AN APPRAISAL OF THE PHYSICAL ENVIRONMENTAL QUALITY OF THE SELEBI – PHIKWE Ni – Cu MINE AREA, SOUTH – EASTERN BOTSWANA

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MAGISTER TECHNOLOGIAE:
ENVIRONMENTAL HEALTH

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BLOEMFONTEIN

February, 2001

DECLARATION OF INDEPENDENT WORK

I, EKOSSE GEORGES-IVO EKOSSE, do hereby declare that this research project submitted to the Technikon Free State for the degree MAGISTER TECHNOLOGIAE: ENVIRONMENTAL HEALTH: is my own independent work that has not been submitted before to any institution by myself or any other person in fulfillment of the requirements for the attainment of any qualification.

.... February, 2001

SIGNATURE OF STUDENT DATE

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SUMMARY

This research project focused on the environmental impact of mining and smelting nickel-copper (Ni-Cu) at the Selebi Phikwe area, south-eastern Botswana. Physico-chemical properties, mineralogical identification and characterisation, and heavy metals concentrations of elements for samples of tailings dump, soils, particulate air matter (PAM), *Colophospermum mopane* (mopane plant), and *Imbrasia belina* (phane caterpillar) were investigated. Physico-chemical properties studied on tailings dump and soil samples included soil texture and colour, particle size distribution (PSD), pH, electrical conductivity (EC), cation exchange capacity (CEC) and descriptive petrography. Identification and characterisation of minerals contained in tailings dump, soil, and PAM samples were performed employing X-ray powder diffraction (XRPD) techniques which included clay size and heavy minerals fractionation. Chemical analyses for heavy metals (cadmium, Cd; cobalt, Co; chromium, Cr; nickel, Ni and selenium, Se) concentrations in tailings dump, soils, PAM, mopane leaves and phane caterpillar were measured with a graphite furnace atomic absorption spectrometer (GFAAS) whereas the flame atomic absorption spectrometer (FAAS) measured copper, Cu; iron, Fe and zinc, Zn concentration levels.

The clay and silt soil components made up to 50 wt % of soil. Very acidic soils were located close to the smelter/concentrator plant, and both soil EC and CEC values were significantly low. Physical tests revealed albite, $NaAlSi_3O_8$; cristobalite, α- SiO_2; chalcopyrite, $CuFeS_2$; pyrrhotite, $Fe_{1-x}S$;

tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$; and pentlandite, $(Fe,Ni)_9S_8$; to be contained in tailings dump. Soil colour varied from pale yellow, reddish yellow to dark reddish brown. The tailings dump comprised of nickelbloedite, $Na_2(Ni(SO_4)_2.4H_2O$; pyrrhotite; quartz, SiO_2; pentlandite; malachite,$Cu_2CO_3(OH)_2$; chalcopyrite; actinolite, $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$; cristobalite; tremolite; kaolinite, $Al_2Si_2O_5(OH)_4$; mica and albite. The PAM consisted of quartz, SiO_2; pyrrhotite; chalcopyrite, $CuFeS_2$; albite, and djurleite, $Cu_{31}S_{16}$. Bulk soil samples consisted of actinolite, albite, quartz, microcline, $KAlSi_3O_8$; pyrrhotite, silicon sulphide, SiS; and cobalt oxide, CoO whereas the < 2 μm fraction was made of kaolinite, smectite, $Na_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.xH_2O$; anorthite, $CaAl_2Si_2O_8$; illite, $KAl_2(Si_3AlO_{10})(OH)_2$ and quartz. Djurleite polymorphs ($Cu_{31}S_{16}$ and $Cu_{1.93}S$) were formed from secondary mineralisation of chalcopyrite and the SO_2 released from concentration/smelting processes. Ambient temperature and an acidic milieu created favourable conditions for the formation of nickelblodite and malachite from the primary ore minerals: pentlandite, chalcopyrite and pyrrhotite in tailings dump. Cobalt oxide and silicon sulphide identified in surface soils were indicative of environmental chemical alteration of mining waste deposited on surface soils.

High concentrations of heavy metals recorded in different environmental media had affected the physical environmental quality at Selebi Phikwe. Heavy metals including Cd, Co, Cr, Cu, Fe, Ni, Se and Zn, which are deleterious to the environment, and pose as health hazards to human beings, were associated with these minerals. Contamination of waterbodies around Selebi Phikwe might have been possible by the heavy ions in solution. Consumption of stunted phane might pose as health hazard. In overcoming pollution problems at Selebi Phikwe, aspects of pollution management such as phytoremediation and phytomining, environmental desulphurisation, phytostabilisation, and biotechnology could be introduced as pollution control measures.

