersal from the tailings or the Hg was wind-blown in the soils during the roasting of ores when the mine was still operative.

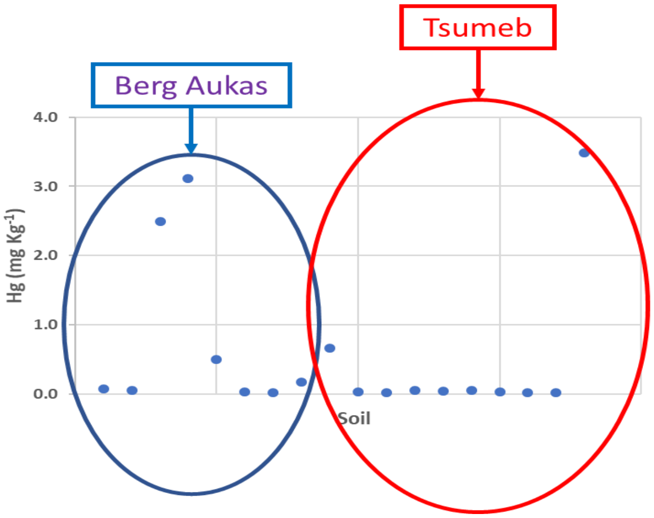

Figure 5.1: Distribution of HgT in surface soils

According to the criteria proposed by the US Environmental Protection Agency (USEPA) for evaluating Hg levels in bulk sediments [71], the threshold effect level (TEL) for Hg, which is the concentration above which there is evidence of potential for observable effects in biota (not necessarily including bioaccumulation and biomagnification) is estimated at 0.174 mg/kg. Based on these criteria, it was found that approximately 40% of the analysed soils from both study areas (i.e. 6 of 15 samples) had HgT beyond TEL; two samples (S5 and S7), i.e. about 13% of all the samples, had HgT falling within the Probable Effect Level (PEL) of 0.486 mg/kg representing the concentration above which adverse effects are expected to occur frequently, and three samples (S3, S4 and S16) i.e. 20% of samples falling into the Toxic Effect Threshold (TET) concentration of 1 mg/kg where sediments are considered to be heavily polluted.

It was observed that the background Hg values in uncontaminated areas were relatively low, in the range of 0.015 to 0.055 mg/kg which agrees with the background value of 0.060 mg/kg reported by Hornberger *et al* [72], which is lower than the generally accepted natural background for soils of 0.1 mg/kg [73].

Moreover, the study conducted by Mapani *et al* [33] reported Hg concentrations in soils from Berg Aukas reaching up to a maximum value of 6.9 mg/kg, a value higher than any value reported in this study for Berg Aukas soils. Water runoff and other dispersion mechanisms such as wind which are believed to be responsible of the Hg mobility in the area could also explain the changes in Hg loads in surface soils. However, Mapani *et al*. [33] mainly attributed the elevated Hg levels observed in their study in upper soils to in situ roasting of fossil fuel as Hg is known to represent highly volatile products of ore roasting and smelting. Sample S4, collected from the area of old mining operations in Berg Aukas exhibited the highest HgT suggesting that past roasting operations could be the principal cause of Hg deposition in the proximity of the old smelter. Additionally, elevated Hg and other metals were also observed in wetland soil (S3). This is believed to be the consequence of the drainage of contaminated particles from pollution sources.

In Tsumeb, two samples (S6 and S7) showed high concentrations of HgT. The high concentrations could be attributed to the fact that these samples were collected alongside the road near the old Tsumeb open pit mine. Additionally, the sample collected from the area of the Dros restaurant had a total Hg concentration of 3.49 mg/kg, a value that is dangerously high. This might indicate the presence of an ore body in the vicinity where the sample was collected. Cinnabar, a sulphide of Hg, is known to occur naturally in the ores of the Tsumeb deposit. All the above-mentioned samples were collected from areas that are close to human settlement with constant movement of people, thus posing a high exposure risk.

Finally, Berg Aukas slag samples (i.e. SL1 and SL2) had a mean HgT of 0.027 mg/kg, similar to the one of 0.028 mg/kg reported by Mapani *et al* [33].

HgT measured in both surface and borehole waters in Berg Aukas exceeded international criteria for Hg in water, such as the World Health Organization Guideline Value (WHO GV) for drinkable water of 1 µg/L [74] and the USEPA Maximum Contaminant Level (MCL) of Hg in drinking water of 2 µg/L [75]. Berg Aukas waters had Hg values similar to those encountered in streams draining areas with concentrated geologic sources of Hg or with large accumulation of Hg-contaminating tailings from Hg or Au mining [76]. The highest HgT was measured in borehole samples (W1 to W3: mean Hg: 6 µg/L). These findings are in line with the observation made by Kortatsi [77] during his study of several boreholes near the Ankora River Basin (Ghana) that is affected by gold mining. The study correlated HgT in the wells to the wet season recharge regimes of polluted surface water and concluded that the occurrence of Hg in the groundwater bodies was largely due to contamination from surface sources. Similar observations were made by Lusilao *et al* [78] in the study of borehole waters from the Vaal River gold mine in South Africa. An alternate explanation would be that the borehole is sited in a fractured zone of the primary ore body at Berg Aukas, which contains sulphides of Zn, Pb, V and Hg. This was observed at Farm Dornhugel, some 60 km west of Berg Aukas, whose borehole water contained sulphides of Zn, Pb and minor As. This borehole was sited directly through the ore zone of the Berg Aukas formation [79]. Boreholes (groundwater) are a source of drinking water in the Berg Aukas area and also water for agricultural and other domestic purposes.

Although Hg in Berg Aukas waters showed concentrations that are worrisome, other physico-chemical parameters of these waters (e.g. pH and EC) fell within the A category (i.e. excellent quality) of the Namibian Guideline Values for drinking water [79]. On the Eh-pH diagram of Hg species (Figure 5.2), elemental Hg (Hg^0) is likely to be the predominant species in Berg Aukas waters.

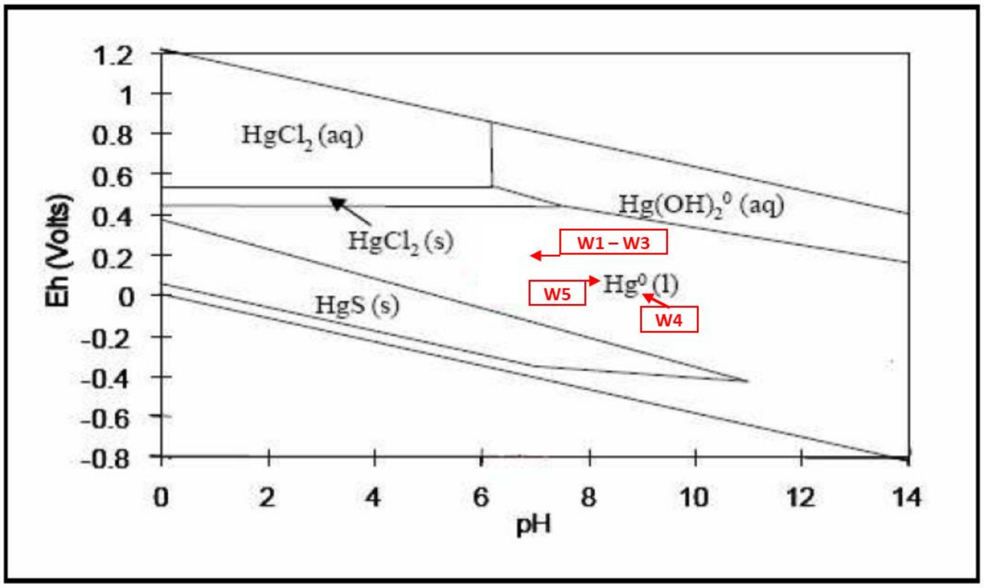

Figure 5.2: Eh-pH diagram of Berg Aukas waters (The red arrows show the exact points of the Eh-pH values for the corresponding samples)

Since the conditions, at the time of the sampling (late rainy season or fall) were quite reducing, it is believed that under oxidizing conditions (summer) Hg^0 may be converted to higher oxidation state (e.g. Hg^{2+}) where complex transformation may affect its mobility and ultimate fate in the environment [80,81].

Plants absorb Hg from air, water and soil through their roots and leaves. The source of Hg, its chemical form as well as the physiology of the plant species are all factors that may affect the amount of Hg found in plants [39]. All plants analysed in this study had

HgT concentrations of less than 1 mg/kg. The mean Hg value obtained in this study was 0.058 mg/kg, which is slightly higher than that obtained in a study by Soltani *et al* [82] which reported a mean Hg concentration of 0.04 mg/kg in plants.

The lowest concentration of Hg in this study (i.e. 0.004 mg/kg) was recorded in *Sclerocarya birrea* from Tsumeb. Eucalyptus plant collected at Tsumeb had a mean Hg concentration of 0.007 mg/kg, which is much lower than the mean concentration (0.081 mg/kg) of Eucalyptus collected at the Rietfontein landfill in South Africa as reported by Lusilao [39].

A plant (P22) sample collected from a pond wetland (where S3 was collected) had the highest recorded amount of HgT of 0.703 mg/kg. Studies have shown that the uptake of Hg tends to be plant specific, with plants like lichens, woody plants, crop plants and wetland plants known to take up a lot of Hg [19].

Heavy metal transfer from soil to plant is dependent on the plant species and metal type. Once heavy metals have accumulated in the soil, there are several factors that may influence the transfer of metals to plants. These factors include total concentration of metals, specific geochemical form, and chemical speciation of metals, pH, EC, redox states and soil organic matter (SOM**)** [82]. Properties of soil such as texture, pH-value, and ion exchange capacity have a strong influence on the availability of metals to plants. Even though Hg is strongly fixed in soils, if conditions allow, it can be absorbed by plants.

To quantify the amount of heavy metal that a plant can take up from the soil its growing in, the transfer coefficient (TC), which is a function of both soils and plant properties, must be determined.

The TC is given by the expression below [83]:

$$TC = C_{plant} / C_{soil} \qquad (5.1)$$

where C_{plant} is the concentration of the metal in the plant and C_{soil} is the concentration of the metal in the soil.

Table 5.1 summarises the TC of four plants that were collected at the same area as S3 in Berg Aukas. Only one of the four plant species was identified. The TC of Hg in unimpacted soils ranges between 0.01 and 0.1 [84]. Two plants, P20 and P22, exceeded this range, with a TC of 0.118 and 0.283, respectively. This means that there is more Hg available for uptake by the plant. These values are however low, compared to TC values obtained by Lusilao [39] in Rietfontein (South Africa) that were 0.743 and 0.882 for two Eucalyptus plant species. The same study reported TC values of 0.053 and 0.102 in two algae plants from Randfontein, with the former having a value equivalent to the TC in *Combretum imberbe* in the present study. A study conducted in Ethiopia by Duressa and Leta [85] reported TC values ranging from 0.112 to 0.266 for Hg in vegetables, which is a smaller range than the one from the present study. Duressa and Leta [85] also found that if the pH of the soil is higher than 6.5, adsorption of metals to soil is usually very high and only traces of the element will be available for uptake by the plant. The pH of the soil sample (S3) used for the TC calculation was 8.0, thus explaining the low TC values.

Table 5.1: Transfer coefficients of mercury for selected plants in Berg Aukas

Soil ID	Hg (mg/kg)	Plant ID	Hg (mg/kg)	TC
S3	2.487	P16 (unidentified)	0.103	0.041
		P18 *Combretum imberbe*	0.126	0.051
		P20 (unidentified)	0.293	0.118
		P22 (unidentified	0.703	0.283

TC= Transfer Coefficient

Taking into consideration that some parts of Berg Aukas is used for agricultural purposes, the TC can be used to predict before planting if it is safe to plant vegetables and crops in that area based on the concentrations of the heavy metals in soil. A higher TC value indicates that more of the element is available for accumulation by the plant. However, it must be noted that the TC alone is not sufficient to conclude on the metal bioavailability because some of the Hg in the leaves originates from the atmosphere [39].

