

## Contamination of Agricultural Products in the Surrounding of the Tsumeb Smelter Complex

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Since the turn of the last century, the Tsumeb area was a major mining hub until 1999, and still continues to be a smelting centre for ores originating from the Democratic Republic of Congo, Zambia, Mauritania, Bulgaria and Chile. This has brought about a situation where the top soils surrounding the smelter, especially in the down wind direction, are highly contaminated with lead, zinc, copper, arsenic and cadmium. The contamination of the top soils and crops is a result of historical smelter emissions as well as due to windborne dust derived from the tailings and slag dumps of the smelter complex. A total of 43 samples of vegetative material were collected in areas with potential soil contamination in the surroundings of the Tsumeb smelter complex. The samples comprise fruit crops (marula, papaya), vegetable (tomato, parsley, carrot, bean, pumpkin, chillies) and a field crop (maize). Twelve topsoil samples were collected at specific sampling sites for correlation with vegetation samples. The concentrations of arsenic, lead and cadmium of most of the fruits and vegetables (marula fruits, pumpkins, chilli, and tomato) correlate with the heavy metal values of the underlying contaminated top soils. The guideline values of the WHO (Codex Alimentarius) and EU were applied for the interpretation of eventual health risks. All plant samples are characterised by high lead concentrations exceeding the guideline values. Crops from Tsumeb-Nomtsoub and the agricultural land to the west of the smelter show critical contaminations.

### Introduction

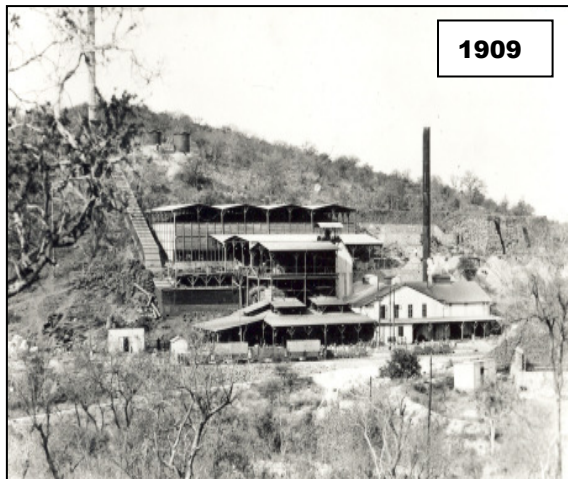
The contamination of the agricultural land in the surroundings of the Tsumeb smelter complex has been well known for many years, though no quantitative data had been available. It can be traced back to emissions from the historical smelter activities as well as to windborne dust derived from the mine tailings and slag dumps in the smelter area.

The Geological Survey of Namibia monitored the environmental situation in Tsumeb in cooperation with the Czech Geological Survey (Kříbek and Kamona, 2005) and the University of Namibia in the past few years. This research has now revealed the exact extent and severity of soil contamination in the Tsumeb area (Geological Survey of Namibia, 2006a; 2006b; 2007a; 2007b; Iipinge, 2008). The previous research included groundwater quality, soil contamination, quality of fresh water fish and to a limited extent the contamination of grasses on surrounding farms.

For this study, a plant sampling campaign assisted by students from the Department of Geology at the University of Namibia (UNAM) was carried out in the Tsumeb area. The following metals were analysed: arsenic, cadmium, copper, lead, molybdenum and zinc.

Soil is a crucial component of rural and urban environments in a setting such as Tsumeb, as it forms the basis for crop cultivation and grazing of domestic animals. Heavy metals occur naturally in soils but rarely at toxic levels. In the case of Tsumeb, critical soil contamination with a number of metals has been caused by mining and processing of poly-metallic ores over a period of more than 100 years. Heavy metals have a deleterious effect on bacteria which are key players in nutrient turnovers in soil (Gremion, 2003). Due to the prevailing carbonate lithologies, the soils in the Tsumeb area have high a pH which is generally reducing the metal uptake of the plants (USDA-NRCS, 2000).

The study had two objectives: (i) The investigation of bioaccumulation of heavy metals in fruits and crops, and (ii) the determination of the specific contaminant uptake by various crops. In the absence of Namibia's own Minimum Risk Levels (MRLs), the UN Food and Agricultural Organisation (FAO)/World Health Organisation (WHO)



guidelines were used to evaluate crop contamination, together with German and Canadian guidelines for soil contamination.

### History

Construction of a first smelter at Tsumeb started in 1906. This first smelter comprised two lead-copper blast furnaces with a cast iron water jacket, and the initial ignition of the first furnace took place in September 1907.

In the beginning, the smelter was not operating continuously, and also at a deficit. The reasons for this deficit were the enormous costs for first-class coke imported



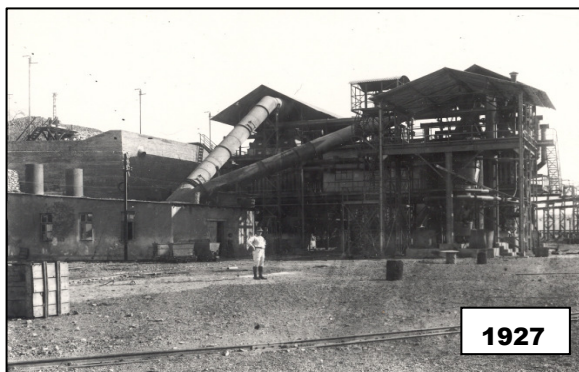
from Germany, and for the additives, e.g. galena, which had to be mixed into the oxide ores, and which were imported from Norway. However, during World War I, when coke was imported from South Africa, and iron ore for flux was found near Kalkfeld close to the railway linking Tsumeb with the coast, the smelter became profitable. In 1923, a third blast furnace was added, and in 1924 one of the old furnaces was enlarged. In 1925, an electric Cottrell precipitator and a Dwight-Lloyd sinter plant for the recovery of cadmium and lead in flue dust in the off-gases were installed. This increased the lead production by 1 000 t annually. 1928 saw the enlargement of the third blast furnace, and the addition of a small rotary furnace as well as an oil-fired furnace for the smelting of lead bearing waste. Finally, in 1931, following the acquisition of a small reverberatory furnace to roast the cadmium-bearing flue dust, the first cadmium was produced (Schneider, 1992a). Due to the worldwide



recession of the 1930ies with its associated low metal prices, the smelter came to a standstill, and remained inactive throughout World War II.

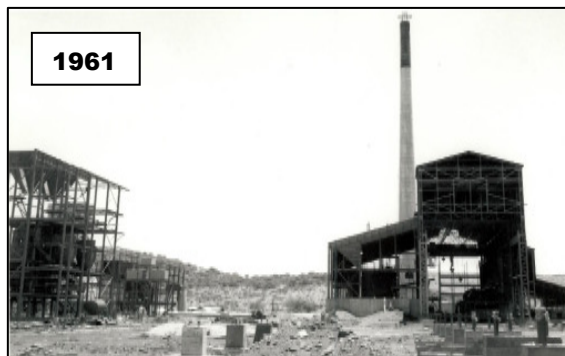
The smelting process at the first smelter at Tsumeb comprised the following steps: The dolomitic run-off-mine ore was stored in heaps of 8 000 t each, from where it was transferred by hand into charging trolleys with a capacity of 3 500 kg. After being mixed with aplite from the mine as silica flux, and hematite from Kalkfeld as iron flux, and after 12-13% of coke were added, the blast furnaces were charged with the material. Air was supplied to the furnaces with

their open throats by 5 rotary piston compressors. After tapping the molten charge flew out onto a settler furnace made from clay. During this process, lead and copper settled according to their specific gravity at the bottom, and the slag, which still contained 0.3% copper and 1.5% lead, remained on top. Once the settler furnace was full, it was also tapped, the copper was allowed to flow onto an iron tray for cooling and was subsequently crushed. The lead was collected in a container, from where it was transferred into forms to solidify. Lead and copper were then exported to Europe without any further value addition. The slag was removed for deposition as waste, but sometimes it was also crushed and used locally as aggregate for concrete (Bürg, 1942). The