OPSOMMING

Hierdie navorsingsprojek het gefokus op die omgewingsimpak van die delf en smelt van nikkel-koper (Ni-Cu) in die Selebi Phikwe-omgewing, suidoostelike Botswana. Fisies-chemiese eienskappe, mineralogiese/delfstofkundige identifikasies en karakterisering asook swaarmetaal konsentrasies van chemiese substansies is ondersoek vir monsters van slak, grond, partikulêre lugdeeltjies (PAM), *Colophospermum mopane* (mopane plant) asook *Imbrasia belina* (faneruspers). Fisies-chemiese eienskappe van stortingsterrein monsters, het tekstuur en kleur, partikelgroottedistribusie (PSD), pH elektrisiteitsgeleidingsvermoë (EC), katioonwisselingkapasiteit (CEC) en beskrywende petrografie ingesluit. Identifikasie en karakterisering van minerale, wat in slak, grond en PAM monsters vervat is, was uitgevoer deur gebruik te maak van X-straaldiffraksie (XRPD)-tegnieke, insluitende leemgrootte en swaarmineraal fraksionering. Chemiese analise vir swaarmetaal (Cd, Co, Cr, Ni en Se) konsentrasies in slak, grond, PAM, mopaneblare en faneruspers is met ‘n atoom absorpsie spektrofotometer (GFAAS) bepaal. Cu, Fe en Zn konsentrasievlakke is met behulp van ‘n vlam-atoom absorpsie spektrometer (FAAS) gemeet.

Die klei- en slakkomponente maak tot 50% (massa) van die grond uit. Suurvormende grond word naby die smeltery/konsentrator-aanleg gevind en beide die EC en CEC-waardes van die grond is aansienlik laag. Fisiese toetse het aangedui dat die slakstortingsterrein, albiet, cristobaliet,

chalkopiriet, pirrotiet, tremoliet en pentlandiet bevat. Die grondkleur wissel van bleekgeel, rooigeel tot donker rooibruin. Die slak bevat nikkelbloediet, $Na_2Ni(SO_4)_2.4H_2O$; pirrotiet, kwarts, pentlandiet, $(Fe,Ni)_9S_8$; malagiet, $Cu_2CO_3(OH)_2$ chalkopiriet, aktinoliet, $CA_2(MG,Fe)_5Si_8O_{22}(OH)_2$; cristobaliet, SiO_2; tremoliet, $Ca_2Mg_5Si_8O_{22}(OH)_2$; kaoliniet, $Al_2Si_2O_5(OH)_4$; mika en albiet. Die PAM bestaan uit kwarts, SiO_2; pirrotiet, $Fe_1\text{ -x}S$; chalkopiriet, $CuFeS_2$; albiet, $NaAlSi_3O_8$; en djurliet, $Cu_{31}S_{16}$. Grondmonsters bestaan uit aktinoliet, albiet, kwarts, mikrokline, $KAlSi_3O_8$; pirrotiet, sillikoonsulphide en kobaltoksied, aangesien die < 2μ m fraksie saamgestel is uit kaoliniet, illiet, $KAl_2(Si_3AlO_{10})(OH)_2$; smektiet, $Na_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.xH_2O$; anortiet, $CaAl_2Si_2O_8$ en kwarts. Djurliet polimorfe ($Cu_{31}S_{16}$ en $Cu_{1.93}S$) is van sekondêre mineralisering van chalkopiriet gevorm en SO_2 word vrygestel van konsentrasie/smeltingsprosesse. Omgewingstemperature en 'n suuragtige milieu het gunstige toestande vir die formasie van nikkelblodiet en malagiet van die primêre ertsminerale pentlandiet, chalkopiriet/koperkies en pirrotiet in uitskothope geskep. Kobaltoksiede en sillikoonsulfiedes wat in oppervlakgrond geïdentifiseer is, is indikatief van die chemiese veranderinge in die omgewing van mynafval wat op die oppervlak afgesak het.

Hoë konsentrasies van swaarmetale, wat ook in verskillende omgewingsmedia aangeteken is, het die fisiese omgewingskwaliteit van Selebi Phikwe geaffekteer. Swaar metale, insluitende Cd, Co, Cr, Cu, Fe, Ni, Se en Zn, wat nadelig is vir die omgewing is, word ook met menslike gesondheidsrisiko's geassosieer. Kontaminasie van watermassas rondom Selebi Phikwe word gerealiseer deur die swaar ione in oplossing. Menslike verbruik van dwergagtige fane mag ook 'n gesondheidsrisiko inhou. Ten einde die besoedelingsprobleme in Selebi Phikwe te oorkom, kan aspekte van besoedelingsbestuur soos fitoremediëring en fitomynbou asook omgewingsdesulfirisasie as besoedelingsbeheermaatreëls ingestel word.