5.2 Heavy metal concentrations

5.2.1 Soils and tailings

Soils are the reservoir for many harmful constituents, elemental and biological, including heavy metals [44]. Results for the soil analyses revealed the occurrence of pollution at both sites, and that soils from Tsumeb had generally lower concentrations of total metal in comparison to soil samples from Berg Aukas. The Berg Aukas large scale contamination by heavy metals in soils is likely related to past ore roasting activities and to water and wind dispersal of fine grain particles from the metal-rich unprotected and poorly designed tailings dams in the area.

Since Namibia has no guidelines on soil quality, the Canadian guidelines [86] were used for comparison. This study reveals that the soils at Berg Aukas and Tsumeb are highly polluted according to Canadian soil quality guidelines for land use as shown in Table 5.2

Table 5.2: Canadian soil quality guidelines for protection of environmental and human health (mg/kg) [86]

Element	**Land use**		
	Residential	**Commercial**	**Industrial**
Arsenic	12	12	12
Chromium	10	22	22
Cadmium	64	87	87
Copper	63	91	91
Lead	140	260	600
Nickel	50	50	50
Zinc	200	360	360
Mercury	6.6	24	50

Other soil references, such as the measured background metal values in soil collected from Oshakati, Northern Namibia, (collected during a different study and used as a negative control in this study) were also used for comparison (Table 5.3) and they all highlighted the pollution occurring in both areas.

Table 5.3: Concentrations (±SD) of trace metals from Oshakati, Northern Namibia, unpolluted soils and other published mean sediments/soils values (in mg/kg)

Source	Cr	Mn	Ni	Cd	Cu	Zn	As	Pb
Oshakati (n = 9)	1.3 ± 1.4	10 ± 13	5.0 ± 4.7	ns	7.1 ± 8.4	29 ± 32	0.9 ± 0.8	1.2 ± 1.2
China Type 1(*)	90	ns(***)	40	0.2	35	100	ns	35
China Type III (*)	400	ns	200	1.0	400	500	ns	500
Agricultural (**)	≤350	2000	50	3.0	150	300	20	100

(*): Type I = unpolluted soil & Type III = heavily polluted soil [87]

(**): WHO except for Cr [88] and Ni [89]

(***): not specified

Cd in tailing samples from Berg Aukas had a mean concentration of 320 mg/kg. A study that aimed at assessing potential human risks associated with historic ore processing at Berg Aukas found a mean concentration of 352 mg/kg for Cd in tailings [33], which was slightly higher than the mean concentration found in this study. Moreover, a study conducted at Rosh Pinah by Kribek *et al* [63] found a mean concentration of 37 mg/kg for Cd in the tailings, a value much less than what was reported for Berg Aukas previously[33] and the current study.

Zn, on the other hand, was observed in very high amounts in tailing samples from Berg Aukas with a mean concentration of 1476 mg/kg. When Kribek *et al* [63] studied the soils from tailing dams in Rosh Pinah, they found a mean value of Zn to be 14030 mg/kg. The high mean value in Rosh Pinah is attributed to the fact that Rosh Pinah is an active Zn mine, whereas Berg Aukas has been closed for more than 30 years [60] and large amounts of minerals has now been dispersed and leached out.

The data presented in Tables 5.2 and 5.3 show that the maximum permissible limits were exceeded for most, if not all, toxic metals except Mn. The high levels recorded indicated that the area is highly contaminated and unsuitable for agricultural use and may also cause some adverse health effects. The general trend observed in descending order is Al > Fe > Zn > Pb > Mn > Cu > Cr > As > Cd > Ni > Co.

Tsumeb soils generally indicated, as mentioned above, much lower heavy metal content compared to Berg Aukas soils. Most of its soils had Zn and Pb below threshold values, except for samples S6, S7, S10 and S11, which exceeded the permissible limits. These four soils were collected in areas with constant human movement (S6 and S7 alongside the road near the old mining pit, and S10 and S11 in and around an informal residential area). Exposure to high toxic metal concentrations poses high risk to people living in the area. Exposure to Pb can affect brain and central nervous system, consequently leading to death. Cd exceeded the permissible limits reported above in all samples in which it was detected. Cu and As were also found to exceed the guideline values. The high concentrations (especially in Cu) can be attributed to the fact that Tsumeb is a Cu mining town.

Furthermore, research has shown that concentration of metals cannot provide extensive indications about the state of contamination in soils [90]. For this reason, the enrichment factors (EF) is usually calculated. The EF is defined as a means of quantifying the enrichment of a potentially contaminant-derived element in an environmental sample relative to a user-defined background position [90]. Once EF is calculated, the state of soil quality can be indicated by different values as seen in Table 5.4.

Table 5.4: EF categories [90]

Value	**Soil dust quality**
EF < 2	Deficiency to minimal enrichment
2 < EF < 5	Moderate enrichment
5 < EF < 20	Significant enrichment
20 < EF < 40	Very high enrichment
EF > 40	Extremely high enrichment

The EF in this study was calculated for Hg, Pb, Cd, As and Zn and was expressed as follows:

$$EF = [Metal/RE]_{soil} / [Metal/RE]_{background} \qquad (5.2)$$

where, *RE* is the value of metal, adopted as *Reference Element*.

The mean concentrations of the elements mentioned above were calculated for each site and used in the above expression (5.2). Table 5.4 shows the classification of EF values. Soils from Berg Aukas have EF values > 40 for Hg, Cd, As and Zn. These values indicate that Berg Aukas soils are extremely enriched with these heavy metals (Table 5.4). Onjefu *et al* [91] also reported very high EF values (20 < EF < 40) for Cd in sediments from Walvis Bay. The EF of Pb in Berg Aukas was 0.35, which shows some deficiency to minimal enrichment. However, in Tsumeb soils the EF for Pb was 88. This value indicated that Tsumeb soils are extremely rich in Pb. EF for Cd in Tsumeb soils was by Onjefu [33] reported as 2.9, which indicated that Tsumeb soils are moderately enriched with Cd. Additionally, the EF values obtained for As and Zn showed significant enrichment whereas Hg had an EF value of 22, which indicated very high enrichment. A study conducted in South Africa by Okedeyi *et al* [92] in 2014 reported moderate enrichment of Hg (2.3 - 4.2) in three coal fired plants, values that are lower than those obtained in the present study for both Berg Aukas and Tsumeb.

Table 5.5: Enrichment Factors of selected heavy metals in Berg Aukas and Tsumeb soils

	Berg Aukas					**Tsumeb**				
	Soil		**Background**			**Soil**		**Background**		
Element	Mean	RE	Mean	RE	EF	Mean	RE	Mean	RE	EF
Hg	1.285	12082	0.06	27,954 **	**49**	0.418	8807	0.06	27,954 **	**22**
Pb	2342	12082	1.223	2212	**0.35**	427	8807	1.223	2212	**88**
Cd*	115	12082	0.857	5192	**58**	4.23	8807	0.857	5192	**2.9**
As	438	12082	0.924	2212	**87**	51.3	8807	0.924	2212	**14**
Zn	14447	12082	43.3	2212	**61**	116.9	8807	43.3	2212	**0.67**

*Cd background values [93]

**Hg *RE* value [94]

For this study, Fe was used as a reference material for background concentrations in the earth's crust. The assumption used is that no anthropogenic activities have disturbed its content in the crust. Additionally, it is an acceptable element for normalization when calculating EF values [95]. The correlation coefficients between the total trace metal concentrations in the study soils are shown in Table 5.6.

A relatively strong positive correlation was found between Fe, As and Cr with all other metals with the exception of Cd and Al. This may suggest a mineral association between these metals such as the reported association between Cr, Cu, Ni, Pb and Zn to Fe oxide minerals (e.g. haematite or magnetite) or to Fe and Mn oxyhydroxide minerals (e.g. goethite, ferrihydrite, and manganite).

Table 5.6: Correlation (Pearson correlation coefficients at $P < 0.05$) matrix between metal concentrations in Berg Aukas and Tsumeb soils

	Cr	*Cd*	*Ni*	*Co*	*Al*	*Fe*	*Cu*	*Zn*	*As*	*Pb*	*Hg*
Cr	1										
Cd	-0.003	1									
Ni	0.803	-0.246	1								
Co	0.824	-0.217	0.965	1							
Al	-0.327	-0.578	0.149	0.140	1						
Fe	0.996	-0.017	0.837	0.854	-0.285	1					
Cu	0.616	-0.018	0.416	0.413	-0.357	0.578	1				
Zn	0.752	0.452	0.301	0.382	-0.707	0.737	0.390	1			
As	0.910	0.120	0.547	0.584	-0.528	0.880	0.763	0.832	1		
Pb	0.415	0.488	-0.061	0.047	-0.687	0.402	0.182	0.891	0.590	1	
Hg	0.586	0.645	0.286	0.305	-0.552	0.577	0.391	0.735	0.615	0.587	1

There is a good correlation between Hg and Cd, suggesting that they are associated together in the ores that were mined at Berg Aukas. In Pb-Zn mines, Cd is generally associated with Pb and Hg. It has also been stated that metals with a highly positive correlation are possibly from the same pollution source, and metals with a highly negative correlation (which was not observed in the present study) are possibly from the different pollution source [96]. An extended correlation analysis between metals in Berg Aukas tailings and other parameters such as total sulphur and anion contents (Table 5.7) also revealed strong positive correlations between almost all the analyzed metals (Hg included), and between metals and total sulphur (S_T), sulphate and chloride.

This can be an indication of the predominance of metal sulphide and metal chloride phases in the tailings. These correlations are further discussed in metal fractionation.

Table 5.7: Correlation matrix between metal concentrations, total sulphur and anions in Berg Aukas tailings

	Cr	*Cd*	*Cu*	*Mn*	*As*	*Fe*	*Zn*	*Pb*	*Hg*	S_T	Cl^-	NO_3^-	SO_4^{2-}
Cr	1												
Cd	0.868	1											
Cu	0.971	0.917	1										
Mn	0.780	0.966	0.852	1									
As	0.934	0.730	0.909	0.575	1								
Fe	0.949	0.795	0.905	0.635	0.978	1							
Zn	0.868	0.549	0.833	0.448	0.919	0.838	1						
Pb	0.973	0.868	0.988	0.769	0.961	0.948	0.880	1					
Hg	0.588	0.153	0.452	-0.045	0.763	0.715	0.791	0.569	1				
S_T	0.929	0.643	0.853	0.574	0.872	0.847	0.941	0.869	0.716	1			
Cl^-	0.806	0.706	0.838	0.531	0.938	0.910	0.776	0.899	0.638	0.654	1		
NO_3^-	0.102	0.037	-0.041	0.156	-0.187	-0.089	-0.058	-0.118	-0.093	0.254	-0.487	1	
SO_4^{2-}	0.794	0.839	0.912	0.793	0.793	0.745	0.709	0.899	0.257	0.622	0.845	-0.373	1

The pH values of the tailings and soils were measured and ranged between 7.4 and 8.9 that is typical of carbonate phases (calcite and dolomite) [97]. No particular correlation was observed between the pH (as well as EC and TDS) with the metal's concentrations. Sipos *et al.* (2014) [98] also observed a negative correlation between their study soils and metal concentrations. They also noted a weak negative correlation between the carbonate and trace metal content of the soil and concluded that carbonate phases are not the characteristic host phases for these elements although carbonate phases are common components of non-Luvisol samples. Additionally, carbonate rocks have a tendency to buffer acidic solutions emanating from weathering of sulphides, significantly increasing the pH.