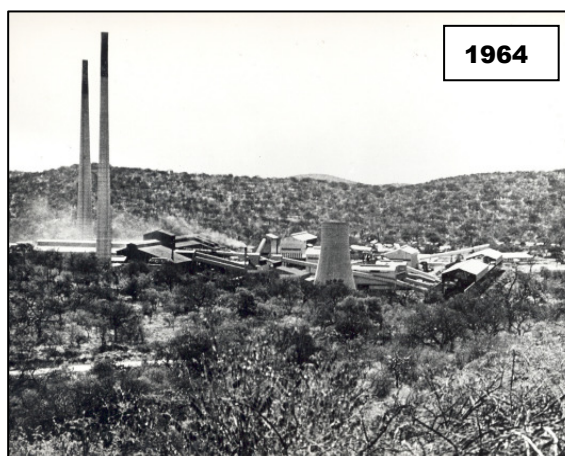


Tsumeb ores have always been very complex ores, containing a variety of accessory metals such as silver, arsenic, antimony, cadmium, cobalt, germanium, gallium, mercury, molybdenum, nickel, tin, tungsten and vanadium, some of which are highly toxic. Apart from cadmium, there was no effort made during the period of operation of the first smelter to recover other metals. During the smelting process, some of these metals went into the smelter products, and some into the slag, but others reached the environment via the smelter stack. All silver and nickel, stayed with the copper, while 100% of the germanium, gallium, tungsten and vanadium, 95% of the cobalt, and 30% of the tin were retained by the slag. However, only 50% of the molybdenum, 20% of the arsenic and the antimony, and 10% of the tin went with the copper, leaving 5% of the cobalt, 60% of the tin, 50% of the molybdenum, 80% of the ar-

senic and antimony, and an alarming 100% of the mercury to enter the atmosphere (pers. comm. H Nolte, September 2013).



During the 1950ies, the Tsumeb concentrates were smelted and refined at a smelter in the USA. However, the ever-increasing transportation costs made it necessary to erect a new and larger smelter in Tsumeb between 1960 and 1962 (Schneider & Seeger, 1992). This smelter was built as an identical copy of the smelter used in the USA. It was commissioned in 1963, and featured integrated copper and lead sections, the latter with an associated lead refinery with an annual capacity of 90 000 tons. The copper section consisted of a reverberatory furnace with waste heat boiler, two converters, a holding furnace, a casting machine and a bag house. Modern filters were placed in the stacks and all areas where pollutants could reach the environment. Production started officially in March 1964, and at that stage the smelter produced more than 3 500 tons of blister copper and 6 000 tons of lead per month (Namibia Custom Smelters, 2013).



The smelter also featured an integrated arsenic plant consisting of four Godfrey roasters



with condensing kitchens and a common bag house, which produced 99% pure arsenic trioxide (Schneider & Genis, 1992).

Also in 1960, a separate germanium reduction plant was introduced. The tailings of the bulk-sulphide flotation circuit were treated with a magnetic separator to recover germanium concentrate. Germanium dioxide was produced from this germanium concentrate in the germanium reduction plant by complex leaching, evaporation, distillation and hydrolysis (Schneider, 1992b).

In 1965, an on-line cadmium plant was commissioned. It consisted of leaching, purification, precipitation, filtering, cementation, melting, refining and casting facilities and produced refined cadmium metal of 99.7% purity (Schneider, 1992a).

In 1986, the production of sodium antimonate was introduced. Antimony concentrates together with arsenic within the copper circuit in the Pierce-Smith converter in the dust which is subsequently fed, via the bag house and the arsenic plant into the lead circuit of the smelter. From the lead refinery, the antimony compounds, together with the arsenic go into the Wet Harris Plant, where they are reduced. The resulting native antimony is then treated with soda to remove impurities (Schneider, 1992c). Nevertheless, by the late 1970s, the modern filters that were installed when the smelter was built in the early 1960s, had become old and not



enough investment took place to replace them and to keep the smelter in an environmentally friendly condition. This state of affairs persisted up until the 1990s (pers. comm. H Nolte, September 2013).

Over the years, production had declined considerably, and by 1988 the annual output was some 13 000 tons of blister copper and 9 000 tons of lead only. In 1992, the lead section was closed. But in 1996, a new lead smelting furnace was built and commissioned. Based on Top Submerged Lance (TSL) technology, the Ausmelt TSL Process is an efficient, environmentally friendly and highly flexible pyro-metallurgical process for treating a wide range of feed materials. The process is based on injecting air, oxygen



and fuel directly into the molten slag bath via a vertically suspended lance. Critical process phenomena, such as feed material dissolution, energy transfer, reaction and primary combustion, take place in the intensely agitated slag layer ([www.outotech.com](http://www.outotech.com)).

But then, and due to industrial action, the smelter was out of operation between 1996 and 2000. From 2000 to 2008, only the copper section of the smelter was operational, while the arsenic plant was run on a small scale. When the Namibian copper mining operations came to a standstill due to the world economic crisis in 2008, a decision was taken to divert to custom smelting, which was realised at the beginning of 2009.

However, the original lead smelting Ausmelt furnace had been refurbished to smelt copper concentrates and was re-

commissioned in 2008. The furnace is now charged with copper concentrates and various fluxes and fuelled with locally produced charcoal and heavy furnace oil. The iron and sulphur in the feed is utilised as the main energy source for smelting the concentrates. Oxygen enriched air is used for combustion. The molten material from the Ausmelt is tapped from tap holes and introduced to the reverberatory furnace –for holding and slag cleaning or alternatively slag is granulated while matte from the TSL can go directly to the converters. Molten matte tapped from the reverberatory furnace is transferred to the Pierce Smith converters for the production of blister copper. Air is blown into the matte and the oxygen reacts with sulphur, iron, lead and zinc. The sulphur from the metal sulphides provides the energy to complete the conversion of matte to blister copper. The blister copper (98.5 % Cu) is cast into 1.62 t bars for shipment to refiner-

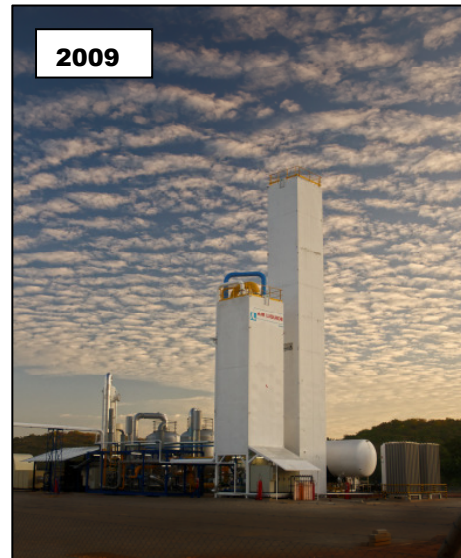


ies.

The granulated slag goes to the Slag Milling Plant for processing. Off-gases from the Ausmelt pass through a spray cooling system to cool it down to 120°C before entering the bag house where dust is separated from gas before the cleaned gas is released to the atmosphere via a second stack. Dust recovered at the bag house is taken to the arsenic plant for processing.