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AIEA	Association Internationale pour les Etudes d'Argiles
AMD	Acid mine drainage
BCL	Bamangwato Concessions Ltd
CCN	Cloud condensation nuclei
CEC	Cation exchange capacity
DAR	Department of Agricultural Research
DMSO	Dimethyl sulphoxide
DPAM	Deposited particulate air matter
DSI	DMSO solvation index
EC	Electrical conductivity
EDTA	Ethylene diamine tetra acetic acid
EPA	Environmental Protection Agency
FAAS	Flame atomic absorption spectrometer
GFAAS	Graphite furnace atomic absorption spectrometer
HI	Hinckley crystallinity index
ICDD	International Centre for Powder Diffraction Data
IR	Infra-red
MAS	Mean annual standard
NIOSH	National Institute of Occupational Safety and Health
NP	Neutralisation potential
PAM	Particulate air matter
pH	Hydrogen ion concentration
PHMH	Plant heavy metal hyperaccumulator

PPAMP	Primary particulate air matter pollutant
ppb	Parts per billion
ppm	Parts per million
PSA	Particle size analyser
PSD	Particle size distribution
SPAMP	Secondary particulate air matter pollutant
TDS	Total dissolved salts
US	United States
USDA	United States Department of Agriculture
VOC	Volatile organic compound
VRPAM	Visibility reducing particulate air matter
WHO	World Health Organisation
XRPD	X-ray powder diffraction
Å	Angstrom
esd	Euhedral spherical diameter
µm	Micro metre
µS/cm	Micro siemens per centimeter

Chapter 1

Introduction

1.1 Background

Botswana has a population of 1 500 000 inhabitants with a 3.1% population growth rate and a population density of 2 persons per km^2 in 1996 (Mbendi, 2000). The country has the fastest growing economy in Africa and among the less developed countries of the world. It is one of Africa's top three mineral producers by value, including South Africa and the Democratic Republic of Congo. Its mining industry provides employment for 10 000 Batswana. It exports mainly diamonds, nickel-copper-cobalt (Ni-Cu-Co) matte and beef, and imports petroleum products, food products, chemicals and textiles.

Diamond, soda ash, gold and Ni-Cu remain the mainstay of the mining industry in Botswana. Growth in mining activities in the country has generated a corresponding increase in tailings dump and other contaminants, that are considered as environmental pollutants. The Selebi Phikwe Ni-Cu mine area, where mining and smelting activities may pose as sources of environmental contamination, is of particular concern. Previous studies at Selebi Phikwe were directed at understanding the petrogenesis (Brown, 1987), structural geology (Gallon, 1986), and mineralogy (Nkoma and Ekosse, 1998; 1999; 2000) of the orebodies. Research work geared at understanding various aspects of environmental pollution around the mine area, however, is not documented. At the Cu-Ni and Cu-Zn mining areas in Canada, it was found that the mining activities contaminated the environment (Bowles and Jambor, 1990; Al *et al.*, 1994; Bowles *et al.*, 1998). This study addressed the effects of mining and processing of Ni-Cu ore bodies on the physical environmental quality of the area.

1.2 Problem statement

Previous X-ray powder diffraction studies of Ni-Cu orebodies from Selebi Phikwe identified transition sulphide minerals, which included chalcopyrite $CuFeS_2$, pentlandite $(Fe,Ni)_9S_8$, pyrrhotite $(Fe_{1-x}S)$, bunsenite (NiO), chalcocite (Cu_2S), penroseite $(Ni,Cu)Se_2$ and magnetite (Fe_3O_4) (Nkoma and Ekosse, 2000; 1999). Similar findings were not reported on in the literature. In the present study, an attempt was made to link information on mineralogy of the transition sulphide minerals from the ore bodies to the physical environment. Furthermore, the physical environmental quality around the Selebi Phikwe Ni-Cu mine area was assessed physico-chemically and chemically.

More specifically, the following concerns were addressed:

Did the mining of Ni-Cu ore bodies, and the concentration and smelting of Ni-Cu-Co affect the physical environmental quality of the Selebi Phikwe mine area?

- If the physical environmental quality were affected, to what extend were the soils, biomass and air affected qualitatively and quantitatively?