5.2.2 Plants

Plants are known to take up and accumulate trace metals from contaminated soil. The results of the analysis of heavy metals in plants for the present study revealed that the mean concentration of Mn in Berg Aukas plants was 136.2 mg/kg while Tsumeb had a mean concentration of 50.6 mg/kg. A study conducted by Ho *et al* [99] in 2013 found the mean concentration of Mn to be 69.4 mg/kg. Background concentration of Mn in grass is in the range of 17 to 334 mg/kg [100]. The values obtained in this study for both Berg Aukas and Tsumeb fall within this range (17- 334 mg/kg).

On another hand, Cd was not detected in plant samples in Tsumeb but a mean concentration of 4.53 mg/kg was reported in plants from Berg Aukas. This mean was slightly higher than that of 0.1 mg/kg reported in Nigeria from a study conducted by Ogundele *et al* [101] in plants from Shao, while plants from Asomu, Okolowo, Idofian, Ganmo, Olooru all had Cd mean below 0.028 mg/kg. The same study reported mean concentration of Cd to be 0.40 and 0.35 mg/kg in plant samples from Elemere and Jebba, respectively. According to WHO [102], the recommended permissible limit of Cd in plants is 0.02 mg/kg. Additionally, all the plant samples analysed in the present study had Cd above the permissible limit, thus indicating contamination.

Results also showed high levels of Zn in plants from Berg Aukas and Tsumeb with the mean concentration of 404.1 and 21.7 mg/kg, respectively. The average Zn concentration in plants at Berg Aukas is almost 400 times higher than the permissible limit allowed by the WHO [102] for plants of 0.6 mg/kg. This high amount can be attributed to the fact that Berg Aukas was a Zn mine. The concentrations of Zn in plants growing on mine tailings in central Mexico were reported to be 51.3 and 102.8 mg/kg in roots and shoots, respectively [103].

The plants collected in Tsumeb exhibited low levels of Pb, with only one sample (P31), identified as *Sclerocarya birrea* (common name Marula tree), showing Pb with an amount of 1.4 mg/kg, a concentration below the WHO permissible concentration of 2 mg/kg. A study conducted in Ethiopia by Duressa *et al* [85] reported mean Pb concentrations of 0.62, 0.30, 0.37, 0.69 and 0.60 mg/kg in garlic, kale, onion, pepper and potato, respectively. These low values of Pb can be attributed to the fact that plants, in general, are less likely to absorb or accumulate Pb due to its low bioavailability, But, if these plants are grown in soils with high levels of Pb, it is possible for some Pb to be taken up. Therefore, poisoning of Pb from plants is usually from Pb-containing dust particles that settles on plant surfaces rather than the uptake of Pb by plants [104].

Ricinus communis is a medicinal plant that grow in soils with high concentrations of heavy metals [105]. This plant species was commonly found vegetating the mine tailings that showed high levels of heavy metals in Berg Aukas. Only one of the three samples of this species had detectable Cd (1.3 mg/kg) which is low compared to the Cd concentration of 13 mg/kg found in a study conducted by González-Terreros *et al* [105] in Mexico. On the other hand, Mn, Zn and Pb mean concentrations were reported to be 80, 187 and 7.5 mg/kg, respectively. In a study conducted on the same plant species growing on contaminated sites in industrial areas of the Islamabad and Rawalpindi by Nazir *et al* in 2011 [106],the mean concentrations of Zn and Pb were 48 and 20 mg/kg, respectively.

Additionally, another plant species that is commonly found in Berg Aukas tailings and wetland is *Combretum imberbe*, also a medicinal plant. The mean levels of Pb and Zn reported in this study were high (36 mg/kg for Pb and 227 mg/kg for Zn) compared to mean levels obtained in the same plant species by Dzomba *et al* [107] in central Zimbabwe, where mean concentrations of Pb and Zn were reported to be of 0.56 and 0.30 mg/kg, respectively.

The results showed that different parts of a plant absorb and accumulates heavy metals differently. The general trend was that leaves of a plant tended to accumulate higher concentrations of heavy metals in comparison to the fruits of the same plant. This may be explained by the mechanism adopted by plants to remove heavy metals from the plant via leaf shedding every year [108]. A plant sample (P20) collected in a pond wetland at Berg Aukas measured high concentrations of most heavy metals studied (Table 4.10. These high concentrations can be due to the fact that wetlands are known to have an ability to accumulate heavy metals (thus they are called "sink of pollutants'') [109]. Besides, the corresponding soil sample (S3) showed little or none of the exchangeable fraction for all the metals, meaning all the likely existing F1 could already have been transferred into the supernatant water (since it is water soluble) thus facilitating the uptake of this bioavailable fraction by the wetland plants. Simply, there is likely high amounts of soluble, bioavailable metals in the pond.

5.3 Distribution and fractionation of mercury

The speciation of Hg, which includes most phase minerals, secondary phases, gaseous and aqueous species, is very important to assess the Hg transport (i.e. mobilisation) and impact in the environment. For instance, the incidental ingestion of contaminated soils is thought to be one of the main terrestrial exposure pathways to metal burdens in the human body. Often, the total soil metal concentration has been assumed to represent the bioavailable dose, but as mentioned earlier, it is well known that inorganic (IHg), elemental (Hg^0), and organic Hg (RHgX) have different chemical and physical properties, routes of exposure and toxicological effects. Hence, the form of ingested Hg is important to assess the absorbed dose. Elemental speciation, therefore, provides important data to predict metal bioavailability that appears to be site, media and matrix specific.

Tailings and soils from Berg Aukas and Tsumeb were subjected to sequential extraction to study Hg and other metals distribution and forms of occurrence. As stated earlier, Hg in tailings mainly occurred in the residual (non-soluble) fraction, i.e. F4 at about 92% of the HgT while the exchangeable (F1) and reducible (F2) fractions counted for 7.6 and 0.4%, respectively.

The variability observed in Hg fractionation in soils from Berg Aukas and Tsumeb illustrates the matrix dependency of metal speciation in soil. In general, Tsumeb soils showed the occurrence of 3 fractions: F1, F3 and F4. Berg Aukas exhibited all four fractions but in very different proportions. For instance, S3 from the wetland only had the residual, S4 and S5 essentially had the reducible fraction (F2) while S1 and S2 showed almost an equipartition between F1, F3 and F4 with a slight predominance of F3.

Different fractions of Hg have different mobility as well as bioavailability characteristics. The most active and mobile as well as bioavailable fraction is the exchangeable Hg (F1).

Davis, Bloom and Que Hee [110] stated that more than 98% of Hg in soils is present as non-alkyl (i.e. inorganic, IHg or Hg^{2+}) compounds and complexes. Considering that Hg bound to organic substances is assumed to be found in F2, this statement applies almost perfectly with Tsumeb soils where no F2 was observed. In the case of Berg Aukas, soils

S4 and S5 showed an average of 78% for F2. This high fraction of Hg could be the combination of Hg bound to Mn and Fe oxides together with the Hg complexed to humic substances, hydroxide and chloro-hydroxide (HgOH and HgClOH) species. Davis *et al* [110] also observed that Hg speciation in contaminated soils is dependent on the nature of the release, the Hg physical and chemical properties, and the chemistry of the receiving soil. The modeling of inorganic Hg(II) species has demonstrated the importance of species such as HgClOH and Hg(OH) when the pH becomes more neutral as it was the case for the Berg Aukas soils.

Neculita *et al* [111] investigated Hg partitioning and speciation in three highly contaminated soils from chlor-alkali plants and found that there was a low mobility of Hg, with a range of 2.6 to 12% of HgT. This amount of the mobile fraction of Hg (F1) is close to the amount measured in both Berg Aukas (mean F1: 12.1%) and Tsumeb (mean F1: 14.1%) soils. Furthermore, high percentages of mobile Hg increase its chances of migration to deeper soil layers. Gavilán-García *et al* [17] looked at Hg speciation in contaminated soils from old mining activities in Mexico and found the fractions that represent a greater potential risk of environmental pollution, such as F1, to be present in low concentrations in contaminated soils. This fraction (F1) may explain the presence of Hg measured in the surrounding plants and is of concern due to the risk of further uptake of the soluble Hg forms by other living species.

The different Hg fractions also positively correlated with HgT with the lowest correlation (r: 0.582) observed with F2 which could be a further indication of the predominance of inorganic Hg species and of the fact that F2 may contain Hg bound to organic radical (Table 5.6) since organo-Hg species are known to generally represent less than 5% of

HgT [112]. Besides, F2 was the only fraction that showed a positive correlation with both total sulphur (S_T) and sulphide. This may imply the occurrence of methyl Hg compounds through the formation of thiol (SH). The level of sulphide is known to control methylation, with amorphous mercury thiols predominating in more reducing environments as in the case of Tsumeb and Berg Aukas soils. It has been reported that in the presence of excess free sulphide, soluble Hg-sulphide complexes can increase HgS solubility by forming thiols, e.g. $Hg(SH)_2$ [110].

Table 5.8: Correlation data between Hg fractions and other physico-chemical parameters

	HgT	S_T	S^{2-}	Cl^-	NO_3^-	SO_4^{2-}	*pH*	*EC*	*F1*	*F2*	*F3*	*F4*
HgT	1											
S_T	0.446	1										
S^{2-}	0.445	1.000	1									
Cl^-	-0.306	-0.547	-0.554	1								
NO_3^-	-0.904	-0.752	-0.752	0.597	1							
SO_4^{2-}	-0.153	-0.464	-0.476	0.755	0.381	1						
pH	-0.435	-0.619	-0.613	-0.284	0.444	-0.130	1					
EC	0.508	0.010	0.012	0.373	-0.246	-0.090	-0.543	1				
F1	0.938	0.121	0.119	-0.092	-0.714	0.089	-0.282	0.528	1			
F2	0.526	0.571	0.571	-0.793	-0.743	-0.240	0.056	-0.447	0.384	1		
F3	0.588	-0.143	-0.143	0.425	-0.250	0.094	-0.443	0.957	0.687	-0.372	1	
F4	0.755	0.090	0.090	0.253	-0.481	0.000	-0.558	0.937	0.787	-0.160	0.967	1

HgT= Total Hg

S_T = Total Sulfur

Sample S3 in Berg Aukas was the only one that showed 100% residual (non-labile) Hg. This could be due to the fact that this sample was collected at the bottom of a pond in a wetland. Hence, all soluble forms of Hg that could have been found in that bottom soil had probably migrated to the water as labile or were converted, under the reducing conditions characteristic of the wetland (Eh ~0.1 V), to either methyl mercury or Hg^0, both being highly volatile. The lack (or the reduced amount) of soluble species in S3 has also been observed for all the other metals studied. There is a possibility that this wetland, where S3 was collected, is likely to contain elevated proportion of the deadly methylmercury (MeHg) since the conversion of IHg to MeHg is essentially a biologically driven process under typical wetland sediment conditions. The production of MeHg is controlled by bacterial activity as well as the bioavailability of IHg species to the microbial community. Under reducing conditions typical of wetland sediments, dissolved Hg speciation and concentration is controlled by the presence of reduced sulphur, and the uncharged dissolved Hg-S species that are the species able to diffuse into bacterial cells, will be readily available for methylation [113].

Results of SEP for Berg Aukas tailings revealed that about 8% of Hg present in the tailings was exchangeable and that almost 92% of Hg was residual. This means that F2 and particularly F3 were almost not present in tailings. Potential Hg species that can be found in the residual fraction are HgS, which is very toxic, even in low doses. Malehase *et al* [45] also reported that the residual fraction was the most dominant fraction in tailings from Randfontein in South Africa, with ranges between 38.7 and 50.4% although many authors have reported residual Hg, that is mainly Hg^0 and, to a certain extent, strongly matrix bound species such as HgS and HgSe, to be in the 90% range [37]. The residual Hg in tailings had a positive correlation with both total sulphur (r = 0.770) and sulphide (r = 0.708), clearly showing the presence of Hg-S type of association (Table 5.9). A positive correlation was also observed between F4 and chloride concentration in tailings.

