An assessment of the foliar heavy metal contamination in the Palabora mining region

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Declaration

This study was conceived and designed by my advisor I. Weiersbye. I declare that this research report is my own, unaided work. It is being submitted for the Degree of Masters of Environmental Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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Abstract

This study was conducted in order to ascertain the levels of elemental concentrations in tree leaf and leaf litter samples collected in two areas at the Rio Tinto Palabora Mining Company. The elemental content in leaves from trees growing in the smelter plume deposition area and in the area around the main copper tailings was determined. The study will provide further insight into the extent of the contamination in these areas exhibiting high visible contamination and potentially high impacts.

Sampling was carried out in November 2008, April 2011 and November 2011. A total of 135 leaf samples from three tree species (*Lonchocarpus capassa, Colophospermum mopane and Euclea divinorum*) were analysed, of which 74 samples were from the smelter plume deposition area, 51 samples were from the main copper tailings seepage area and 10 were leaf litter samples. Elemental concentrations in the leaves were measured and total percentages of C, H, N and S were determined.

The highest concentrations of elements were found in the leaf litter samples from the smelter plume deposition area in 2008, with the average concentrations being: 1.57 ug/g of Ni, 9.44 ug/g of Bi, 16.3 ug/g of Pb, 110 ug/g of Mn, 122 ug/g of Ti, 483 ug/g of Al, 1463 ug/g of Cu, 2812 ug/g of S and 5611 ug/g of Fe. Element concentrations in trees varied with the tree species, higher levels were found in *L. capassa* and *E. divinorum* leaves than in *C. mopane* leaves. In the leaves analysed from the smelter plume deposition area the element concentrations decreased in the order S > Fe > Al > Cu > Mn > Ti > Pb > Ni > Bi. In the leaves from the Cu tailings seepage area the element concentrations decreased in the order S > Fe > Mn > Cu > Al > Ti > Ni > Bi > Pb. Significant differences were observed for the concentrations of certain metals and elements in the leaves between the three years (2008 to 2011) and between seasons (April to November). The concentrations generally decreased from 2008 to 2011and from April to November 2011.

The findings from this study indicate that both of the high impact areas investigated are contaminated by the mining activities, with trees growing in the smelter plume deposition area showing higher contamination than trees in the Cu tailings seepage area. The leaves and leaf litter sampled in this study can be used as bioindicators of the contamination in this region.

Contents

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Table 1: Symbols of elements referred to in this report

Symbol	Element	Symbol	Element	Symbol	Element	Symbol	Element
N	Nitrogen	**Mo**	Molybdenum	**Pd**	Palladium	**Li**	Lithium
P	Phosphorus	**Cl**	Chlorine	**H**	Hydrogen	**Ti**	Titanium
K	Potassium	**Ni**	Nickel	**He**	Helium	**V**	Vanadium
S	Sulfur	**Na**	Sodium	**C**	Carbon	**Cr**	Chromium
Mg	Magnesium	**Co**	Cobalt	**O**	Oxygen	**Br**	Bromine
Ca	Calcium	**Cd**	Cadmium	**F**	Fluorine	**Rb**	Rubidium
Fe	Iron	**U**	Uranium	**Ne**	Neon	**Sr**	Strontium
Mn	Manganese	**Zr**	Zirconium	**Cl**	Chlorine	**Se**	Selenium
B	Boron	**Au**	Gold	**Al**	Aluminium	**Cd**	Cadmium
Zn	Zinc	**Ag**	Silver	**Pb**	Lead	**Sb**	Antimony
Cu	Copper	**Pt**	Platinum	**As**	Arsenic		
Bi	Bismuth	**W**	Tungsten	**Ba**	Barium		

1. Introduction

The Rio Tinto Palabora Mining Company (RTPMC) commenced operations in 1964 and is a member of the worldwide Rio Tinto Group of Companies. Copper, vermiculite, magnetite, rock phosphate (apatite) and other by-products are extracted and beneficiated from surface and underground workings of the mine. The RTPMC is located near the town of Phalaborwa in the Limpopo Province of the Republic of South Africa. The mine shares a border with the Kruger National Park. Since the mine is in such close proximity to the Kruger National Park, the company's operations and potential impacts on the surrounding environment are closely scrutinised by government, environmental groups, the National Parks Board and the local community. Potentially elevated concentrations of metals occurring in and on leaves in the vicinity of the RTPMC mine as a result of the mine and its operations could have a direct effect on organisms feeding on these leaves. Such contaminants could also accumulate and transfer to higher trophic levels with consequent negative impacts. It is therefore important to understand the implications that the emissions from the RTPMC could have on the natural environment in the surrounding areas as well as the impact on the human population.

Many of the essential elements required by plants are enriched in the commonly occurring minerals at RTPMC. This is why Ni, Ti, Mn, Al, Cu, Fe, S, P, K, Mg and Ca were chosen for assessment. Due to the mining activities in this area, these commonly occurring elements may be present at elevated concentrations. However, elevated total concentrations in the environment do not imply that these elements will be more bioavailable for plant uptake. Of these elements Ti, Al and Fe are classified as dust elements. Cu and S are also important as RTPMC is a copper mine, with the copper coming from sulphide ores, thus there could be elevated concentrations of these elements from the mining and processing of the ore.

Some potential impacts of the mining activities include animal deaths which have occurred in the surrounding areas of the mine that could be associated or are perceived to be related to the heavy metals originating from the mine (Grobler 1999). Deposition of S could also lead to soil acidification and people could eat Mopane worms (*Imbrasia belina*) containing heavy metals.

2. Literature Review

2.1. Metals in the environment

Metals are an important class of pollutants because they can be toxic to organisms at relatively low concentrations and can have harmful ecological outcomes (Boyd et al. 2006). Heavy metals have serious negative environmental consequences, however humans continue to depend on them which results in large concentrations of heavy metals accumulating in the environment (Han et al. 2002). The negative effects of heavy metals on organisms can often result in serious toxicological symptoms and even mortality. Some influences that heavy metals have on organisms include info-disruption between individuals, changes to immune responses and interferences to immune system functions (Boyd 2010). Although these effects are generally dose-dependent, some heavy metals are required in relatively small quantities as micronutrients; therefore the low doses can actually have positive direct effects for many organisms (Boyd 2010).

When studying heavy metals in plants, it is important to note that substances that are deposited on the surface of plants from the atmosphere by wet or dry deposition will follow different laws and mechanisms of uptake into the plant from the mechanisms that determine the accumulation of heavy metals through uptake by roots from the soil (Kovář 1990). It is therefore important to distinguish between these two forms of contamination (Kovář 1990). High levels of particle, gas and solution deposition can increase the danger of food chain contamination (Kovář 1990).

The elements required for complete plant nutrition include the macronutrients: N, P, K, S, Mg and Ca and the micronutrients: Fe, Mn, B, Zn, Cu, Mo, Cl, Ni and Na (Morgan 2011). These elements are necessary and beneficial for plant growth and the elimination of any of these will results in abnormalities of growth, deficiency symptoms and abnormal reproduction (Morgan 2011). Heavy metals such as Fe, Cu, Ni and Zn are therefore essential for normal plant growth, however elevated concentrations of these essential metals can inhibit growth and cause toxicity symptoms (Hall 2002). Many plants possess several potential cellular mechanisms that may be involved in the detoxification of heavy metals and thus tolerance to metal stress (Hall

2002). Other research has shown that short and long-term exposure to metals results in toxicity as evidenced by a reduction of microbial diversity and activities in soil (Wang et al. 2007).

Copper in soil occurs almost exclusively in the divalent form. The largest fraction of copper is usually present in the crystal lattices of primary and secondary minerals. Copper also occurs in organic compounds, is present as an exchangeable cation on soil colloids and is a constituent of the soil solution. Copper is more strongly bound to organic matter than other micronutrient cations and the copper complexes present in soil play an important role in regulating copper mobility and availability (Mengel and Kirkby 2001).

2.2. Biomonitoring of metals

Biomonitoring is an important tool that can be used to assess the impact that any activity has on the environment (Lange and Lambert 1995). Such monitoring techniques can be ecologically orientated, and should take into account factors such as bioavailability, bioconcentration and bioaccessibility as well as organisms from different trophic levels (bacteria, algae, herbivores and carnivores) (Steinberg et al. 1994). Bioavailability can be defined as the proportion of total metals that are available for incorporation into biota (John and Leventhal 1994). Total metal concentrations do not necessarily correspond with metal bioavailability (John and Leventhal 1994). Mammals and insects can be used to access the degree of heavy metal contamination in both aquatic and terrestrial environments.

Some examples of studies in which biomonitoring techniques have been applied include: determining the distribution of Cu smelter emissions using the honey mesquite (*Prosopis juliflora*) as a bioindicator of the Cu concentrations; characterising the deposition from nuclear accidents and weapons testing using concentration analyses in pine trees (*Pinus ponderosa* and *Pinus radiata*); mapping of Hg vapours from an abandoned mining area using azalea leaves (*Azalea indica*) which act as vapour traps, and in the investigation of atmospheric deposition of heavy metals using moss as an indicator organism as it has a high metal binding capacity (Lange and Lambert 1995). The levels of metals in the Kruger National Park have also been assessed in topsoil, dust, leaves, grass, lichen and bark in a previous study. It was found that dust, lichen

and bark reflected the levels of air pollution better than grasses or leaves of trees. From this study it was suggested that bark and lichens could be used as bioindicators of air pollution from point sources in remote areas (McCrindle and Panichev 2004).

2.3. Risk Assessment of metals in the environment

Ecological Risk Assessment is defined as the process that evaluates the likelihood that adverse effects may occur, or are occurring as a result of exposure to one or more stressors (U.S. EPA 1998). Some examples of environmental stressors include: seasonal influences, stochastic events, chemicals, land change, disease, invasive species and climate change (Lee 1999). Ecological risk assessments are developed within a risk management context to evaluate human-induced changes that are considered undesirable (U.S. EPA 1998). Such risk assessments deal with the probability and cost of an event causing a potentially undesirable effect on the natural environment. Risk can be defined as exposure to the consequence of uncertainty. It is comprised of two elements: the probability of a risk occurring and the consequence if it were to take place (Risk = Probability x Consequence) (Lee 1999). Risk assessments can be both qualitative and quantitative and can be used to improve environmental planning and the outcomes of a business, resulting in improved environmental and financial performance for both the short and long term (U.S. EPA 1998).

The objectives of a risk assessment are to reduce the risk of exposure, mitigate the impacts and improve the chances of achieving the planned objectives (Lee 1999). An acceptable level of risk is determined for the present and in the future. The Ecological Risk assessment framework involves the following five steps: formulating the problem (establishes the context and identifies the risks), analyse the risks (stressor response and exposure analysis), assess and prioritise the risks (risk characterisation), treat the risks (communication and control) and finally review, monitor and access the effectiveness of treatments (Lee 1999). It is important that a reasonably good understanding of the environmental baseline conditions is developed prior to risk assessment (Lee 1999). Ecological risk assessments are becoming increasingly important in evaluating the effects of historical mining as well as in predicting the potential effects of present and future mining (Lee 1999).

2.4. Sources of metals in the environment

2.4.1. Smelters and refineries

The dilution of air contaminants in the atmosphere is an important process that assists in preventing undesirable levels of pollutants in the ambient air (Neveling 2011). Hunter et al. (1987) gave evidence as to how Cu and Cd contamination presented itself in soil and vegetation in a grassland ecosystem at a refinery complex in north-west England. Cd was found to be more mobile than Cu in the soil and vegetation, and the contamination of both metals was widespread with elevated levels persisting up to 3km from the refinery (Hunter et al. 1987). The soil profiles indicated that there was surface retention of Cu and a low diversity of indigenous vegetation was found in the complex (Hunter et al. 1987). Seasonal variations in the concentrations of the metals were found with peaks occurring in the winter months. It was concluded that this winter peak reflected the translocation of Cu into older shoots and leaves prior to the shedding of these leaves and incorporation into the litter layer. The Cu concentrations are then diluted as new leaves grow in spring (Hunter et al. 1987). The winter peak Cu concentration in the shoots and leaves of *Agrostis stolonifera* was 330 ug/g. This high concentration of Cu at the refinery site was thought to be due to surface deposition of particulates derived from atmospheric deposition and splash back of particles from the soil surface. These particles are deposited onto the leaf surface and retained by physical sites such as leaf veins, hairs and axils (Hunter et al. 1987). It was also found that 25% of Cu is incorporated into the plant as protein bound or ionic species and 75% is present as a superficial deposit of metal rich soil particulates (Hunter et al. 1987). Such retention of these metal particles suggests that there is a great potential for food chain movement. Hunter et al. (1987) concluded that detritivorous animals feeding on senescent plant material at the refinery site would ingest four times more Cu than herbivorous animals feeding on live plant material at the same site.

Furthermore, airborne Cu aerosols have a relatively short residence time and it is thought that the build up of Cu in the atmosphere is not a major phytotoxic factor originating from Cu smelters. Cu smelters often release much larger quantities of As than Cu (Ayres et al. 2002).

Other emissions from Cu and Ni smelters can include Cd, Hg, Mn, Ni, Pb, Sb, Se and Zn (Ayres et al. 2002).

2.4.2. Tailings storage facilities

When studying metal contamination at a mine it is important to understand the geochemical weathering processes that are occurring. Such processes acting upon metallurgical wastes and by-products initiate the process of transporting heavy metals from contaminated areas and redistributing them to surrounding soils, streams and groundwater (Wang et al. 2007). The pH of seepage water from tailings storage facilities reflects the balance between acid producing and neutralizing minerals in the tailings (Heikkinen et al. 2008). The overall geochemistry depends on the mineralogical composition of the tailings solids and dissolution of acid buffering minerals. The distribution of heavy metals and metalloids in seepage and pore waters is largely dictated by the deposit geology and exposure to oxygen (redox behaviour) (Lottermoser and Ashley 2005).

In a study by Heikkinen et al. (2008) at Luikonlahti, a Cu and talc mine and processing plant in Finland, the factors influencing tailings seepage quality, such as seepage and drainage water geochemistry (pH, EC, O_2, redox, alkalinity, dissolved cations and trace metals, major anions and total element concentrations) were analysed. It was found that seepage quality was largely influenced by the tailings mineralogy (Heikkinen et al. 2008). Drainage from the high sulphide, multi-metal tailings of Luikonlahti represented typical acid mine drainage with elevated contents of Zn, Ni, Cu, and Co (Heikkinen et al. 2008). Other factors affecting the seepage quality included weathering rate of the tailings along the seepage flow path, process water input, local hydrological settings, and structural changes in the tailings impoundment. The quality of the seepage water also adjusts and changes as modifications are made to the tailings facilities (Heikkinen et al. 2008).

2.5. Rio Tinto Palabora Mining Company

The Rio Tinto Palabora Mining Company (RTPMC) beneficiates Cu, vermiculite, magnetite and other by-products from surface and underground workings. The Phalaborwa Complex is the only economically viable carbonatite- hosted Cu deposit in the world (Usher and Moukodi 2008). The ore body outcropping at a small saddleback hill, called Loolekop, contains a unique variety of minerals. Two other volcanic pipes nearby contain vermiculite and phosphate (Usher and Moukodi 2008).

The soils occurring on Palabora's property are generally shallow and eutrophic, with high clay content (Usher and Moukodi 2008). Eutrophic soils are soils, which have suffered little or no leaching and consequently have a high base status which means they are relatively fertile and have a good supply of essential plant nutrients (Posnik 2002).

The temperatures in this area range between 8 to 40˚C, but it is mostly warm with high humidity. Rainfall varies between 250 mm to 700 mm with maximum volumes falling from December to February mainly in the form of thunderstorms and heavy showers (Mucina and Rutherford 2006; RTPMC 2011).

2.5.1. RTPMC Mining and Waste Disposal

RTPMC operates one of the largest underground Cu mines in the world. The mine runs a concentrator, smelter and refinery to produce refined Cu products. A variety of by-products are released in the Cu recovery process. Some of these by-products include phosphate, magnetite, U, Zr, Au, Ag, Pt, Pd and Ni. At the RTPMC, Cu concentrate is smelted in the reverberatory, converter and anode furnaces. Reverberatory gas, which is not rich in sulfur dioxide (SO_2), is emitted to the atmosphere via a tall stack. Converter off-gas, which is rich in SO_2, is routed to the acid plant for conversion to sulfuric acid and only a fraction is emitted into the atmosphere. Approximately 75% of S contained in concentrate is captured during the smelting process (RTPMC 2001). The smelting process also yields significant quantities of sulfuric acid (RTPMC 2001). RTPMC is a market leader in the production and sale of vermiculite. Vermiculite occurs in a separate ore body that is in the same geological complex as the Cu ore body (RTPMC 2001).

2.5.2. RTPMC Environmental Impacts

Some of the significant environmental issues monitored and controlled by RTPMC include air pollution, water pollution and consumption and land disturbance (Posnik 2002). RTPMC maintains a dynamic environmental management system committing the company to the undertaking of mining activities in an environmentally accepted manner. RTPMC aims to evaluate the environmental risks associated with the mining activities and products and take appropriate action to minimise the potential risks (Posnik 2002).

The most significant air quality impact occurs as a result of the Cu smelting process. The particulate matter suspended in air can be comprised of the following: suspended particles; fine and ultra-fine particles; diesel particulate matter; coal fly-ash; mineral dusts such as coal, asbestos, limestone and cement; metal dusts and fumes such as Zn, Cu, Fe and Pb; acid mists for example sulfuric acid; fluoride particles; paint pigments; pesticide mists; oil smoke and many others (Neveling 2011). The wind at the mine blows mainly from the south east (23.8%) but sometimes blows from the south south-east (15.2%) and from the east south-east (7.4%) (Neveling 2011). This is important as the smoke plume from the Cu smelter predominanlty blows in a north westerly direction and the town of Phalaborwa is located north of the mine.

Waste and by-products of the RTMPC are stored or disposed of in the magnetite storage dam, the ore stockpiles, a waste rock dump or in the Cu tailings dam (RTPMC 2001)**.** The potential pollutants that are produced and distributed via the various pathways during mining operations and metal production are: metals from the mined ore (Cu and Cu-associated metals such as Pb, Cr, Ni, Zn, Cd and Hg); radioactive material from the tailings dams; acids in the soils from spillages and leakage of sulfuric, hydrochloric and nitric acid and their respective salts and petroleum products, such as diesel and petrol from spillages, leakages, run off and wash down water during cleaning or rain (Posnik 2002).

2.5.3. Previous studies conducted at RTPMC

The mine has numerous air monitoring stations as well as several boreholes where the water quality is monitored. Ambient dust deposition was examined near the operations of RTPMC

during the period 23 June 2009 to 23 June 2011 by Environmental and Health Risk Consulting (Neveling 2011). Some of the objectives of this monitoring programme were: to determine the exposure of human populations in the residential, agricultural and industrial settings near RTPMC's operations; to identify threats to natural ecosystems; to determine compliance with local, provincial and national standards; to identify future problems and to determine the progress against management/control targets. The results from this monitoring programme indicated that there is a general reduction in deposition rates from north to south as well as a reduction with increasing distance from the smelter. The deposition pattern concurs with the predominant wind directions for the Phalaborwa area and confirms that the RTPMC operations are the primary anthropogenic source of ambient Cu (Neveling 2011).

The South African National Standard annual target level of dust is 300 mg/m^2/day and the industrial action level of dust is 1200 mg/m^2/day (SANS 2005). Table 2 is a summary of the monthly dust deposition rates around the smelter, vermiculite operations (VO) plant and in Phalaborwa Town as presented by Neveling (2011). The average deposition is very high at the smelter and VO plant.

Table 2: Summary of monthly dust deposition rates 23 June 2009 to 23 June 2010 (Neveling 2011)

Parameter	Smelter	VO Plant	Phalaborwa Town
Months	12	12	9
Minimum (mg/m^2/day)	528.58	3175.99	101.37
Maximum (mg/m^2/day)	2643.58	6462.93	430.39
Average (mg/m^2/day)	**1376.57**	**4890.71**	**224.01**

Dust deposition samples associated with the Kruger National Park were also collected to determine the insoluble Cu content. Cu deposition rates varied between 0.004 and 1.006 mg/m^2/day, and of the samples collected 75 % fell within the typical background Cu deposition range of 0.005 to 0.136 mg/m^2/day, however fourteen samples exceeded the upper threshold of the range (Neveling 2011).

As part of the Environmental Management Programme Report (EMPR) of RTPMC, soil samples were taken in 18 locations within a radius of 22 km from the mine (Posnik 2002). One sample

location chosen for background sampling was situated to the south of the mining complex. The soil pH was determined and it was found that the pH of most samples was neutral to alkaline (pH 6.5 to 8.6) (Posnik 2002). Two locations (in the area near the smelter and the area northwest of the smelter towards Phalaborwa) showed significantly lower pH's (Posnik 2002). The slightly acidic soil pH in the smelter area was ascribed to deposition of SO_2 and SO_3, which are oxidised in the soil to form sulfuric acid (Posnik 2002).

Another study conducted in 2008 determined the mineralogy of the mineral waste deposits at the RTPMC through X-ray diffraction and X-ray fluorescence (Usher and Moukodi 2008). The acid or alkaline producing potential of each of the tailings and waste rock dumps was also calculated. The long-term risk of sulfate and metal release from each waste material was then determined to predict the long-term contaminant loads that may be released (Usher and Moukodi 2008). Usher & Moukodi (2008) found that most of the samples had insufficient sulfides to result in the long-term generation of acidity and that the low sulfides should limit high rates of sulfate generation from the waste. Consideration of the acid potentials versus the neutralisation potentials illustrated that acid mine drainage associated problems were considered to be highly unlikely at RTPMC (Usher and Moukodi 2008).

Geobotanical data which could facilitate the evaluation of the mines monitoring programmes was obtained in another study (RTPMC 2008). This Statistical and Geostatistical Evaluation Report aimed to statistically determine and evaluate the temporal and spatial variation for the database period. This would directly reflect on management actions and mitigating measures (RTPMC 2008). The RTPMC 2008 study determined the geographic areas at risk where the threshold value of 100 ug/g of Cu was most likely to be exceeded. During surveys conducted in 1999 – 2002, sampling plots of ± 15 m × 15 m were selected at each monitoring locality. Samples (grass, tree leaves and soil) were collected systematically across the extent of each plot (RTPMC 2008). The total Cu concentration was then determined for unwashed vegetation (Cu deposited on the surface of the vegetation) and washed vegetation (Cu absorbed by vegetation) separately (RTPMC 2008). The results for the Cu concentration determined from the unwashed vegetation samples, gives an indication of the atmospheric deposition of Cu on plant material due to the nearby mining activities. The Cu concentration determined for the

washed vegetation gives an indication of the amount of Cu accumulated in the vegetation composite at the Phalaborwa monitoring localities (RTPMC 2008). The 2008 study concluded that the intrinsic variation of Cu in plant material was not solely dependent on the atmospheric deposition of Cu (RTPMC 2008). The observed dynamics of the Cu content of the vegetation could be dependent on the rate of atmospheric Cu deposition, natural soil Cu content, internal nutrient cycling of vegetation, growth stage of vegetation, type (population, community, species) of vegetation sampled, plant part sampled (roots, stems, leaves), sampling design, methodology and climatological conditions (rainfall, wind speed and wind direction) (RTPMC 2008).