- Investigations leading to the answers of the above question queried related issues, such as the concentrations of the different heavy ions and how they vary in the particulate air matter (PAM), soils, and biomass?
- Were there any alterations of the physico-chemical properties of the soil and the clay fraction of soil due to the mining and extraction metallurgical activities?
- What was the mineralogy of the soil and how was it linked with the mineralogy of the orebodies?
- What values are obtained from the PAM and how do these values compare with international standards?
- Were the results obtained from laboratory analyses indicative of contamination of the environmental quality due to mining activities?
- If contamination of the physical environment had occurred, how could it be contained?
- Could mining activities continue without an effect on the physical environmental quality?

1.3 Aims and objectives

The primary objective of this study was to characterise the tailings dump, soil, PAM, mopane and phane around the Selebi Phikwe area in order to understand how mining and extraction metallurgical activities affect the physical environmental quality of the surroundings. The physical parameters of soil and ionic concentrations of some elements in tailings dump, soil, vegetation and worms were investigated because of their possible effects on living organisms. It was achieved by the following analyses and characterisation.

1.3.1 Analyses of physical parameters

- The electrical conductivity (EC), temperature, pH, particle size distribution (PSD) and CEC were determined in the soil samples obtained from the mine area.

1.3.2 Qualitative and quantitative analyses

Analyses focused on the following heavy metals: cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), selenium (Se) and zinc (Zn).

- Samples of tailings dump from the processing of Ni-Cu orebodies at the Selebi Phikwe smelter/concentrator plant were analysed for concentrations of the following heavy metals: Cd, Co, Cr, Cu, Fe, Ni, Se and Zn.

- Qualitative and quantitative analyses of soil samples within the Selebi Phikwe environment were performed. The concentration of ions of heavy metals analysed included Cd, Co, Cr, Cu, Fe, Ni, Se and Zn. The analyses were carried out for both whole and clay fraction of soils.

- Qualitative and quantitative determination of samples of PAM from the air (atmosphere) within the Selebi Phikwe environment were conducted for the following heavy metals: Cd, Co, Cr, Cu, Fe, Ni, Se and Zn.

- Qualitative and quantitative determination of heavy ion concentrations in samples of mopane leaves from the Selebi Phikwe environment were carried out. The ions analysed were for the following heavy metals: Cd, Co, Cr, Cu, Fe, Ni, Se and Zn.

- Qualitative and quantitative determination of heavy ion concentrations in samples of phane within the Selebi Phikwe environment were conducted. The tests for ions included the following heavy metals: Cd, Co, Cr, Cu, Fe, Ni, Se and Zn.

1.3.3 Mineralogical identification and characterisation

- The mineralogy of samples of tailings dump from the surroundings of Selebi Phikwe was identified and characterised.
- The mineralogy of soil samples from the surroundings of Selebi Phikwe was identified and characterised.
- The clay fraction of soil samples were mineralogically identified and characterised.
- Samples of PAM were mineralogically analysed and characterised.

1.3.4 Interpretation of results

Values obtained from the field observations and laboratory analyses of samples were compared with international standards and related contextually to similar studies elsewhere. From the interpretation of the data and discussions on the subject, reasonable scientific recommendations on the appraisal of the physical environmental quality were advanced.

1.4 Hypothesis

Mining and smelting of Ni-Cu at Selebi Phikwe is likely to affect the quality of the physical environment through the introduction of different types of contaminants. This study attempted to consolidate the hypothesis by investigating the physico-chemistry, mineralogy and chemistry of the physical environment around the Selebi Phikwe Ni-Cu mine area.

Chapter 2

The Selebi Phikwe study area and study materials

2.1 Regional and site geography

Selebi Phikwe is located in southeastern Botswana (Figure 2.1). The country covers an area of 600 370 km^2 and it shares boundaries with Zambia in the north, Zimbabwe in the north - west, Namibia in the west and South Africa in the south and south – east (CIA, 2000). The country is situated between longitudes 20° 00' E and 29° 00' E, and latitudes 17° 45' S and 27° 00' S. Botswana is part of the African continental plateau, which has a low relief and extends to parts of Angola, Namibia and South Africa (Carney *et al.,* 1994).