Table 5.9: Correlation data between Hg and physico-chemical parameters in Berg Aukas tailings

	HgT	*S_T*	*S^{2-}*	*Cl^-*	*NO_3^-*	*SO_4^{2-}*	*pH*	*Ec*	*F1*	*F2*	*F4*
HgT	1										
S_T	0.716	1									
S^{2-}	0.698	0.756	1								
Cl^-	0.638	0.654	0.128	1							
NO_3^-	-0.093	0.254	0.636	-0.487	1						
SO_4^{2-}	0.257	0.622	-0.042	0.845	-0.373	1					
pH	0.458	0.647	0.631	0.110	0.245	0.234	1				
Ec	-0.722	-0.169	-0.610	0.023	-0.093	0.471	-0.289	1			
F1	-0.498	-0.911	-0.663	-0.589	-0.411	-0.599	-0.349	-0.054	1		
F2	0.752	0.782	0.915	0.362	0.522	0.099	0.340	-0.531	-0.793	1	
F4	0.996	0.770	0.708	0.683	-0.077	0.329	0.473	-0.663	-0.567	0.772	1

HgT= Total Hg

S_T = Total Sulfur

Navarro [114] reported that the main Hg phase minerals in mine waste are cinnabar (HgS), metacinnabar (cubic HgS), metallic Hg^0, corderoite ($Hg_3S_2Cl_2$), livingstonite ($HgSb_4S_8$), calomel (Hg_2Cl_2) and schuetteite ($Hg_3(SO_4)O_2$). This author also described three mechanisms through which HgS can be converted into mobile Hg forms:

- During ore roasting (at 500 – 600 °C) HgS can be converted into Hg^0 as follows:

  $HgS(s) + O_2(g) \rightarrow SO_2(g) + Hg^0(g)$
- Under oxidative (acidic) conditions, HgS can dissolve as follows:

  $HgS(s) + 2O_2(g) + 2H_2O \rightarrow Hg(OH)_2^0 + SO_4^{2-} + 2H^+$
- HgS can also dissolve in the presence of organic matter by means of surface complexation.

The complex formation, Eh-pH conditions, and organic matter and iron oxyhydroxide content control the aqueous mobilization of Hg in mine waste. Atmospheric emission of Hg^0 as well the leaching of waste through episodic high intensity precipitation, characteristic of semi-arid regions, favour possible transport of Hg from mine waste and under such conditions, Hg can be mobilized to pore water, surface water or groundwater. When Hg-soluble phases (chlorides and oxychlorides) are present, essentially in F1 and also as observed in Berg Aukas tailings, mobilization of Hg may be enhanced. Moreover, heavy metals such as Hg, Fe, Pb and Zn may be mobilized by atmospheric emissions of Hg^0 present in mine waste, which may be significant, and by dissolution of Hg^0 and metal-sulphate salts during episodic runoff events caused by semi-arid conditions [114].

On the basis of the collected data, it is quite clear that the main source of Hg pollution in Berg Aukas is the poorly maintained tailing dumps found in the area which release Hg mainly through runoff as well as through wind dispersion of Hg^0. The same mechanisms could explain the presence of Hg in Tsumeb soils where the main source of Hg is believed to be stored waste from smelting processes occurring in the area. The only exception to this could be the soil near the Dros restaurant (S16) where an abnormal Hg load is thought to occur from a Pb-Zn-Hg ore located in the area.

5.4 Distribution and fractionation of co-occurring metals

The chemical form (species) of an element, which determines its ecotoxicological risk to biota and the solubility (availability) of a given elemental species are generally the two aspects to be considered in the risk assessment of heavy metal contamination of water, sediment, soil or other environmental samples [115]. Sequential extraction, therefore, provides information that can enable the identification of the main binding sites of an element, the strength of metal binding to the particulates and the phase associations of elements in soil/sediment [116].

In their study on the human health risks associated with historic ore processing at Berg Aukas, Mapani *et al* [33] identified primary sulphides such as sphalerite [(Zn,Fe)S], galena (PbS) and subordinate pyrite [FeS_2]. Correlation analysis of the data from Berg Aukas tailings (Figure 5.7) showed a relatively strong positive correlation between the identified metals and total Sulphur, suggesting an eventual presence of metal sulphides, which in many cases, was confirmed with sequential extraction data discussed below.

Table 5.10: Correlation analysis of data from Berg Aukas tailings

	Cr	*Cd*	*Cu*	*Mn*	*As*	*Fe*	*Al*	*Zn*	*Pb*	*Hg*	*ST*
Cr	1										
Cd	0.868	1									
Cu	0.971	0.917	1								
Mn	0.780	0.966	0.852	1							
As	0.934	0.730	0.909	0.575	1						
Fe	0.949	0.795	0.905	0.635	0.978	1					
Al	0.512	0.846	0.644	0.933	0.292	0.354	1				
Zn	0.868	0.549	0.833	0.448	0.919	0.838	0.148	1			
Pb	0.973	0.868	0.988	0.769	0.961	0.948	0.534	0.880	1		
Hg	0.588	0.153	0.452	-0.045	0.763	0.715	-0.382	0.791	0.569	1	
ST	0.929	0.643	0.853	0.574	0.872	0.847	0.257	0.941	0.869	0.716	1

Due to the number of elements discussed in the following section, which led to the treatment of a great number of data, the relevant corresponding correlation tables will only appear in appendices.

Besides the positive correlation between metal concentrations and sulphur content, strong correlations were also observed between some metals (Table 5.7) which could be an indication of the co-occurrence of certain metals within the same mineral. For instance, correlations between Zn-Fe (r = 0.838) and Pb-Zn (r = 0.880) could suggest the occurrence of sphalerite [(Zn,Fe)S] and descloizite [$(Pb,Zn)_2VO_4$), respectively. Both of these correlations were identified by Mapani *et al* [33] whereas the correlation between Pb-As (r = 0.961) could indicate the presence of mimetite [$(Pb_5(ASO_4)_3Cl$], which was deduced from sequential extraction data.

5.4.1 Arsenic (As)

As is an element that combines with other elements to form inorganic and organic compounds, with the inorganic As compounds being thought to be more toxic. There are various ways in which people living in the area could be exposed to As. This includes breathing in dust that may contain the toxic metal, eating or touching soil that contains arsenic. Children playing in the area are at a higher risk of exposure as they tend to eat the dirt. The allowable concentration of As in soil is 5.0 mg/kg, according to WHO guidelines. Although the total As concentrations exceeded this limit, the data indicate that As is mostly associated with the residual fraction, therefore it is in a form that is mostly immobile and does not present a problem to the environment, even if an average of 1.6% of exchangeable As (i.e. about 2.5 mg/kg) was also measured in soil. These results are very similar to those reported by Sracek *et al* [51] who found that most of the As present in mine tailings from Kombat mine (Namibia) is residual. Additionally, As in the reducible fraction (F2) is correlated with the chloride in the soil (r = 0.973). This led to the suggestion of the likely occurrence of mimetite since a positive correlation (r = 0.761 for As-Cl and r = 0.966 for Pb-Cl) was also observed between As, Pb and chloride contents in the residual fraction of Berg Aukas tailings. The oxidisable fraction of As was mostly present in tailings.

5.4.2 Cobalt (Co)

The majority of Co in soil (53% in Berg Aukas and 55% in Tsumeb) was reported to be residual (F4), with a considerable concentration, also occurring as reducible (F2), especially in Tsumeb soil (25%). Tashakor *et al* [117] also reported that, in addition to its abundance in the residual fraction, Co also was tightly bound to Mn-oxide fraction (F2) in soil.

Co is found with minerals containing a possible variety of elements such as Ni, As, S, Fe, Cr, Cu, Pb, and Mn in the form of oxide, sulphide or arsenide. The total concentration of Co indeed correlated with most of the concentrations of these elements with the exception of Cu where a relatively poor correlation (r = 0.401) was obtained.

In the present study, Co in F2 was also correlated with the sulphate content (r = 0.976). This may indicate a Co-SO_4 type of binding observed in minerals such as cobaltkieserite, aplowite, moorhouseite and bieberite.

5.4.3 Cadmium (Cd)

Cd is not found in its pure state in nature, but is mainly associated with sulphide ores of Pb, Cu and Zn. The contamination may be attributed to roasting of ores, dust fallout emissions from slimes dams and slag deposits [33]. Since Cd is usually a by-product of Zn and Cu smelting, its high occurrence could be a result of emissions from ore roasting. Total Cd in soil positively correlated with Zn (r = 0.509), Pb (r = 0.940) and Hg (r = 0.540). Strong correlations between Cd and metals such as Cu (r = 0.917), Mn (r = 0.966), As (r = 0.730), Fe (r = 0.795), Zn (r = 0.549) and Pb (r = 0.868) were also observed in Berg Aukas tailing materials.

The results presented earlier indicate that there is a significant amount of Cd at both sampling sites occurring as exchangeable (22 to 59%). This suggested the presence of Cd bound to carbonate that is easily soluble in water and causing Cd to be highly mobile and available for uptake by living species, which poses a serious environmental risk at the study sites.

The presence of metal carbonate species can be explained by the abundant occurrence of carbonate minerals, such as dolomite ($CaMg(CO_3)_2$] in the area as stated by Mapani *et al* [33]. It has been reported that the most important factor affecting Cd mobility are pH and total soil content [118]. According to the Atlas of Eh-pH diagrams (National Institute of Advanced Industrial Science and Technology [119], Cd should exist in water as free Cd^{2+} under the Eh-pH conditions of the study sites (Figure 5.3). This is understandable due to the relatively weak bond between Cd and carbonate characteristic of the species found in the exchangeable fraction.

Depending on soil types, free Cd (Cd^{2+}), and the organically complexed forms (i.e. Cd in F1 and F2) are the most abundant species followed by inorganic soluble species such as sulphates and chlorides [118]. Note that Cd in F1 and F2 soils occurred at 43 and 79% in Berg Aukas and Tsumeb, respectively. Additionally, the correlations were observed between Cd in F4 and chloride ($r = 0.852$) and sulphate ($r = 0.992$) ions in Berg Aukas tailings.

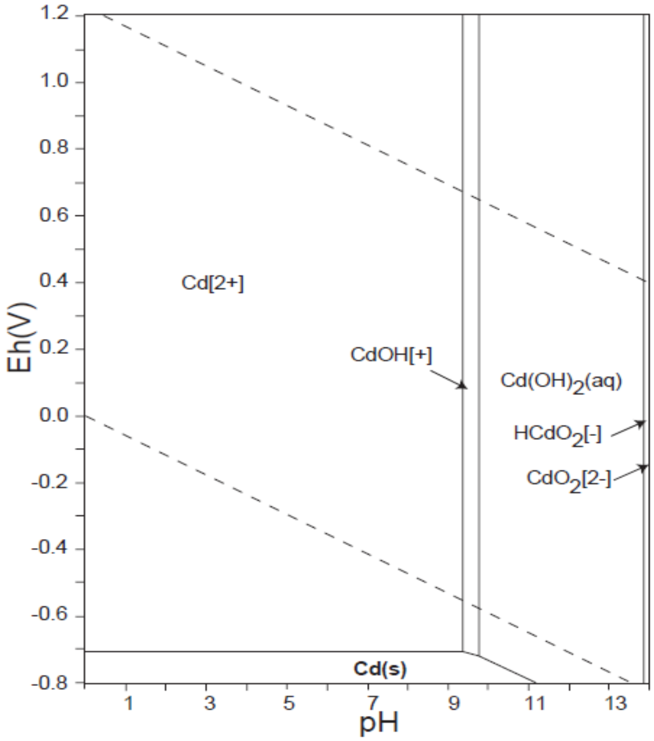

Figure 5.3: Eh-pH diagram showing Cd speciation in water [119]

Authors have also reported significant correlations between Cd, and other soil properties such as cation exchange capacity (CEC), clay or organic matter and metal contents. Fe and Mn (hydr)oxides were found to be the main carriers for Cd, Zn and Ni (F2) under toxic conditions, whereas the organic fraction was most important for Cu. This metal mobility can seriously be reduced by the formation of metal sulphide precipitates (F3) under anoxic conditions. Plants can also affect metal mobility by oxidising their rhizosphere and taking up metals [120].