An investigation was carried out to determine the potential for Cu poisoning in wild ruminants in the Phalaborwa area in the Kruger National Park (Grobler 1999). Atmospheric deposition of Cu onto the surface of certain plant species and onto the surface of soil can be detrimental as growth can be inhibited and plant roots can be killed (Grobler 1999). High, moderate and low risk zones were related to the distance from the Cu smelter. Grobler (1999) found that topsoil Cu concentrations were significantly higher than subsoil Cu concentrations. There was also a significant linear decrease in the concentration of Cu relative to distance from the Cu smelter (Grobler 1999). The results for the plant material revealed that the Cu concentrations of unwashed plant material were significantly higher than washed plant material at the same sites (Grobler 1999). Therefore Cu deposition from the smelter was deposited on the plant surfaces. From the investigation it was concluded that the emissions from the Cu smelter were sufficient in amount and appropriate in direction to have contributed significantly to the topsoil Cu concentrations and unwashed plant Cu concentrations (Grobler 1999). Grobler (1999) also stated that the environmental Cu pollution and poisoning was associated with the smelting operations at the mine and consumers of the Cu enriched plant material could be adversely affected.

Table 3 gives an indication of the Cu requirements and maximum tolerance for various animals. Cu poisoning causes severe gastroenteritis in animals and is characterized by abdominal pain, diarrhoea, anorexia, dehydration and shock (National Research Council 1984). As can be seen in the table the maximum tolerance of Cu for cattle is 100 ug/g of feed.

Table 3: The Cu required and maximum tolerance concentrations for growing animals
(National Research Council 1984)

	Cu requirements (ug/g of feed)	**Cu maximum tolerance** (ug/g of feed)
Horses	10	800
Chicken	5	300
Pigs	3-6	250
Cattle	10	100
Sheep	7-11	25

Posnik (2002) reported on the water-soluble and plant available Cu in the RTPMC area (Table 4). The water-soluble Cu simulates the Cu that is in the soil solution and is thus likely to migrate freely in the soil whereas the plant available Cu gives an indication of the plants potential to excrete chelators which make minor elements bound in the soil matrix available for metabolism by the plant (Posnik 2002). The water-soluble Cu concentrations in the soils were generally low indicating that the Cu movement into the deeper soil during rain events is minor. In addition, Posnik (2002) found that the highest concentrations of water-soluble Cu were near the smelter. A concentration gradient from the source (smelter) to the background (situated to the south of the mining complex) was also clearly seen as the concentration of water-soluble Cu at the pollution source was about 350 times higher than at the background sampling location (Posnik 2002).

Table 4: Total Cu concentrations in soil samples taken for the Environmental Management Programme Report for the Rio Tinto Palbora Mining Company (Posnik 2002)

Cu concentration (ug/g)	**Water-soluble Cu**	**Plant available Cu**
Range in the smelter area	1.0 – 9.0	610 – 4100
Average in the smelter area	0.01 – 0.2	9 - 214
Background	0.003 – 0.06	3.0 - 15

The total Cu concentrations were also determined by Posnik (2002) in leaves from grasses and from trees and shrubs around the mine (Table 5). The leaves from the trees and shrubs had higher Cu concentrations than the leaves from the grasses (Posnik 2002).

Table 5: Total Cu concentrations in plant samples taken for the Environmental Management Programme Report for the Rio Tinto Palbora Mining Company (Posnik 2002)

Cu concentration (ug/g)	**Unwashed grass leaves**	**Unwashed tree and shrub leaves**
Range in the smelter area	83 - 2000	1.3 - 3700
Average in the smelter area	2.1 - 244	184 - 3700
Control	2.1 – 34.3	1,4 – 4.2

3. Aim

The aim of this study was to assess the concentration of metals and other elements found in leaves and leaf litter samples collected in two high impact areas of the Rio Tinto Palabora Mining Company. Leaves from three naturally occurring and abundant tree species (*Lonchocarpus capassa*, *Colophospermum mopane* and *Euclea divinorum*) sampled at different time periods (November 2008, April 2011 and November 2011) on two polluted sites at the RTPMC were compared. This study also aimed to contribute towards establishing the context of the potential contamination at the Rio Tinto Palabora Mine, the first step of the Ecological Risk assessment framework.

3.1. Key Questions

- Was there a decrease in the concentration of heavy metals, dust elements and other elements deposited on or within the leaves from the three tree species relative to the distance from the smelter?
- How do the concentrations of elements deposited on or within the leaves in the smelter plume deposition area compare to the concentrations in the leaves from the Cu tailings seepage area?
- Does the concentration of elements in the leaves differ over time (3 years) or between seasons (late and early wet)?
- How do the concentrations of the elements deposited on or within the leaves of the three different tree species compare?
- Can the tree leaves in the contaminated areas around RTPMC be used as a bioindicator?

4. Rationale for this study

The current study formed part of RTPMC's on-going environmental assessments and the wider remote-sensing and risk assessment survey. The study will provide further insight into the extent of the contamination in two areas exhibiting high visible contamination and potentially high impacts. The results will access the significance of the elemental deposition from the smelter plumes as well as from the seepage off the Cu tailings.

Since the smelter plume continues past the mine boundaries and the town of Phalaborwa it is important to understand the implications that the emissions and the elements contained in the smoke plume could have on people and the natural environment. Animal deaths occurring in the surrounding areas could be associated or are perceived to be related to the heavy metals originating from the mine. S deposition could lead to soil acidification and people could eat Mopane worms (*Imbrasia belina*) containing heavy metals. It was an intention of the study to assess the Mopane worms in relation to Mopane leaves, however, for two years running, worms could not be collected and so the study was refocused to the quality of browse for three common tree species.

5. Methodology

From the aim of the project, the experimental design was set up to determine whether there are differences between three tree species, sampled at different time periods, on two polluted sites at the RTPMC. Previous studies have already looked at polluted versus control sites and from these studies the polluted sites were established.

5.1. Study Site

The study site for this project was the Rio Tinto Palabora Mining Company (RTPMC) which is located near the town of Phalaborwa in the Limpopo Province of the Republic of South Africa. Figure 1 is a Google Earth image of the mining complex on the east, with Foskor to the west. The red arrow gives an indication of the dominant direction in which the smelter plume travels.

Figure 1: Rio Tinto Palabora Mining Company with Foskor to the west
Smelter stack plume is in the north western region of the property shown by the red arrow, with the smelter stacks represented by the red oval (Source: Google Earth April 2011)

5.1.1. Smelter plume deposition area

The first high impact area in which sampling was carried out was in the smelter plume deposition area. The contaminants that are deposited from the air onto the soil and vegetation originate from the five smelter stacks shown in Figures 2 and 3.

Figure 2: Smelter stacks at Rio Tinto Palabora Mining Company

Figure 3: Plume from smelter stack at Rio Tinto Palabora Mining Company

The predominant wind direction in Phalaborwa is SE and SSE and the sampling area was therefore NW of the smelter stacks (Figure 4). The samples from this region give an indication of the elements deposited on the plants and potentially taken up into the plants from the soil solution (due to rainfall and wash down of the contaminants into the soil and also from litter fall and decomposition).

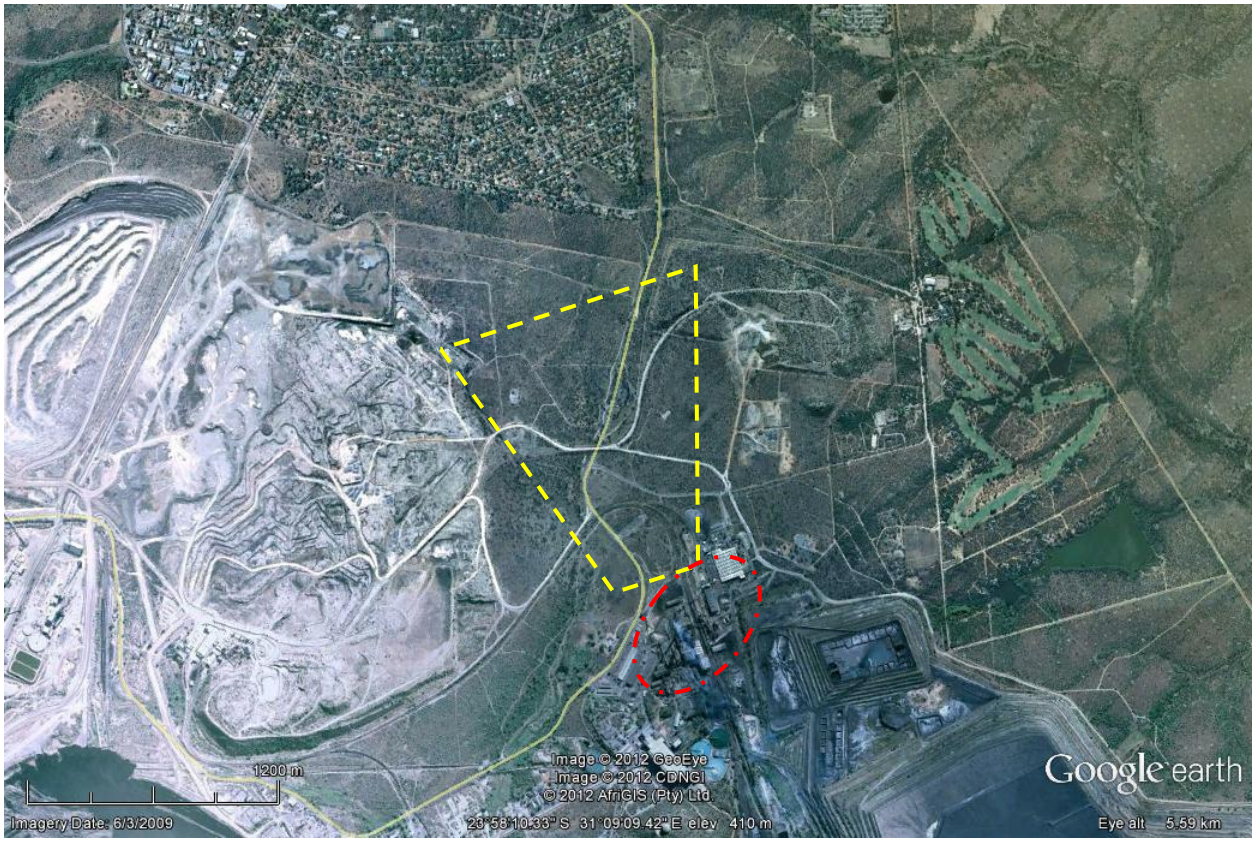

Figure 4: Smelter stacks (red) **and study area** (yellow) (Source: Google Earth July 2011)

5.1.2. Main Cu tailings dam seepage area

The second high impact area in which sampling was carried out was in the area around the main Cu tailings dam (Figure 5, 6, 7). In this area heavy metals could leach out of the tailings into the soil solution, groundwater and surface water. Trees were sampled on either side of the road on the edge of the tailings dam (i.e. close to as well as a bit further away from the tailings). The samples in this region give an indication of the elements taken up by the roots of plants, as well as elements deposited on the surface of vegetation from tailings dust.

Figure 5: Side of main Cu tailings dam, Rio Tinto Palabora Mining Company

Figure 6: Top of main Cu tailings dam, Rio Tinto Palabora Mining Company

Figure 7: Rio Tinto Palabora Mining Company main Cu tailings dam in the centre of the image with the sampling area in yellow (Source: Google Earth July 2011)

5.1.3. Study Period

The study utilised leaf and leaf litter samples collected in November 2008 (Weiersbye et al. 2008), repeats of the November 2008 samples collected in November 2011, April 2011 and repeats of the April 2011 samples collected in November 2011. These collections were used to make comparisons between two time periods in the same season (November 2008 and November 2011) and between two different seasons in the same year (April 2011 and November 2011). Sampling in November 2008 was carried out after a severe acid mist occurrence in March 2008 (Surmon and Weiersbye 2012). The hydronium ions of acid rain can mobilise metal ions such as Al^{3+} and leach away essential nutrients and ions such as Mg^{2+} (Davies and Mundalamo 2010). It was expected that this acid mist event would have a large impact on the concentrations of certain elements in the leaves.

5.2. Tree species sampled

- *Lonchocarpus capassa* (**AB**)

Lonchocarpus capassa is a medium to tall deciduous or semi-deciduous tree with a sparse crown. It occurs in bushveld and woodlands and is often found at low altitudes along river banks. The leaves have a large surface area and are shiny above and grey- green below. *L. capassa* leaves are browsed by stock and game and the roots are used medicinally (Van Wyk and Van Wyk 2007). This species was chosen for this study as these trees were found in both of the high impact areas. The leaves also have large surface areas and would thus give a good indication of the elements deposited on the surface of the leaves from the smelter plumes and from dust blown off the tailings.

Figure 8: *L. capassa* tree (above) **and leaves** (below)

- *Colophospermum mopane* (**Mop**)

Colophospermum mopane is a shrub or medium to tall deciduous tree, thus the leaves are seldom more than one year old and provide a useful indicator of cumulative impacts on the tree leaves within that period. These trees occur in almost pure *C. mopane* stands in hot, low-lying areas, often on alluvial or lime rich soils (Van Wyk and Van Wyk 2007). Leaves are glabrous and have a medium sized surface area, which is intermediate between *L. capassa* and *E. divinorum* leaves. *C. mopane* are browsed by cattle (*Bos taurus*) and game, particularly elephants (*Loxodonta africana*). Caterpillars otherwise known as *Mopane* worms, of the emperor moth (*Imbrasia belina)*, feed on the leaves and in turn are widely eaten by people and animals (Van Wyk and Van Wyk 2007). *C. mopane* is a legume tree and is therefore a nitrogen fixer. Nitrogen fixing trees have high requirements for Fe and Co. Since Co and Cu have similar characteristics (both are transition metals from period 4 block d), Cu concentrations could be high in *C. mopane* trees in the RTPMC area as a result of the abundance of Cu.

Figure 9: *C. mopane* tree (left) **and leaf** (right)

- *Euclea divinorum* (**Euc**)

Euclea divinorum is a small evergreen tree or bush, and the leaves are therefore long lived. Since this tree is evergreen it may be more useful as a bioindicator than *C. mopane* over longer time periods. The sexes occur on separate plants (dioecious). *E. divinorum* often occurs on brackish floodplains along rivers or on termitaria. The leaves are coriaceous, elliptic and undulate with a small surface area. The fruit and roots are used medicinally (Van Wyk and Van Wyk 2007). This tree species was chosen as it was abundant in the smelter plume area. The leaves also have a small surface area and are long lived and would therefore provide a good contrast to both *L. capassa* and *C. mopane* leaves.

Figure 10: *E. divinorum* tree (above) **and leaves** (below)

5.3. Sampling method

Leaves from between 6 to 10 trees of each of the three species were sampled in the two high impact sites (Figures 11 and 12). Systematic sampling was used in this study, where a random start was chosen and trees were then sampled every 50 to 400 m along the roads, with trees selected at varying distances from the road.

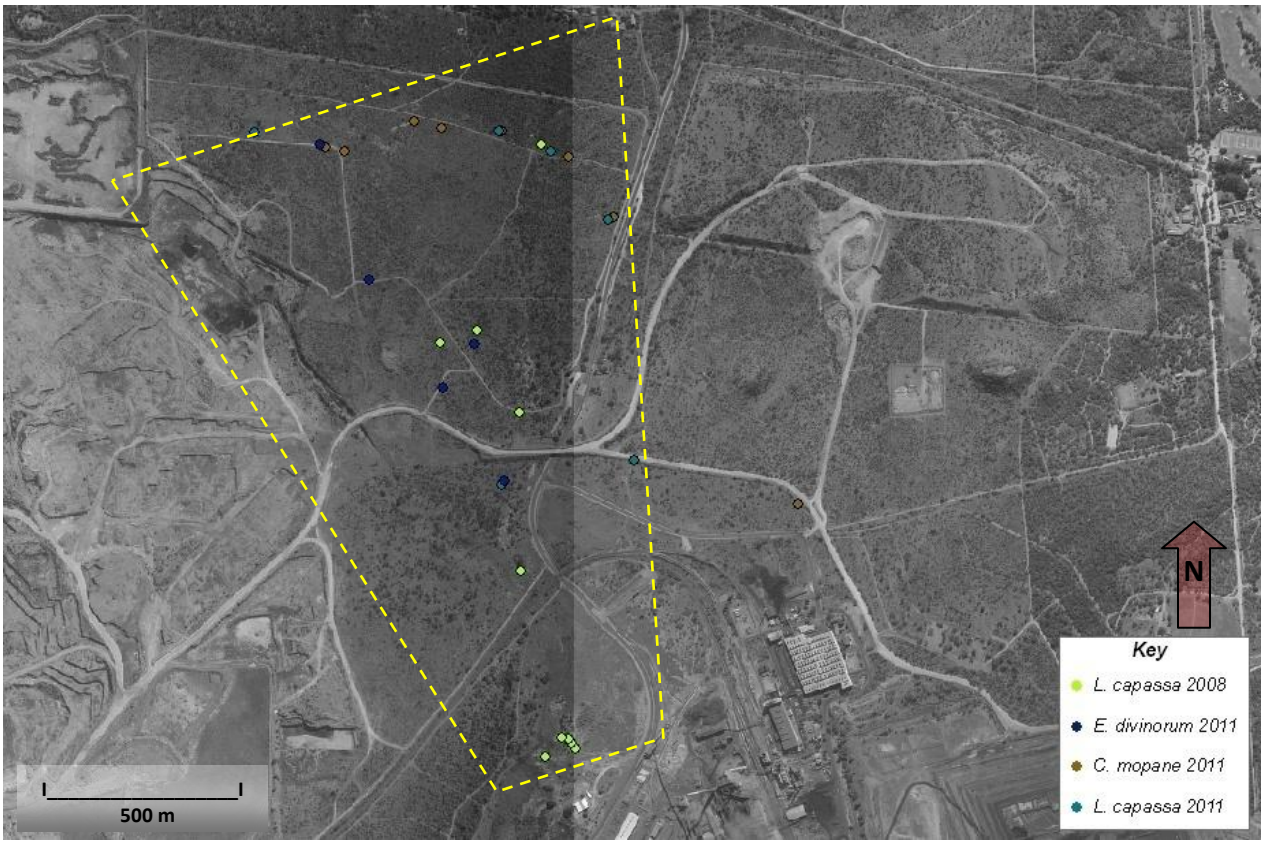

Figure 11: Aerial photograph showing sampling locations in the smelter plume deposition area at the Rio Tinto Palabora Mining Company (Source: Weiersbye et al. 2008)

Figure 12: Aerial photograph showing sampling locations in the seepage area around the main Cu tailings at the Rio Tinto Palabora Mining Company (Source: Weiersbye et al. 2008)

Leaves were collected randomly from each tree. At least 20 leaves, mainly older where possible, were collected to ensure that a representative sample was obtained. GPS coordinates of each tree as well as an estimate of the trees height was recorded. After the leaves were collected they were then combined to form one composite sample for each tree.

The unwashed leaves were freeze dried rather than oven dried to avoid losing volatile elements. The samples were then crushed to form a homogenous sample from which a representative subsample was sent to the Environmental Analytical Chemistry laboratory, School of Chemistry at Wits University for microwave digestion and elemental analyses. Approximately 0.1 g of the crushed homogenous sample was weighed and the exact mass was recorded. An excess of nitric acid was then added to the liner with the sample for digestion. A *Multiwave 3000 SOLV* instrument was used to digest the samples. The maximum power was 600 W with the temperature limit set at 190 ˚C and the pressure limit set at 20 bars. After digestion the liners were rinsed and the samples were made up to 25 ml with deionised water.

Leaf litter, consisting of mainly old and dry litter, was also collected from below a subset of the trees that were sampled for leaves in 2008 and 2011. Elemental analyses of these leaf litter samples from both of the high impact areas were then completed. The same sample preparation was followed for the leaf litter as for the unwashed leaf samples. Leaf litter was analysed to determine the concentrations that detritivores feeding on this matter may be exposed to.

Surface soil was also sampled however analyses of these samples was beyond the scope of this study, which focused on the potential for element transport from plants to consumers and not on element transfer from the soil to plants or the potential bioavailability of metals and other elements in the substrate.

5.4. Elemental analyses

The plant material was analysed using inductively coupled plasma optical emission spectrometry (ICP-OES). ICP-OES is a major technique that is used for trace elemental analysis (Manahan 2004). About 70 elements can be measured in an aqueous solution; however this technique is also used for a standard environmental analysis which involves a full screening for heavy metals whereby about 32- 36 metals are analysed. ICP-OES cannot be used to measure H, He, C, N, O, F, Ne, Cl and some other elements. For a linear response to the elements concentration the optimum working range is 0.5- 100 ug/g and the total dissolved solids in the solution need to be less than 1.5% (Manahan 2004).

The elements of interest included: Li, Na, Mg, Al, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Mo, Se, Cd, Sb, Ba, Pb, Bi and U. The elements prioritised for this study in terms of toxicity and mobility were: Cr, Co, Zn, As, U, Ni, Bi, Pb, Mn, Ti, Al, Cu, S and Fe. The detection limits for some of the elements analysed are shown below in Table 6.

Table 6: Detection Limits for ICP-OES as obtained from Environmental Analytical Chemistry laboratory, School of Chemistry at Wits University

	Al	**Bi**	**Cu**	**Mn**	**Ni**	**Pb**	**Sr**	**Ti**
Minimum (ug/g)	0.006	0.011	0.005	0.001	0.004	0.014	0.002	0.001

NBS Orchard Leaves 1571 Certified Reference Material was analysed together with the samples to monitor the accuracy and reliability of the analyses (Table 7). A small subset of the samples from this study, including the Certified Reference Material, were also sent to the Agricultural Research Council (ARC) Laboratories in Pretoria to verify the results received from Wits University. The concentrations obtained for the elements in NBS Orchard Leaves 1571 Certified Reference Material from Wits University and ARC Laboratories shown in Table 7 are very similar to the certified concentrations. See Tables 22 and 23 in Appendix for all ICP-OES results.

Table 7: Concentrations obtained and certified concentrations (ug/g) for the elements described in this report for the NBS Orchard Leaves 1571 Certified Reference Material reported by the Environmental Analytical Chemistry laboratory, School of Chemistry at Wits University (Wits CRM) and Agricultural Research Council Laboratories in Pretoria (ARC CRM)

Element	Wits CRM (ug/g)	ARC CRM (ug/g)	Certified Content (ug/g)
Bi	0.09	-	0.1
Ni	1.3	1.4	1.3 ± 0.2
Ti	22.7	10.3	-
Pb	49.0	43.1	45 ± 3
Mn	81.0	94.9	91 ± 4
Al	106	282	-
Cu	13.4	13.6	12 ± 1
Sr	32.5	33.4	37 ± 1
Fe	320	298	300 ± 20
S	1769	-	1900
P	2011	2374	2100 ± 100
Mg	5139	6557	6200 ± 200
K	14539	14310	14700 ± 300

Total percentage analyses for C, H, N and S in subsamples of the homogenised leaf material were carried out using the Leco CHNS- 932 instrument.