Until recently, the smelter complex consisted of two primary smelting furnaces, namely the old reverberatory furnace and the refurbished Ausmelt furnace; three Pierce–Smith converter furnaces, bag houses and cooling towers, the arsenic treatment plant, and a slag milling plant. The Tsumeb smelter

is one of only five commercial-scale smelters in Africa, and one of only few in the world that are able to treat arsenic- and lead-bearing copper concentrates and other polymetallic ores. An oxygen plant was commissioned in 2012, and programmes to improve emissions control, such as the reduction of dust emissions from the converter furnaces, increase of baghouse capacity, upgrading of

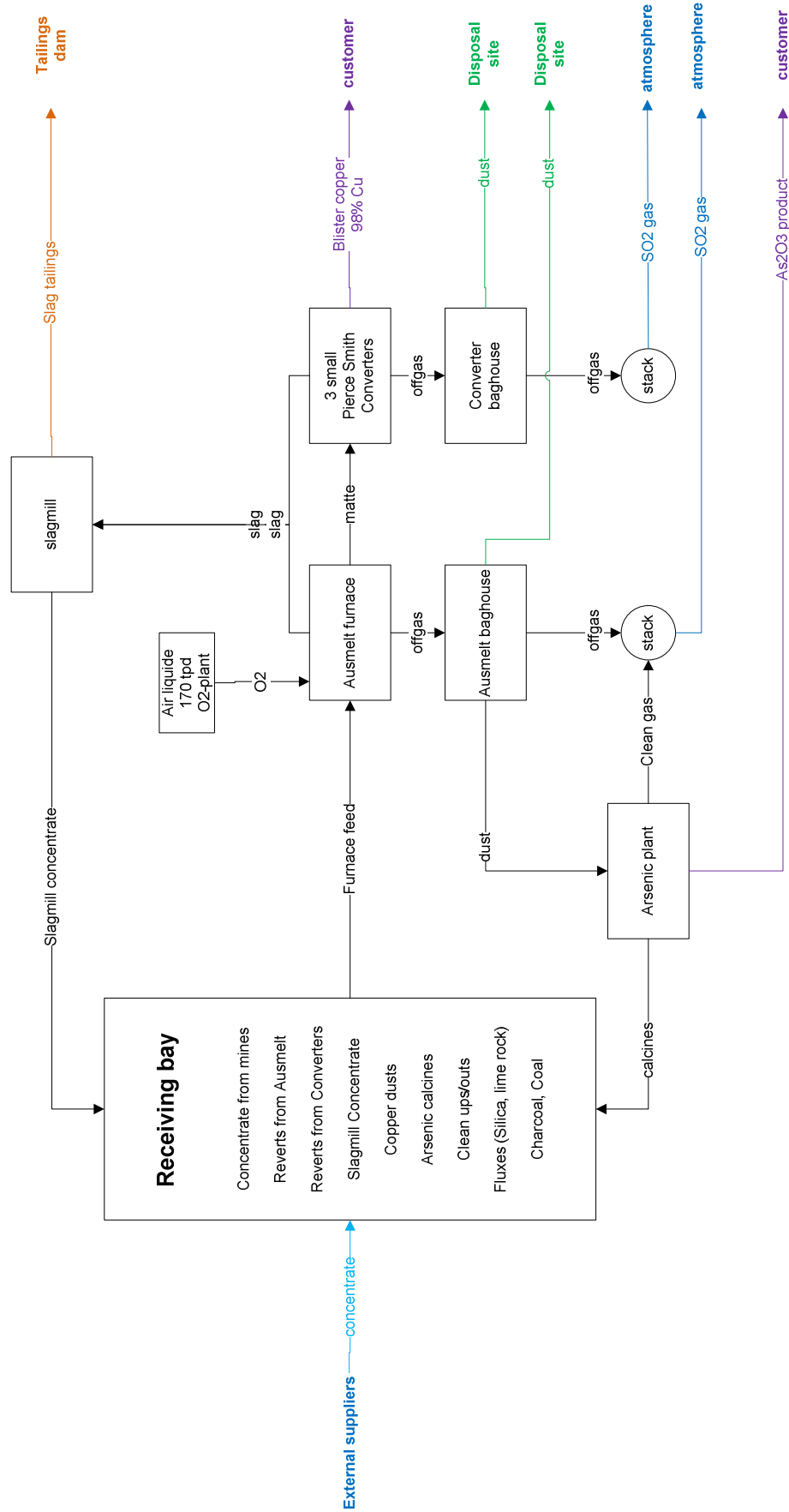


fume extraction systems, and a new extraction system at the arsenic plant are ongoing ([www.dundee-precious.com](http://www.dundee-precious.com)).

In August 2013, the old reverberatory furnace was shut down completely because of its poor compliance to the improved environmental conditions. It will not be started up again, and thus the Ausmelt has become the only smelting furnace. An acid plant to



capture the SO<sub>2</sub> emissions is currently under construction and will be commissioned towards the end of 2014 (pers. comm. H Nolte, September 2013).