Here again, S3, from Berg Aukas wetland had no exchangeable Cd. It is, therefore, safe to assume that the whole soluble Cd has dissolved into the pond, which is possibly used as a drinking water source for animals in the surrounding area. This explains why little to no trace of the metal was found in the exchangeable fraction for this sample (as for Hg).

The presence of soluble Cd in the wetland can explain the relatively elevated Cd content found in some of the collected wetland plants. For instance, a Cd concentration of 3.4 mg/kg was measured in sample P20 from the wetland whereas sample P17 from the same wetland had Cd at a concentration as high as 14.2 mg/kg. According to guidelines set by the WHO, the maximum permissible concentration of Cd in soil should fall in the range of 0.3 - 1.0 mg/kg. The data obtained show that Cd exceeded the threshold limit, especially in the Berg Aukas settlement.

5.4.4 Copper (Cu)

Despite the total toxic metal content of Cu exceeding the maximum permissible limits, the high concentrations of Cu in soil may not necessarily be a cause for concern. The data shows that Cu is mostly introduced into the environment in a form that is stable or one that is not an environmental risk. Results indicate that Cu is associated with the fraction that is bound to silicates i.e. the residual fraction, with an average of 51% in Berg Aukas and 66% in Tsumeb soil. This is consistent with findings of Ogunbajo *et al* [121]. However, the tailings indicate that there may be a significant amount that is associated with the mobile phases, with 67% being reported as the maximum in the reducible fraction.

The relatively high percentage of Cu in the oxidisable fraction in soil (up to 21% in Berg Aukas) is in accordance with its strong covalent interaction with organic matter [122]. Moreover, Rutkowska, Szulc and Bomze [123] found that Cu in soil solutions occurred mainly as metalorganic complexes and that soil texture and soil Cu contamination had no influence on the percentages of different Cu forms in the soil solution.

Finally, Cu positively correlated with sulphide in F2 (r = 0.685) and F3 (r = 0.857) indicating the eventual occurrence of Cu – sulphide association such as those found in chalcopyrite ($CuFeS_2$) and covellite (CuS). Note that Cu positively correlated with Fe at both soils (r = 0.539) and tailings (r = 0.905). Cu also had a slight positive correlation with fluoride in F1 (r = 0.552). Fluoride-containing secondary Cu sulphide ores have recently been reported by Rodrigues *et al* [124].

5.4.5 Lead (Pb)

Pb is naturally occurring in soil and is usually tightly bound on surfaces of organic matter and fine clay particles and has a tendency to accumulate in the upper soil horizons. Soil Pb availability is dependent on how tightly it is held by soil particles and its solubility [125]. On the other hand, since pH values were generally above 7, it can be said that very little of the Pb that is found in the studied soils was bioavailable. The lower the pH of the soil, the higher the bioavailability [46]. Under acidic conditions, it is held less tightly and thus more soluble, but at neutral to basic conditions, it is held more tightly and is less soluble. Pb was predominantly found in the reducible fractions, which may be attributed to Pb forming stable complexes and an indication that it is associated with Fe-Mn oxides and bound to organic matter. Manceau *et al* [126] studied soils contaminated by different industrial activities including Pb-Zn smelting and found Pb to be divalent and coordinated to O, OH ligands and that it was present in different forms which could not be identified individually.

The results also show that the Berg Aukas tailings contain some Pb that is water soluble, with 32.8% being the maximum, which is an indication that Pb is bioavailable for plant uptake. The study showed that soil samples from Berg Aukas and Tsumeb had slightly elevated results of exchangeable Pb (about 9% on average at both sites), with the highest amount of about 36% observed in Tsumeb. The exchangeable Pb is believed to be Pb bound to carbonate. Additionally, cerussite ($PbCO_3$) has been identified as a secondary mineral occurring in Berg Aukas [33].

Similar studies done in Tunisia by Wali *et al* [48] showed that most of the Pb (about 60%) was found in the residual fraction of contaminated soil. Pb in soil was correlated with sulphide for all four fractions, but more especially with F3 (r = 0.907) which may indicate the presence of Pb sulphide minerals such as galena (PbS). Finally, Pb in tailing materials showed a strong correlation with both chloride (r = 0.966) and sulphate (r = 0.805) ions in the residual fraction implying the likely occurrence of Pb-Cl and Pb-SO_4 types of association such as those found in cotunnite ($PbCl_2$) and the diverse minerals of Pb sulphate species.

5.4.6 Manganese (Mn)

Mn is an element that occurs naturally and is classified as an essential nutrient, but it does not exist in its elemental form. Mn is mainly found as carbonates, oxides and silicates. Mn, in both study areas was predominantly observed in the reducible and exchangeable fractions implying the occurrence of Mn bound to oxide, organic substrate and carbonate. Kalembkiewicz and Sitarz-Palczak [127] found that the contribution of the chemical fractions of Mn in soil follows the order: Mn (oxide) > Mn (residual) > Mn (organic) > Mn (carbonate) > Mn (exchangeable). Considering that the BCR SEP classifies the oxide and organic bound as F2 (reducible) while the carbonate and exchangeable fractions are grouped in F1 (exchangeable), the sequence proposed by Kalembkiewicz and Sitarz-

Palczak [127] is a quasi-perfect match of the situation observed in the present study. The only exception to this sequence was the relatively high fraction of exchangeable Mn in Berg Aukas soil (about 43%) which could be attributed to the Eh-pH conditions at the time of the sampling, which suggests the occurrence of Mn mainly as Mn^{2+} (i.e. soluble in water), but also to the input of soluble fractions during rainy season from the surrounding tailings dams. Although the total Mn concentration is below the maximum permissible limit (MPL), the chemical speciation data of Mn shows that the metal is mostly present in the highly mobile fractions i.e. exchangeable and reducible fractions. This is a cause for concern as the toxic metal can easily be leached into waterways, inhaled as dust and poses a risk for children playing in the contaminated area, which may lead to adverse health effects.

Mn was also present in the oxidisable fraction in soil (F3) where it correlated with the sulphide content (r = 0.834) whereas in Berg Aukas tailings the residual Mn (F4) correlated with chloride (r = 0.883) and sulphate (r = 0.845). This type of Mn association is found in minerals such as alabandite, browneite, rambergite (both MnS), scacchite ($MnCl_2$) and the diverse valid mineral species of Mn sulphate.

5.4.7 Nickel (Ni) and chromium (Cr)

Ni, which occurred at low concentrations in soil was predominantly found as reducible (i.e. bound to Fe and/or Mn oxides) and residual (i.e. bound to crystal lattice). Ni, Cr and Fe were the metals that exhibited, in increasing order, the highest proportions of residual fractions. The combination of selective sequential extraction (SSE) analysis and X-ray diffraction (XRD) of soil powders carried out by Tashakor *et al* [117] showed that Cr and Ni are primarily associated with the residual fraction of soil which is inherited from resistant silicates and that the crystalline Fe-oxide fraction of soil is the second substantial scavenger of Cr and Ni. The correlations between total Ni with Cr (r = 0.872) and Fe (r = 0.913) and between total Cr and Fe (r = 0.996) are in line with the above findings.

5.4.8 Zinc (Zn)

Zn exhibits similar properties as those of Cd and is also soluble in water. It is an essential nutrient for plant growth but only in minimal concentrations. When it exceeds its maximum concentration, it becomes toxic and begins to compete with Mn, Fe, P or Cu for plant uptake and may cause deficiencies in plant tissues. Zn was found to be present in all the investigated soil and tailings samples. Given that Zn behaves in a similar manner to Cd, the exchangeable fraction of Zn in sample S3 was extremely low, which is an indication that it is bioavailable for plants in the pond. The metal was found to be above the permissible concentrations and mainly associated with the exchangeable and reducible fractions of the soil, an indication that Zn is weakly binding, associated with carbonates and oxides of Fe and Mn. The occurrence of smithsonite ($ZnCO_3$) was actually identified by Mapani *et al* [33] in Berg Aukas soil. Diesing *et al* [128] in their study of Zn speciation and its exchangeability in soils polluted with heavy metals distinguished three pools of exchangeable Zn: the pool of Zn exchangeable within first minute observed in all the study soils, Zn exchangeable on the medium term, as well as the slowly and not exchangeable Zn. The values of Zn in the first two pools were said to be similar to those obtained in soil/plants system. The study also showed that more than half of the Zn was present in species weakly bound to organic compounds and/or outer sphere inorganic and organic complexes while other species included strongly sorbed and crystalline mineral

Zn species. Finally, the study also highlighted the dependency of the extraction efficiency to the soil properties.

Conversely, over 50% of the total Zn in the present study is associated with the less mobile (F3) and residual fractions (F4) in soil. The positive correlation between Zn and sulphide in F3 ($r = 0.888$) may suggest the presence of Zn-S bond found in minerals such as sphalerite, wurtzite whereas the residual Zn could indicate the occurrence of strongly silicate bound willemite (Zn_2SiO_4) which was identified by Mapani *et al* [33]. These authors also reported the occurrence of descloizite [$(Pb,Zn)_2VO_4$] which could be deduced by the positive correlation noted between total Zn and Pb ($r = 0.768$).

As mentioned earlier, although not discussed in depth in the present study the speciation of Cr and Fe showed essentially the occurrence of the residual fraction in soils and tailings at proportions greater than 90%. Such high proportions of F4 have been reported in the literature stated that this is a general observation for Fe in most soils [98,129,130].

Chapter 6

Conclusions and recommendations

6.1 Conclusions

The main purpose of this study was to characterise the occurrence and distribution of mercury and other metals that occur in association with Hg, in selected local environmental compartments affected by old and current mining activities. This study showed evidence that past mining activities continue to pollute the soils, water and plants in Berg Aukas and Tsumeb with heavy metals mainly through mine tailings even years after the activities have ceased, as it is the case for Berg Aukas. Water and mine tailings from Berg Aukas as well as soils and plants from both Berg Aukas and Tsumeb showed elevated concentrations of Hg and other co-occurring heavy metals. The recorded Hg values were, in many cases, higher than the threshold or permissible levels reported in international guidelines. Total metal concentrations also showed that Zn and Pb appeared in concentrations that are way above the maximum permissible concentrations in the Berg Aukas area, which is a result of the past ore roasting emissions. The Tsumeb sampling sites recorded concentrations of Cd and Cu that also exceeded guideline values. In general, it is observable that the Berg Aukas area is more severely contaminated than the Tsumeb area. This is an indication that there was improper management of the mine and tailings at the time of closure and thus, it became a source of toxic metals in the environment. This pollution as well as prolonged exposure to heavy metals pose a serious ecosystem and health risk not only to people working and/or living in both Berg Aukas and Tsumeb, but also to plants and animals.

The impact of anthropogenic heavy metal pollution on Berg Aukas and Tsumeb soils were evaluated using enrichment factors (EF). EF of Hg, Cd, As and Zn in Berg Aukas soils and Hg, Pb and As for Tsumeb soils indicate that the degree of enrichment in these two towns is between significant to extreme enrichment, thus it can be concluded that the heavy metal pollution is predominantly from anthropogenic sources.

Moreover, the TC of Hg from soil to plant was found to be low, indicating reduced mobility of ions, which could be due to the alkalinity of the soil. Even though the plants used to calculate the TC were all from the same area, they had different TC values. This proved that some plant species have greater ability to take up Hg from soil than others. Conclusions about the bioavailability of metals could not be made based on the TC index alone because bioavailability of metals can be affected by factors such as plant species, growth period, cation exchange capacity, soil pH and organic matter.