5.5. Data analysis, statistical limitations and assumptions

From the elemental concentrations in the leaves and leaf litter collected from RTPMC in November 2008, April 2011 and November 2011, comparisons between the three tree species in the two areas with different sources of contamination could be made. The relationship between the contamination levels and the distance from the source and whether there was an effect of sampling year or season could also be determined for unwashed leaves.

These factors are important in designing appropriate monitoring protocols that use bioindicators to determine the spread of contaminants form smelter plume deposition and Cu tailings seepage.

Data were analysed using Microsoft Excel and the statistical program SAS, Enterprise Guide 4.2.

The data analyses were based on:

- Varying distances from point source (leaves in smelter plume deposition area)
- High impact areas (smelter plume deposition area and Cu tailings seepage area)
- Late wet season and early wet season (April and November 2011)
- Time periods (November 2008 and November 2011, i.e. for the early wet season)
- Tree species (*Lonchocarpus capassa, Colophospermum mopane* and *Euclea divinorum)*
- Leaf litter layer samples (November 2008, April 2011 and November 2011)

From the above list of categories the Pearson's R correlation analysis, Wilcoxon- Mann Whitney Test and the Wilcoxon signed rank test were used. Analyses were limited to non parametric tests since the majority of data within the categories was not normally distributed. There were also many different monitoring localities and different monitoring periods, thus limited replicates per category.

6. Results

A total of 135 leaf samples were analysed from the two RTPMC regions, of which 51 were from the Cu tailings seepage area, 74 from the smelter plume deposition area and 10 were leaf litter samples (Table 8 and Table 21 in Appendix). The samples were collected in November 2008 (N= 23), replicated samples were obtained from the same trees in November 2011 (N= 19) and additional sampling was carried out in April 2011 (N= 58) and November 2011 (N= 35).

Table 8: Summary of the number of samples collected for the study and the number of samples in the smelter plume that were collected close to and far from the smelter stacks

Tree type	Time of collection	Cu tailings seepage area	Smelter plume	Of the smelter plume samples those that were close to or far away from the smelter stacks:	
				Close (< 1000 m)	Far (> 1000 m)
L. capassa	2008	0	9	5	4
	Repeats of 2008 in Nov 2011	0	8	5	3
	April 2011	12	11	3	8
	November 2011	10	6	2	4
C. mopane	2008	6	0	0	0
	Repeats of 2008 in Nov 2011	2	0	0	0
	April 2011	13	12	2	10
	November 2011	8	8	1	7
E. divinorum	2008	0	3	0	3
	Repeats of 2008 in Nov 2011	0	4	0	4
	April 2011	0	10	2	8
	November 2011	0	4	1	3
Leaf litter	2008	2	3	1	2
	2011	2	3	1	2

L. capassa leaves were not collected from the Cu tailings seepage area in 2008. *E. divinorum* trees were very rare in the Cu tailings seepage area and were therefore not sampled. Most of the samples collected in the smelter plume area were collected from a distance of more than 1000 m away from the smelter smoke stacks.

From the ICP-OES analyses of the RTPMC leaf samples the elements that fell below the minimum detection limits were: As, Co, Cr, Zn, Ag, Au, Ba, Be, Eu, Ga, Gd, Ge, Hg, Ir, In, Li, Mo, Os, Pd, Pt, Rb, Ru, Rh, Sb, Sc, Se, Sn, Ta, Te, Th, Tl, U, V, Y and Zr.

As shown in Table 9 many of the essential elements required by plants are enriched in the commonly occurring minerals at RTPMC which is why Ni, Al, Cu, S, Fe, P and K were chosen for assessment. Due to the abundance and mining of these minerals in this area, these commonly occurring elements may be present at elevated concentrations in the environment. From the table it is obvious that there is an abundance of Al, Cu and Fe in the RTPMC area. There may also be elevated concentrations of Ni, Ti, S, Mg and P. However, elevated total concentrations in the environment do not imply that these elements will be more bioavailable for plant uptake.

Table 9: Common minerals found and by products produced at the RTPMC

Name	Chemical formula
Cu in carbonatite (chalcopyrite and bornite)	$CuFeS_2$ and Cu_5FeS_4
Vermiculite	$(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$
Phlogopite	$KMg_3(AlSi_3O_{10})(F,OH)_2$
Magnetite	Fe_3O_4
Baddeleyite (Titanium dioxide)	TiO_2
Phosphate rock (apatite)	$Ca_5(PO_4)_3(F,Cl,OH)$
Ni sulphate	$NiSO_4$

6.1. Element concentration in leaves versus distance of tree from smelter

The Pearson's R correlation analysis between the concentrations of elements in leaves and the distance of the tree from the contamination source, the smelter stacks, revealed that both positive and negative correlations are present (Table 10 and Table 24 in Appendix). Pearson's R values range from - 1 to + 1. Strong correlations are regarded as Pearson's R values greater than ± 0.4 and weak correlations are regarded as Pearson's R values less than ± 0.3.

The furthest distance from the smelter fell close to the main road and industrial area of the town of Palabora. Cu showed strong negative correlations in *L. capassa* and *E. divinorum* in both April and November 2011. Therefore Cu concentrations declined with increasing distance

from the smelter in these tree species. Bi, Ti and S were also present at higher concentrations closer to the smelter (strong negative Pearson's R values) in *E. divinorum* and *L. capassa* in April and November 2011. The number of positive correlations increased from April to November and the number of negative correlations decreased from April to November in all three tree species (Table 10).

The correlation results for April 2011, from the late wet to early dry season, when the leaves were mainly older thus expecting the concentration of elements in the leaves to be higher than the November 2011 leaves, are producing mainly negative correlations. The results for November 2011, from the early wet season, when the leaves were mainly new and we thus expect the concentration of elements in the leaves to be lower than the April 2011 leaves, indicate that, except for *E. divinorum* which is an evergreen tree, there are mainly positive correlations.

Table 10: Pearson's R correlation analysis of element concentration in leaves versus distance of tree from smelter for the three tree species in April and November 2011

Element	*L. capassa*		*C. mopane*		*E. divinorum*	
	Apr-11	Nov-11	Apr-11	Nov-11	Apr-11	Nov-11
Al	-0.35	0.76	-0.64	-0.67	-0.63	-0.40
Cu	-0.64	-0.65	0.55	0.24	-0.46	-0.87
Fe	0.09	0.44	0.11	-0.25	-0.69	-0.07
Mn	0.50	0.66	0.30	0.33	-0.65	-0.42
Bi	-0.60	-0.69	0.91	0.45	-0.65	-0.84
K	-0.80	0.11	-0.41	0.63	-0.96	0.66
Mg	0.23	0.74	0.35	0.60	-0.56	-0.68
Ni	-0.23	0.53	0.20	0.47	-0.36	-0.40
Sr	-0.04	0.75	0.13	0.56	0.15	-0.39
Ti	-0.90	0.57	-0.75	0.25	-0.87	0.10
W	-0.86	0.66	-0.39	0.54	0.20	0.87
P	-0.30	-0.16	0.38	0.60	-0.98	0.76
S	-0.72	-0.40	0.49	0.68	-0.92	-0.96
Positive correlations	**1**	**8**	**3**	**8**	**0**	**3**
Negative correlations	**6**	**3**	**4**	**1**	**10**	**7**

Red cells indicate a strong positive correlation and green cells indicate a strong negative correlation

6.2. Leaves in the smelter plume deposition area and the Cu tailings seepage area

Comparisons of the concentrations of various elements in the smelter plume deposition area and the Cu tailings seepage area from April 2011 using *L. capassa* and *C. mopane* leaves as representative species revealed that the concentrations of Bi, Ni, Al and Cu were higher in the smelter plume area for both species (Table 11). The mean concentration of Cu in leaves of *L. capassa* in the smelter plume area was higher than the recommended maximum of 100 ug/g, which is the maximum tolerable level of Cu in cattle feed (National Research Council 1984).

Significant differences were found between the concentrations of Bi, Ti, Cu and Fe in *L. capassa* leaves and between the concentrations Bi and S in *C. mopane* leaves from the smelter plume area and Cu tailings seepage area ($P < 0.05$).

Table 11: The mean, median and range of concentrations in ug/g of some elements found in leaves of *L. capassa* and *C. mopane* in the smelter plume deposition area and Cu tailings seepage area in April 2011

L. capassa	**Smelter plume deposition area** (N= 6)			**Cu tailings seepage area** (N= 8)			**Wilcoxon-Mann-Whitney Test**		
	Mean	**Median**	**Range**	**Mean**	**Median**	**Range**	**W (x)**	**Z**	***P***
Bi	0.72	0.64	0.32- 1.20	0.15	0.15	0.09- 0.23	W(1)= 6	-2.19	**< 0.05**
Ni	1.15	1.18	0.87- 1.39	1.00	0.98	0.84- 1.24	W(1)= 53	0.97	> 0.05
Ti	14.4	14.9	6.72- 21.3	5.60	5.60	2.93- 8.26	W(1)= 4	-1.50	**< 0.05**
Al	35.2	36.0	12.2- 49.5	21.3	14.8	8.08- 40.5	W(1)= 29	-1.52	> 0.05
Cu	106	94.4	18.9- 197	14.8	9.29	2.63- 38.1	W(1)= 11	-2.24	**< 0.05**
Fe	561	443	411- 1058	347	358	216- 517	W(1)= 60	1.87	**< 0.05**
S	2175	1976	203- 4254	2179	1725	1366- 4381	W(1)= 47	0.19	> 0.05
C. mopane	**Smelter plume deposition area** (N= 8)			**Cu tailings seepage area** (N= 7)			**Wilcoxon-Mann-Whitney Test**		
	Mean	**Median**	**Range**	**Mean**	**Median**	**Range**	**W (x)**	**Z**	***P***
Bi	0.24	0.23	0.17- 0.35	0.05	0.05	0.05- 0.06	W(1)= 3	-1.91	**< 0.05**
Ni	1.11	1.02	0.71- 1.95	0.97	1.03	0.70- 1.07	W(1)= 51	-0.52	> 0.05
Ti	10.3	8.55	4.52- 17.9	13.7	9.82	8.58- 22.6	W(1)= 13	0.87	> 0.05
Al	24.6	14.3	9.17- 53.2	23.6	23.6	23.6	W(1)= 4	0	> 0.05
Cu	33.8	24.2	8.39- 77.8	14.5	14.5	14.5	W(1)= 2	-0.75	> 0.05
Fe	323	284	167- 660	360	181	121- 986	W(1)= 49	-0.75	> 0.05
S	1963	1863	1265- 3379	1495	1453	1180- 1853	W(1)= 35	-2.37	**< 0.05**

Comparisons of the concentrations of various elements in the smelter plume area and the Cu tailings seepage area from November 2011 using *L. capassa* and *C. mopane* leaves as representative species yielded numerous significant differences between the two areas (Table 12). The Cu levels measured in both the tree leaf species were below the recommended 100 ug/g as stated previously for ruminant cattle consumption (National Research Council 1984). The concentrations of Bi, Ni, Cu and S were higher in the smelter plume area in both *L. capassa* and *C. mopane* leaves.

Significant differences were found between the concentrations of Bi, Sr and Fe in the *L. capassa* leaves and between Ni, Cu and Fe in the *C. mopane* leaves from the smelter plume area and Cu tailings seepage area ($P < 0.05$).

Table 12: The mean, median and range of concentrations in ug/g of some elements found in leaves of *L. capassa* and *C. mopane* in the smelter plume deposition area and Cu tailings seepage area in November 2011

L. capassa	**Smelter plume deposition area** (N= 6)			**Cu tailings seepage area** (N= 10)			**Wilcoxon-Mann-Whitney Test**		
	Mean	**Median**	**Range**	**Mean**	**Median**	**Range**	**W (x)**	**Z**	***P***
Bi	0.45	0.37	0.17 - 0.86	0.39	0.10	0.08 - 1.30	W(1)= 21	-1.75	**< 0.05**
Ni	1.47	1.28	1.18 - 2.02	1.24	1.28	0.91 - 1.49	W(1)= 99	-0.54	> 0.05
Ti	16.2	15.3	13.2 - 21.9	17.3	12.3	10.9 - 37.3	W(1)= 27	-1.53	> 0.05
Al	27.2	28.0	13.2 - 40.0	31.4	25.1	16.4 - 60.7	W(1)= 45	-0.20	> 0.05
Cu	69.5	62.6	27.4 - 125	68.7	13.7	8.67 - 184	W(1)= 17	-0.94	> 0.05
Fe	295	268	230 - 452	373	170	33.9 - 1969	W(1)= 79	-2.66	**< 0.05**
S	2141	1940	1729 - 2799	1986	2091	641 - 2573	W(1)= 98	-1.55	> 0.05
C. mopane	**Smelter plume deposition area** (N= 8)			**Cu tailings seepage area** (N= 7)			**Wilcoxon-Mann-Whitney Test**		
	Mean	**Median**	**Range**	**Mean**	**Median**	**Range**	**W (x)**	**Z**	***P***
Bi	0.13	0.15	0.07 - 0.16	0.07	0.07	0.06 - 0.07	W(1)= 4.5	-1.18	> 0.05
Ni	1.20	1.16	0.97 - 1.44	1.04	1.00	0.92 - 1.27	W(1)= 97	1.82	**< 0.05**
Ti	14.6	15.1	11.4 - 17.3	12.4	12.5	10.2 - 14.4	W(1)= 19	-1.10	> 0.05
Al	12.1	13.6	7.86 - 15.2	13.9	13.9	11.0 - 16.7	W(1)= 18	1.19	> 0.05
Cu	21.5	22.6	17.6 - 24.2	12.1	12.1	11.5 - 12.6	W(1)= 3	-1.44	**< 0.05**
Fe	232	214	173 - 374	149	147	108 - 204	W(1)= 102	2.27	**< 0.05**
S	1543	1541	1038 - 2124	1495	1453	1180 - 1853	W(1)= 82	0.49	> 0.05

6.3. Leaves sampled in November 2008 and November 2011

Comparisons of the concentrations of various elements in *L. capassa* and *E. divinorum* leaves within the smelter plume deposition area from 2008 and 2011 revealed that the concentrations of all of the elements in the samples were higher in 2008 except for Ni and P in *L. capassa* leaves and for Mn, Ti, P and Mg in *E. divinorum* leaves.

Significant differences in the concentrations of Bi, Ti, Sr, Cu and Fe in *L. capassa* leaves from 2008 and 2011 were found ($P < 0.05$). There was also a significant difference in the concentrations of Bi, Cu and Fe in *E. divinorum* leaves from 2008 and 2011 ($P < 0.05$) (Table 13). The concentration of Cu in leaves of *L. capassa* from 2008 and 2011 and of *E. divinorum* from 2008 was found to be higher than or very near to the recommended maximum of 100 ug/g in cattle feed (National Research Council 1984). No significant differences were picked up for S between 2008 and 2011 and the S concentrations remain high in both leaf types.

Table 13: The mean, median and range of concentrations in ug/g of some elements found in leaves of *L. capassa* and *E. divinorum* in the smelter plume deposition area in November 2008 and November 2011

L. capassa	**2008** (N= 8)			**2011** (N= 8)			**Wilcoxon signed rank test**	
	Mean	**Median**	**Range**	**Mean**	**Median**	**Range**	**W**	***P***
Bi	3.74	3.61	0.08 - 7.40	1.57	1.14	0.18 - 4.16	> 17	**< 0.05**
Ni	1.33	1.20	1.03 - 1.92	1.58	1.30	1.05 - 3.73	< -1	> 0.05
Ti	27.3	26.4	8.23 - 68.1	16.6	16.2	13.5 - 20.5	> 14	**< 0.05**
Al	77.1	65.7	28.4 - 179	54.8	30.9	12.5 - 212	< 9	> 0.05
Cu	734	722	174 - 1391	236	159	2.64 - 671	> 17	**< 0.05**
Fe	1682	1149	224 - 5059	664	355	230 - 2352	> 17	**< 0.05**
S	3253	2697	1613 - 8797	2569	2692	1943 - 3102	< -3	> 0.05
E. divinorum	**2008** (N= 3)			**2011** (N= 4)			**Wilcoxon signed rank test**	
	Mean	**Median**	**Range**	**Mean**	**Median**	**Range**	**W**	**P**
Bi	0.72	0.66	0.62 -0.89	0.26	0.26	0.04 - 0.47	> 8	**< 0.05**
Ni	1.05	0.98	0.91 - 1.26	0.91	0.86	0.84 - 1.01	< 2	> 0.05
Ti	11.1	12.6	5.12 - 15.4	12.9	12.9	12.3 - 13.4	< 3	> 0.05
Al	34.1	34.1	31.2 - 37.0	12.0	12.0	12.0	< 1.5	> 0.05
Cu	95.3	83.4	71.6 - 131	31.7	32.7	19.3 - 42.2	> 4	**< 0.05**
Fe	682	712	509 - 826	398	351	209 - 683	> 4	**< 0.05**
S	2336	2264	2087 - 2656	2233	2168	1786 - 2809	< 3	> 0.05

6.4. *Leaves sampled in April and November 2011*

Comparisons of the concentrations of various elements in leaves of *L. capassa* in the smelter plume deposition area from the late wet season (April) and the early wet season (November) revealed that the concentrations of all of the elements detected in the samples were higher in April except for Ni, Ti, P and K. Significant differences in the concentrations of Bi, Ni, Mn, Cu and Fe in the *L. capassa* leaves from April and November 2011 were found ($P < 0.05$) (Table 14).

Table 14: The mean, median and range of concentrations in ug/g of some elements found in leaves of *L. capassa* in the smelter plume deposition area in April and November 2011

L. capassa	**April** (N= 6)			**November** (N= 6)			**Wilcoxon signed rank test**	
	Mean	**Median**	**Range**	**Mean**	**Median**	**Range**	**W**	***P***
Bi	0.72	0.64	0.32 - 1.20	0.45	0.37	0.17 - 0.86	> -8.5	**< 0.05**
Ni	1.15	1.18	0.87 - 1.39	1.47	1.28	1.18 - 2.02	> 8.5	**< 0.05**
Ti	14.4	14.9	6.72 - 21.3	16.2	15.3	13.2 - 21.9	< 3.5	> 0.05
Mn	80.1	64.6	29.5 - 207	35.6	30.6	11.7 - 75.1	> -9.5	**< 0.05**
Al	35.2	36.0	12.2 - 49.5	27.2	28.0	13.2 - 40.0	< -5.5	> 0.05
Cu	106	94.4	18.9 - 197	69.5	62.6	27.4 - 125	> -8.5	**< 0.05**
Fe	561	443	411 - 1058	295	268	230 - 452	> -10.5	**< 0.05**
S	2175	1976	203 - 4254	2141	1940	1729 - 2799	< 1.5	> 0.05

Comparisons of the concentrations of various elements in leaves of *C. mopane* in the smelter plume deposition area from April and November 2011 revealed that the concentrations of all of the elements detected in the samples were higher in April except for Ni, Ti, Mn, P and K. Significant differences in the concentrations of Bi, Ti and S in the *C. mopane* leaves from April and November 2011 were found ($P < 0.05$) (Table 15).

Table 15: The mean, median and range of concentrations in ug/g of some elements found in leaves of *C. mopane* in the smelter plume deposition area in April and November 2011

C. mopane	**April** (N= 8)			**November** (N= 8)			**Wilcoxon signed rank test**	
	Mean	**Median**	**Range**	**Mean**	**Median**	**Range**	**W**	***P***
Bi	0.24	0.23	0.17 - 0.35	0.13	0.15	0.07 - 0.16	> -14	**< 0.05**
Ni	1.11	1.02	0.71 - 1.95	1.20	1.16	0.97 - 1.44	< 9	> 0.05
Ti	10.3	8.55	4.52 - 17.9	14.6	15.1	11.4 - 17.3	> 17	**< 0.05**
Mn	23.0	11.9	4.81 - 62.9	24.6	19.3	11.4 - 61.1	< 10	> 0.05
Al	24.6	14.3	9.17 - 53.2	12.1	13.6	7.86 - 15.2	< -6	> 0.05
Cu	33.8	24.2	8.39 - 77.8	21.5	22.6	17.6 - 24.2	< -9	> 0.05
Fe	323	284	167 - 660	232	214	173 - 374	< -6	> 0.05
S	1963	1863	1265 - 3379	1543	1541	1038 - 2124	> -13	**< 0.05**

Comparisons of the concentrations of various elements in leaves of *E. divinorum* in the smelter plume deposition area from April and November 2011 revealed that the concentrations of all of the elements detected in the samples were higher in November. Significant differences in the concentrations of Bi, Ni, Ti, Cu and Fe in the *E. divinorum* leaves from April and November 2011 were found ($P < 0.06$) (Table 16). Here a 6 % level of significance was used whereas previously a 5 % level of significance was used, however these findings are still useful and important.

Table 16: The mean, median and range of concentrations in ug/g of some elements found in leaves of *E. divinorum* in the smelter plume deposition area in April and November 2011

E. divinorum	**April** (N= 5)			**November** (N= 4)			**Wilcoxon signed rank test**	
	Mean	**Median**	**Range**	**Mean**	**Median**	**Range**	**W**	***P***
Bi	0.41	0.33	0.27 - 0.65	0.57	0.67	0.33 - 0.72	> 7.5	**< 0.06**
Ni	1.02	1.02	0.94 - 1.11	1.27	1.29	1.18 - 1.33	> 7.5	**< 0.06**
Ti	15.4	14.6	14.2 - 18.1	18.7	19.1	16.9 - 20.0	> 7.5	**< 0.06**
Mn	31.6	28.1	22.0 -52.9	33.0	37.6	15.9 - 45.6	< 1.5	> 0.06
Al	27.2	27.0	9.84 - 49.0	31.4	32.3	17.2 - 44.8	< 1.5	> 0.06
Cu	47.1	42.9	26.6 - 90.3	72.0	84.5	35.4 - 96.0	> 7.5	**< 0.06**
Fe	309	258	236 - 415	448	498	326 - 519	> 7.5	**< 0.06**
S	2336	2299	1314 - 3010	2631	1870	1696 - 4327	< 2.5	> 0.06

The results from the analysis of the leaf samples taken from trees in the Cu tailings seepage area, revealed that the concentrations of all of the elements detected were higher in November than in April 2011, except for Mn, Sr, S and Mg in *L. capassa* leaves and for Ti, Sr, Al, Cu, Fe and Mg in *C. mopane* leaves. Significant differences were found between the concentrations of Fe ($W > -14$, $P < 0.05$) and Sr ($W > -17$, $P < 0.05$) in the *L. capassa* leaves sampled from the Cu tailings seepage area in April and November 2011.

6.5. Comparing the elemental concentrations in leaves from the three tree species

Since the trees that were sampled in this study are all quite different with regard to growth, size, leaf shape and surface texture, it was expected that there would be differences between the tree species with respect to the concentrations of elements in the leaves. Such concentration differences were observed for Bi, Ti, Mn, Al and Cu. The general trend of these element concentrations was *L. capassa* > *E. divinorum* > *C. mopane* leaves.