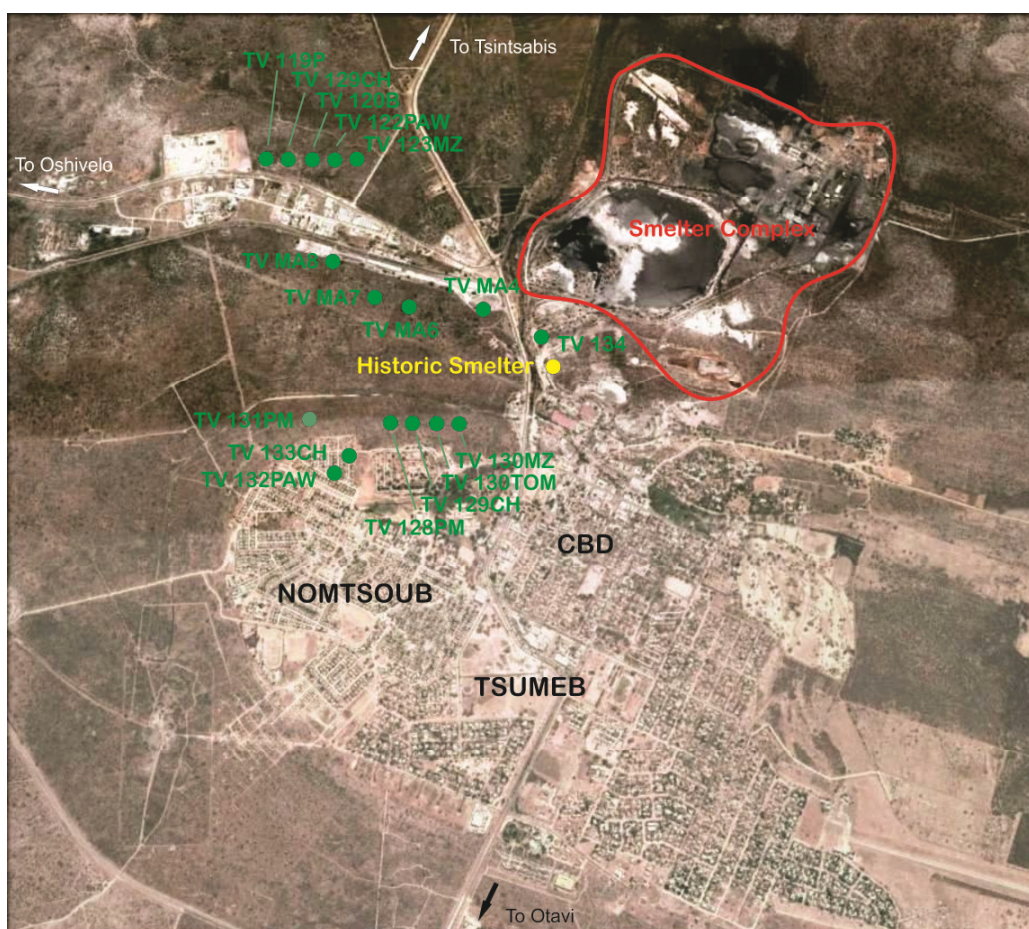


### Plant sampling and analysis

A total of 43 plant samples were collected (Fig. 1) comprising of field crops (pumpkin – *Cucurbita sp.*, (Fig. 2a); maize – *Zea mays* (Fig. 2b)); fruit crops (marula – *Sclerocarya birrea* (Fig. 3); papaya – *Carica papaya* (Fig. 4a); chilli pepper – *Capsicum sp* (Fig. 4b)); vegetables (tomato – *Solanum lycopersicum*, parsley – *Petroselinum crispum*(Fig. 5a); bean – genus *Fabaceae*; and carrot – *Daucus carota* (Fig. 5b)). Most of the vegetable and fruit samples were taken from commercial farms 1 to 1.5 km to the west of the smelter complex as well as private plantations in gardens between 0.3 and 1.5 km to the southwest of the historical smelter, in the Nomtsoub township of Tsumeb (Fig. 1). Marula fruits (Fig. 3), indigenous to the area, were also collected at distances between 200 m and 600 m from the fence of the smelter complex.

### Sampling and Analytical Methods

There are several sampling methods available to analyze heavy metals in soil samples. In this study, *x-ray fluorescence spectroscopy* (XRF) was used to quantify the contamination of the soil samples. The vegetative samples were analysed by *inductively coupled plasma-mass spectroscopy* (ICP-AES).



**Figure 1:** Plant sample locations marked by green points, Tsumeb, north-central Namibia (image Google Earth)

Two types of samples were collected from each sampling point, one plant sample was cleaned with distilled water while the other sample was not cleaned in order to investigate the eventual effect of superficial adsorption of dust. All samples were air dried.

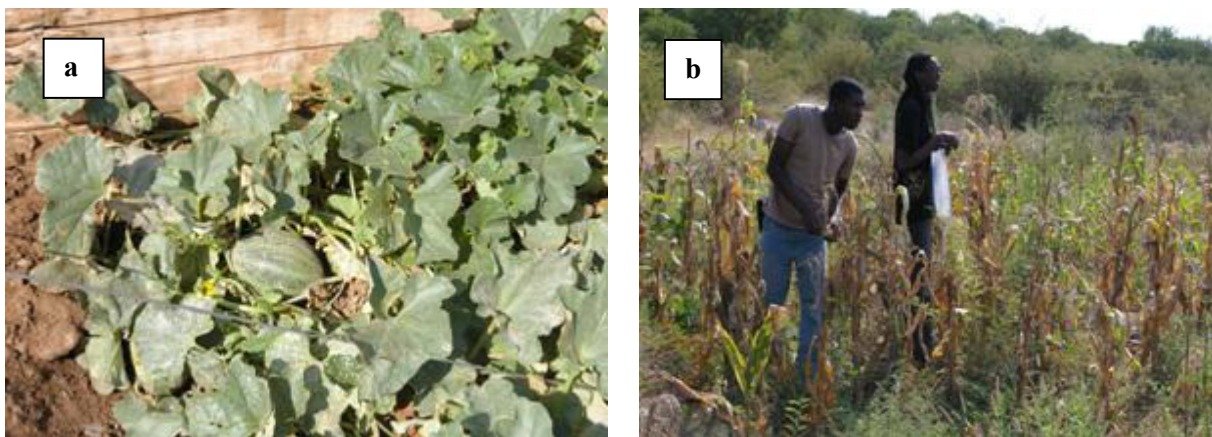
The analyses of the vegetative material were performed by the Institute for Soil, Climate and Water in Pretoria, South Africa. Acid digestion of the material was applied. All samples were analysed for each element in duplicate, and mean values were calculated.

### Soil Sampling and Analysis

The collection of the 12 soil samples was confined to the topsoil. Vegetation (leaves, branches) from sampling plots was removed and the upper three centimetres of the soil profile were taken. The <2 mm and <0.18 mm fractions of each homogenised soil sample were collected by sieving at each site. Previous studies showed a trend of only

slight enrichment of arsenic, copper, lead, cadmium and zinc in the fine fraction compared to the coarser fraction (Geological Survey of Namibia, 2006b). Therefore, the <0.18 mm fraction was chosen as representative soil sample and used for analysis. The <2 mm fraction was taken to the Geological Survey of Namibia for analysis.

The semi-quantitative analysis of the soil samples took place onsite with a portable x-ray fluorescence (XRF) spectrometer XLt 700 Series Environmental Analyzer Version 4.2 of NITON Corporation, USA. The instrument is pre-calibrated by the manufacturer and the measurements taken were compared with readings from international standard samples (NIST 2709, NIST 2710, and RCRA). The detection limits vary between 10 and 30 mg/kg for the different elements. The confidence intervals (2 sigma; 95 %) depend on the measuring time, and typically range from  $\pm 5$  to  $\pm 50\%$ , using a measuring time of 60 seconds. Extended periods of measuring for 120 seconds to 180 seconds lower the range drastically to acceptable levels of 5-25%.

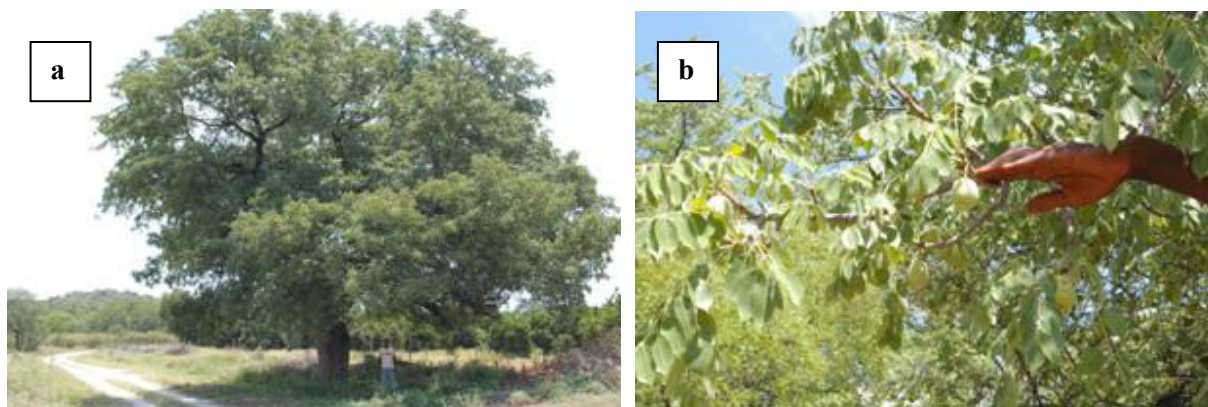


**Figure 2:** (a) Pumpkin (sample TV-131PM); and (b) maize (sample TV-130MZ) in gardens of Tsumeb - Nomsoub, north of Rand Street