Additionally, some studies have shown that there are certain plant species that can take up as much heavy metals as possible to regulate the amount of heavy metals that can be taken up from the environment. Planting of such plant species can be used for mitigation and remediation purposes in order to reduce and regulate the contamination of the environment by heavy metals [131]. There were generally low concentrations of Hg measured in plants in this study. This could be because not all plant families are metal-accumulating species. Moreover, most of the Hg that is taken up by metal-accumulating plant species, tend to accumulate in the roots.

One of the plant species studied, namely *R. communis*, that was commonly found growing on and around tailings in Berg Aukas, grows well in metal-contaminated soil and has a potential of phytoremediation. However, it is not known whether it is an accumulator or an excluder [132].

The results of sequential extraction procedures indicated that most Hg found in soils and tailings from Berg Aukas and Tsumeb is residual. Even though exchangeable Hg measured amounts as low as 3%, this fraction is a high environmental risk due to availability in the environment. Correlation data and Eh-pH models enabled the prediction of the occurrence of several Hg species such as elemental Hg (Hg^0), several inorganic Hg forms (e.g. $HgCl_2$, HgClOH, $Hg(OH)_2$, HgS, $Hg(SH)_2$, etc.) as well as organomercurials such MeHg in wetland. This, in turn, permitted to explain the likely mechanisms of Hg transport and transformation within the study area which is critical for eco-toxicological assessment and remediation purposes.

The forms of occurrence of other toxic metals in soil (and tailings) samples also were studied. Cd, Zn and Mn were found to be the most labile (mobile) metals, as they were mostly present in the water soluble and reducible fractions, while As came in a form that is relatively immobile and therefore not a substantial risk to the environment. Pb was predominantly found in the reducible fractions, showing that it is bound to Fe-Mn oxides and organic matter. The least mobile, amongst the identified elements, were Fe followed by Cr. The trends observed in the mobile and bioavailable fractions of Berg Aukas and Tsumeb were Mn > Cd > Zn > Pb > Cu > As > Cr >Fe and Cd > Mn > Zn > Pb > Cu > As > Cr > Fe, respectively. These data are an indication that the modified BCR method is reliable for assessing the risk of toxic metals present in soil (and tailings).

Moreover, it appeared that the type of heavy metal contamination found in the study soils is dependent on the mining operation that occurred on site, as well as disposal patterns of contaminated waste. Moreover , as stated by Wuana and Okieimen [104], even though the presence of heavy metals persists in soils for years after initial introduction, the chemical species in which the metal is found in the soil, may make it more bioavailable. This study also revealed the level of bioavailability of metals in tailings and soils from the two mining towns. If environmental conditions are favorable, the bioavailable metals in soils will be taken up by plants, thus entering the food chain.

In brief, the present study revealed that both Berg Aukas and Tsumeb have relatively high amounts of Hg and other toxic heavy metals in their plants and soils. The general trend was that there were higher concentrations in Berg Aukas soils in comparison to Tsumeb soil. Even though mining activities have ceased at Berg Aukas, the mine tailings that are not properly walled-in are believed to cause fine particles that contain Hg and other toxic metals to be dispersed by the wind and water to surrounding soils, thus increasing soil concentration levels. Finally, mining activities are still active in Tsumeb and thus continue to cause ecosystem pollution in the surroundings.

6.2 Recommendations

The following recommendations are proposed for a better insight but also as partial remedial approaches in the pollution occurring at both study areas:

a) Analyse more water samples for better characterisation of the Hg pollution impact on watersheds

b) Development of environmentally friendly and low-cost technologies (e.g. Phytoremediation) to remediate contaminated sites, depending on the physical characteristics of the site

c) Perform seasonal sampling to understand how seasonality is affecting Hg behaviour at the sites

d) Characterisation of Hg methylation in the study areas

e) Conduct further studies to find which plant species can regulate the amount of heavy metals taken up from the environment as a form of mitigation and remediation

f) Conduct further studies on speciation of Hg on agricultural plants at Berg Aukas to assess what forms of Hg are found in plants eaten by humans

g) Walling-in the tailing dams in order to reduce additional contamination to the surrounding areas

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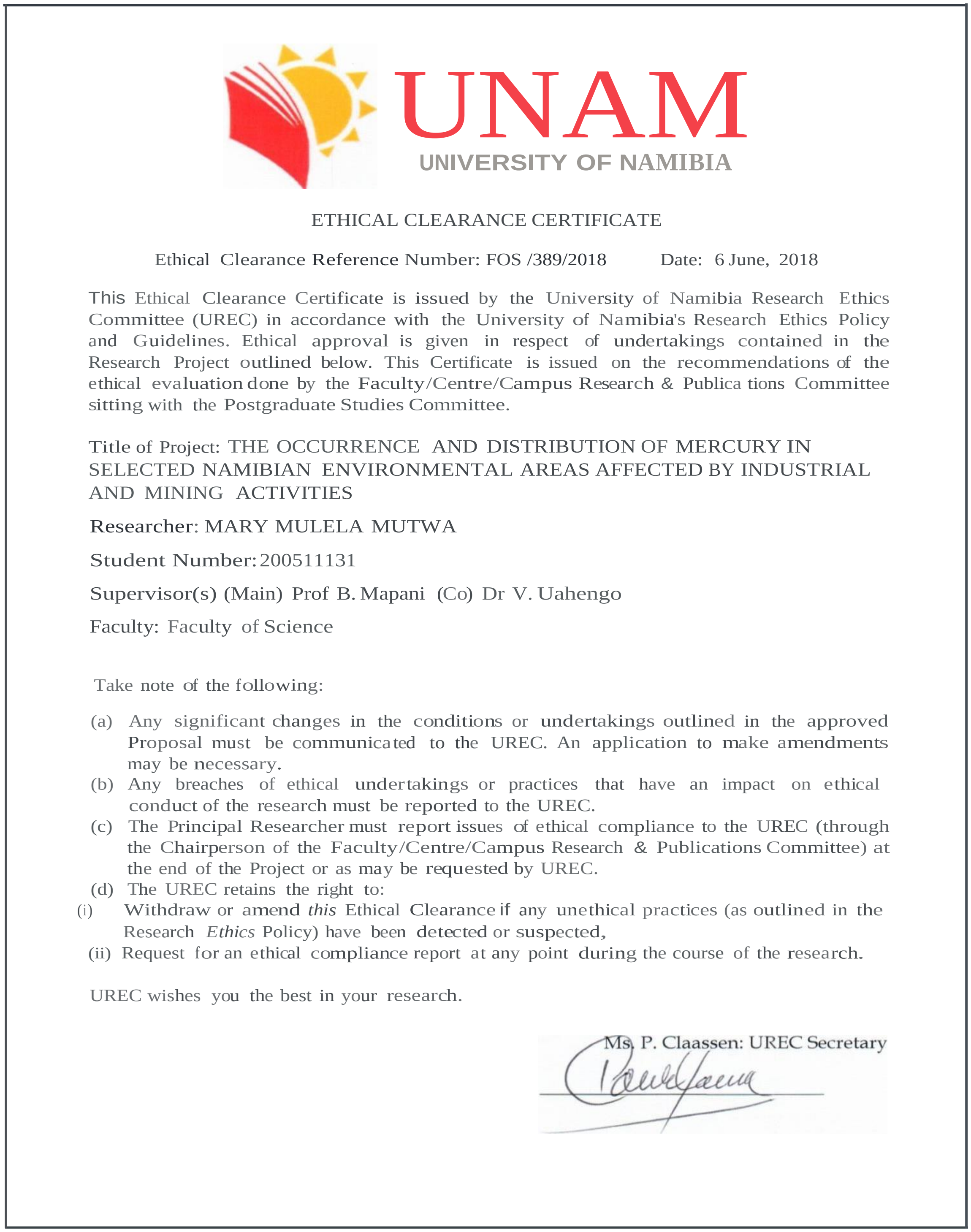
Appendices

Appendix 1: Ethical Clearance Certificate



UNAM
UNIVERSITY OF NAMIBIA

ETHICAL CLEARANCE CERTIFICATE

Ethical Clearance Reference Number: FOS /389/2018 Date: 6 June, 2018

This Ethical Clearance Certificate is issued by the University of Namibia Research Ethics Committee (UREC) in accordance with the University of Namibia's Research Ethics Policy and Guidelines. Ethical approval is given in respect of undertakings contained in the Research Project outlined below. This Certificate is issued on the recommendations of the ethical evaluation done by the Faculty/Centre/Campus Research & Publications Committee sitting with the Postgraduate Studies Committee.

Title of Project: THE OCCURRENCE AND DISTRIBUTION OF MERCURY IN SELECTED NAMIBIAN ENVIRONMENTAL AREAS AFFECTED BY INDUSTRIAL AND MINING ACTIVITIES

Researcher: MARY MULELA MUTWA

Student Number: 200511131

Supervisor(s) (Main) Prof B. Mapani (Co) Dr V. Uahengo

Faculty: Faculty of Science

Take note of the following:

(a) Any significant changes in the conditions or undertakings outlined in the approved Proposal must be communicated to the UREC. An application to make amendments may be necessary.
(b) Any breaches of ethical undertakings or practices that have an impact on ethical conduct of the research must be reported to the UREC.
(c) The Principal Researcher must report issues of ethical compliance to the UREC (through the Chairperson of the Faculty/Centre/Campus Research & Publications Committee) at the end of the Project or as may be requested by UREC.
(d) The UREC retains the right to:
(i) Withdraw or amend *this* Ethical Clearance if any unethical practices (as outlined in the Research *Ethics* Policy) have been detected or suspected,
(ii) Request for an ethical compliance report at any point during the course of the research.

UREC wishes you the best in your research.

Ms. P. Claassen: UREC Secretary

Appendix 2: Tables 1-18

Table 1: Hg concentration for soils, tailings, plants and water from Berg Aukas and Tsumeb using DMA 80

Sample Type	Sample name	HgT (mg/Kg)	SD (mg/kg)	RSD (%)
Soil	S1 BA	0.074	0.001	0.9
Soil	S2 BA	0.055	0.016	29.3
Soil	S3Pond BA	2.487	0.069	2.8
Soil	S4 BA	3.113	0.401	12.9
Soil	S5 BA	0.498	0.069	13.8
Soil	S6 TB	0.175	0.008	4.4
Soil	S7 TB	0.663	0.049	7.4
Soil	S8(I.S.under Tree)	0.033	0.002	7.0
Soil	S9(I.S.OA)	0.015	0.001	8.8
Soil	S10(I.S.OA)	0.057	0.005	9.1
Soil	S11(B.Compound)	0.043	0.001	1.6
Soil	S11(I.S.soilI)	0.055	0.006	10.6
Soil	S12 (B.cpd)	0.026	0.017	65.0
Soil	S13	0.022	0.001	6.4
Soil	SL1	0.033	0.001	2.8
Soil	SL2	0.020	0.001	3.3
Soil	S15(soil)	0.022	0.000	0.8
Soil	S16	3.487	0.277	8.0
	Mean Soils	0.604	0.051	

Table 2: Hg concentration for tailings from Berg Aukas using DMA 80

Sample Type	Sample name	HgT (mg/Kg)	SD (mg/kg)	RSD (%)
Tailings	T1 Bottom	1.166	0.008	0.7
Tailings	T2 Middle	1.185	0.104	8.8
Tailings	T3 top	1.394	0.060	4.3
Tailings	T4 S/C	0.817	0.048	5.9
Tailings	T5	1.709	0.143	8.3
Tailings	T6	2.238	0.150	6.7
Tailings	T7	1.750	0.049	2.8
Tailings	T8	1.338	0.023	1.7
Tailings	T9 B cliff	0.975	0.080	8.2
Tailings	T10 cliff	0.955	0.016	1.7
Tailings	T11	1.032	0.111	10.7
Tailings	T12	1.619	0.684	42.3
Tailings	TT13	1.323	0.065	5.0
Tailings	TT14	1.717	0.008	0.5
Tailings	TT15	2.061	0.407	19.8
Tailings	TT16	1.051	0.032	3.1
Tailings	TT17	0.037	0.004	10.5
	Mean T	1.396	0.416	