Significant differences in the concentrations of Bi, Mn, Cu and Fe were found between the leaves of the three tree species (*L. capassa, C. mopane* and *E. divinorum)* in the smelter plume area from April 2011 ($p < 0.05$). Significant differences in the concentrations of Bi, Al, Cu, Fe and S were found between the leaves of the three tree species (*L. capassa, C. mopane* and *E. divinorum)* in the smelter plume area from November 2011 ($p < 0.05$).

Significant differences in the concentrations of Bi, Ti, Mn and S were found between the leaves of the *C. mopane* and *L. capassa* in the Cu tailings seepage area from April 2011 ($p < 0.05$). Significant differences in the concentrations of Bi, Ni, Mn and S were found between the leaves of *C. mopane* and *L. capassa* in the Cu tailings seepage area from November 2011 ($p < 0.05$).

The concentrations of Mn, Al, Cu and Fe in ug/g, found in the leaves of the three different tree species (**AB**: *L. capassa*, **Mop**: *C. mopane* and **Euc**: *E. divinorum* in Figures 13, 14, 15 and 16) in the Cu tailings seepage area (**Cu Tail** in Figures 13, 14, 15 and 16) and in the smelter plume deposition area (**Plume** in Figures 13, 14, 15 and 16) from the various sampling periods are shown below.

The highest mean concentration of Mn was 120 + 37.9 ug/g, from *L. capassa* leaves sampled in April 2011 in the Cu tailings seepage area (**Apr-11 AB Cu Tail**) (Figure 13).

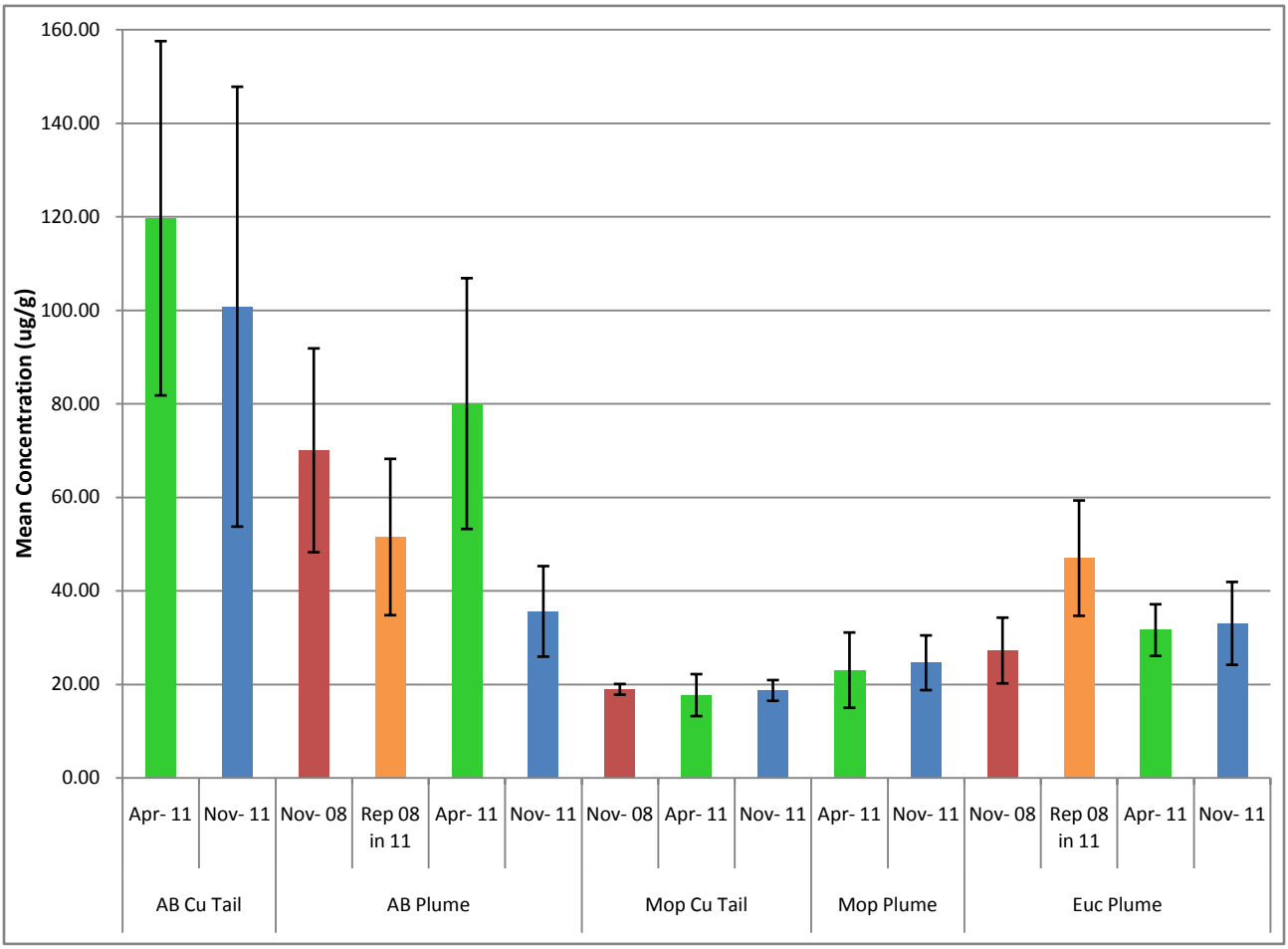

Figure 13: Mean concentrations of Mn (ug/g with SE bars) in the leaves of the three tree species (AB: *L. capassa*, Mop: *C. mopane* and Euc: *E. divinorum*) in the two high impact areas, Cu Tail and Plume at Rio Tinto Palabora Mining Company

The concentrations of Al, Cu and Fe were highest in the leaves from *L. capassa* in the smelter plume area, for November 2008 and repeats of November 2008 in November 2011 (**AB Plume**) (Figures 14- 16). The concentrations of Al, Cu and Fe in leaves from November 2011 were highest in *E. divinorum* from the smelter plume deposition area (**Nov- 11 Euc Plume**).

The highest mean concentration of Al was 77.1 + 19.8 ug/g, from *L. capassa* leaves sampled in November 2008 in the smelter plume area (**Nov- 08 AB Plume**) (Figure 14).

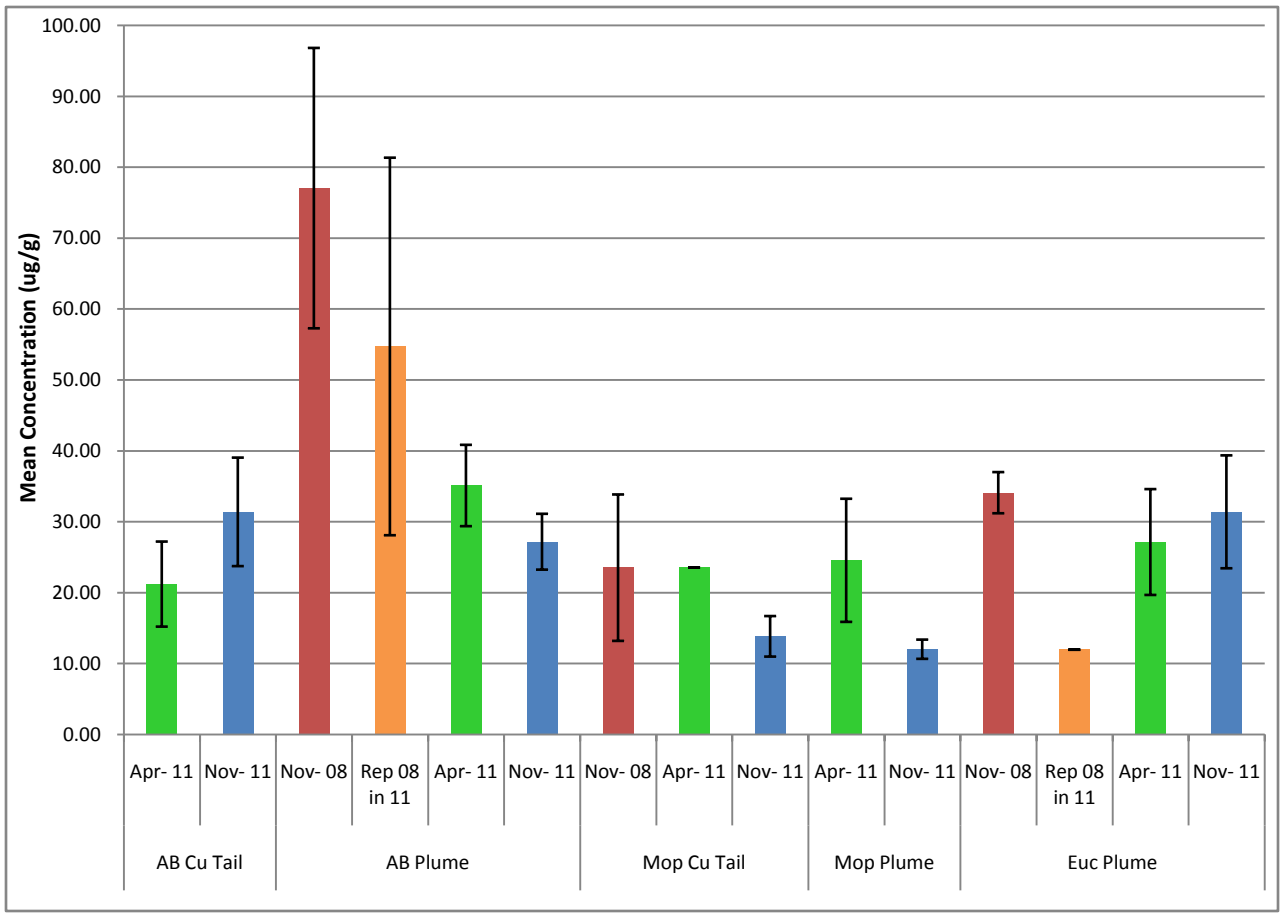

Figure 14: Mean concentrations of Al (ug/g with SE bars) in the leaves of the three tree species (AB: *L. capassa*, Mop: *C. mopane* and Euc: *E. divinorum*) in the two high impact areas, Cu Tail and Plume at Rio Tinto Palabora Mining Company

Cu concentrations in *L. capassa* leaves were higher in the samples taken from the smelter plume area than in the samples from the Cu tailings seepage area. The highest mean concentration of Cu was 734 + 173 ug/g, from *L. capassa* leaves sampled in November 2008 in the smelter plume area (**Nov- 08 AB Plume**) (Figure 15).

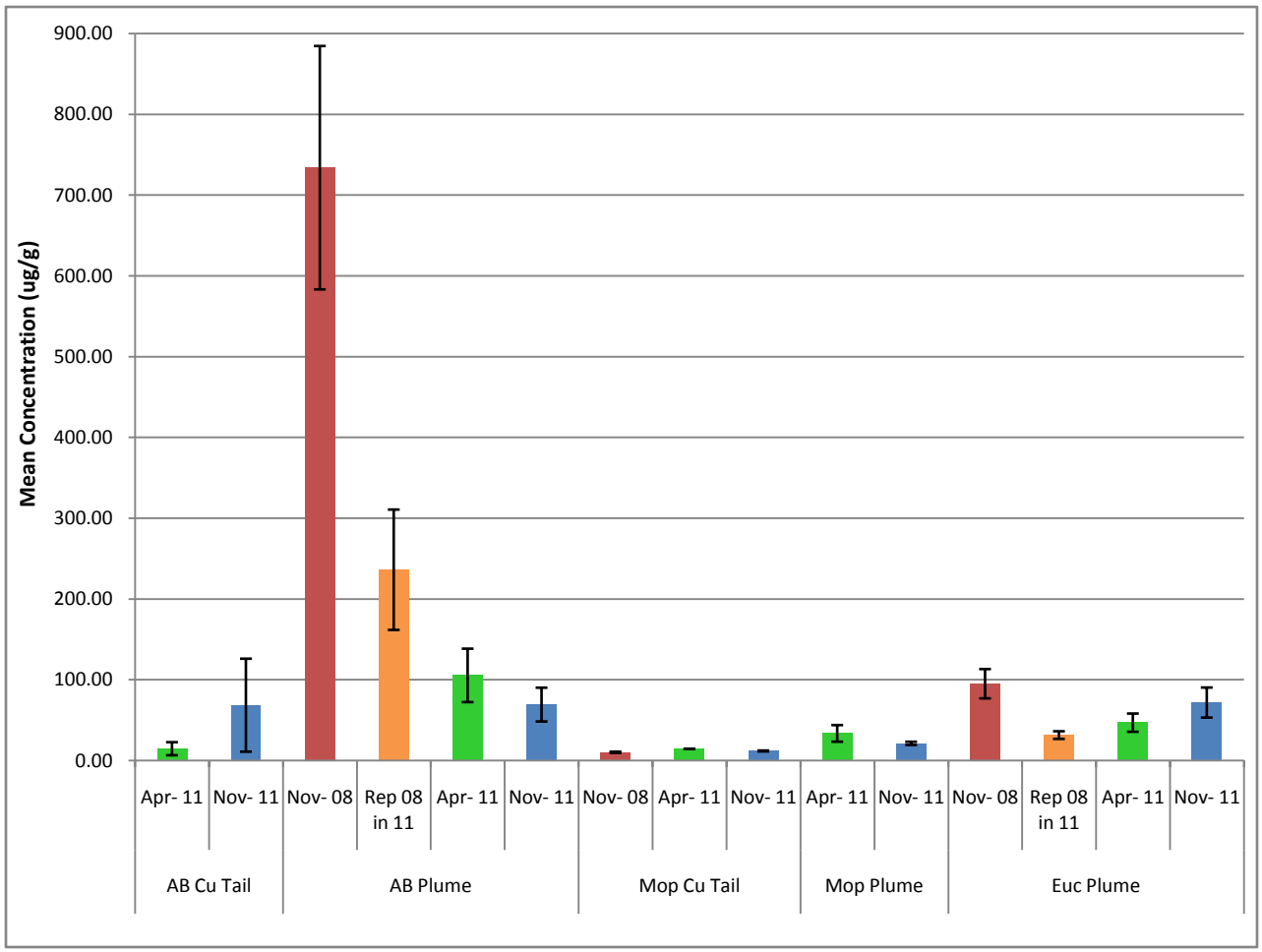

Figure 15: Mean concentrations of Cu (ug/g with SE bars) in the leaves of the three tree species (AB: *L. capassa*, Mop: *C. mopane* and Euc: *E. divinorum*) in the two high impact areas, Cu Tail and Plume at Rio Tinto Palabora Mining Company

Fe was found in all samples with the minimum mean concentration of Fe occurring in *C. mopane* leaves from the Cu tailings seepage area (**Mop Cu Tail**). No significant differences were found between the concentrations of Fe in the leaves from the smelter plume deposition area and Cu tailings seepage area.

The highest mean concentration of Fe was 1682 + 541 ug/g, from *L. capassa* leaves sampled in November 2008 in the smelter plume area (**Nov- 08 AB Plume**) (Figure 16).

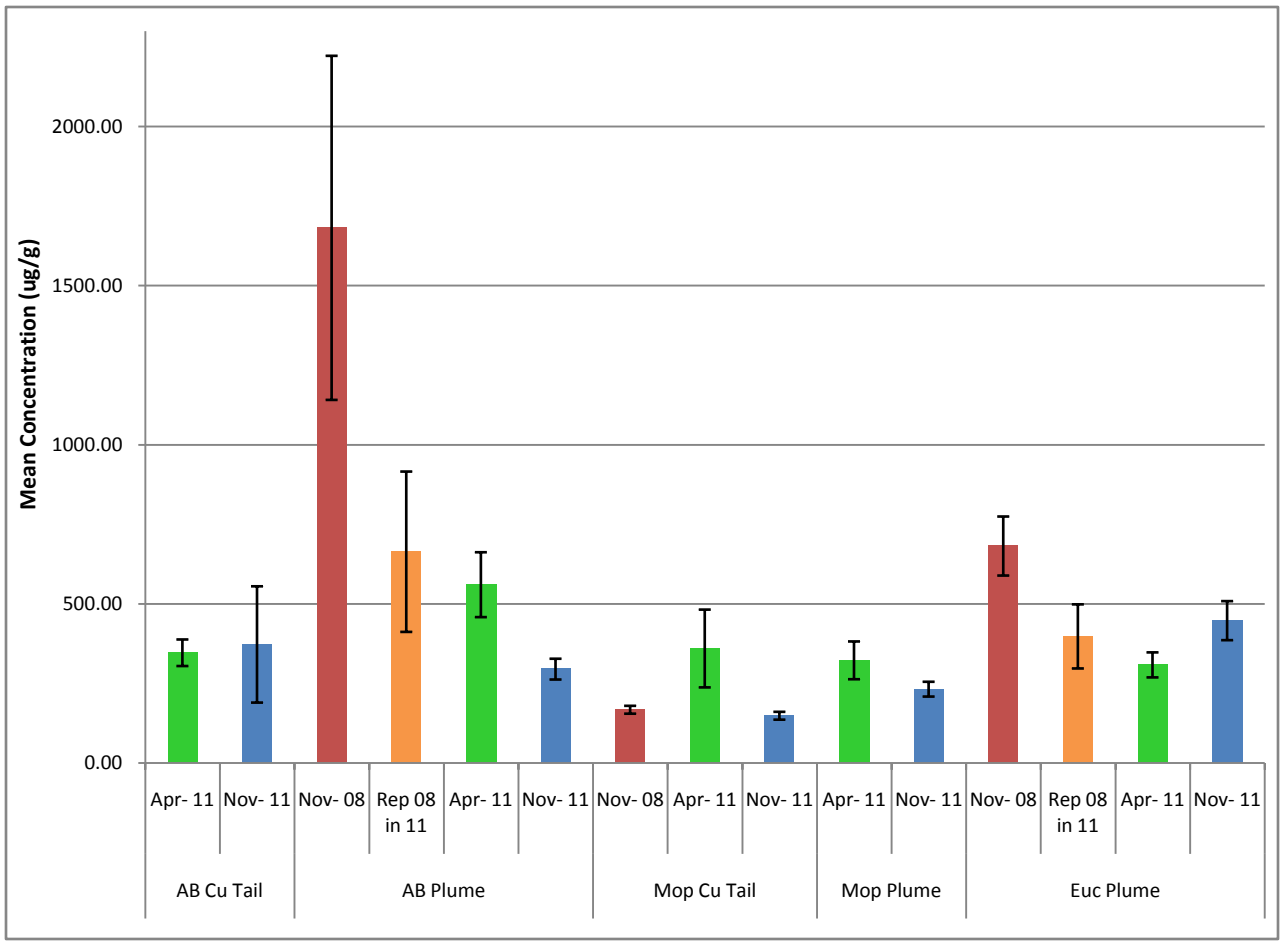

Figure 16: Mean concentration of Fe (ug/g with SE bars) in the leaves of the three tree species (AB: *L. capassa*, Mop: *C. mopane* and Euc: *E. divinorum*) in the two high impact areas, Cu Tail and Plume at Rio Tinto Palabora Mining Company

6.6. Elemental analysis of the leaf litter

The leaf litter samples taken from underneath some of the trees that were sampled for leaves proved to have high concentrations of heavy metals and dust elements. Throughout the study it was observed that there was little decomposition of the leaf litter, resulting in a deep layer of litter. The highest concentrations of the heavy metals such as Pb, Al, Cu and Fe were found in the leaf litter (Table 17). Pb was very low in most samples; however the highest concentrations of Pb were detected in the leaf litter sampled from the smelter plume deposition area in 2008. The concentrations of all of the elements of interest in the leaf litter decreased from 2008 to 2011. Significant differences in the concentrations of Bi, Ti, Cu and Fe were found between the leaf litter samples from November 2008 and November 2011 ($p < 0.05$).

Table 17: The mean, median and range of concentrations in ug/g of some elements found in leaf litter samples from 2008 and 2011

Leaf Litter	**2008** (N= 5)			**2011** (N= 5)			**Wilcoxon signed rank test**	
	Mean	**Median**	**Range**	**Mean**	**Median**	**Range**	**W**	***P***
Bi	9.44	1.96	0.78 - 25.4	1.70	1.26	0.29 - 3.56	> 7.5	**< 0.05**
Ni	1.57	1.42	0.81 - 2.62	1.11	1.10	0.95 - 1.30	< 6.5	> 0.05
Ti	122	103	17.6 - 218	40.8	50.5	15.5 - 54.5	> 6.5	**< 0.05**
Pb	16.3	16.3	15.2 - 17.3	Below Detection Limit				
Mn	110	106	27.8 - 166	67.4	56.7	30.3 - 104	< 3.5	> 0.05
Al	483	395	95.1 - 997	246	226	102 - 353	< 2.5	> 0.05
Cu	1463	382	101 - 3401	273	194	25.0 - 573	> 7.5	**< 0.05**
Fe	5611	6136	751 - 8515	1683	2061	681 - 2749	> 6.5	**< 0.05**
S	2812	1642	1346 - 5022	1485	1461	835 - 2487	< 6.5	> 0.05

6.7. Results from the C, H, N and S analyses in leaves and leaf litter

The total percentage of C, H, N and S in 44 leaf samples and 5 leaf litter samples was determined (Figures 17 and 18). The dry substance of the plant body is mainly composed of the following elements: C (44.5 %), oxygen (42.5 %), hydrogen (6.5 %), N (2.5 %), P (0.2 %), S (0.3 %) and the alkali and alkaline-earth metals K (1.9 %), Ca (1.0 %) and Mg (0.2 %) (Markert 1992). Oxygen is therefore most likely making up most of the "% other" in the results for this study as plants are made up of about 43 % oxygen (Markert 1992).