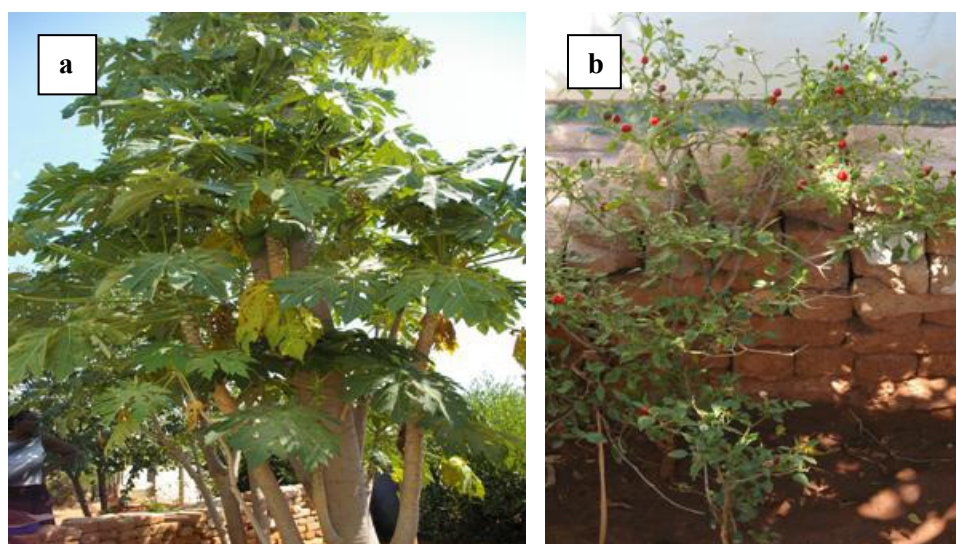
For standard analysis, about 100 g of the <0.18 mm fraction of each sample were used. The samples were placed into plastic bags and analysed in direct contact with the shutter window of the XRF. The samples were analysed for 60 seconds.

For the purpose of quality control, the soil samples were analysed in parallel at Analytical Laboratory Services in Windhoek applying inductively coupled plasma mass spectrometry (ICP). The reference method was EPA3050B (Environmental Protection Agency).

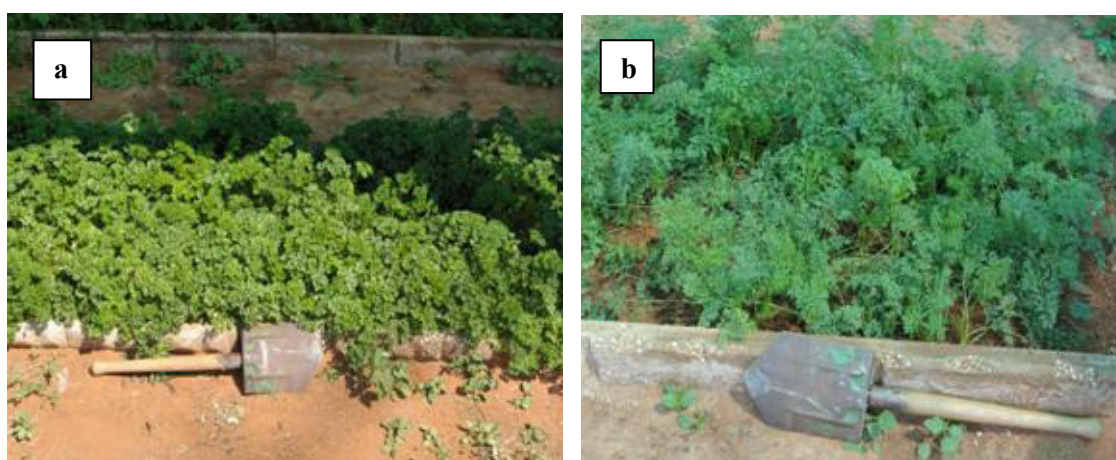




**Figure 3:** (a) Marula tree (person for scale under the tree); and (b) fruit, from the northern part of the Tsumeb town (hand for scale)



**Figure 4:** (a) Papaya fruit tree (TV-132PAW); and (b) chilli plants (TV-133CH), grown in the Nomtsoub township to the west of the smelter complex



**Figure 5:** (a) Parsley plants (TV-119P); and (b) carrots (TV-120C) in a vegetable green house bed of the farm to the west of the smelter

### Results of the Soil Survey

When comparing the ICP analysis of the top soils with the XRF spectrometer measurements, it becomes obvious that low to moderate concentrations of the heavy metals show an acceptable correlation. However,

discrepancies between the two analytical methods exist with respect to the higher concentrations (Table 1). The data in Table 1 suggests that the portable XRF Niton XLt 700 version 4.2 series is sufficiently reliable. The matrix effect appears to be the main factor for major discrepancies.

Sample No	As mg/kg ICP	As* mg/kg	Cd mg/kg ICP	Cd* mg/kg	Cu mg/kg ICP	Cu* mg/kg	Pb mg/kg ICP	Pb* mg/kg	Zn mg/kg ICP	Zn* mg/kg	Mo mg/kg ICP
TSV-119	34	30	3		111	111	260	240	221	238	2
TSV-120	26	21	2		77	75	173	153	151	139	1
TSV-122	68	88	7		232	246	458	431	437	419	2
TSV-123	63	49	5		159	143	320	340	368	239	3
TSV-124	204	169	39		615	544	1090	1226	1580	858	4
TSV-125	849	929	224	214	2500	3308	3020	7315	6420	3231	23
TSV-126	307	192	49		531	457	831	1356	1520	606	6
TSV-127	393	366	63	28	915	1042	1190	2327	2300	1130	9
TSV-128	57	61	11		170	188	269	363	394	248	1
TSV-130	47	46	7		168	162	249	333	425	235	1
TSV-131	47	51	10		125	158	131	495	413	164	1
TSV-132	19	25	2		56	55	100	102	101	109	<1

- Portable XRF spectrometer

**Table 1:** Heavy metal concentrations of topsoil samples (180 µm fraction) of the Tsumeb area: Comparison between ICP values (Shaded) and semi-quantitative XRF spectrometer values

The evaluation of the hazardous potential of the top soils with respect to heavy metal contamination is based on German (Eikmann and Kloke, 1993) and Canadian (Canadian Environmental Council of Ministers of the Environment, 1999) guideline values for agricultural land use and gardening. These guidelines give the maximum allowable levels for toxic metals in soils and have been applied in this study (Table 2).

The majority of the topsoil samples revealed critical heavy metal contamination (Table 2). Concerning the strict Canadian

guideline values, none of the investigated soils is suitable for agricultural land use. The top soils at the old railway station and to the west of it showed very high values for arsenic, cadmium, lead, copper and zinc, exceeding both, Canadian and German guideline values by far. The severe contamination in that area most probably traces back to metal-rich emissions derived from the historical smelter.

Arsenic ranges from 19-849mg/kg, thus some samples are below the German (50mg/kg) but still above the Canadian

guideline values (12mg/kg). Cadmium ranges from 2-224mg/kg, 67% of the soil samples are below the German guideline of 20mg/kg, while all are still above the Canadian guideline of 1.2mg/kg. Copper ranges from 56-2500mg/kg, 92% of the samples are below the German (1000mg/kg) guidelines, while 92% are above the Canadian guideline values of 63mg/kg. Lead values range from 100-3020mg/kg, whereby 25% are above German guideline values of 1000mg/kg, and 100% of samples are above the Canadian guideline of 70mg/kg. Zinc ranges from 101 to the extreme of 6420mg/kg and 33% of the samples are below the German guideline values of 600mg/kg, and 17% are below the Canadian value of 200mg/kg. In highly contaminated soils, the elements showed a trend with arsenic being widely distributed.

Garden soils from houses of the suburb of Tsumeb-Nomtsoub Extension 1 indicated elevated concentrations of the elements of concern but most values are slightly below the German guideline value. The agricultural land to the west and downwind of the Tsumeb smelter complex is in parts critically contaminated by arsenic and copper (Table 2).