Table 3: Hg concentration for plants from Berg Aukas and Tsumeb using DMA 80

Sample Type	Sample name	HgT (mg/Kg)	SD (mg/kg)	RSD (%)
Plant	P1	0.041	0.009	22.3
Plant	P2	0.086	0.017	19.7
Plant	P3	0.025	0.003	11.2
Plant	P4	0.069	0.008	11.8
Plant	P5(T8)	0.037	0.002	4.5
Plant	P6	0.064	0.005	8.0
Plant	P7	0.042	0.001	2.4
Plant	P9	0.035	0.001	3.9
Plant	P5F	0.049	0.033	66.3
Plant	P8F	0.038	0.022	57.7
Plant	P8(T11) l	0.050	0.000	0.6
Plant	P10F	0.014	0.002	12.9
Plant	P10(T12) L	0.051	0.015	28.5
Plant	P11(T12)	0.046	0.018	39.8
Plant	P12F	0.009	0.001	9.1
Plant	P12(TT13) L	0.033	0.002	5.8
Plant	P13L	0.033	0.001	3.7
Plant	P13(TT13) F	0.010	0.005	50.7
Plant	P14F	0.008	0.001	16.1
Plant	P15L	0.026	0.002	8.1
Plant	P15(TT16)	0.010	0.004	36.2
Plant	P16 Pond	0.103	0.009	9.1
Plant	P17	0.073	0.001	1.8
Plant	P18	0.126	0.002	1.5
Plant	P18 SeedPond	0.017	0.001	5.1
Plant	P19 LeavePond	0.036	0.000	0.0
Plant	P20 Pond Wetland	0.293	0.001	0.4
Plant	P21(P.WL)	0.023	0.001	5.5
Plant	P22 Pond Wetland	0.703	0.011	1.6
Plant	P23	0.048	0.008	16.8
Plant	P24 L	0.042	0.005	11.8
Plant	P24 F	0.009	0.003	29.9
Plant	P25 L	0.028	0.003	8.9
Plant	P25 F	0.008	0.001	14.0
Plant	P26 Euc	0.007	0.000	3.1
Plant	P27 EU.	0.007	0.001	20.2
Plant	P28 Euc	0.006	0.000	7.0
Plant	P29 M.L	0.025	0.000	1.5
Plant	P30 M.L	0.025	0.000	1.1
Plant	P31 Mar Leaves	0.030	0.000	1.0
Plant	P32 Mar Fruits	0.004	0.000	8.1
	Mean	0.058	0.005	

Table 4: Hg concentration for water from Berg Aukas using DMA 80

Sample Type	Sample name	HgT (mg/Kg)	SD (mg/kg)	RSD (%)
water	W1	0.006	0.002	33.1
water	S3 water	0.003	0.000	4.9
water	W4	0.002	0.000	24.5
water	W5	0.002	0.001	37.0
	mean	0.003	0.001	

Table 5: Hg sequential extraction results for soils and tailings

Sample Id	F1 (mg/kg)	F2 (mg/kg)	F3 (mg/kg)	F4 (mg/kg)	HgT (mg/Kg)	
S1	**0.026**	**0.000**	**0.027**	**0.021**	0.074	
S2	**0.098**	**0.044**	**0.215**	**0.000**	0.055	
S3	**0.000**	**0.000**	**0.000**	**2.487**	2.487	X
S4	**0.068**	**2.618**	**0.000**	**0.427**	3.113	
S5	**0.000**	**3.617**	**0.000**	**0.000**	0.498	X
S6	**0.075**	**0.000**	**0.185**	**-0.085**	0.175	
S7	**0.072**	**0.000**	**0.461**	**0.130**	0.663	
S8	**0.057**	**0.000**	**0.124**	**-0.148**	0.033	
S9	**0.042**	**0.000**	**0.175**	**-0.203**	0.015	
S10	**0.040**	**0.000**	**0.145**	**-0.129**	0.057	
S11	**0.030**	**0.000**	**0.077**	**-0.052**	0.055	
S12	**0.020**	**0.000**	**0.015**	**-0.009**	0.026	
S13	**0.023**	**0.000**	**0.036**	**-0.037**	0.022	
S14	**0.026**	**0.000**	**0.214**	**-0.207**	0.033	
S15	**0.023**	**0.000**	**0.000**	**-0.001**	0.022	
S16	**0.087**	**0.034**	**0.221**	**3.146**	3.487	X
T1	**0.105**	**0.000**	**0.000**	**1.061**	1.166	
T2	**0.142**	**0.000**	**0.000**	**1.043**	1.185	
T3	**0.032**	**0.000**	**0.000**	**1.362**	1.394	X
T4	**0.103**	**0.000**	**0.000**	**0.714**	0.817	
T5	**0.050**	**0.000**	**0.000**	**1.659**	1.709	
T6	**0.000**	**0.000**	**0.000**	**2.238**	2.238	X
T7	**0.139**	**0.000**	**0.000**	**1.611**	1.750	
T8	**0.133**	**0.000**	**0.000**	**1.206**	1.338	
T9	**0.085**	**0.000**	**0.000**	**0.889**	0.975	
T10	**0.114**	**0.000**	**0.000**	**0.842**	0.955	
T11	**0.091**	**0.000**	**0.000**	**0.941**	1.032	
T12	**0.000**	**0.000**	**0.000**	**1.619**	1.619	X
TT13	**0.123**	**0.000**	**0.000**	**1.199**	1.323	
TT14	**0.000**	**0.027**	**0.000**	**1.690**	1.717	X
TT15	**0.000**	**0.084**	**0.000**	**1.977**	2.061	X
TT16	**0.121**	**0.000**	**0.000**	**0.930**	1.051	
TT17	**0.085**	**0.000**	**0.000**	**0.000**	0.037	

Table 6: Correlation data between As fractions and other physico-chemical data in Berg Aukas and Tsumeb soils

	AsT	S_T	S^{2-}	F^-	Cl^-	NO_3^-	SO_4^{2-}	*pH*	*Ec*	*F1*	*F2*	*F3*	*F4*
AsT	1												
S_T	-0.347	1											
S^{2-}	-0.350	1.000	1										
F^-	0.014	0.335	0.337	1									
Cl^-	-0.842	-0.193	-0.191	-0.340	1								
NO_3^-	-0.802	0.834	0.835	0.132	0.380	1							
SO_4^{2-}	-0.713	0.553	0.556	0.686	0.339	0.717	1						
pH	0.766	-0.824	-0.826	-0.432	-0.300	-0.948	-0.891	1					
EC	-0.906	0.162	0.166	0.292	0.788	0.600	0.836	-0.692	1				
F1	-0.302	0.131	0.129	-0.882	0.383	0.332	-0.367	-0.015	-0.103	1			
F2	-0.943	0.024	0.026	-0.196	0.973	0.570	0.524	-0.513	0.880	0.343	1		
F3	0.951	-0.041	-0.044	0.147	-0.964	-0.582	-0.563	0.540	-0.903	-0.301	-0.999	1	
F4	0.997	-0.411	-0.413	0.026	-0.810	-0.843	-0.709	0.795	-0.876	-0.340	-0.921	0.928	1

AsT = Total Arsenic
S_T = Total Sulfur

Table 7: Correlation matrix between metal concentrations in Berg Aukas and Tsumeb soils

	Cr	*Cd*	*Ni*	*Co*	*Al*	*Fe*	*Cu*	*Zn*	*As*	*Pb*	*Hg*
Cr	1										
Cd	-0.191	1									
Ni	0.872	-0.379	1								
Co	0.854	-0.316	0.986	1							
Al	0.181	-0.590	0.550	0.547	1						
Fe	0.996	-0.220	0.913	0.895	0.258	1					
Cu	0.582	-0.203	0.333	0.401	-0.077	0.539	1				
Zn	0.734	0.509	0.453	0.459	-0.314	0.703	0.333	1			
As	0.932	-0.043	0.655	0.660	-0.046	0.898	0.764	0.786	1		
Pb	0.148	0.940	-0.079	-0.030	-0.539	0.119	-0.052	0.768	0.260	1	
Hg	0.703	0.540	0.387	0.411	-0.342	0.664	0.430	0.987	0.806	0.778	1

Table 8: Correlation data between Co fractions and other physico-chemical data in Berg Aukas and Tsumeb soils

	CoT	S_T	S^{2-}	F^-	Cl^-	NO_3^-	SO_4^{2-}	*pH*	*Ec*	*F1*	*F2*	*F3*	*F4*
CoT	1												
S_T	0.138	1											
S^{2-}	0.126	1.000	1										
F^-	0.429	-0.531	-0.537	1									
Cl^-	0.296	-0.547	-0.554	0.148	1								
NO_3^-	-0.006	-0.752	-0.752	0.042	0.597	1							
SO_4^{2-}	0.762	-0.464	-0.476	0.640	0.755	0.381	1						
pH	-0.324	-0.619	-0.613	0.404	-0.284	0.444	-0.130	1					
EC	-0.420	0.010	0.012	-0.260	0.373	-0.246	-0.090	-0.543	1				
F1	0.100	0.137	0.137	-0.680	0.284	0.541	-0.028	-0.211	-0.202	1			
F2	0.606	-0.610	-0.620	0.613	0.848	0.491	0.976	-0.069	0.032	-0.027	1		
F3	0.254	0.467	0.466	0.386	-0.767	-0.718	-0.193	0.134	-0.435	-0.590	-0.352	1	
F4	0.217	0.730	0.730	0.096	-0.804	-0.847	-0.342	-0.125	-0.306	-0.424	-0.514	0.944	1

CoT = Total Cobalt
S_T = Total Sulfur

Table 9: Correlation data between Cd fractions and other physico-chemical data in Berg Aukas and Tsumeb soils

	CdT	S_T	S^{2-}	F^-	Cl^-	NO_3^-	SO_4^{2-}	*pH*	*Ec*	*F1*	*F2*	*F3*	*F4*
CdT	1												
S_T	0.459	1											
S^{2-}	0.459	1.000	1										
F^-	0.352	-0.531	-0.537	1									
Cl^-	-0.785	-0.547	-0.554	0.148	1								
NO_3^-	-0.618	-0.752	-0.752	0.042	0.597	1							
SO_4^{2-}	-0.192	-0.464	-0.476	0.640	0.755	0.381	1						
pH	0.201	-0.619	-0.613	0.404	-0.284	0.444	-0.130	1					
EC	-0.578	0.010	0.012	-0.260	0.373	-0.246	-0.090	-0.543	1				
F1	0.992	0.518	0.518	0.281	-0.836	-0.693	-0.290	0.162	-0.495	1			
F2	0.986	0.577	0.577	0.264	-0.799	-0.733	-0.247	0.061	-0.463	0.994	1		
F3	0.906	0.780	0.779	-0.026	-0.791	-0.711	-0.332	-0.122	-0.480	0.918	0.941	1	
F4	0.564	-0.397	-0.399	0.750	-0.202	0.240	0.355	0.716	-0.816	0.472	0.425	0.247	1

CdT = Total Cadmium
S_T = Total Sulfur

Table 10: Correlation data between Cu fractions and other physico-chemical data in Berg Aukas and Tsumeb soils