In Botswana, the plateau lies at about 1000 m above sea level, and is covered extensively by aeolian sands (Gallon, 1986). Except for the Okavango Delta, the Chobe River in the north, and the Limpopo River in the east, the country is without permanent surface waters (Carney *et al.*, 1994). The rivers are ephemeral. Flow of surface water on riverbeds is observed after sporadic rainfalls from October to April. At the Selebi Phikwe area, streams are feeders that discharge northwards into the Motloutse River (Holmgren, 1991). The Motloutse and Shashe Rivers flow east to the Limpopo River. Linear ridges and smaller outcrops dominate the geomorphology of the study site. The area slopes towards Motloutse and Selibe Rivers, which are ephemeral. Kopjes and inselbergs of granitoid rocks rise above flat pediment dipping to the north in a gentle manner (De Wit and Bekker, 1990). About two-thirds of Botswana is covered with Kalahari Sands (Adliss *et al.*, 1989). Approximately 80 % of the population of the country (1 500 000 people) is living in the eastern part of the country where there is availability of water; which is a very scarce natural commodity (CIA, 2000). Although the country is said to have an annual population growth of 3.5 %, recent nagging health concerns related to AIDS may turn to decrease the figure substantially (CIA, 2000). Extreme distances in the country are from north to south 1 100 km and east to west 1 000 km.

2.2 Regional and site Geology

Botswana is located at the center of the southern section of the African continental plate. The eastern part of Botswana is made up of the Archaean Zimbabwe and Kaapvaal Cratons and the intervening Limpopo Mobile Belt, dating from about 3500 Ma (Carney *et al.,* 1994). The overlying thick sediments in Central Botswana obscure the termination of the cratonic area in the north-west of the country, but aeromagnetic studies reveal a vertical fault known as the Makgadikgadi Line that runs from north-east to south-west with a downthrow of around 2000 m (Reeves, 1978). The Zontfontein Fault, with a downthrow of about 400 m to the north, separates the Zimbabwe and Kaapvaal Cratons. The Kalahari Line, a major north-south dislocation, truncates the craton in the west. The Ghanzi-Chobe Orogenic Belt can be found protruding from the Central West district in a northeastern direction.

The Zimbabwe Craton covers about 60 000 km^2 and consists of the Francistown Granite-Greenstone Complex, the Motloutse Complex and the Mosetse Complex with the latter being the youngest. The Francistown Granite-Greenstone Complex consists of three groups (Table 2.1). The Tati Volcanic Group, which occurs as metamorphosed volcanic and sedimentary sequences in the northwest and southeast of Francistown, is the oldest unit of the complex. The Tati Volcanic Group is succeeded by metavolcanic, ultramafic to felsic rocks, named the Vumba Volcanic Group. The Maitengwe Volcanic Group, which consists mainly of ultramafic rocks, succeeds the Vumba Volcanic Group.

The Limpopo Mobile Belt is subdivided into four complexes: Phikwe, Semolale, Baines Drift and Mahalapye Complexes. Carney *et al.*, (1994) suggested that the evolution of the Limpopo Mobile Belt in Botswana started with the deposition of the Baines Drift Complex supracrustal sequences between 3570 Ma and 3270 Ma. Between 500 Ma and 300 Ma later, both the Phikwe complex supracrustal sequences and the Semolale Complex Greenstone Assemblages were deposited. The Mahalapye Migmatite and the Mokgware Granite of the Mahalapye Complex were also formed around 2700 Ma (Carney *et al.*, 1994).

The geology of the Selebi Phikwe area is characterised by metasediments of the Limpopo Mobile Belt. Banded gneisses, quartzofeldspathic gneisses, amphibolites, basic granulites, quartzites, marbles and calc-silicate rocks, anorthositic gneisses, granitic gneisses, gneissic granites, leucocratic granulites and ultrabasic bodies dominate the geology rock types. The metasedimentary amphibolites serve as the host rock of orebodies that contain the exploited Ni and Cu minerals (Carney *et al.*, 1994; Gallon, 1986).

2.3 Climatic setting

There is lack of detailed data concerning rainfall and temperature in Botswana. Patterns as reported by Bhalotra (1987), show an average annual rainfall of 250 mm in the south and 500 mm in the north. Highest rainfall recorded in the country is 650 mm per year at the Chobe area, which is, located northwest, and the lowest rainfall data is 250 mm per year at the southwestern part of the country. The country, being landlocked, experiences very low rainfall. This is mainly because moist coastal air does not attain the 600 km distance from the nearest coast, and penetrates the high atmospheric pressure that builds up over the country (Bhalotra, 1987).

Temperatures in Botswana reach an annual maximum of 44 °C during the months of October to April. Temperatures during the day attain 35 °C to 40 °C and very seldom falls below 26 °C during the night. Winter temperatures during the coldest months (June to September) are between 26 °C during the day and + or - 6 °C during the night, with an average maximum of 15 °C. It is common to find ground frost in the early mornings during the winter months. The months of August and September have very low humidity and are characterised by frequent dust storms all over the country (Potenhaner, 1994).