### Results of Plant Analysis

For interpretation purposes the guideline values of the WHO (Codex Alimentarius) and EU were applied (Table 3A).

All plant samples showed *lead* contaminations exceeding the EU and WHO guideline values of 0.3 and 0.4 mg/kg, respectively. The highest concentrations were found in parsley and carrots exceeding the WHO guideline value by up to almost 20 times for the un-cleaned vegetable. Proper washing of vegetables before preparation leads to a significant decrease of the contamination by approximately 50%. It showed that lead adhered more than the other elements to the surface of those crops and also that its chemical adsorption was high. However, both types of vegetable still exceed the WHO guideline value by roughly 7 times after cleaning with distilled water (Table

3B). Absorption of lead from soil is less than from lead dissolved in aqueous solutions. If ingested together with meals, absorption decreases (26% fasted; 2.5% when ingested with a meal) (ATSDR, 2005). In the Tsumeb area another major source of lead ingestion is through wind that has a high volume of suspended particles (Laidlaw and Filippelli, 2008).

The flesh of the marula samples ("cleaned samples") exceeds the WHO guideline value in all cases by 50% to 200% (Table 3B). Maize, beans and paw-paws are the least contaminated crops concerning lead in comparison to chilli, pumpkin and carrot. However, the lead concentrations in the cleaned samples still exceed the WHO guideline value in most cases.

The highest concentrations of cadmium were found in chilli, pumpkin and carrots, and are exceeding the EU guideline (0.2 mg/kg) value by four to six times. In contrast, maize and paw-paw samples contain cadmium in very low quantities far below the EU guideline value. Marula fruits are not critically contaminated with cadmium, except for one sample taken a few metres directly opposite of the historical smelter.

Parsley, carrots and pumpkin samples are significantly high in arsenic values (Table 3A). The washed vegetable samples exceeded the WHO guideline value of 0.5 mg/kg by two to four times (Table 3B). In contrast arsenic concentrations of maize, beans, chilli, and tomatoes are below the WHO guideline values. All analyses for maize are below the detection limit of the ICP-MS (<0.1 mg/kg). The arsenic concentrations in paw-paw and marula vary between 0.3 and 1.1 mg/kg, and, thus, exceed the guideline value only moderately.

None of the analysed plant samples show critical contamination in copper as they contained below 20mg/kg and zinc values were found to be below 50mg/kg though the soil was heavily contaminated.

The relative uptake of arsenic, lead and cadmium from the soil into the plant is shown by soil-plant transfer coefficients



Sample No.	Description	Latitude	Longitude	As mg/kg	Cd mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg
TS V119t	Farm west of smelter	-19.20389	17.70638	34	3	111	260	221
TS V120t	Farm west of smelter	-19.20389	17.70638	26	2	77	173	151
TS V122t	Farm west of smelter	-19.20389	17.70638	68	7	232	458	437
TS V123t	Farm west of smelter	-19.20673	17.70670	63	5	159	320	368
TS V124t	Old railway station, garden	-19.23484	17.70846	204	39	615	1090	1580
TS V125t	West of old railway stat.	-19.23485	17.70639	849	224	2500	3020	6420
TS V126t	West of old railway stat.	-19.23368	17.70337	307	49	531	831	1520
TS V127t	West of old railway stat.	-19.23173	17.70379	393	63	915	1190	2300
TS V128t	Nomtsoub	-19.24031	17.70393	57	11	170	269	394
TS V130t	Nomtsoub	-19.24031	17.70213	47	7	168	249	425
TS V131t	Nomtsoub	-19.24016	17.69930	47	10	125	131	413
TS V132t	Nomtsoub	-19.24169	17.69968	19	2	56	100	101
<b>Eikmann-Kloke Values for Soil Contamination, 1993 (“German guideline values”)</b>								
BW III = “Soil Values III” point to human-, phyto-, zoo-, ecotoxicological risks: remediation required								
				<b>As mg/kg</b>	<b>Cd mg/kg</b>	<b>Cu mg/kg</b>	<b>Pb mg/kg</b>	<b>Zn mg/kg</b>
BW III	Agriculture, gardening, crops, fruits			50	20	200	1000	600
BW III	Multifunction soils (parks, recreation)			80	50	600	2000	3000
BW III	Multifunction soils (industry)			200	60	2000	2000	3000
<b>Germany – Soil Protection Law, 1999</b>								
Test values for the soil – human pathway (direct contact)								
Playground for children				25	10		200	
Residential areas (including house gardens)				50	20		400	
<b>Canada – Soil Quality Guidelines for the Protection of Environmental and Human Health, 1999</b>								
Agriculture				12	1.2	63	70	200
Residential				12	1.2	63	140	200
Commercial				12		91	260	360
Industrial				12		91	600	360

**Table 2:** Analytical results of the top soils and evaluation concerning the German (red) and Canadian (yellow) guideline value for agriculture, gardening, crops and fruits

Sample No.	Crop/ Topsoil	Zn mg/kg	Cu mg/kg	As mg/kg	Cd mg/kg	Pb mg/kg	Mo mg/kg
WHO Guidelines		50	20	0.5	-	0.4	-
EU Guidelines		50	20	-	0.20	0.3	-
TV-MA4 uncleaned	Marula fruit	17	10	0.9	0.37	2.7	0.5
TV-MA4 cleaned	Marula fruit	16	9	0.8	0.33	2.3	0.5
TSOS-114t	Topsoil	3279	2899	658.0	67.00	6471.0	---
TV-MA6 uncleaned	Marula fruit	19	6	1.1	0.13	2.2	0.6
TV-MA6 cleaned	Marula fruit	12	6	0.6	0.13	2.1	0.6
TSV-125t	Topsoil	6420	2500	849.0	224.00	3020.0	23.0
TV-MA7 uncleaned	Marula fruit	15	7	0.9	0.08	1.2	0.5
TV-MA7 cleaned	Marula fruit	14	6	0.8	0.10	0.9	0.5
TSV-126t	Topsoil	1520	531	307.0	49.00	831.0	6.0
TV-MA8 uncleaned	Marula fruit	13	8	1.2	0.08	2.7	0.4
TV-MA8 cleaned	Marula fruit	18	8	1.1	0.08	1.9	0.5
TSV-127t	Topsoil	2300	915	393.0	63.00	1190.0	9.0
TV-128PM uncleaned	Pumpkin	28	10	0.6	0.38	0.7	1.6
TV-128PM cleaned	Pumpkin	33	11	0.6	0.42	1.0	1.5
TV-129CH uncleaned	Chilli	21	9	0.2	1.21	0.8	1.0
TV-129CH cleaned	Chilli	16	8	0.1	1.31	0.7	0.8
TS-128t	Topsoil	394	170	57.0	11.00	269.0	1.0
TV-130TOM unclean.	Tomato	47	13	0.3	0.66	1.1	2.5
TV-130TOM cleaned	Tomato	45	14	0.2	0.58	0.6	2.3
TS-130t	Topsoil	425	168	47.0	7.00	249.0	1.0
TV-131PM unclean.	Pumpkin	46	12	1.1	0.75	2.0	0.5
TV-131PM cleaned	Pumpkin	44	11	1.2	0.80	1.5	0.5
TS-131t	Topsoil	413	125	47.0	10.00	131.0	1.0

**Table 3A: Selected** analysis for crops with heavy metal concentrations exceeding WHO and EU guidelines for agricultural plants (shaded) and associated top soils exceeding the German guideline values

(Tables 4 and 5). The metal distribution, in general, decreases from root to stem and leaf to edible parts (Adriano, 2001). Our study also shows that toxic elements are virtually excluded from the seed parts of the plant, as is shown by the maize sample.