	CuT	S_T	S^{2-}	F^-	Cl^-	NO_3^-	SO_4^{2-}	*pH*	*Ec*	*F1*	*F2*	*F3*	*F4*
CuT	1												
S_T	0.603	1											
S^{2-}	0.600	1.000	1										
F^-	0.279	-0.531	-0.537	1									
Cl^-	-0.671	-0.547	-0.554	0.148	1								
NO_3^-	-0.666	-0.752	-0.752	0.042	0.597	1							
SO_4^{2-}	-0.076	-0.464	-0.476	0.640	0.755	0.381	1						
pH	-0.047	-0.619	-0.613	0.404	-0.284	0.444	-0.130	1					
EC	-0.534	0.010	0.012	-0.260	0.373	-0.246	-0.090	-0.543	1				
F1	0.947	0.349	0.346	0.553	-0.595	-0.605	0.059	0.128	-0.507	1			
F2	0.989	0.688	0.685	0.149	-0.680	-0.655	-0.128	-0.113	-0.545	0.891	1		
F3	0.862	0.858	0.857	-0.223	-0.673	-0.599	-0.303	-0.269	-0.487	0.655	0.926	1	
F4	0.980	0.463	0.459	0.451	-0.627	-0.654	0.009	0.040	-0.502	0.992	0.940	0.743	1

CuT = Total Copper
S_T = Total Sulfur

Table 11: Correlation data between Pb fractions and other physico-chemical data in Berg Aukas and Tsumeb soils

	PbT	S_T	S^{2-}	F^-	Cl^-	NO_3^-	SO_4^{2-}	*pH*	*Ec*	*F1*	*F2*	*F3*	*F4*
PbT	1												
S_T	0.669	1											
S^{2-}	0.669	1.000	1										
F^-	0.143	-0.531	-0.537	1									
Cl^-	-0.807	-0.547	-0.554	0.148	1								
NO_3^-	-0.723	-0.752	-0.752	0.042	0.597	1							
SO_4^{2-}	-0.285	-0.464	-0.476	0.640	0.755	0.381	1						
pH	-0.009	-0.619	-0.613	0.404	-0.284	0.444	-0.130	1					
EC	-0.492	0.010	0.012	-0.260	0.373	-0.246	-0.090	-0.543	1				
F1	0.995	0.611	0.611	0.210	-0.818	-0.728	-0.281	0.051	-0.479	1			
F2	0.979	0.772	0.771	-0.024	-0.785	-0.690	-0.321	-0.112	-0.504	0.955	1		
F3	0.713	0.907	0.907	-0.499	-0.581	-0.492	-0.399	-0.383	-0.379	0.643	0.839	1	
F4	0.972	0.512	0.512	0.335	-0.785	-0.719	-0.217	0.111	-0.458	0.990	0.905	0.529	1

PbT = Total Lead
S_T = Total Sulfur

Table 12: Correlation data between Mn fractions and other physico-chemical data in Berg Aukas and Tsumeb soils

	MnT	*S_T*	*S^{2-}*	*F^-*	*Cl^-*	*NO_3^-*	*SO_4^{2-}*	*pH*	*Ec*	*F1*	*F2*	*F3*	*F4*
MnT	1												
S_T	0.266	1											
S^{2-}	0.257	1.000	1										
F^-	0.639	-0.531	-0.537	1									
Cl^-	-0.232	-0.547	-0.554	0.148	1								
NO_3^-	-0.443	-0.752	-0.752	0.042	0.597	1							
SO_4^{2-}	0.436	-0.464	-0.476	0.640	0.755	0.381	1						
pH	-0.077	-0.619	-0.613	0.404	-0.284	0.444	-0.130	1					
EC	-0.477	0.010	0.012	-0.260	0.373	-0.246	-0.090	-0.543	1				
F1	0.896	0.732	0.727	0.571	-0.653	-0.606	-0.041	-0.002	-0.596	1			
F2	0.768	-0.118	-0.130	0.744	0.406	-0.150	0.849	-0.277	-0.043	0.391	1		
F3	0.791	0.835	0.834	0.372	-0.785	-0.727	-0.250	-0.006	-0.485	0.974	0.230	1	
F4	-0.099	0.383	0.377	-0.574	0.347	0.253	0.183	-0.573	-0.115	-0.174	-0.034	-0.384	1

MnT = Total Manganese
S_T = Total Sulfur

Table 13: Correlation data between Zn fractions and other physico-chemical data in Berg Aukas and Tsumeb soils

	ZnT	*ST*	*S^{2-}*	*F^-*	*Cl^-*	*NO_3^-*	*SO_4^{2-}*	*pH*	*Ec*	*F1*	*F2*	*F3*	*F4*
ZnT	1												
ST	0.745	1											
S^{2-}	0.745	1.000	1										
F^-	0.023	-0.531	-0.537	1									
Cl^-	-0.805	-0.547	-0.554	0.148	1								
NO_3^-	-0.710	-0.752	-0.752	0.042	0.597	1							
SO_4^{2-}	-0.326	-0.464	-0.476	0.640	0.755	0.381	1						
pH	-0.077	-0.619	-0.613	0.404	-0.284	0.444	-0.130	1					
EC	-0.494	0.010	0.012	-0.260	0.373	-0.246	-0.090	-0.543	1				
F1	0.946	0.610	0.611	-0.013	-0.832	-0.465	-0.367	0.162	-0.714	1			
F2	0.998	0.761	0.761	-0.014	-0.794	-0.686	-0.326	-0.092	-0.512	0.953	1		
F3	0.912	0.889	0.888	-0.328	-0.685	-0.588	-0.382	-0.289	-0.447	0.885	0.932	1	
F4	0.997	0.708	0.708	0.091	-0.805	-0.726	-0.301	-0.048	-0.485	0.934	0.991	0.877	1

ZnT = Total Zinc
S_T = Total Sulfur

Table 14: Correlation matrix between metal concentrations, total sulphur and anions in Berg Aukas tailings

	Cr	*Cd*	*Cu*	*Mn*	*As*	*Fe*	*Al*	*Zn*	*Pb*	*Hg*	S_T
Cr	1										
Cd	0.868	1									
Cu	0.971	0.917	1								
Mn	0.780	0.966	0.852	1							
As	0.934	0.730	0.909	0.575	1						
Fe	0.949	0.795	0.905	0.635	0.978	1					
Al	0.512	0.846	0.644	0.933	0.292	0.354	1				
Zn	0.868	0.549	0.833	0.448	0.919	0.838	0.148	1			
Pb	0.973	0.868	0.988	0.769	0.961	0.948	0.534	0.880	1		
Hg	0.588	0.153	0.452	-0.045	0.763	0.715	-0.382	0.791	0.569	1	
S_T	0.929	0.643	0.853	0.574	0.872	0.847	0.257	0.941	0.869	0.716	1

S_T = Total Sulfur

Table 15: Correlation data between Cd fractions and other physico-chemical data in Berg Aukas tailings

	CdT	S_T	S^{2-}	F^-	Cl^-	NO_3^-	SO_4^{2-}	*pH*	*Ec*	*F1*	*F2*	*F3*	*F4*
CdT	1												
S_T	0.643	1											
S^{2-}	0.12	0.756	1										
F^-	0.024	-0.665	-0.703	1									
Cl^-	0.706	0.654	0.128	-0.081	1								
NO_3^-	0.037	0.254	0.636	-0.321	-0.487	1							
SO_4^{2-}	0.839	0.622	-0.042	-0.175	0.845	-0.373	1						
pH	-0.009	0.647	0.631	-0.995	0.110	0.245	0.234	1					
EC	0.521	-0.169	-0.610	0.349	0.023	-0.093	0.471	-0.289	1				
F1	-0.808	-0.962	-0.559	0.523	-0.758	-0.122	-0.800	-0.526	-0.073	1			
F2	0.712	0.387	0.299	0.135	0.093	0.643	0.233	-0.179	0.407	-0.452	1		
F3	0.72	0.670	0.564	0.024	0.533	0.370	0.349	-0.081	-0.087	-0.671	0.768	1	
F4	0.9	0.647	-0.003	-0.125	0.852	-0.302	0.992	0.174	0.480	-0.826	0.343	0.455	1

CdT = Total Cadmium
S_T = Total Sulfur

Table 16: Correlation data between Cu fractions and other physico-chemical data

	CuT	*S_T*	*S^{2-}*	*F^-*	*Cl^-*	*NO_3^-*	*SO_4^{2-}*	*pH*	*Ec*	*F1*	*F2*	*F3*	*F4*
CuT	1												
S_T	0.853	1											
S^{2-}	0.326	0.756	1										
F^-	-0.307	-0.665	-0.703	1									
Cl^-	0.838	0.654	0.128	-0.081	1								
NO_3^-	-0.041	0.254	0.636	-0.321	-0.487	1							
SO_4^{2-}	0.912	0.622	-0.042	-0.175	0.845	-0.373	1						
pH	0.326	0.647	0.631	-0.995	0.11	0.245	0.234	1					
EC	0.273	-0.169	-0.61	0.349	0.023	-0.093	0.471	-0.289	1				
F1	-0.46	-0.229	0.101	-0.429	-0.812	0.565	-0.471	0.422	0.093	1			
F2	-0.564	-0.557	-0.345	-0.02	-0.845	0.331	-0.438	0.038	0.416	0.888	1		
F3	0.909	0.829	0.479	-0.142	0.754	0.175	0.692	0.121	0.108	-0.553	-0.677	1	
F4	0.92	0.797	0.323	-0.171	0.965	-0.242	0.83	0.181	0.011	-0.737	-0.838	0.894	1

CuT = Total Copper
S_T = Total Sulfur

Table 17: Correlation data between Pb fractions and other physico-chemical data in Berg Aukas tailings

	PbT	*S_T*	*S2-*	*F^-*	*Cl^-*	*NO_3^-*	*SO_4^{2-}*	*pH*	*Ec*	*F1*	*F2*	*F3*	*F4*
PbT	1												
S_T	0.869	1											
S^{2-}	0.358	0.756	1										
F^-	-0.317	-0.665	-0.703	1									
Cl^-	0.899	0.654	0.128	-0.081	1								
NO_3^-	-0.118	0.254	0.636	-0.321	-0.487	1							
SO_4^{2-}	0.899	0.622	-0.042	-0.175	0.845	-0.373	1						
pH	0.334	0.647	0.631	-0.995	0.110	0.245	0.234	1					
EC	0.151	-0.169	-0.61	0.349	0.023	-0.093	0.471	-0.289	1				
F1	0.086	0.126	0.131	0.129	-0.260	0.734	0.035	-0.164	0.554	1			
F2	-0.741	-0.683	-0.46	0.167	-0.865	0.276	-0.493	-0.15	0.448	0.363	1		
F3	0.552	0.584	0.55	0.077	0.388	0.488	0.234	-0.142	-0.049	0.564	-0.524	1	
F4	0.924	0.797	0.344	-0.321	0.966	-0.355	0.805	0.341	-0.129	-0.287	-0.898	0.391	1

PbT = Total Lead
S_T = Total Sulfur

Table 18: Correlation data between Mn fractions and other physico-chemical data in Berg Aukas tailings

	MnT	S_T	S^{2-}	F^{-}	Cl^{-}	NO_3^{-}	SO_4^{2-}	*pH*	*Ec*	*F1*	*F2*	*F3*	*F4*
MnT	1												
S_T	0.574	1											
S^{2-}	0.070	0.756	1										
F^{-}	-0.024	-0.665	-0.703	1									
Cl^{-}	0.531	0.654	0.128	-0.081	1								
NO_3^{-}	0.156	0.254	0.636	-0.321	-0.487	1							
SO_4^{2-}	0.793	0.622	-0.042	-0.175	0.845	-0.373	1						
pH	0.043	0.647	0.631	-0.995	0.110	0.245	0.234	1					
EC	0.666	-0.169	-0.610	0.349	0.023	-0.093	0.471	-0.289	1				
F1	0.721	0.440	0.479	-0.356	-0.994	0.994	-0.864	0.338	0.741	1			
F2	0.351	0.424	0.534	-0.651	-0.334	0.808	0.009	0.626	0.171	0.956	1		
F3	0.999	-0.338	-0.298	0.423	-0.613	0.771	-0.239	-0.441	0.998	0.696	0.455	1	
F4	0.811	0.809	0.327	-0.137	0.883	-0.064	0.845	0.142	0.185	-0.324	0.039	0.454	1

MnT = Total Manganese
S_T = Total Sulfur