The study area of Selebi Phikwe has a semi-arid climate with two dominant seasons. The summer months from October to April are characterised with about 90 % of the annual rainfall, which usually average 450 mm per annum (Potenhaner, 1994). Rainfalls result from convectional instability with short stormy sporadic spells of a few minutes to about 4 days. Year 2000 particularly has had more rains due to the effect of Tropical Eline Cyclone that devastated Mozambique. Seasonal variation of rainfall does occur. The winter months are from May to September (Bhalotra, 1987).

The temperature of Selebi Phikwe ranges from 18 °C to 35 °C with highest values recorded during the months between October and April. Night frosts are common from mid-May to August with temperatures rising to 26 °C by mid day during winter months. Radiation values are high throughout the year. The summer months have higher levels of evapotranspiration (>5.5 mm - <6.5mm) compared to the winter months of <2.5 mm. Prevailing winds are generally easterly and northeasterly except during summer storms when they are southeasterly (Potenhaner, 1994).

2.4 Aspects of vegetation

In Botswana, conspicuous changes in vegetation cover are observed from the hardveld to the sandveld regions. The interspersed areas of the hardveld are covered with woodland and trees, and the thin grass, savanna type vegetation is found on the sandveld areas of the country (Tietema *et al.*, 1991). Climate and vegetation are not major contributors to the development of the soils in the country. This is partly due to the general aridity, which affects the leaching processes. Additionally, oxidation being a prevalent factor in the given climatic conditions in the country, soil organic matter is very low (Tietema, 1993).

The vegetation cover of the Selebi Phikwe area is the savanna type. The area is covered with mopane, *Colophospermum mopane* and a variety of acacia species namely the *Acacia Karoo*, *Acacia galpinti*, and *Acacia tortilis*. Other identified vegetation types are *Combretum sp., Zizphus mucronata, Commipphora kirkia*, and *Burkea sp.*, which are commonly found on the rocky outcrops (Timberlake *et al.*, 1993). They are broad-leaved deciduous trees. Tufted perennial grass cover dominates the herbaceous layer. The grass is commonly found where trees and shrubs are lacking. The biomass is between 2000 kg/hectare and 3000 kg/hectare. Residents allege that over the years, noticeable decrease in vegetation cover at the Selebi Phikwe area has been observed (Department of Town and Regional Planning, 1996). The allegation may be generally attributed to mining activities. This observation has not been scientifically substantiated (Tietema *et al.*, 1992; Timberlake *et al.*, 1993).

2.5 Selebi Phikwe township

Selebi Phikwe is one of the main urbanised townships of Botswana (Figure 2.2), rated after Gaborone, Francistown, Maun, and Lobatse (Grant and Grant, 1995).

The study area is located in the north-eastern part of Botswana between longitudes 27° 47'E and 27° 53'E, and latitudes 22° 55'S and 22° 00'S. Selebi Phikwe which is the principal town of the area, is located 465 Km from Gaborone, 160 Km from Francistown and 60 Km east of Serule on the Gaborone-Francistown Highway (Department of Town and Regional Planning, 1996). The railway line, which runs from Mafeking, South Africa to Harare, Zimbabwe, passes through the township. It is positioned 100 Km from Baines Drift and Zanzibar which are border settlements with South Africa.

The study area of about 250 km^2 has a population of about 50,000 with a 2.4% constant growth rate (National Census, 1991) since 1991. Population projection for 2021 is 78, 000. Rapid population expansion from < 5,000 in 1971 to the present population size characterised by 52.5 % male and 47.5 % female, has led to pressure on existing social and economic infrastructures (Department of Town and Regional Planning, 1996). The male population will probably continue to increase, as it is the dominant sex for mine labour. Twenty six percent of the labour force of < 20, 000 (National Census, 1991) is engaged in mining of Ni-Cu.

Large scale and small scale industries, commercial businesses and agricultural farms are other economic activities in the region (Figure 2.3). The women and children are gainfully engaged in the harvesting and selling of phane worms. Government has provided primary and secondary schools. The area also has a vocational college for the learning of trades. The mine runs a hospital in town (Department of Town and Regional Planning, 1996). Quite unfortunately, common health problems are cardio-respiratory, tuberculosis, colds, influenza, bronchitis, and pneumonia (Gazette, 2000). Aids-related diseases are not as high as in Francistown and Gaborone cities (Mmegi, 2000).