The relative plant uptake for *lead* is very low. The lead concentration in the crops is between 0.15% and 2% of the lead concentration of the soil in which the crop grows. The higher value for *carrots* confirms

that lead primarily accumulates in the roots and is less trans-located to other parts of the plant as was found by Adriano (2001). Stem vegetables like *maize*, *beans* and *tomatoes* are less prone to lead contamination through the soil-plant pathway.

The coefficients for *cadmium* are significantly higher than those for lead which is supported by several other studies on the mobility of cadmium (Ramos et al., 2002; Smolders, 2001). The highest relative cad-

Sample No.	Crop	Zn mg/kg	Cu mg/kg	As mg/kg	Cd mg/kg	Pb mg/kg	Mo mg/kg
WHO Guidelines		50	20	0.5	-	0.4	-
EU Guidelines		50	20	-	0.2	0.3	-
TV-MA1 uncleaned	Marula fruit	12.2	7.40	0.47	0.03	1.45	0.20
TV-MA1 cleaned	Marula fruit	16.5	7.30	0.34	0.03	0.67	0.12
TV-MA2 uncleaned	Marula fruit	11.2	4.32	0.50	0.04	1.33	0.22
TV-MA2 cleaned	Marula fruit	13.0	4.37	0.61	0.06	0.84	0.23
TV-MA3 uncleaned	Marula fruit	12.4	7.42	0.80	0.06	1.28	0.71
TV-MA3 cleaned	Marula fruit	10.3	5.96	0.76	0.06	1.10	0.65
TV-MA4 uncleaned	Marula fruit	16.8	9.52	0.92	0.37	2.42	0.52
TV-MA4 cleaned	Marula fruit	15.8	8.50	0.77	0.33	2.25	0.51
TV-MA5 uncleaned	Marula fruit	10.1	3.55	0.54	0.05	0.67	0.17
TV-MA5 cleaned	Marula fruit	13.0	4.58	0.53	0.15	0.73	0.26
TV-MA6 uncleaned	Marula fruit	18.6	6.35	1.09	0.13	2.20	0.57
TV-MA6 cleaned	Marula fruit	11.5	5.62	0.58	0.13	2.05	0.56
TV-MA7 uncleaned	Marula fruit	14.6	6.80	0.91	0.08	1.20	0.47
TV-MA7 cleaned	Marula fruit	13.8	6.45	0.75	0.10	0.94	0.50
TV-MA8 uncleaned	Marula fruit	13.0	8.15	1.19	0.08	2.66	0.36
TV-MA8 cleaned	Marula fruit	17.5	8.25	1.13	0.08	1.94	0.47
TV-119P uncleaned	Parsley	34.0	14.61	3.9	0.66	5.50	10.41
TV-119P cleaned	Parsley	31.1	10.14	2.1	0.44	2.67	9.48
TV-120C uncleaned	Carrot	29.4	7.81	1.70	0.71	7.51	1.25
TV-120C cleaned	Carrot	28.1	6.85	1.21	0.96	2.96	4.33
TV-120BS uncleaned	Bean seeds	24.1	9.08	0.12	0.18	0.33	2.51
TV-120B uncleaned	Bean skin	11.0	6.83	0.20	0.16	0.52	1.54
TV-120B cleaned	Bean skin	13.8	6.60	0.25	0.16	0.52	1.56
TV-122PAW unclean.	Pawpaw	18.0	4.77	0.94	0.06	2.35	2.21
TV-122PAW cleaned	Pawpaw	16.4	3.45	0.59	0.04	0.86	1.98
TV-123MZ uncleaned	Maize	31.2	2.78	<0.1	0.03	0.38	0.94
TV-123MZ cleaned	Maize	30.9	3.20	<0.1	0.03	0.40	0.93
TV-128PM uncleaned	Pumpkin	27.9	10.47	0.62	0.38	0.73	1.55
TV-128PM cleaned	Pumpkin	32.8	10.91	0.62	0.42	0.97	1.52
TV-129CH uncleaned	Chilli	20.5	8.84	0.19	1.21	0.84	1.01
TV-129CH cleaned	Chilli	16.4	7.54	0.13	1.31	0.69	0.79
TV-130MZ uncleaned	Maize	40.1	3.44	<0.1	0.04	0.49	1.01
TV-130MZ cleaned	Maize	37.7	3.68	<0.1	0.04	0.50	1.02
TV-130TOM uncleaned	Tomato	46.6	13.36	0.34	0.66	1.10	2.45
TV-130TOM cleaned	Tomato	44.9	13.78	0.16	0.58	0.62	2.26
TV-131PM uncleaned	Pumpkin	46.3	12.30	1.10	0.75	2.00	0.53
TV-131PM cleaned	Pumpkin	44.0	11.04	1.17	0.80	1.46	0.54
TV-132PAW uncleaned	Pawpaw	15.8	2.75	0.63	0.08	0.66	2.39
TV-132PAW cleaned	Pawpaw	18.0	2.80	0.55	0.07	0.73	1.95
TV-133CH uncleaned	Chilli	29.6	15.80	0.27	0.85	1.15	1.10
TV-133CH cleaned	Chilli	26.9	14.50	0.21	0.89	0.71	1.12
TV-134 cleaned	Ximenia Am.	10.3	5.80	0.64	0.28	0.98	1.40
TV-135MZ uncleaned	Maize	33.5	2.48	<0.1	0.03	0.61	0.80

Table 3B: Analytical results of uncleaned and cleaned vegetative material (Shaded: results exceeding guidelines)



mium uptake was found in *carrots*, *chilli* and *parsley* (Table 4). Following its uptake by the roots, cadmium translocation is rather limited throughout the plant. Cadmium uptake is influenced by the presence of zinc in soils and chloride salinity (Smolders, 2001). Cadmium distribution is very limited in cereal grains like *maize* and fruits of trees like *paw-paw* and *marula*. In areas where manganese is present in soils, as is the case in most

tropical soils, the presence of Cd inhibits its uptake (Ramos *et al.*, 2002).

The coefficients for arsenic reveal a generally low degree of contaminant uptake by the plants (Table 4). Stem crops (maize, chilli, tomato, beans) and fruit trees (marula, paw-paw) show the lowest values (Table 4). In contrast, arsenic uptake by root vegetables like carrots and leafy vegetables like parsley is high (Table 4).

Crop	Lead	Cadmium	Arsenic
Beans	0.25	8.50	0.80
Carrot	2.00	48.00	6.00
Chilli	0.50	28.50	0.50
Maize	0.15	0.60	<0.2
Marula fruit	0.46	0.21	0.96
Parsley	1.00	15.00	7.00
Pawpaw	0.50	2.30	1.30
Pumpkin	0.70	6.00	1.50
Tomato	0.20	8.00	0.30

**Table 4:** Plant uptake of contaminants from soil (concentration in plant material/concentration in soil in %)

Sample No.	Crop	Arsenic	Lead	Cadmium
TV-MA1	Marula fruit	0.02	0.01	-
TV-MA2	Marula fruit	0.02	0.01	-
TV-MA3	Marula fruit	0.01	0.01	-
TV-MA4	Marula fruit	0.001	0.0003	0.005
TV-MA5	Marula fruit	0.02	0.003	-
TV-MA6	Marula fruit	0.0007	0.0006	0.0005
TV-MA7	Marula fruit	0.002	0.001	0.002
TV-MA8	Marula fruit	0.003	0.002	0.001
TV-119P	Parsley	0.07	0.01	0.15
TV-120C	Carrot	0.06	0.02	0.48
TV-120B	Bean Skin	0.01	0.003	0.08
TV-120BS	Bean Seeds	0.006	0.002	0.09
TV-122PAW	Pawpaw	0.006	0.003	0.006
TV-123MZ	Maize	<0.002	0.001	0.006
TV-128PM	Pumpkin	0.01	0.004	0.04
TV-129CH	Chilli	0.002	0.003	0.12
TV-130TOM	Tomato	0.003	0.002	0.08
TV-130MZ	Maize	<0.002	0.002	0.006
TV-131PM	Pumpkin	0.02	0.01	0.08
TV-132PAW	Pawpaw	0.02	0.007	0.04
TV-133CH	Chilli	0.008	0.007	0.45