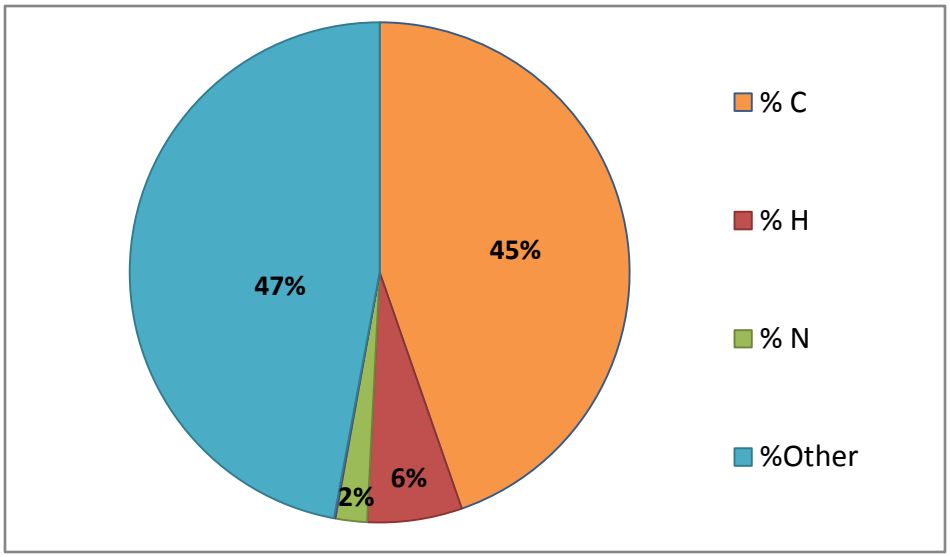

Figure 17: Mean CHNS results for the leaves from all sources combined

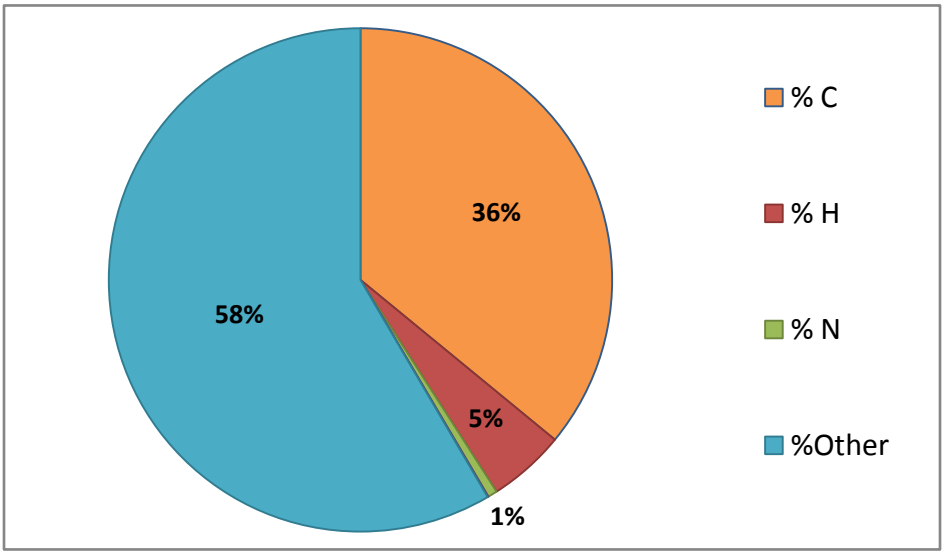

Figure 18: Mean CHNS results for the leaf litter from all sources combined

The percentage of C in the leaf litter is lower than in the leaves and there is a large increase in the "% other" in the leaf litter compared to the leaves because C, N and S are utilized during decomposition. The concentration of heavy metals in the leaf litter was higher than in the leaves, therefore the "% other" in the leaf litter would also include these heavy metals.

7. Discussion

The leaf samples collected at the Rio Tinto Palabora Mining Company produced interesting and comparable results to other studies. Using the concentrations and percentages given in Table 18 as a guide to the global average concentrations occurring in all plants, the concentrations found in the leaves from trees at RTPMC can be accessed. There were higher than average concentrations of K, S, Fe, Cu and Bi and lower than average concentrations of Al and Mn in the leaves sampled at the RTPMC. Although Cu is essential for plant growth, only a very small amount of Cu is required. The plants growing in the contaminated areas around the RTPMC mine have elevated amounts of Cu. Literature also indicates that in plants, the amounts of N, P and K should be greater than Ca in addition to Mg and S being greater than Fe, Mn, Zn, Cu, B, Mo and Cl (Morgan 2011).

Table 18: Global average concentration of some elements in all plants compared to ranges found in leaf and leaf litter samples from RTPMC (compiled from Adriano 1986, Cali 1977 and Markert 1992)

Element	Average Concentration	Range in leaves	Range in leaf litter
C	44 %	35 – 52 %	33 – 38 %
O	44 %	–	–
H	6 %	5 – 7 %	5 %
N	1.5 – 2.8 %	0.3 – 4 %	0.1 – 1 %
P	0.2 %	0.08 – 0.30 %	0.07 – 0.13 %
K	1 – 1.5 %	0.61 – 1.72 %	0.11 – 0.42 %
Mg	0.2 – 0.6 %	0.15 – 0.40 %	0.27 – 0.63 %
S	0.1 %	0.12 – 0.33 %	0.15 – 0.28 %
Fe	100 – 300 ug/g	149 – 1682 ug/g	1683 – 5611 ug/g
Cu	5 – 20 ug/g	10 – 734 ug/g	273 – 1463 ug/g
Al	90 – 530 ug/g	12 – 77 ug/g	246 – 483 ug/g
Mn	50 – 700 ug/g	18 – 120 ug/g	67 – 110 ug/g
Ti	0.02 – 56 ug/g	6 – 27 ug/g	41 – 122 ug/g
Ni	0.5 – 4 ug/g	0.9 – 1.6 ug/g	1.1 – 1.6 ug/g
Bi	0.05 – 0.2 ug/g	0.05 – 3.7 ug/g	1.7 – 9.4 ug/g

Red indicates concentrations at the higher end of global average concentrations and blue indicates concentrations at the lower end of global average concentrations.

The hyper-accumulation thresholds for commonly studied metals in plants are: 10 000 ug/g of Mn or Zn; 1000 ug/g of Ni, Cu , Se, Al and As; and 100 ug/g of Cd, Cr, Pb or Co, therefore none of the tree species sampled in this study can be classified as hyper-accumulators (Boyd 2004). However, the concentrations of some of the element in the leaves were at the upper end of the global average.

pH is a significant environmental factor controlling the availability of metals (John and Leventhal 1994). Due to the calcite composition of the host rock at RTPMC there is natural alkalinity. In open veld areas at RTPMC, where there is an absence of degrading organic soil components and elevated alkalinity, the Ca, Al and P buffer capacity of the soil should mitigate acid generation and thus the mobilisation of metals (Posnik 2002).

It is a positive finding that very little Pb, mostly below the detection limit, was found in the majority of the leaf samples as Pb can have serious negative impacts on the environment (John and Leventhal 1994). However the plant Pb content may have been very low due to the low bioavailability of Pb.

7.1. Element concentration in leaves versus distance of tree from smelter

From the correlation analysis of element concentration in the leaves versus distance of the tree from the smelter smoke stacks, it was expected that the deposition would mostly occur closer to the smelter therefore a negative correlation would be likely. The correlation results presented in Table 10, show that most of the elements did have a negative correlation. Such results are in agreement with the findings from studies carried out at RTPMC and other Cu mines (Hunter et al. 1987; RTPMC 2008). In these studies it was also found that the contamination from the Cu smelting process was widespread with elevated levels evident within 3 - 10 kms away from the refineries (Hunter et al. 1987; RTPMC 2008).

In a similar correlation study on *C. mopane* leaves around the Selebi Phikwe Ni-Cu mine in Botswana, strong associations were observed for Cu and Fe, for concentrations of the metals and distance to the smelter plant (Ekosse et al. 2005). The concentrations of heavy metals were found to be inversely related to distance from the contamination site for the eight metals (Cu, Ni, Fe, Cr, Co, Cd, Zn and Se) studied. Stronger associations generally existed between concentrations in the soil than in the leaves (Ekosse et al. 2005).

L. capassa and *E. divinorum* leaves from this study had the highest number of correlations with element concentrations and distance from the smelter. Except for Bi, Cu and S the correlation for the other elements in *L. capassa* leaves either changed from a weak correlation in April to a positive correlation in November or from a negative correlation in April to a positive correlation in November. *E. divinorum* leaves showed a strong negative correlation for S in April and November. This may be due to the SO_2 which is emitted from the smelter stacks (mainly reverberatory and some converter off-gas) and the fact that *E. divinorum* is evergreen, thus S can accumulate on and in the leaves throughout the year. Elements in *C. mopane* leaves

showed a small number of correlations. The concentrations of most of the elements analysed were also lower in the *C. mopane* leaves, both close to and far away from the smelter stacks.

E. divinorum is an evergreen tree, therefore the leaves collected were generally older, and in both April and November 2011 the correlations were mainly negative, however there were fewer significant correlations in November. This is of interest as in April, which is at the end of the wet season, when *L. capassa, C. mopane* and *E. divinorum* all had older leaves, there were mainly negative correlations while in November, which is at the end of the dry season, when *L. capassa* and *C. mopane* had flushed with new leaves, there were mainly positive correlations. Also *L. capassa* and *C. mopane* are deciduous. Therefore it is possible that the canopy surface area for interception and deposition is smaller at the end of the dry season (November) than at the end of the wet season (April) and this could produce the observed pattern. From the results of this study it appears that the correlation between concentration and distance from the smelter is most strongly associated with leaf age. Other factors that determine the correlations may also be rainfall and wind (speed and frequency).

The wind frequencies and speeds obtained in a study at RTPMC found that in spring and summer the wind speeds are higher and the wind blows more frequently than in autumn and winter (Neveling 2011). The results from the current study found that more negative correlations existed at the end of the wet season (more wind) and more positive correlations existed at the end of the dry season (less wind). This was also found in the Palabora Mining Company Statistical and Geostatistical Evaluation Report that investigated the concentrations of Cu, where an increase in wind speed correlated with an increase in Cu concentration as more Cu gets transported and deposited.

7.2. Smelter plume deposition area versus the Cu tailings seepage area

In the 2002 EMPR update for RTPMC it was stated that it is difficult to differentiate between airborne deposition and that from spillages as well as that the contribution to total pollution from airborne sources is significant (Posnik 2002). Cu dust emitted from the smelter stacks has historically been relatively significant, with higher deposition close to the smelter. Dust is also

emitted from the various stockpiles on site, the tailings dam and the magnetite stockpiles to the north and northwest and east of the site (Posnik 2002).

The findings from this study for the comparison of leaves sampled in the smelter plume deposition area and the Cu tailings seepage area indicate that the concentrations of the metals Bi, Ni and Cu are higher in the smelter plume deposition area in all three of the tree species. Therefore, the pollution generated from the Cu smelting process is most likely the cause of these elevated concentrations. Bi is commonly found in areas with air pollution. Bi, which has a very low melting temperature and low boiling point, is volatilised during the Cu smelting process and forms part of the gaseous waste stream (Ayres et al. 2002). It is generally not regarded as environmentally hazardous, but there have been suspicions of a relationship with brain disease leading to a ban in France (1978) and a ban on cosmetic use in Austria (1986) (Ayres et al. 2002). The presence of elevated concentrations of Bi and Cu in the smelter plume area indicates that there is contamination from the smelter plume, thus from airborne deposition.

7.3. November 2008 versus November 2011

The sampling in November 2008 was carried out after a severe acid mist occurrence (Surmon and Weiersbye 2012). The leaves of many of the trees that were sampled in 2008 showed signs of stress, acid damage and defoliation (Surmon and Weiersbye 2012). Aerosol deposits may have contained a combination of $SO_{2,}$ heavy metals and soot.

This acid mist occurrence may be the reason that the concentrations of the heavy metals and other elements of interest were so much higher in 2008 than in 2011. The acid mist could have lowered the pH of the soil solution causing the metals to mobilise and be taken up by the trees. This was found in a study that investigated the effects of acid precipitation on the toxicity of metals. By decreasing the pH, the corrosiveness of water increased, enhancing the mobilisation of metal salts from soil and metallic compounds from minerals (Nordberg et al. 1985).

7.4. Late versus early wet season

The results obtained for the comparisons of leaves from April 2011 and November 2011 show that there is a difference between the concentrations of elements over different seasons. Leaves collected in April from *L. capassa* and *C. mopane*, at the end of the wet growing season when the leaves were older, generally had higher concentrations of elements as compared to the leaves of those same trees collected in November, the start of the wet growing season when the leaves were new. Leaves collected from *E. divinorum,* which were mostly older in April and November as *E. divinorum* is an evergreen tree, had higher concentration of elements in November after the dry season.

The rainy season in Phalaborwa is between November and March with the maximum rainfall falling in January (Neveling 2011). The Statistical and Geostatistical Evaluation Report, January 2002 – October 2008, concluded that higher Cu concentrations are recorded in unwashed plant material during the drier winter months, than in the wetter summer months and that the transport of the duct from the smelter plume is a function of the wind and rainfall pattern (RTPMC 2008). When there was an increase in the rainfall the Cu concentration afterwards decreased, suggesting that the Cu is washed away from the vegetation surface and perhaps drained into the soils (RTPMC 2008). In another similar study investigating Cu, it was concluded that the winter peak of Cu in leaves reflected the translocation of Cu into older shoots and leaves prior to the shedding of these leaves and the incorporation into the litter layer where the Cu concentrations are then diluted as new leaves grow in spring (Hunter et al. 1987).

The differences in the concentrations of certain elements such as Bi, Ni, Ti, Cu, Fe and S in this study are most likely influenced by dust deposition, rainfall patterns and growth of new leaves. Titanium dioxide, from the mineral Baddeleyite which commonly occurs at RTPMC, has a very small grain size and is classified as dust pollution (Markert 1992). Therefore, the significant differences picked up for Ti as well as Bi, Ni, Cu and Fe in *E. divinorum* leaves between April and November 2011 in the smelter plume deposition area indicate that in April, after there has been rainfall, the windblown dust and particles deposited on the leaves are washed off while in November after the dry season the dust has accumulated. In *L. capassa* and *C. mopane* leaves

the metals Ni and Ti were also found to be higher in November than in April 2011 in the smelter plume deposition area.

7.5. Tree species

When comparing the concentrations of Bi, Ni, Ti, Mn, Al, Cu, Fe and S in the leaves of the three different tree species, significant differences were found. Since the leaves of the three trees species have different shapes, surface areas and surface properties it was expected that the concentrations of certain elements would differ. The trees also have diverse growth patterns and life histories (Table 19). The general trend of the concentrations of these elements in the leaves was *L. capassa* > *E. divinorum* > *C. mopane*.

Table 19: Summary of some distinguishing characteristics of the three tree species sampled in this study (summarised from Van Wyk 2007 with own observations included)

Tree	***L. capassa***		***C. mopane***		***E. divinorum***	
Leaf surface area	Large		Medium		Small	
Average leaf age	**<** one year		**<** one year		**>** one year	
Leaf surface	Slightly hairy		Glabrous		Coriaceous with wavy edges	
Animal consumers	Game		Mopane worms, cattle, game		Insect larvae, birds	
Nitrogen fixing	No		Yes		No	
Average height of trees sampled for leaves (m)	Smelter plume	Cu Tail	Smelter plume	Cu Tail	Smelter plume	Cu Tail
	6.1	5.9	2.3	5.8	1.8	-
Mean ratio of Fe/Mn for samples in this study based on ug/g	8.5	4.9	18	18	13	-

The ratio of Fe/Mn in vegetal tissue should be between 1.5 and 2.5 since both elements are involved in metabolic processes and should thus be present in suitable proportions for adequate plant growth (Kabata-Pendias and Pendias 1993). The ratios of Fe/Mn in leaves from this study was higher than 2.5 in both of the sampling areas. The ratios are most likely elevated

due to the presence of Fe and Mn on the surface as well as on the inside of the leaves. However, this high ratio could indicate that there are elevated concentrations of Fe and low concentrations of Mn found in the leaves. Another study found that within reasonable limits the absolute concentrations of Fe and Mn in the plant can be of no great importance as long as they are both present in the correct relation to one another (Somers et al. 1942). However, the trees at RTPMC may be susceptible to Fe toxicity and Mn deficiencies as these two elements are antagonistic therefore one will inhibit the uptake of the other (Somers et al. 1942).

Comparing the concentrations of Cu, Fe and Ni found in *C. mopane* leaves from this study (Cu- 10 to 34 ug/g, Fe- 149 to 360 ug/g and Ni- 0.97 to 1.20 ug/g) to the results from a similar study on *C. mopane* leaves at a Ni-Cu mine (Cu- 4 to 116 ug/g, Fe - 31 to 430 ug/g and Ni- 19 to 120 ug/g) one can see that the concentrations of Cu and Ni in the leaves from this study are quite low and that the Fe concentrations from the two studies are comparable (Ekosse et al. 2005).

Leaf size, canopy area and tree height could be determining factors for the high elemental concentrations in *L. capassa* leaves however not for the high elemental concentrations in *E. divinorum* leaves which have the smallest surface area and average tree height. *C. mopane* trees, which are nitrogen fixing, sampled in the smelter plume deposition area were all quite small and the leaves of these trees had the lowest concentrations of all the elements studied. The small tree size may be due to soil degradation as a result of the pollution, which can lead to the extinction of free-living nitrogen fixing organisms and *Rhizobium* causing complete suppression of nitrogen fixation (Giller and Cadisch 1995). Another reason for the low concentrations of elements studied in *C. mopane* leaves may be because these leaves are eaten by Mopane worms and new leaves can flush twice yearly. In a study that focused on litter fall and nutrient return in a woodland dominated by *C. mopane*, it was noted that herbivory was evident at the end of the dry season when new leaves were emerging and that insects were probably attracted by the new, soft and nutrient-rich leaves (Mlambo and Nyathi 2008).

The high concentrations measured in *E. Divinorum* leaves in November 2011 were most likely because the leaves were older and had thus accumulated metals and dust elements for a longer time period, whereas the *L. capassa* and *C. mopane* trees had shed their old leaves and grown new ones.

7.6. Elemental analysis of the leaf litter

The high concentrations of contaminants found in the leaf litter in this study, may have a negative impact on detritivores feeding on this material which is resulting in the low decomposition rates.

Forrow and Maltby, 2009 conducted research to better understand the contaminant induced changes in detritus processing and feeding in streams. They found that the main mechanism responsible for the reduction in feeding was direct toxicity and this was most severe when animals were in contact with contaminated sediments (Forrow and Maltby 2009). From the results of a similar study it was concluded that detritivorous animals feeding on senescent plant material at the refinery site would ingest four times more Cu than herbivorous animals feeding on live plant material at the same site (Hunter et al. 1987). Another study investigated the influence of soil heavy metal pollution on soil microbial biomass, enzyme activity and community composition near a Cu smelter. The results showed that microbial biomass carbon was negatively affected by elevated metal levels and was closely correlated with heavy metal stress (Wang et al. 2007). Enzyme activity was also found to be greatly depressed by conditions in the heavy metal-contaminated sites. Good correlation was also observed between enzyme activity and the distance from the Cu smelter (Wang et al. 2007).

8. Conclusions

The leaves and leaf litter at the Rio Tinto Palabora Mining Company have been contaminated by mining activities in the area. There is evidence that differences exist in the concentrations of some metals, including Cu, in browse and litter with distance from the smelter point source. There is also evidence that the concentrations of certain elements vary between the two contaminated sites, the three tree species and the two seasons. The concentrations generally decreased from April to November 2011 and from 2008 to 2011. The findings of this study contribute to the formulation of the problem statement in an ecological risk assessment. The risks are therefore that these contaminants (surface and intrinsic) may have an impact on leaf and leaf litter consumers. These factors should be taken cognisance of, in the design of the risk assessment with respect to herbivores and detritivores, surrounding communities and ecosystem goods and services.

The highest concentrations of elements were found in the leaf litter samples from the smelter plume deposition area in 2008, with the average concentrations being: 1.57 ug/g of Ni, 9.44 ug/g of Bi, 16.3 ug/g of Pb, 110 ug/g of Mn, 122 ug/g of Ti, 483 ug/g of Al, 1463 ug/g of Cu, 2812 ug/g of S and 5611 ug/g of Fe. Element concentrations in leaves varied with the tree species, higher levels were found in *L. capassa* and *E. divinorum* leaves than in *C. mopane* leaves. In the leaves analysed from the smelter plume deposition area, element concentrations decreased in the order S > Fe > Al > W > Cu > Mn > Ti > Pb > Ni > Bi. Both positive and negative correlations were found for the relationship between the distance from the smelter and the concentrations of elements in the leaves. In April negative correlations dominated while in November more positive correlations were present. In the leaves from the Cu tailings seepage area the element concentrations decreased in the order S > Fe > W> Mn > Cu > Al > Ti > Ni > Bi > Pb. These differences in the concentrations between the high impact sites are probably due to differences in the sources of the contamination, the total metal concentrations in soils and the bioavailability of the elements.

In conclusion the leaves sampled from the smelter plume deposition area showed the highest contamination. The leaves and leaf litter sampled in this study can be used as bioindicators of the contamination in this region. It may be beneficial to include the bark and roots of trees in

future bioindicator studies, especially for deciduous trees such as *C. mopane* where the leaves alone may not give a true indication of the contaminants occurring in the tree. The findings from this study can be used in future studies to better understand the flow of these contaminants to leaf and leaf litter consumers in the area.

9. Recommendations for future studies

- Carry out a washed versus unwashed comparison of leaves collected in the smelter plume deposition area and in the Cu tailings area in the dry and wet season. By comparing the washed and unwashed leaf samples one can distinguish external from internal contamination as far as possible, and determine how extensive the surface contamination is.
- Determine the concentrations of heavy metals present in the soil from total concentration and water soluble fraction analyses. This could be measured as the water soluble and plant available metal concentrations and would give an indication of the metals that would be immediately available to roots and organisms in the soil.
- Determine the bioaccumulation factor and the translocation factor. The bioaccumulation factor is defined as the ratio of a metal concentration in shoots (total dry weight) versus that in the soil and is a measure of the ability of a plant to take up and transport metals to the foliage. The translocation factor is the measure of the ability of the plant to transport metals from the roots to the shoots (Kříbek et al. 2011).
- Determine the concentration of heavy metals in the roots of the trees. This would give an indication of overall bioavailability as much higher concentrations of heavy metals are generally taken up into roots, but not translocated to the shoots.
- Once the concentrations in the leaves, roots and soil are determined, a study on the pathways of heavy metals could be carried out.
- Mammals and insects can be used to access the degree of heavy metal contamination in both aquatic and terrestrial environments. Use the findings from this study as the baseline for another study on Mopane worms (*Imbrasia belina*) which eat *C. mopane* leaves. By evaluating the diet of Mopane worms as well as the elemental concentrations in the worms the mechanisms of transport of elements in the food chain can be determined.