2.6 Nickel-copper (Ni-Cu) mines

Most of the working population of Selebi Phikwe is employed in mining activities (Department of Town and Regional Planning, 1996). The Bamangwato Concessions Limited (BCL), formed in 1956, are the managers of the mines. Its shareholders are the Anglo American Corporation and De Beers Consolidated Mines and Associated Companies (30 % share capital), the Botswana Government (30 % share capital) and members of public (40 % share capital) (Department of Town and Regional Planning, 1996; Gallon, 1986). The BCL is the largest employer of the industrial workforce in Botswana with > 5,000 employees of which 160 are expatriates. It operates four mines: Selebi, Selebi North, Phikwe and Selkirk (Mbendi, 2000). The Phoenix mine is operated by the Tati Nickel Mining Company in which Anglo American Corporation and investors from the United Kingdom are the major partners. The Phoenix mine utilises dry ore separation technique to derive concentrate from 1 700 000 tonnes of mine ore per annum. A sixth mine, the Thakadu/Makal copper-silver (Cu-Ag) mine with reserves of over 8 000 000 tonnes is being developed (Mbendi, 2000).

All the mines are located in the northeast of Botswana. Mining activities carried out between 1973 and 1980 were by opencast method. From 1974, underground mining was introduced as a cost-efficient method. Currently there are four shafts at the Selebi Phikwe mining are, which are operational some as deep as 820 m below the surface (BCL, 1997). The shafts are used for movement of miners, waste and transportation of ore.

Three ore types based on their sulphide contents and effects of tectonic deformation are mined (Gallon, 1986). These are massive sulphides, semi sulphides and disseminated sulphides. The massive sulphides are orebodies in which the host rock has been totally replaced by sulphides and consist of pentlandite and pyrrhotite S-bearing minerals. Boulders of amphibolites constitute the remnants of the host rock. The semi-massive sulphides contain between 40 wt % and 70 wt % sulphide in a matrix of host amphibolites, and garnets are commonly found at the sulphide/amphibolite contacts. The disseminated sulphides are orebodies having 0 wt % to 40 wt % low-grade sulphide ore with poorly developed mineral zoning (Gallon, 1986).

2.6.1 Minerals association of Ni-Cu orebodies at Selebi Phikwe

The host rock constitutes phlogopite mica-rich amphibolite. Other minerals constituting the Ni-Cu orebodies include chalcopyrite, bunsenite, chalcocite, penroseite and magnetite (Table 2.2). The minerals associations are classified as sulphides, oxides and selenides. Co and Cr are major impurities in most of the minerals (Gallon, 1986).

Chalcopyrite and chalcocite are the main sources of Cu at Selebi Phikwe. Chalcopyrite is not ferromagnetic and is usually confused for gold (Au). It is the most widely occurring Cu-bearing mineral (Deer *et al.*, 1983) and it has a very significant economic importance as an ore mineral. It is formed with other sulphide minerals of primary magmatic origin and in metalliferous veins of igneous rocks. Chalcocite is very heavy with conchoidal fractures and almost malleable in its natural state (Coggans *et al.*, 1999). At Selebi Phikwe, they are both considered to have formed by metasomatic and contact metamorphic replacement due to magmatic sulphide solutions (Gallon, 1986). Chalcopyrite and chalcocite are easily altered to malachite, $Cu_2CO_3(OH)_2$ and azurite, $Cu_2(CO_3)_2(OH)_2$. Chalcocite can also be altered to cuprite, Cu_2O (Deer *et al.*, 1983). The changes occur in acidic environments with the release of associated ions of heavy metals (Coggans *et al.*, 1999).

Pentlandite, is the main source of Ni at Selebi Phikwe with bunsenite and penroseite being less dominant (Nkoma and Ekosse, 1999). The minerals are usually associated with Co, Cr, Mn and Cu as impurities. Pentlandite is an opaque iron nickel sulphide mineral, usually associated with pyrrhotite as exsolution intergrowths. There are two pseudomorphs of penroseite: the nickel copper selenide, $(Ni,Cu)Se_2$ and the cobalt copper nickel selenide sulphide,

$(Ni,Co,Cu)(Se,S)_2$. The Co-containing pseudomorph is likely to be the form present, and the only Se-carrying mineral at Selebi Phikwe (Nkoma and Ekosse, 1999). Its ionisation leads to the contribution of S, Se, Ni, Co, Cu and Mn into the environment (Coggans *et al.*, 1999).

Pyrrhotite and magnetite are Fe-bearing minerals, which are not exploited economically at Selebi Phikwe (Nkoma and Ekosse, 1999). Pyrrhotite is yellow-bronze, massive, granular aggregates easily distinguished from pyrite by its ferromagnetic nature. It is associated with pentlandite and Co-bearing minerals. It is found in high-grade metamorphic rocks. Magnetite in metamorphic terrain is formed by the reduction of hematite derived from the dissociation of sulphides. Magnetite is a hard, heavy mineral, which dissolves, slowly in an acidic environment (Coggans *et al.*, 1999; Deer *et al.*, 1983). Both minerals are present in very significant proportions in the Selebi Phikwe area and likely influence the environmental contamination chemistry.