**Table 5:** Coefficients for contaminants in the crop samples compared to the adjacent soil

Element	WHO (2002)	EU (2001)
As (mg/kg)	0.5	-
Cu (mg/kg)	20	20
Pb (mg/kg)	0.4	0.3
Zn (mg/kg)	50	50
Cd (mg/kg)	Not available	0.2
Mo (mg/kg)	Not available	Not available

**Table 6:** Guideline values of the WHO (Codex Alimentarius) and the EU for agricultural plants

### Conclusions

The selection of sample materials was based on some fruits and vegetables which are abundant on farms and in gardens in the area. The analysed fruit crops (marula, paw-paw), vegetables (tomato, parsley, carrot, bean, pumpkin, chilli) and field crops (maize) were collected from moderately to severely contaminated soils in the surroundings of the Tsumeb smelter complex.

Bioaccumulation of the toxic elements lead, cadmium and arsenic is evident in all plant samples. These elements can severely impact human health if contaminated fruits and vegetables are consumed regularly or in significant quantities.

All cleaned fruit and vegetable samples exceed the WHO and EU guideline values for lead by up to seven (7) times, and, thus, are not suitable for human consumption.

Parsley and carrot as well as chilli and pumpkin accumulated high concentrations of lead, arsenic and cadmium despite the fact that the underlying soils are only moderately contaminated. In addition, the crops were grown in green house structures where wind-borne contamination is reduced (Table 5). Thus, leaf vegetables like parsley and root vegetables like carrots seem to be extremely prone to the accumulation of the investigated toxic elements.

In contrast, maize and to a lesser extend stem vegetables like tomatoes and beans as well as fruits of paw-paw contain relatively low concentrations of the hazardous elements.

Thus, it is recommended to strictly cease any agricultural land use and vegetable gardening for human consumption in the blue zone of figure 6. Especially critical is the area towards the west and north of the smelter, where a buffer zone of 3 to 6 km should be established where no crops and vegetables should be grown at all.

Growing of leaf vegetables (parsley, spinach, lettuce) and root vegetables (carrots, potatoes) should be generally restricted in the wider surroundings of the smelter including the whole town and the farmland up to 10 km to the west of the smelter (red zone in figure 6). For those areas, especially maize but also stem vegetables (beans, tomatoes, green pepper) and fruit trees could serve as alternatives.

Heavy metal concentrations of uncleaned and cleaned vegetative material showed generally moderate differences. Some pesticides such [monosodium methyl arsenate](#) (MSMA) and [disodium methyl arsenate](#) (DSMA) contain arsenic, and may have been used in the past. At present, widely used in the area is the herbicide Methylchlorophenoxyacetic acid (MCPA) and the pesticide Cypermethrin, both of which are organic compounds without any heavy metals (pers. comm. AGRA, September 2013) However, the effect of dust adsorption on the surface of parsley and carrots is significant. Thus, leaf and root vegetables grown in the Tsumeb area have to be intensively washed before consumption. Farmer and supermarkets are advised to clean all root vegetables properly before distribution.

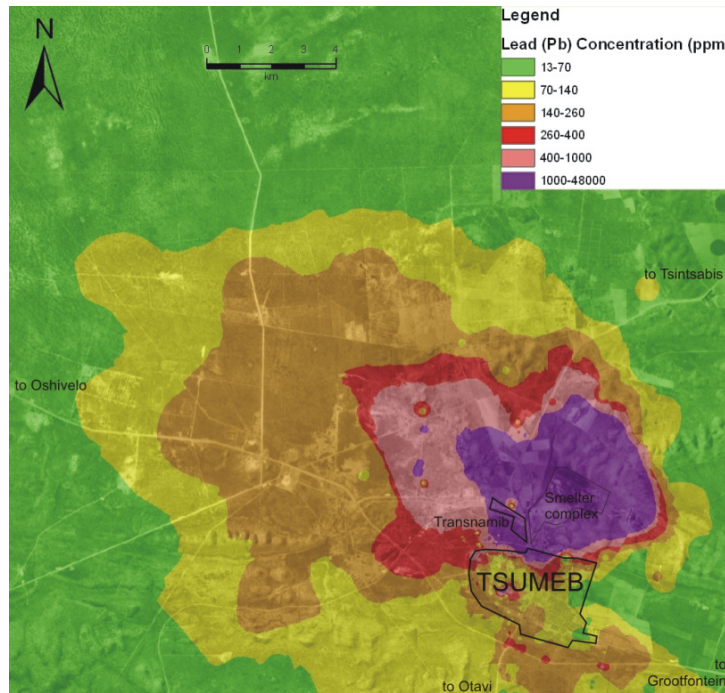


Figure 6: Lead contamination of surface soils in the Tsumeb area

Another issue of concern is the collection of marula fruit containing the contaminants directly in the flesh and in the adsorbed dust on the fruit’s surface. Awareness has to be created on the severe hazardous

risks posed by marula fruits collected in highly contaminated areas. Marula collection should be prevented in a radius of approximately 1 km around the smelter.

Element	Route of exposure	Duration	MRLs	Endpoint	Detected
Arsenic	Inhalation Ingestion Dermal	Acute Chronic	0.005mg/kg/day 0.0003mg/kg/day	Cancer, liver cardiovascular, gastrointestinal, kidney, neurological, Pulmonary, reproductive	Blood Urine Nails Hair
Cadmium	Ingestion Inhalation	Chronic	0.0002mg/kg/day TTD <sub>NEURO</sub> = 0.0002mg/kg/day TTD <sub>CARDIO</sub> = 0.005mg/kg/day TTD <sub>HEMATO</sub> = 0.0008mg/kg/day TTD <sub>TESTIC</sub> = 0.003mg/kg/day	Lung damage, stomach irritation, kidneys (main target), fragile bones, delayed development in children, testicular effects (necrosis & atrophy), BP	Blood, hair, urine or nails
Copper	Ingestion Inhalation	Acute	0.01mg/kg/day	gastrointestinal	Hair, nails, blood, urine and other tissues.
Lead	Inhalation Ingestion. Dermal (organic Pd)	Chronic	MRLs threshold not yet determined	Reduced fertility $\geq 40\mu\text{g/dL}$ Gastrointestinal Colic in children $60-100\mu\text{g/dL}$ Cardiovascular $\leq 10\mu\text{g/dL}$	Blood, urine

Table 7: Minimal Risk Levels (ATSDR) - TTD – Target Organ Toxicity Dose, NEURO – Neurological effect, CARDIO – Cardiovascular effect, HEMA – Haematological effect, TESTIC – Testicular effect



Soil treatment can be done *in situ* (on-site) or *ex situ* (removed and treated elsewhere) e.g. by phyto-extraction. None of the metals investigated are biodegradable (USDA, 2000), which means that they will be resident in soils for some time to come. The best mitigation is zoning off areas that show the highest and unsafe levels of contamination of toxic metals such as arsenic, lead and cadmium. The path of exposure, effects and minimal risk levels for selected metals are given in Table 7.

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