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11. Appendix

Table 20: Abbreviations used in Appendix

AB	*L. capassa*
Mop	*C. mopane*
Euc	*E. divinorum*
U	Unwashed leaves
W	Washed leaves
I (X) L	Leaves collected in 2008
N (X) L	Leaves collected in November 2011
Li and Lip	Leaf litter

Table 21: Sample descriptions and GPS Coordinates

Sample	Tree	Height (m)	Time of collection	Sample type	Place	Dist from smelter stacks (m)	GPS lat	GPS long
17	AB	7.5	2011 Nov	leaves	Cu Tail		-23.9893	31.1929
19	AB	4	2011 Nov	leaves	Cu Tail		-23.9897	31.1934
21	AB	2.5	2011 Nov	leaves	Cu Tail		-23.9907	31.1947
24	AB	3.7	2011 Nov	leaves	Cu Tail		-23.9921	31.1943
27	AB	4	2011 Nov	leaves	Cu Tail		-23.9940	31.1935
29	AB	10	2011 Nov	leaves	Cu Tail		-23.9897	31.1926
31	AB	8	2011 Nov	leaves	Cu Tail		-23.9893	31.1906
33	AB	9	2011 Nov	leaves	Cu Tail		-23.9891	31.1901
34	AB	8.5	2011 Nov	leaves	Cu Tail		-23.9891	31.1900
35	AB	5	2011 Nov	leaves	Cu Tail		-23.9887	31.1883
20	Mop	6	2011 Nov	leaves	Cu Tail		-23.9894	31.1935
22	Mop	6	2011 Nov	leaves	Cu Tail		-23.9907	31.1947
23	Mop	3	2011 Nov	leaves	Cu Tail		-23.9921	31.1946
26	Mop	7.7	2011 Nov	leaves	Cu Tail		-23.9942	31.1942
28	Mop	4	2011 Nov	leaves	Cu Tail		-23.9938	31.1935
30	Mop	6	2011 Nov	leaves	Cu Tail		-23.9898	31.1927
32	Mop	6.5	2011 Nov	leaves	Cu Tail		-23.9894	31.1907
36	Mop	5	2011 Nov	leaves	Cu Tail		-23.9887	31.1882
37	AB	6	2011 Nov	leaves	Plume	1497	-23.9653	31.1523
39	AB	4	2011 Nov	leaves	Plume	1699	-23.9637	31.1509
41	AB	7	2011 Nov	leaves	Plume	1773	-23.9632	31.1497
48	AB	8	2011 Nov	leaves	Plume	2029	-23.9633	31.1440
61	AB	6.5	2011 Nov	leaves	Plume	868	-23.9709	31.1529
67	AB	5	2011 Nov	leaves	Plume	938	-23.9715	31.1498
50	Euc	1.5	2011 Nov	leaves	Plume	1920	-23.9636	31.1455
55	Euc	1.5	2011 Nov	leaves	Plume	1576	-23.9667	31.1467
66	Euc	2.2	2011 Nov	leaves	Plume	948	-23.9714	31.1498
38	Mop	3	2011 Nov	leaves	Plume	1504	-23.9652	31.1524
40	Mop	2.5	2011 Nov	leaves	Plume	1674	-23.9639	31.1513
42	Mop	2	2011 Nov	leaves	Plume	1784	-23.9632	31.1498
45	Mop	2	2011 Nov	leaves	Plume	1823	-23.9632	31.1484

46	Mop	4	2011 Nov	leaves	Plume	1873	-23.9630	31.1477
51	Mop	3	2011 Nov	leaves	Plume	1912	-23.9636	31.1456
53	Mop	3	2011 Nov	leaves	Plume	1875	-23.9637	31.1461
63	Mop	2.5	2011 Nov	leaves	Plume	871	-23.9720	31.1567
017 U	AB	7.5	2011 April	leaves	Cu Tail		-23.9893	31.1929
017 W	AB	7.5	2011 April	leaves	Cu Tail		-23.9893	31.1929
019 U	AB	4	2011 April	leaves	Cu Tail		-23.9897	31.1934
021 U	AB	2.5	2011 April	leaves	Cu Tail		-23.9907	31.1947
021 W	AB	2.5	2011 April	leaves	Cu Tail		-23.9907	31.1947
024 U	AB	3.7	2011 April	leaves	Cu Tail		-23.9921	31.1943
027 U	AB	4	2011 April	leaves	Cu Tail		-23.9940	31.1935
031 U	AB	8	2011 April	leaves	Cu Tail		-23.9893	31.1906
031 W	AB	8	2011 April	leaves	Cu Tail		-23.9893	31.1906
033 U	AB	9	2011 April	leaves	Cu Tail		-23.9891	31.1901
035 U	AB	5	2011 April	leaves	Cu Tail		-23.9887	31.1883
035 W	AB	5	2011 April	leaves	Cu Tail		-23.9887	31.1883
037 U	AB	6	2011 April	leaves	Plume	1497	-23.9653	31.1523
037 W	AB	6	2011 April	leaves	Plume	1497	-23.9653	31.1523
039 U	AB	4	2011 April	leaves	Plume	1699	-23.9637	31.1509
039 W	AB	4	2011 April	leaves	Plume	1699	-23.9637	31.1509
041 U	AB	7	2011 April	leaves	Plume	1773	-23.9632	31.1497
041 W	AB	7	2011 April	leaves	Plume	1773	-23.9632	31.1497
048 U	AB	8	2011 April	leaves	Plume	2029	-23.9633	31.1440
048 W	AB	8	2011 April	leaves	Plume	2029	-23.9633	31.1440
061 U	AB	6.5	2011 April	leaves	Plume	868	-23.9709	31.1529
061 W	AB	6.5	2011 April	leaves	Plume	868	-23.9709	31.1529
067 U	AB	5	2011 April	leaves	Plume	938	-23.9715	31.1498
050 U	Euc	1.5	2011 April	leaves	Plume	1920	-23.9636	31.1455
050 W	Euc	1.5	2011 April	leaves	Plume	1920	-23.9636	31.1455
055 U	Euc	1.5	2011 April	leaves	Plume	1576	-23.9667	31.1467
055 W	Euc	1.5	2011 April	leaves	Plume	1576	-23.9667	31.1467
059 U	Euc	1.8	2011 April	leaves	Plume	1296	-23.9682	31.1491
059 W	Euc	1.8	2011 April	leaves	Plume	1296	-23.9682	31.1491
060 U	Euc	2.2	2011 April	leaves	Plume	1235	-23.9692	31.1484
060 W	Euc	2.2	2011 April	leaves	Plume	1235	-23.9692	31.1484
066 U	Euc	2.2	2011 April	leaves	Plume	948	-23.9714	31.1498
066 W	Euc	2.2	2011 April	leaves	Plume	948	-23.9714	31.1498
018 U	Mop	5	2011 April	leaves	Cu Tail		-23.9896	31.1929
018 W	Mop	5	2011 April	leaves	Cu Tail		-23.9896	31.1929
020 U	Mop	6	2011 April	leaves	Cu Tail		-23.9894	31.1935
022 W	Mop	6	2011 April	leaves	Cu Tail		-23.9907	31.1947
023 U	Mop	3	2011 April	leaves	Cu Tail		-23.9921	31.1946
026 U	Mop	7.7	2011 April	leaves	Cu Tail		-23.9942	31.1942
026 W	Mop	7.7	2011 April	leaves	Cu Tail		-23.9942	31.1942
028 U	Mop	4	2011 April	leaves	Cu Tail		-23.9938	31.1935
030 W	Mop	6	2011 April	leaves	Cu Tail		-23.9898	31.1927
034 U	Mop	8.5	2011 April	leaves	Cu Tail		-23.9891	31.1900
034 W	Mop	8.5	2011 April	leaves	Cu Tail		-23.9891	31.1900
036 U	Mop	5	2011 April	leaves	Cu Tail		-23.9887	31.1882
036 W	Mop	5	2011 April	leaves	Cu Tail		-23.9887	31.1882

038 U	Mop	3	2011 April	leaves	Plume	1504	-23.9652	31.1524
038 W	Mop	3	2011 April	leaves	Plume	1504	-23.9652	31.1524
040 U	Mop	2.5	2011 April	leaves	Plume	1674	-23.9639	31.1513
042 U	Mop	2	2011 April	leaves	Plume	1784	-23.9632	31.1498
045 U	Mop	2	2011 April	leaves	Plume	1823	-23.9632	31.1484
046 U	Mop	4	2011 April	leaves	Plume	1873	-23.9630	31.1477
046 W	Mop	4	2011 April	leaves	Plume	1873	-23.9630	31.1477
051 U	Mop	3	2011 April	leaves	Plume	1912	-23.9636	31.1456
053 U	Mop	2	2011 April	leaves	Plume	1875	-23.9637	31.1461
053 W	Mop	2	2011 April	leaves	Plume	1875	-23.9637	31.1461
063 U	Mop	2.5	2011 April	leaves	Plume	871	-23.9720	31.1567
063 W	Mop	2.5	2011 April	leaves	Plume	871	-23.9720	31.1567
I 44 L	AB		2008	leaves	Plume	1728	-23.9860	31.1585
I 52 L	AB		2008	leaves	Plume	1339	-23.9874	31.1598
I 56 L	AB		2008	leaves	Plume	1076	-23.9874	31.1596
I 59 L	AB		2008	leaves	Plume	1076	-23.9875	31.1595
I 60 L	AB		2008	leaves	Plume	740	-23.9906	31.1597
I 64 L	AB		2008	leaves	Plume	373	-23.9906	31.1597
I 66 L	AB		2008	leaves	Plume	383	-23.9909	31.1598
I 67 L	AB		2008	leaves	Plume	373	-23.9908	31.1600
I 68 L	AB		2008	leaves	Plume	399	-23.9911	31.1603
I 48 L	Euc		2008	leaves	Plume	1311	-23.9860	31.1586
I 49 L	Euc		2008	leaves	Plume	1311	-23.9860	31.1586
I 50 L	Euc		2008	leaves	Plume	1311	-23.9874	31.1596
I 59 L	Euc		2008	leaves	Plume	1296	-23.9682	31.1491
I 76 L	Mop		2008	leaves	Cu Tail		-24.0187	31.1548
I 77 L	Mop		2008	leaves	Cu Tail		-24.0184	31.1547
I 79 L	Mop		2008	leaves	Cu Tail		-24.0146	31.1612
I 88 L	Mop		2008	leaves	Cu Tail		-24.0052	31.1611
I 90 L	Mop		2008	leaves	Cu Tail		-24.0052	31.1611
I 91 L	Mop		2008	leaves	Cu Tail		-24.0052	31.1611
I 44 Li	NA		2008	leaf litter			-23.9860	31.1586
I 52 Li	NA		2008	leaf litter			-23.9874	31.1598
I 64 Li	NA		2008	leaf litter			-23.9906	31.1597
I 80 Li	NA		2008	leaf litter			-24.0113	31.1594
I 94 Li	NA		2008	leaf litter			-23.9908	31.1420
N 44 L	AB		2011 Nov	leaves	Plume	1728	-23.9860	31.1585
N 52 L	AB		2011 Nov	leaves	Plume	1339	-23.9874	31.1598
N 56 L	AB		2011 Nov	leaves	Plume	1076	-23.9874	31.1596
N 60 L	AB		2011 Nov	leaves	Plume	740	-23.9906	31.1597
N 64 L	AB		2011 Nov	leaves	Plume	373	-23.9906	31.1597
N 66 L	AB		2011 Nov	leaves	Plume	383	-23.9909	31.1598
N 67 L	AB		2011 Nov	leaves	Plume	373	-23.9908	31.1600
N 68 L	AB		2011 Nov	leaves	Plume	399	-23.9911	31.1603
N 48 L	Euc		2011 Nov	leaves	Plume	1311	-23.9860	31.1586
N 49 L	Euc		2011 Nov	leaves	Plume	1311	-23.9860	31.1586
N 50 L	Euc		2011 Nov	leaves	Plume	1311	-23.9874	31.1596
N 51 L	Euc		2011 Nov	leaves	Plume	1311	-23.9874	31.1596
N 76 L	Mop		2011 Nov	leaves	Cu Tail		-24.0187	31.1548
N 77 L	Mop		2011 Nov	leaves	Cu Tail		-24.0184	31.1547

N 44 Lip	NA		2011 Nov	leaf litter			-23.9860	31.1586
N 52 Lip	NA		2011 Nov	leaf litter			-23.9874	31.1598
N 70 Lip	NA		2011 Nov	leaf litter				
N 71 Lip	NA		2011 Nov	leaf litter				
N 80 Lip	NA		2011 Nov	leaf litter			-24.0113	31.1594
Orchard leaf CRM			**NBS Orchard leaves (1571)**					

Table 22: Concentrations (ug/g) and relative standard deviations obtained for Al, Cu, Fe, Mn, Pb, S, Bi, Ca, K and Mg from ICP-OES analyses

Sample	Tree	Al	RSD	Cu	RSD	Fe	RSD	Mn	RSD	Pb	RSD	S	RSD	Bi	RSD	Ca	RSD	K	RSD	Mg	RSD
17	AB	nd	0.00	nd	0.00	33.85	3.35	nd	0.00	nd	0.00	641.37	1.51	nd	0.00	1037.99	1.57	3713.69	2.28	803.66	1.60
19	AB	nd	0.00	nd	0.00	152.28	2.71	25.67	2.20	nd	0.00	2147.34	1.62	nd	0.00	3221.86	2.39	12157.70	1.52	2768.44	1.94
21	AB	30.29	3.51	nd	0.00	161.69	1.89	25.15	0.63	nd	0.00	1904.37	0.68	0.08	6.58	2990.02	0.63	16075.27	0.88	2369.94	0.72
24	AB	24.77	7.11	nd	0.00	169.93	1.69	50.04	2.92	nd	0.00	2417.61	1.27	nd	0.00	3220.18	3.08	14152.95	3.49	2761.93	2.89
27	AB	nd	0.00	nd	0.00	566.01	0.63	60.34	0.56	nd	0.00	2100.85	0.72	nd	0.00	2332.86	0.46	11282.72	1.52	2108.50	0.64
29	AB	60.69	2.40	183.82	0.92	1969.08	0.75	32.08	0.67	nd	0.00	1898.84	0.29	1.30	0.54	4728.03	2.84	10134.97	1.56	2539.60	2.57
31	AB	nd	0.00	8.67	7.05	198.64	0.47	635.63	1.73	nd	0.00	2080.26	0.31	0.09	8.06	2701.44	0.47	11203.05	1.60	2145.26	0.25
33	AB	nd	0.00	nd	0.00	121.10	3.25	9.58	5.98	nd	0.00	1695.45	2.29	nd	0.00	918.30	9.04	14482.77	9.96	1345.21	8.06
34	AB	25.08	3.16	nd	0.00	169.15	2.18	33.62	6.47	nd	0.00	2395.85	0.42	nd	0.00	3686.09	2.98	15968.95	1.28	2415.59	3.03
35	AB	16.35	1.73	13.71	3.40	187.73	2.03	34.80	1.59	nd	0.00	2573.44	0.17	0.10	8.73	2982.13	0.23	16705.72	2.54	2010.23	0.18
20	Mop	nd	0.00	nd	0.00	116.84	0.85	30.48	0.71	nd	0.00	1308.09	1.56	nd	0.00	4560.96	0.51	8244.78	0.76	1828.79	0.18
22	Mop	nd	0.00	12.62	1.38	135.42	0.47	10.09	2.07	nd	0.00	1463.55	0.68	nd	0.00	1675.51	0.79	13039.07	0.74	1556.92	0.23
23	Mop	nd	0.00	nd	0.00	184.40	0.76	20.30	0.82	nd	0.00	1443.05	0.82	nd	0.00	3324.25	0.59	7875.00	1.68	1859.21	1.22
26	Mop	16.74	8.09	nd	0.00	118.14	1.54	22.79	0.93	nd	0.00	1748.84	0.45	0.07	6.62	4432.56	0.94	13926.98	1.48	1726.05	0.76
28	Mop	nd	0.00	nd	0.00	108.15	0.69	14.37	0.62	nd	0.00	1759.16	0.57	nd	0.00	1175.29	1.08	17141.60	1.79	1499.75	1.11
30	Mop	nd	0.00	nd	6.86	203.82	0.69	14.00	1.41	nd	0.00	1201.12	0.82	nd	0.00	8530.29	0.21	6517.24	1.29	1476.23	0.53
32	Mop	11.03	3.76	11.51	3.35	158.74	3.63	19.66	4.52	nd	0.00	1180.23	2.64	0.06	7.27	5714.60	2.80	7069.88	3.63	1702.01	3.04
36	Mop	nd	0.00	nd	0.00	165.92	1.27	17.88	0.44	nd	0.00	1852.99	0.45	nd	0.00	2310.03	0.96	20828.00	0.76	1750.65	0.92
37	AB	29.06	5.59	nd	0.00	259.43	2.67	41.74	4.12	nd	0.00	1933.86	1.26	0.17	4.07	3325.07	0.28	13383.23	1.77	1744.17	0.39
39	AB	34.25	6.81	nd	0.00	452.23	2.33	19.27	0.43	nd	0.00	1728.64	0.61	0.30	4.43	2426.52	0.61	22214.39	0.67	2414.75	0.66
41	AB	39.95	4.06	27.43	5.06	297.43	5.74	75.08	0.78	nd	0.00	2507.49	0.42	0.31	3.94	4080.32	0.70	23830.75	1.03	2799.14	0.61
48	AB	27.00	4.93	50.68	4.24	276.63	2.86	46.42	2.81	nd	0.00	1942.11	1.26	0.44	3.92	8019.00	0.09	11499.63	2.95	3541.74	1.84
61	AB	19.89	5.95	74.59	8.32	256.57	4.24	19.39	2.65	8.45	2.94	2799.45	2.26	0.62	2.71	3538.34	1.64	14250.83	2.48	2253.48	1.33
67	AB	13.21	6.18	125.22	2.35	229.89	4.24	11.74	1.16	nd	0.00	1936.96	1.71	0.86	2.16	2089.57	0.65	17936.41	1.84	1732.50	0.96
50	Euc	17.23	6.71	35.37	3.19	519.14	1.96	37.63	2.68	13.15	4.74	1695.72	0.70	0.33	3.69	7609.42	0.01	11617.93	1.62	3459.90	0.85
55	Euc	44.75	2.21	84.53	0.74	325.69	0.31	15.91	1.09	nd	0.00	1869.61	0.84	0.67	1.21	4994.75	1.64	10535.97	1.55	2073.48	1.46
66	Euc	32.34	1.13	96.04	1.26	498.35	0.49	45.57	1.46	nd	0.00	4326.86	0.43	0.72	1.14	8226.91	0.04	10726.01	5.65	5173.61	5.16
38	Mop	13.59	3.50	nd	0.00	374.43	3.97	14.09	0.55	nd	0.00	1346.73	1.05	0.07	10.96	2858.02	5.68	12462.27	0.47	1076.98	0.95
40	Mop	7.86	4.78	17.59	2.93	203.20	0.88	32.56	1.49	13.10	2.56	1519.33	2.05	0.11	6.95	5173.60	1.18	14590.85	3.23	1605.03	1.39
42	Mop	9.99	6.38	24.19	8.03	261.32	1.41	26.29	0.40	15.25	1.20	2124.25	0.25	0.16	6.21	2427.11	0.12	21221.95	0.78	1608.43	0.17
45	Mop	13.76	2.87	22.60	2.35	184.26	1.24	24.08	0.95	nd	0.00	1562.51	0.40	0.00	0.00	2727.02	0.80	19186.46	1.94	1504.04	0.50
46	Mop	nd	0.00	nd	0.00	252.44	1.57	61.07	0.42	nd	0.00	1766.07	0.63	0.16	6.75	6443.36	0.52	22159.85	0.23	2053.63	0.63
51	Mop	nd	0.00	nd	0.00	186.19	3.15	14.44	1.33	nd	0.00	1382.23	1.82	0.15	7.56	6648.65	1.43	17705.50	1.73	2009.40	1.57
53	Mop	nd	0.00	nd	0.00	173.42	4.40	11.42	1.40	nd	0.00	1604.42	1.89	nd	0.00	3126.29	2.48	13616.83	0.94	1222.27	0.63
63	Mop	15.16	8.49	nd	0.00	223.88	10.03	12.99	1.66	8.66	5.94	1037.56	1.74	nd	0.00	1517.37	1.69	11972.67	1.62	1152.75	1.31
017 U	AB	8.06	6.74	nd	0.00	216.13	0.42	86.29	0.71	nd	0.00	1366.13	0.67	nd	0.00	7451.61	0.23	6033.87	0.50	2619.35	1.25
017 W	AB	17.51	7.40	nd	0.00	197.86	10.35	96.30	0.77	nd	0.00	1378.02	1.97	nd	0.00	7564.20	0.36	5305.45	1.59	3370.62	0.84
019 U	AB	nd	0.00	nd	0.00	215.86	0.07	50.48	0.26	nd	0.00	1685.98	0.80	nd	0.00	8098.26	0.09	6418.38	0.35	3430.27	0.34
021 U	AB	18.26	1.42	nd	0.00	517.39	0.91	44.35	0.46	nd	0.00	1738.26	0.81	nd	0.00	7000.00	0.78	6982.61	1.06	4408.70	0.81
021 W	AB	11.06	10.37	nd	0.00	161.63	0.55	44.23	0.74	nd	0.00	1720.04	0.53	nd	0.00	6209.83	0.92	4397.92	1.34	4814.74	0.91
024 U	AB	38.88	6.60	38.14	3.08	457.70	1.13	87.29	0.62	nd	0.00	1711.98	0.46	0.23	5.39	6755.50	0.05	7092.91	1.31	4745.72	0.48
027 U	AB	40.50	4.46	nd	0.00	351.24	2.32	222.31	0.92	nd	0.00	1705.79	0.22	nd	0.00	8144.63	0.59	10327.27	0.54	3371.07	0.69
031 U	AB	nd	0.00	12.98	5.11	223.99	0.37	344.09	0.72	nd	0.00	1891.70	0.41	nd	0.00	7914.16	0.10	3316.77	1.22	3727.41	0.50
031 W	AB	nd	0.00	nd	0.00	175.29	1.44	478.81	5.03	nd	0.00	1901.44	0.90	nd	0.00	16100.99	1.81	3223.44	6.89	4116.95	6.16
033 U	AB	10.40	2.82	5.60	4.41	364.00	1.06	57.60	1.14	nd	0.00	2952.00	0.17	0.09	3.74	7928.80	0.03	8672.80	1.08	3755.20	0.36
035 U	AB	11.41	2.29	2.63	8.95	428.49	1.85	64.98	1.84	nd	0.00	4381.46	1.46	0.15	5.34	8155.32	0.32	9110.63	1.52	6184.98	1.62
035 W	AB	36.55	3.49	nd	0.00	271.46	3.12	100.40	0.79	7.80	6.80	4893.14	1.86	0.09	6.29	8277.40	0.03	15618.09	1.33	8864.68	0.56
037 U	AB	32.34	3.04	38.80	1.80	441.78	4.60	33.55	2.91	nd	0.00	1527.84	0.67	0.37	1.59	3370.15	0.22	13292.65	0.61	1673.76	0.08
037 W	AB	86.11	5.40	346.09	2.14	1211.32	1.11	49.68	1.83	nd	0.00	3485.74	0.96	2.10	3.24	4164.67	0.72	10291.63	2.26	1655.93	0.84

Sample	Tree	Al	RSD	Cu	RSD	Fe	RSD	Mn	RSD	Pb	RSD	S	RSD	Bi	RSD	Ca	RSD	K	RSD	Mg	RSD
039 U	AB	49.47	2.95	190.27	2.98	1057.93	1.76	73.57	0.37	nd	0.00	203.21	0.27	1.20	1.03	19052.85	0.34	5670.19	0.79	5061.31	0.13
039 W	AB	119.87	3.13	247.70	1.89	4969.91	3.62	64.12	1.78	9.96	3.11	1955.31	1.39	1.42	1.58	6763.54	0.05	7463.23	2.86	3823.41	4.12
041 U	AB	39.61	1.07	44.10	2.94	443.21	0.41	207.40	2.11	5.61	4.28	2201.11	2.03	0.35	4.42	6352.19	0.09	9228.96	6.88	2825.56	2.11
041 W	AB	20.65	8.90	67.64	0.99	573.89	1.62	237.10	0.45	nd	0.00	3318.04	1.37	0.43	2.09	6244.46	0.15	7305.38	0.73	3375.00	0.84
048 U	AB	12.22	4.21	18.94	3.20	411.20	3.54	80.65	0.36	nd	0.00	1749.90	0.90	0.32	1.11	10518.33	0.04	4105.91	0.87	3665.99	1.05
048 W	AB	nd	0.00	24.68	3.30	253.73	0.81	70.18	1.95	nd	0.00	1496.92	0.58	0.27	0.68	7480.72	0.04	2154.76	1.21	2764.78	0.15
061 U	AB	28.55	1.49	144.68	2.40	569.03	2.12	55.65	1.52	nd	0.00	3111.29	0.91	0.91	2.63	8121.77	0.03	13393.55	1.36	3607.74	0.83
061 W	AB	16.28	3.82	85.03	0.88	441.41	2.73	59.25	1.77	nd	0.00	3437.19	1.48	0.60	2.45	7629.20	0.04	10924.82	2.36	4130.05	1.24
067 U	AB	48.72	3.44	196.92	3.56	441.33	3.19	29.48	1.90	nd	0.00	4253.68	1.76	1.19	1.98	6961.46	0.06	11899.24	3.55	2548.11	2.17
050 U	Euc	9.84	1.99	42.86	2.71	240.98	1.04	28.10	1.28	nd	0.00	1313.82	0.83	0.27	2.54	6899.30	0.15	6063.23	1.10	3400.47	1.01
050 W	Euc	nd	0.00	48.06	2.74	397.57	0.40	30.58	1.34	nd	0.00	1861.17	0.61	0.21	5.72	21495.15	0.35	3286.89	1.34	4266.99	0.56
055 U	Euc	37.79	1.14	44.00	3.21	258.28	2.09	22.00	0.44	nd	0.00	2276.71	3.59	0.48	1.62	8110.52	0.02	7110.88	0.31	3439.93	0.19
055 W	Euc	nd	0.00	23.10	8.73	331.33	1.00	12.74	1.28	nd	0.00	1440.00	0.26	0.24	6.90	7423.01	0.19	5619.03	1.48	2864.07	0.65
059 U	Euc	12.24	4.14	31.74	10.39	393.14	3.13	30.59	2.01	nd	0.00	2780.31	1.93	0.33	4.85	6429.14	0.09	9624.01	2.28	3996.46	1.05
059 W	Euc	15.63	3.91	nd	0.00	177.31	1.17	34.49	0.64	nd	0.00	2236.53	0.19	0.20	7.47	8366.77	0.78	6097.90	0.73	3220.06	1.05
060 U	Euc	27.04	9.02	26.61	1.93	235.98	7.10	24.43	0.90	nd	0.00	2298.71	0.15	0.33	2.55	7321.41	0.02	11046.01	1.13	2795.53	0.54
060 W	Euc	nd	0.00	nd	0.00	197.92	2.84	17.59	0.46	nd	0.00	1822.81	0.32	0.18	0.86	8298.41	0.09	7719.80	0.43	2122.37	0.87
066 U	Euc	49.01	8.99	90.29	1.04	415.32	1.04	52.88	0.31	nd	0.00	3009.55	0.31	0.65	1.47	7231.96	0.02	11487.90	1.23	5153.65	0.48
066 W	Euc	nd	0.00	28.00	8.28	225.58	1.19	46.84	1.79	nd	0.00	2288.14	0.36	0.29	2.65	9129.93	0.03	10052.18	1.15	4856.23	0.91
018 U	Mop	nd	0.00	nd	0.00	154.78	0.95	13.04	0.83	nd	0.00	941.74	0.56	0.05	1.53	6539.13	0.80	5878.26	0.92	1738.26	0.50
018 W	Mop	nd	0.00	nd	0.00	124.40	0.57	12.87	1.58	nd	0.00	980.65	0.37	0.05	8.83	5362.25	0.71	6478.46	0.68	1489.42	0.26
020 U	Mop	nd	0.00	nd	0.00	121.39	1.20	27.67	1.46	nd	0.00	1040.73	2.47	nd	0.00	6287.21	1.73	4407.02	1.88	1469.60	1.68
022 W	Mop	nd	0.00	nd	0.00	231.60	0.38	7.93	1.06	nd	0.00	875.34	0.30	nd	0.00	6788.75	0.44	4706.07	1.14	1588.65	1.20
023 U	Mop	nd	0.00	nd	0.00	180.61	6.95	nd	0.00	nd	0.00	1426.64	3.65	nd	0.00	5691.40	1.06	5311.97	0.66	1320.40	0.74
026 U	Mop	nd	0.00	nd	0.00	986.06	0.91	32.34	1.91	nd	0.00	1044.58	1.62	0.06	8.04	5512.41	1.07	7201.71	2.27	1355.65	1.06
026 W	Mop	15.44	8.06	8.58	10.63	156.15	1.00	52.34	0.31	nd	0.00	1160.82	0.67	0.08	6.58	6683.51	0.31	8107.72	0.63	1382.17	0.23
028 U	Mop	23.59	2.01	nd	0.00	594.04	1.80	10.01	1.29	nd	0.00	1163.78	0.92	nd	0.00	8126.45	0.24	9207.31	0.18	1939.40	0.29
030 W	Mop	nd	0.00	nd	0.00	184.11	7.37	13.41	8.36	nd	0.00	1186.89	4.76	nd	0.00	8931.18	7.43	7617.38	8.18	1330.78	6.60
034 U	Mop	nd	0.00	nd	0.00	138.20	2.31	3.41	1.66	nd	0.00	987.87	0.62	nd	0.00	7902.09	1.10	5201.23	1.39	2101.14	1.08
034 W	Mop	12.47	8.25	nd	0.00	151.76	0.67	6.24	1.45	nd	0.00	978.13	0.74	nd	0.00	7492.95	0.72	5264.35	2.08	2000.44	0.63
036 U	Mop	nd	0.00	14.52	0.00	346.65	4.69	19.74	5.81	nd	0.00	1637.42	4.76	nd	0.00	5452.26	1.15	5672.90	5.74	3867.10	4.80
036 W	Mop	nd	0.00	nd	0.00	298.87	1.69	9.34	1.00	nd	0.00	1790.66	0.79	nd	0.00	4687.64	0.43	5304.06	0.18	2507.26	0.39
038 U	Mop	nd	0.00	8.39	2.39	219.76	3.41	10.07	0.73	nd	0.00	1264.86	0.21	0.18	3.44	7958.25	0.09	4128.42	0.56	2004.66	0.15
038 W	Mop	nd	0.00	nd	0.00	207.75	8.15	9.52	8.60	nd	0.00	1648.55	5.97	nd	0.00	7650.40	1.29	4897.27	7.22	1901.50	4.57
040 U	Mop	10.07	8.63	20.13	4.86	175.84	6.78	8.72	0.34	nd	0.00	1404.03	0.87	0.21	2.13	5311.41	0.20	5005.37	0.53	975.17	0.18
042 U	Mop	9.17	7.81	22.16	4.44	372.07	0.46	18.34	0.91	nd	0.00	2142.28	0.59	0.23	7.55	6665.96	0.80	5241.85	1.18	1690.75	1.16
045 U	Mop	nd	0.00	nd	0.00	431.36	1.53	62.93	1.58	nd	0.00	3378.82	0.61	0.17	5.16	10401.02	0.01	9285.95	1.54	2743.38	0.52
046 U	Mop	14.34	5.51	26.15	1.05	210.03	6.53	55.67	4.17	nd	0.00	2263.92	0.83	0.27	1.43	7542.46	0.44	4659.42	1.64	2337.30	0.82
046 W	Mop	14.26	1.06	11.00	6.45	321.55	2.28	82.32	0.77	8.97	9.90	2441.21	0.17	0.21	4.25	6839.46	0.03	5563.02	1.00	3143.41	1.72
051 U	Mop	nd	0.00	48.21	3.62	659.77	0.32	11.84	1.93	nd	0.00	1583.46	0.89	0.35	2.73	3768.33	0.81	9823.03	1.02	946.52	0.54
053 U	Mop	36.29	2.26	77.83	2.40	167.32	3.02	4.81	4.56	15.60	1.50	2280.97	3.11	0.28	1.09	13350.61	0.05	5013.77	1.46	1785.43	0.95
053 W	Mop	nd	0.00	nd	0.00	145.60	1.47	1.93	2.04	nd	0.00	1807.09	0.08	nd	0.00	6767.07	0.51	4748.68	1.25	1045.60	0.56
063 U	Mop	53.15	3.72	nd	0.00	347.81	2.64	11.91	1.57	nd	0.00	1386.14	0.10	nd	0.00	6900.94	0.38	10902.90	0.87	1084.68	0.24
063 W	Mop	25.55	7.83	nd	0.00	517.40	1.04	17.20	0.40	nd	0.00	1454.41	1.16	0.17	6.37	8337.32	0.10	8419.38	0.55	2077.45	0.59
I 44 L	AB	nd	0.00	nd	0.00	224.11	0.72	97.83	0.66	nd	0.00	1613.24	0.02	0.08	5.89	8222.73	0.11	7368.08	1.05	4242.98	0.46
I 52 L	AB	28.41	1.84	173.82	0.37	919.22	0.10	20.06	0.20	nd	0.00	1713.09	0.00	1.21	0.56	2289.69	0.43	12165.46	1.03	2856.27	0.60
I 56 L	AB	42.86	1.98	282.35	1.53	1059.66	0.49	19.33	0.22	nd	0.00	2663.87	0.61	1.93	0.71	3331.09	1.04	10642.86	0.75	2727.73	1.19
I 60 L	AB	178.98	2.21	911.19	1.51	5059.32	1.24	158.64	1.09	nd	0.00	8796.61	1.08	4.72	1.99	8550.51	0.02	12342.71	1.77	4479.66	0.81
I 64 L	AB	98.09	2.90	1390.78	1.40	1621.03	1.67	29.43	0.09	nd	0.00	2937.48	0.68	7.40	0.23	2995.30	0.38	16601.13	1.20	1634.97	0.25
I 66 L	AB	35.37	3.11	473.86	2.78	754.39	3.39	27.15	2.81	nd	0.00	2223.67	2.25	3.03	2.97	2695.06	0.68	9876.14	0.26	1304.75	0.82
I 67 L	AB	90.14	8.00	1185.67	0.94	2579.35	0.77	163.64	0.67	nd	0.00	3344.84	1.49	7.32	0.88	5976.89	0.90	12813.56	0.99	2860.86	0.49
I 68 L	AB	65.70	2.03	721.60	1.71	1239.17	1.33	44.33	1.21	nd	0.00	2729.38	0.25	4.20	0.84	6680.83	2.23	10085.34	3.07	2169.08	2.33

Sample	Tree	Al	RSD	Cu	RSD	Fe	RSD	Mn	RSD	Pb	RSD	S	RSD	Bi	RSD	Ca	RSD	K	RSD	Mg	RSD
I 48 L	Euc	nd	0.00	83.41	0.69	711.95	0.81	36.59	0.51	nd	0.00	2656.10	0.05	0.62	0.86	7093.17	0.02	7619.27	1.35	3450.00	0.25
I 49 L	Euc	37.04	1.23	71.56	5.69	825.91	1.40	13.47	2.09	nd	0.00	2087.09	1.80	0.66	0.72	12552.01	0.63	13135.45	2.07	3675.77	0.82
I 50 L	Euc	31.24	7.80	130.94	3.79	508.76	1.78	31.66	2.03	nd	0.00	2263.55	1.67	0.89	3.62	7191.58	0.04	9940.36	3.30	3495.02	1.48
I 76 L	Mop	nd	0.00	nd	0.00	163.41	0.63	17.24	1.49	nd	0.00	3128.65	0.60	nd	0.00	5444.34	0.85	10577.46	1.61	4821.90	0.88
I 77 L	Mop	nd	0.00	11.10	3.47	142.99	1.33	19.10	0.30	nd	0.00	2686.68	0.26	nd	0.00	5826.76	0.68	16079.21	1.38	3603.26	0.56
I 79 L	Mop	33.89	8.38	nd	0.00	225.39	0.62	24.43	1.10	nd	0.00	3727.67	0.90	nd	0.00	5183.27	0.48	22544.13	2.02	4152.45	0.22
I 88 L	Mop	nd	0.00	nd	0.00	158.26	1.52	17.11	4.24	nd	0.00	178.04	2.91	nd	0.00	2189.41	3.03	13189.37	1.66	1231.84	0.31
I 90 L	Mop	13.25	3.44	9.68	2.66	145.19	5.25	17.32	5.47	nd	0.00	1762.64	4.17	nd	0.00	1034.15	9.09	14902.98	9.88	1232.83	7.19
I 91 L	Mop	nd	0.00	nd	0.00	171.15	1.50	18.44	0.50	nd	0.00	1453.28	0.21	nd	0.00	1125.00	0.53	14140.33	0.94	1541.80	0.76
I 44 Li	NA	150.77	2.87	200.00	1.79	4184.62	1.05	94.62	1.34	nd	0.00	1641.54	1.37	1.32	0.68	7573.85	0.49	2933.85	1.70	2940.77	2.33
I 52 Li	NA	779.18	1.24	3230.14	2.42	8515.07	1.03	157.81	1.14	17.26	9.70	5021.92	0.42	17.80	1.16	13952.88	0.11	6576.16	1.88	7589.59	0.66
I 64 Li	NA	395.04	2.61	3400.76	0.81	8467.56	2.15	105.63	1.39	nd	0.00	4611.64	0.75	25.36	1.32	15861.64	1.39	4731.87	1.68	2765.27	0.87
I 80 Li	NA	997.26	4.73	382.35	8.90	6135.97	0.43	165.92	5.90	15.24	9.85	1345.65	2.01	1.96	4.03	2585.90	46.95	3220.40	10.04	15764.08	3.79
I 94 Li	NA	95.12	4.86	100.98	1.85	751.46	1.12	27.80	1.17	nd	0.00	1441.46	1.20	0.78	3.07	6879.51	0.05	3335.12	0.73	2578.54	0.28
N 44 L	AB	14.99	2.48	2.64	8.26	230.07	0.89	19.39	3.43	nd	0.00	1946.33	1.12	0.18	7.74	1804.41	0.33	13640.16	0.50	1547.89	0.47
N 52 L	AB	nd	0.00	91.94	1.94	372.20	1.46	10.61	2.43	nd	0.00	2125.34	0.34	0.73	4.68	2248.23	0.12	15548.43	2.79	2368.47	0.16
N 56 L	AB	30.87	5.63	151.90	7.47	307.85	2.50	23.56	1.95	nd	0.00	2981.05	0.56	1.04	2.19	3232.85	5.41	14328.52	5.92	2526.17	4.42
N 60 L	AB	46.00	4.68	305.50	5.15	573.00	2.72	98.00	3.22	nd	0.00	2765.00	2.91	1.82	3.09	3372.50	0.23	12418.50	0.73	1708.50	0.32
N 64 L	AB	28.64	2.41	129.14	4.70	278.07	0.65	25.52	0.26	nd	0.00	2619.29	0.18	0.94	0.76	3170.74	1.08	10004.84	1.55	1341.93	0.66
N 66 L	AB	12.52	8.58	166.98	1.96	337.29	1.19	10.85	0.81	nd	0.00	1942.76	0.23	1.23	0.70	1643.04	1.08	12106.59	0.81	1348.33	0.67
N 67 L	AB	212.16	3.36	670.72	0.79	2352.36	0.77	125.06	0.89	nd	0.00	3067.00	0.61	4.16	0.79	6365.51	0.55	6116.87	1.14	2482.63	0.65
N 68 L	AB	38.10	8.35	372.65	0.71	863.42	1.06	99.07	0.87	nd	0.00	3101.61	0.52	2.44	0.71	12974.94	0.08	4379.59	1.17	4447.42	1.61
N 48 L	Euc	nd	0.00	33.36	2.26	339.19	0.40	34.95	0.75	nd	0.00	2209.09	0.07	0.32	1.20	7850.57	0.27	5288.00	0.65	3465.75	2.46
N 49 L	Euc	nd	0.00	19.33	1.85	208.76	0.97	25.52	0.64	nd	0.00	1786.08	1.23	0.21	4.58	16809.28	0.08	5311.08	2.14	3283.76	0.61
N 50 L	Euc	12.00	2.73	42.24	2.81	361.92	3.13	45.60	1.56	nd	0.00	2126.40	2.12	0.47	0.94	8053.92	0.01	7089.12	0.13	3085.44	0.60
N 51 L	Euc	nd	0.00	31.94	3.81	682.98	1.89	81.89	1.14	nd	0.00	2808.92	0.71	0.04	2.36	13961.87	0.04	6713.56	1.07	5602.27	0.68
N 76 L	Mop	22.25	3.10	nd	0.00	632.20	3.07	17.71	1.96	nd	0.00	1566.86	1.50	nd	0.00	1198.08	1.69	14037.73	6.44	1488.29	1.28
N 77 L	Mop	nd	0.00	nd	0.00	165.07	0.77	22.83	0.09	nd	0.00	1274.05	0.22	nd	0.00	3643.02	0.27	9463.61	0.75	2508.59	0.38
N 44 Lip	NA	353.24	2.65	194.31	2.28	2060.96	1.36	95.74	1.51	nd	0.00	1100.75	1.05	1.26	0.99	7946.72	0.09	688.09	2.21	1847.79	1.58
N 52 Lip	NA	221.31	1.00	573.08	1.33	2077.22	0.95	56.69	1.38	nd	0.00	1460.66	0.03	3.56	1.11	7655.82	0.12	2215.44	1.35	2817.26	1.05
N 70 Lip	NA	328.05	3.05	542.96	1.68	2748.55	1.86	104.28	1.17	nd	0.00	2486.79	1.55	3.05	2.15	6303.94	6.31	706.77	2.38	3304.18	1.72
N 71 Lip	NA	225.79	0.73	24.98	9.91	848.71	0.33	49.95	1.43	nd	0.00	834.73	0.80	0.33	3.20	8419.70	0.04	882.18	0.56	1846.79	0.72
N 80 Lip	NA	102.41	1.26	28.71	3.67	681.21	0.50	30.26	0.20	nd	0.00	1543.19	0.02	0.29	6.15	7432.76	0.13	959.74	0.74	3600.00	0.66
Orchard Leaf CRM Wits	CRM	106.25	1.42	13.41	6.98	319.77	1.51	80.97	0.37	49.00	5.71	1769.05	0.90	0.09	6.64	8669.40	0.02	14538.74	1.15	5139.03	0.78
Orchard Leaf CRM ARC	CRM	282.40		13.60		298.30		94.90		43.11		-		-		21365.00		14310.00		6557.00	
Certified concentration		-		12 ± 1		300 ± 20		91 ± 4		45 ± 3		1900		0.1		20900 ± 300		14700 ± 300		6200 ± 200	
036 U ARC lab		37.06		14.91		219.80		13.10		0.65		-		-		7108.00		7416.00		3470.00	
038U ARC lab		85.24		28.51		211.90		20.40		nd		-		-		3100.00		7447.00		3100.00	
053U ARC lab		52.74		157.50		42.84		30.18		0.59		-		-		11695.00		5023.00		3457.00	
059U ARC lab		76.93		34.79		273.40		9.00		nd		-		-		16940.00		6360.00		2248.00	

Table 23: Concentrations (ug/g) and relative standard deviations obtained for Ni, P, Sr, Ti, W and Co from ICP-OES analyses

Sample	Tree	Ni	RSD	P	RSD	Sr	RSD	Ti	RSD	W	RSD	Co	RSD
17	AB	nd	0.00	1046.67	3.47	nd	0.00	nd	0.00	11.28	5.19	nd	0.00
19	AB	1.49	2.17	2756.46	0.60	nd	0.00	nd	0.00	nd	0.00	nd	0.00
21	AB	1.37	0.68	3484.85	0.78	21.05	0.94	11.81	4.92	90.34	2.83	nd	0.00
24	AB	1.20	0.86	2096.09	0.58	15.85	3.52	10.90	3.12	82.73	4.95	nd	0.00
27	AB	1.06	2.45	3159.77	0.60	21.25	0.76	nd	0.00	61.19	6.61	nd	0.00
29	AB	1.28	1.68	1857.23	0.55	55.49	0.92	37.28	1.38	43.35	1.33	nd	0.00
31	AB	1.31	1.10	3503.21	3.85	28.89	0.66	nd	0.00	91.01	2.93	nd	0.00
33	AB	0.91	3.45	3632.24	2.23	nd	0.00	nd	0.00	88.87	3.53	nd	0.00
34	AB	1.23	2.28	2034.07	1.63	29.35	0.93	12.27	1.16	91.78	2.87	nd	0.00
35	AB	1.34	3.38	2615.10	0.86	40.61	1.45	14.24	5.77	102.83	1.51	nd	0.00
20	Mop	1.02	5.50	2828.69	1.44	27.09	0.71	nd	0.00	91.44	3.00	nd	0.00
22	Mop	0.93	1.94	3827.94	1.11	10.09	0.74	nd	0.00	86.64	6.57	nd	0.00
23	Mop	1.03	1.22	2901.32	1.35	nd	0.00	nd	0.00	nd	0.00	nd	0.00
26	Mop	0.92	2.23	3247.91	1.20	23.26	1.39	10.23	5.71	78.14	1.56	nd	0.00
28	Mop	0.98	3.59	3141.68	2.53	nd	0.00	nd	0.00	nd	0.00	nd	0.00
30	Mop	1.18	0.78	919.29	1.79	213.05	0.58	nd	0.00	112.40	4.01	nd	0.00
32	Mop	0.99	5.08	813.84	3.08	127.57	2.90	12.47	3.08	90.64	3.05	nd	0.00
36	Mop	1.27	1.70	3334.39	0.55	35.77	0.83	14.41	5.85	121.71	0.30	nd	0.00
37	AB	1.29	1.19	2932.49	1.52	14.79	2.98	14.27	5.49	91.41	7.01	nd	0.00
39	AB	1.88	1.25	2335.00	0.76	17.66	0.61	21.94	4.70	128.98	1.88	nd	0.00
41	AB	2.02	1.44	2925.72	0.30	17.81	3.07	17.33	1.15	113.58	3.69	nd	0.00
48	AB	1.27	0.72	1406.84	1.38	60.16	2.65	16.11	6.37	103.26	6.26	nd	0.00
61	AB	1.18	2.94	2219.67	2.24	8.95	3.26	14.42	6.22	84.03	4.88	nd	0.00
67	AB	1.19	2.11	2265.65	2.61	6.36	1.41	13.21	2.31	92.45	3.09	nd	0.00
50	Euc	1.29	3.25	1340.71	1.67	27.20	0.34	19.95	2.97	100.65	5.78	nd	0.00
55	Euc	1.18	1.45	1656.80	0.41	15.41	1.47	16.91	2.50	92.98	3.49	nd	0.00
66	Euc	1.33	1.69	744.34	3.43	30.87	4.32	19.11	2.88	91.14	4.63	nd	0.00
38	Mop	1.00	1.39	3010.51	0.77	11.58	0.56	12.08	8.20	83.04	0.83	nd	0.00
40	Mop	0.97	0.94	2206.78	4.35	31.81	1.84	12.35	4.67	87.57	6.04	nd	0.00
42	Mop	1.43	2.35	3960.35	0.66	12.62	0.59	16.83	2.53	128.82	2.95	nd	0.00
45	Mop	1.40	1.45	3522.53	0.93	16.21	0.85	16.71	2.65	122.35	1.44	nd	0.00
46	Mop	1.44	0.83	4387.18	4.35	51.40	0.68	17.30	2.61	120.11	0.94	nd	0.00
51	Mop	1.29	2.18	2423.55	3.28	46.42	1.08	15.99	1.79	122.23	2.34	nd	0.00
53	Mop	1.00	1.28	2695.33	1.21	14.54	2.37	11.42	7.60	89.31	3.40	nd	0.00
63	Mop	1.04	2.90	1638.62	3.07	5.63	1.49	14.29	1.98	89.21	4.06	nd	0.00
017 U	AB	0.84	4.04	1190.32	0.56	47.58	0.30	nd	0.00	69.35	4.81	nd	0.00
017 W	AB	0.95	1.65	1034.82	0.91	46.40	1.40	nd	0.00	84.05	6.32	nd	0.00
019 U	AB	0.91	6.21	1527.56	2.80	39.17	0.46	nd	0.00	72.24	7.77	nd	0.00
021 U	AB	1.04	2.23	1271.30	2.28	61.74	0.50	nd	0.00	80.87	2.38	nd	0.00
021 W	AB	0.89	1.09	1259.83	1.98	36.58	0.98	nd	0.00	81.66	3.10	nd	0.00
024 U	AB	1.10	2.38	1246.21	0.79	57.21	0.89	2.93	9.16	89.49	2.44	nd	0.00
027 U	AB	1.24	2.18	1148.76	2.66	nd	0.00	8.26	1.83	nd	0.00	nd	0.00
031 U	AB	0.94	2.58	1088.28	1.21	181.79	0.57	nd	0.00	78.72	1.74	nd	0.00
031 W	AB	1.12	2.01	722.27	4.64	nd	0.00	5.68	1.56	nd	0.00	nd	0.00
033 U	AB	0.98	3.91	1221.60	1.93	121.60	0.10	nd	0.00	83.20	5.08	nd	0.00
035 U	AB	0.97	4.95	1270.54	2.45	158.93	1.53	nd	0.00	82.54	3.80	11.41	5.35
035 W	AB	1.16	4.22	1091.21	2.33	nd	0.00	6.82	6.16	nd	0.00	nd	0.00
037 U	AB	1.21	1.95	1007.25	0.59	20.21	0.40	15.76	0.94	81.65	3.96	nd	0.00
037 W	AB	3.24	2.30	1107.82	1.54	20.70	1.61	10.76	4.79	77.00	7.69	nd	0.00
039 U	AB	1.35	8.50	1221.56	2.62	142.07	0.33	13.95	0.88	nd	0.00	nd	0.00
039 W	AB	1.41	1.97	1269.96	2.99	nd	0.00	56.95	1.39	nd	0.00	nd	0.00
041 U	AB	1.15	4.84	947.71	2.23	nd	0.00	12.33	1.39	nd	0.00	nd	0.00
041 W	AB	1.35	1.92	1075.16	2.36	79.75	0.67	7.12	1.06	90.43	5.91	nd	0.00
048 U	AB	0.87	2.49	906.72	2.93	nd	0.00	6.72	5.18	nd	0.00	nd	0.00
048 W	AB	0.79	1.72	938.56	1.22	47.81	1.36	nd	0.00	68.64	8.45	nd	0.00
061 U	AB	1.39	3.73	1108.55	2.49	39.68	0.66	21.29	1.83	96.77	3.72	nd	0.00
061 W	AB	1.28	2.13	969.20	4.78	49.75	1.67	18.09	5.90	91.36	6.93	nd	0.00
067 U	AB	0.90	3.14	997.30	3.18	27.02	2.08	16.38	2.56	70.42	2.13	nd	0.00
050 U	Euc	1.02	0.59	622.48	2.20	26.70	0.45	nd	0.00	89.23	2.59	nd	0.00
050 W	Euc	1.19	6.35	725.24	6.71	37.86	0.81	nd	0.00	97.57	2.49	nd	0.00
055 U	Euc	1.03	1.33	745.19	0.83	37.79	0.45	14.83	6.83	81.79	9.37	nd	0.00
055 W	Euc	0.83	2.74	649.91	0.65	21.50	0.90	nd	0.00	69.29	1.71	nd	0.00
059 U	Euc	0.94	4.07	782.46	0.85	21.03	1.32	14.15	1.53	76.87	8.18	nd	0.00
059 W	Euc	1.10	1.93	787.90	1.17	17.78	0.26	12.93	2.94	97.01	1.49	nd	0.00
060 U	Euc	1.02	1.18	818.72	0.58	33.59	0.61	14.39	2.72	88.11	1.15	nd	0.00
060 W	Euc	1.02	1.92	801.45	1.23	24.92	0.36	12.71	2.90	83.08	1.02	nd	0.00
066 U	Euc	1.11	1.73	851.27	1.25	26.66	0.91	18.06	5.62	85.99	3.06	nd	0.00
066 W	Euc	1.39	3.37	799.50	0.36	27.46	1.00	17.23	3.86	121.67	5.78	nd	0.00
018 U	Mop	1.04	2.14	1008.70	1.52	82.61	0.52	nd	0.00	99.13	2.44	nd	0.00
018 W	Mop	0.93	5.33	1051.86	0.47	60.92	0.23	nd	0.00	87.51	7.58	nd	0.00
020 U	Mop	0.90	1.38	1147.83	1.54	44.18	0.62	9.82	3.60	76.76	2.54	nd	0.00

Sample	Tree	Ni	RSD	P	RSD	Sr	RSD	Ti	RSD	W	RSD	Co	RSD
022 W	Mop	0.88	6.08	1020.65	3.61	101.27	1.39	nd	0.00	nd	0.00	nd	0.00
023 U	Mop	1.07	4.09	1094.27	7.48	nd	0.00	nd	0.00	94.10	10.39	nd	0.00
026 U	Mop	1.03	3.68	924.98	2.80	59.54	1.04	22.59	1.63	72.89	5.37	nd	0.00
026 W	Mop	1.22	1.94	1114.49	1.52	75.50	0.41	nd	0.00	119.26	6.87	nd	0.00
028 U	Mop	1.00	3.91	1023.67	2.57	nd	0.00	8.58	2.17	nd	0.00	nd	0.00
030 W	Mop	1.17	9.51	925.02	2.22	nd	0.00	nd	0.00	nd	0.00	nd	0.00
034 U	Mop	1.04	2.56	996.40	2.42	nd	0.00	nd	0.00	nd	0.00	nd	0.00
034 W	Mop	1.04	5.34	960.46	1.38	138.25	0.52	11.95	4.52	94.59	2.03	nd	0.00
036 U	Mop	0.70	5.05	1428.39	4.99	270.58	5.77	nd	0.00	59.23	5.00	nd	0.00
036 W	Mop	nd	0.00	1380.57	2.32	nd	0.00	nd	0.00	nd	0.00	nd	0.00
038 U	Mop	0.89	3.24	978.84	3.47	52.00	0.53	nd	0.00	73.81	5.25	nd	0.00
038 W	Mop	1.08	6.82	1074.45	5.52	53.13	6.20	nd	0.00	91.19	4.87	nd	0.00
040 U	Mop	0.71	3.29	1099.33	2.32	36.91	0.39	nd	0.00	62.42	2.64	nd	0.00
042 U	Mop	0.92	0.37	1055.86	1.46	45.08	1.27	nd	0.00	70.29	6.10	nd	0.00
045 U	Mop	1.30	0.94	1369.86	0.85	nd	0.00	8.55	1.52	nd	0.00	nd	0.00
046 U	Mop	1.15	1.37	1597.56	0.81	82.66	2.11	nd	0.00	75.07	5.55	nd	0.00
046 W	Mop	1.23	1.26	1362.02	1.30	124.30	0.91	13.04	7.58	79.06	0.94	nd	0.00
051 U	Mop	1.95	1.90	1783.93	1.38	8.46	1.21	nd	0.00	76.13	5.96	nd	0.00
053 U	Mop	0.85	0.98	1238.87	7.34	53.49	1.35	4.52	7.60	85.26	2.33	nd	0.00
053 W	Mop	0.83	4.67	1271.08	0.81	nd	0.00	3.22	6.30	nd	0.00	nd	0.00
063 U	Mop	1.13	0.32	1227.12	0.76	24.66	0.35	17.86	2.07	97.80	1.85	nd	0.00
063 W	Mop	1.29	0.32	1023.49	1.76	39.31	0.45	20.15	2.35	108.10	3.72	nd	0.00
I 44 L	AB	1.03	5.43	1271.74	0.03	102.27	6.94	nd	0.00	nd	0.00	nd	0.00
I 52 L	AB	1.15	1.67	2411.70	0.53	14.21	0.21	11.70	2.98	72.70	2.95	nd	0.00
I 56 L	AB	1.07	1.72	1876.47	1.04	15.13	0.14	15.97	1.53	58.82	4.94	nd	0.00
I 60 L	AB	1.46	2.23	1272.71	0.44	41.19	1.25	68.14	1.12	nd	0.00	nd	0.00
I 64 L	AB	1.92	1.32	2612.24	1.49	27.88	0.98	33.04	2.08	68.66	0.79	nd	0.00
I 66 L	AB	1.21	2.80	2129.89	1.48	14.81	3.12	8.23	8.23	69.10	6.05	nd	0.00
I 67 L	AB	1.63	2.59	2206.32	1.36	40.22	1.16	26.35	0.70	nd	0.00	nd	0.00
I 68 L	AB	1.20	0.64	1986.94	1.06	46.47	1.80	27.77	2.00	62.49	4.81	nd	0.00
I 48 L	Euc	0.91	0.60	654.88	2.56	48.29	0.99	5.12	6.87	nd	0.00	nd	0.00
I 49 L	Euc	1.26	0.55	729.93	1.62	nd	0.00	12.63	2.79	nd	0.00	nd	0.00
I 50 L	Euc	0.98	3.80	872.90	1.00	38.51	2.05	15.40	7.23	68.46	4.01	nd	0.00
I 76 L	Mop	1.04	8.43	1273.63	0.61	nd	0.00	nd	0.00	nd	0.00	nd	0.00
I 77 L	Mop	0.98	1.28	1524.52	0.64	207.83	0.94	11.55	1.85	87.48	4.68	nd	0.00
I 79 L	Mop	1.48	2.84	3870.32	1.68	nd	0.00	7.09	4.05	nd	0.00	nd	0.00
I 88 L	Mop	1.22	4.59	2262.65	2.14	17.64	1.23	14.44	5.36	117.09	6.36	nd	0.00
I 90 L	Mop	1.05	6.35	3829.42	4.29	nd	0.00	nd	0.00	96.28	5.23	nd	0.00
I 91 L	Mop	1.05	3.81	2935.33	0.51	nd	0.00	3.69	4.85	nd	0.00	nd	0.00
I 44 Li	NA	0.96	2.12	590.77	0.52	120.00	1.89	66.15	5.09	nd	0.00	nd	0.00
I 52 Li	NA	2.62	0.22	2091.78	2.19	nd	0.00	217.81	0.75	nd	0.00	10.68	5.35
I 64 Li	NA	1.89	3.26	1185.11	1.89	110.78	0.85	103.05	2.23	nd	0.00	nd	0.00
I 80 Li	NA	0.00	3.43	1889.13	1.41	nd	0.00	207.73	5.84	nd	0.00	10.45	1.80
I 94 Li	NA	0.81	1.70	863.41	0.48	300.73	1.10	17.56	3.82	49.76	8.93	nd	0.00
N 44 L	AB	1.42	1.72	2861.31	0.55	6.17	0.82	nd	0.00	84.62	6.87	nd	0.00
N 52 L	AB	1.14	0.32	2801.67	0.68	4.42	2.77	nd	0.00	84.87	9.01	nd	0.00
N 56 L	AB	1.18	4.67	1981.95	0.83	6.50	7.42	nd	0.00	87.73	5.41	nd	0.00
N 60 L	AB	1.43	3.33	1879.50	1.10	7.00	4.08	20.50	4.27	99.00	3.04	nd	0.00
N 64 L	AB	1.55	2.49	3377.47	0.65	14.58	0.33	13.54	1.68	89.05	2.57	nd	0.00
N 66 L	AB	1.12	4.09	3147.50	0.62	nd	0.00	nd	0.00	70.96	8.58	nd	0.00
N 67 L	AB	3.73	1.32	1992.80	0.88	46.15	0.63	17.12	2.27	35.73	5.52	nd	0.00
N 68 L	AB	1.05	2.18	1419.73	0.65	nd	0.00	15.24	4.93	nd	0.00	nd	0.00
N 48 L	Euc	0.86	3.16	842.01	2.17	24.62	0.50	nd	0.00	69.90	5.12	nd	0.00
N 49 L	Euc	0.84	3.44	730.67	1.42	24.74	2.31	nd	0.00	72.68	5.71	nd	0.00
N 50 L	Euc	1.01	0.54	972.00	0.57	33.12	0.36	13.44	5.81	72.00	5.61	nd	0.00
N 51 L	Euc	0.00	0.00	811.56	5.33	nd	0.00	12.28	5.54	nd	0.00	nd	0.00
N 76 L	Mop	0.92	2.50	3093.76	1.47	10.45	2.38	12.26	3.16	69.94	1.41	nd	0.00
N 77 L	Mop	1.01	3.94	2585.85	0.86	52.68	0.37	nd	0.00	93.07	4.96	nd	0.00
N 44 Lip	NA	1.14	0.97	515.00	1.23	102.34	1.40	52.35	1.85	41.50	9.15	nd	0.00
N 52 Lip	NA	1.07	0.76	802.16	0.01	57.46	0.00	50.47	3.49	28.73	0.00	nd	0.00
N 70 Lip	NA	1.10	1.70	599.53	5.44	61.64	2.77	54.46	3.67	nd	0.00	nd	0.00
N 71 Lip	NA	1.30	1.34	583.46	2.97	269.75	0.67	30.97	9.00	88.92	5.31	nd	0.00
N 80 Lip	NA	0.95	0.03	1171.55	0.04	309.57	0.74	15.52	2.27	nd	0.00	nd	0.00
Orchard Leaf CRM Wits	CRM	1.32	1.06	2010.74	1.51	32.49	0.91	22.69	3.12	67.61	9.82	nd	0.00
Orchard Leaf CRM ARC	CRM	1.40		2374.00		33.44		10.29		0.13		-	
Certified concentration		1.3 ± 0.2		2100 ± 100		37 ± 1		-		-		0.20	
036 U ARC lab		0.35		1817.00		206.70		-		0.13		-	
038U ARC lab		4.34		961.00		62.76		-		0.08		-	
053U ARC lab		1.65		2027.00		51.74		-		8.16		-	
059U ARC lab		2.10		1208.00		64.83		-		nd		-	

11.1. Statistical data

Table 24: Pearson's R correlation analyses results for element concentration in leaves versus distance of tree from smelter in April and November 2011

L. capassa			
Apr-11	**Dist from smelter (m)**	*Nov-11*	**Dist from smelter (m)**
Dist from smelter (m)	1	**Dist from smelter (m)**	1
Al	-0.34886	**Al**	0.762271
Cu	-0.63943	**Cu**	-0.65286
Fe	0.085213	**Fe**	0.443059
Mn	0.504229	**Mn**	0.662364
Pb	0.318846	**Pb**	-0.62518
S	-0.72461	**S**	-0.39793
Bi	-0.60236	**Bi**	-0.69281
Ca	0.299318	**Ca**	0.633723
K	-0.80212	**K**	0.106395
Mg	0.232557	**Mg**	0.736775
Ni	-0.23237	**Ni**	0.528074
P	-0.29731	**P**	-0.1643
Sr	-0.03657	**Sr**	0.754896
Ti	-0.89773	**Ti**	0.566981
W	-0.85596	**W**	0.664498
C. mopane			
Apr-11	**Dist from smelter (m)**	*Nov-11*	**Dist from smelter (m)**
Dist from smelter (m)	1	**Dist from smelter (m)**	1
Al	-0.6429	**Al**	-0.66523
Cu	0.549005	**Cu**	0.242664
Fe	0.111574	**Fe**	-0.25128
Mn	0.302256	**Mn**	0.33323
Pb	0.244959	**Pb**	-0.30558
S	0.491921	**S**	0.676612
Bi	0.913814	**Bi**	0.448104
Ca	0.146052	**Ca**	0.582253
K	-0.4064	**K**	0.626753
Mg	0.348796	**Mg**	0.60154
Ni	0.197105	**Ni**	0.473354
P	0.382865	**P**	0.599181
Sr	0.129771	**Sr**	0.555894
Ti	-0.75456	**Ti**	0.25185
W	-0.39384	**W**	0.538837

E. divinorum			
Apr-11	**Dist from smelter (m)**	*Nov-11*	**Dist from smelter (m)**
Dist from smelter (m)	1	**Dist from smelter (m)**	1
Al	-0.62781	**Al**	-0.40145
Cu	-0.46462	**Cu**	-0.87219
Fe	-0.68701	**Fe**	-0.069
Mn	-0.65028	**Mn**	-0.41562
Pb	0	**Pb**	0.77079
S	-0.92193	**S**	-0.95611
Bi	-0.65022	**Bi**	-0.83531
Ca	0.054332	**Ca**	-0.34106
K	-0.95863	**K**	0.6555
Mg	-0.56365	**Mg**	-0.6828
Ni	-0.36311	**Ni**	-0.40212
P	-0.97538	**P**	0.761896
Sr	0.153328	**Sr**	-0.38586
Ti	-0.87496	**Ti**	0.102801
W	0.200911	**W**	0.874048

Table 25: Summary of *P* values obtained from the Wilcoxon Signed Rank Test and the Wilcoxon Mann Whitney Test for various elements

***P* values obtained from Statistics Tests**		**Al**	**Cu**	**Fe**	**Mn**	**S**	**Bi**	**Ca**	**K**	**Mg**	**Ni**	**P**	**Sr**	**Ti**	**W**
	PAIRED Tests (Wilcoxon Signed Rank)														
Leaf Litter	2008 vs 2011	0.63	**0.05**	**0.05**	0.44	0.13	**0.05**	0.81	**0.05**	0.13	1.00	**0.06**	0.81	**0.05**	0.25
Seasons Tailings	**AB**_Apr vs Nov 2011 Cu Tailings seepage area	0.31	0.63	**0.05**	0.20	0.74	0.69	**0.01**	**0.02**	**0.01**	0.46	**0.02**	**0.02**	0.38	0.84
	Mop_Apr vs Nov 2011 Cu Tailings seepage area	1.00	1.00	0.30	0.94	0.16	0.75	**0.05**	**0.02**	0.69	0.70	**0.05**	0.63	0.88	0.56
Seasons Plume	**AB**_Apr vs Nov 2011 Smelter Plume	0.31	**0.06**	**0.03**	**0.05**	0.84	**0.05**	**0.03**	**0.03**	**0.05**	**0.05**	**0.03**	0.56	0.56	**0.05**
	Mop_Apr vs Nov 2011 Smelter Plume	0.38	0.16	0.46	0.20	**0.05**	**0.02**	**0.04**	**0.01**	0.55	0.25	**0.01**	0.20	**0.02**	**0.02**
	Euc_Apr vs Nov 2011 Smelter Plume	0.81	**0.06**	**0.06**	0.81	0.63	**0.06**	0.81	0.44	1.00	**0.06**	0.44	1.00	**0.06**	**0.06**
Over 3 years	**AB**_2008 vs Nov 2011 Smelter Plume	0.25	**0.02**	**0.02**	0.20	0.74	**0.02**	0.64	0.84	0.15	0.95	0.11	**0.02**	**0.02**	0.11
	Euc_2008 vs Nov 2011 Smelter plume	0.20	**0.05**	**0.05**	0.38	0.12	**0.01**	0.25	0.25	0.50	0.14	0.25	0.75	0.10	0.25
Washed versus unwashed	**AB**_Cu Tailings seepage area	0.50	0.50	0.13	0.13	0.63	1.00				0.38		0.13	0.18	1.00
	AB_Smelter Plume	0.81	0.44	0.44	0.63	0.13	0.63	0.31	0.13	0.63	0.63	0.63	0.63	0.63	0.63
	Mop_Cu Tailings seepage area	0.50	1.00	0.25	0.88	0.25	1.00	0.63	0.38	0.25	0.63	0.88	0.88	1.00	0.88
	Mop_Smelter Plume	0.25	0.25	0.63	0.63	0.88	0.38	0.63	1.00	0.63	0.25	0.63	0.88	0.50	0.88
	Euc_Smelter Plume	0.13	0.13	0.63	0.31	0.31	**0.06**	0.13	**0.06**	0.63	0.63	0.81	0.63	0.13	0.44
	INDEPENDENT Tests (Wilcoxon Mann Whitney)														
Smelter Plume versus Cu Tailings seepage area	**AB**_ Cu Tailings seepage area vs Smelter Plume Apr 2011	0.11	**0.02**	**0.05**	0.30	0.80	**0.02**	0.90	0.25	0.20	0.30	**0.01**	0.13	**0.05**	0.73
	Mop_ Cu Tailings seepage area vs Smelter Plume Apr 2011	0.77	0.32	0.42	0.73	**0.02**	**0.04**	0.42	0.82	0.64	0.56	0.11	0.95	0.28	0.68
	AB_ Cu Tailings seepage area vs Smelter Plume Nov 2011	0.81	0.31	**0.01**	0.53	0.11	**0.05**	0.29	0.77	0.95	0.57	0.45	**0.02**	0.11	0.27
	Mop_ Cu Tailings seepage area vs Smelter Plume Nov 2011	0.18	**0.05**	**0.02**	0.77	0.59	0.17	0.72	**0.05**	0.33	**0.05**	0.79	0.29	0.23	0.29
Tree Species	**AB_Mop_Euc** in Smelter Plume Apr 2011	0.54	**0.01**	**0.02**	**0.02**	0.57	**0.01**	0.90	0.19	**0.01**	0.57	**0.00**	0.48	0.54	0.26
	AB_Mop_Euc in Smelter Plume Nov 2011	**0.04**	**0.02**	**0.01**	0.28	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.10	**0.00**	0.39	0.40	0.24
	AB_Mop in Cu Tailings seepage area Apr 2011	0.62	0.48	0.30	**0.00**	**0.00**	**0.05**	**0.03**	0.20	**0.01**	1.00	**0.03**	0.22	**0.05**	0.94
	AB_Mop in Cu Tailings seepage area Nov 2011	0.12	0.56	0.21	**0.01**	**0.01**	**0.06**	0.29	0.59	**0.03**	**0.02**	0.86	0.73	0.88	0.19