2.7 Selebi Phikwe Concentrator and smelter plant

Extracted ore from the five producing mines are processed at the only Ni-Cu concentrator/smelter plant in the country located at the Selebi Phikwe area (Figure 2.4). The ore is processed in three stages: crushing and grinding, flotation and concentration, and smelting. There are primary, secondary and tertiary crushers, which reduce particle size of ore to < 12mm. The crushed particles are ground in a ball mill to desirable size and then conveyed to flotation tanks. At the flotation tanks, Ni, Cu and Co are concentrated. With the addition of calcium hydroxide, potassium amylxamthate, and tri-ethoxy-butane extracted minerals float to the surface whereas the heavier wasted material settles at the bottom and through pipes is deposited as tailings dump. After concentration, the metals are separated using high voltage magnetic separators. The concentrated base metals are dried in separate spray dryers. The concentrate is smelted in a furnace at 1350 °C whereby waste fumes of S and Fe are released, and the matte packaged upon cooling for export (Modisanyane, 1998).

In 1994, profits from Ni-Cu amounted to 5.7% (US $ 99 000 000) of principal export earnings, and in 1996 the Ni-Cu products contributed US$124 000 000 to export earnings. The average grade of mined ore is 0.75 wt % Cu and 0.69 wt % Ni. More than 95 wt % constitutes the tailings dump. An average of 40 000 tonnes per year of metal-in-matte (Cu, Ni and Co) is produced and exported to both Zimbabwe and Europe for refining (Modisanyane, 1998).

2.8 Notes on study materials

The tailings dump, soils, PAM, mopane plant and phane caterpillar (worm) found around the Ni-Cu mining area and concentrator/smelter plant are discussed briefly in corresponding sections below.

2.8.1 Tailings dump

Tailings dump from Ni-Cu mining and processing is known to promote acid mine drainage (AMD) (Bowles *et al.*, 1994). Groundwater is contaminated and the fauna and flora of the environment are affected (Bowles *et al.*, 1995). AMD may be defined as drainage occurring as a result of sulphide oxidation in rock exposed to air and water (Benner *et al.*, 1997). The rocks become acidic in a low pH environment, leading to precipitation of ions including those of heavy metals. Pyrrhotite (Fe_7S_8-FeS) and pyrite (FeS_2) in tailings dump are oxidised on exposure to water to form sulphate and sulphuric acid as indicated in equations 1.1 and 1.2 below (Al *et al.*, 1994 and 1994a; Benner *et al.*, 1997; Bowles *et al.*, 1995):

$$2FeS_2 + 16H2O \rightarrow 2FeSO_4 + 2H_2SO_4 + 14H^+ \qquad \text{(equation 1.1)}$$

$$4FeSO_4 + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 4H_2SO_4 \qquad \text{(equation 1.2)}$$

The acidification reactions could be accelerated by the bacterium *Thiobacillus ferroxidans*, the absence of neutralising minerals such as calcite ($CaCO_3$), and the release of heavy metals into their ionic state (Bowles *et al.*, 1998). Piles of tailings dump such as shown in Figure 2.5 from around the mines at Selebi Phikwe and the concentrator/smelter plant stay for years probably without proper disposal. During stockpiling, ions of heavy metals leached into the soils and water bodies, and could eventually be absorbed by plants.

Finer particles from the tailings dump could be windblown to distant environments, and eventually affect the ecosystem. Tailings dump from Ni-Cu mines and smelter/concentrator plants leach out ions of heavy metals that could contaminate soils and cause the development of dead zones; depleted of vegetation growth where plants died due to heavy metal poisoning.

2.8.2 Soils

The soils at Selebi Phikwe are classified as Eutric Regosols and Haplic Luvisols as illustrated and described by the Soil Mapping and Advisory Service Project (1990). The Eutric Regosols are deep to very deep, very dark greyish brown to brown fine sandy loam soil. The Haplic Luvisols are shallow to moderate well-drained, reddish brown to strong brown sandy clay to clay, undulating to rolling on basalt. Figure 2.6 illustrates Haplic Luvisol soil around the Selebi Phikwe mine area. Both soils are shallow with an average depth of 1 m.

The primary minerals (quartz, mica and feldspars) and secondary minerals (kaolin, illite and smectites) are the main mineral components in the types of soils found at Selebi Phikwe (Tan, 1998). Kaolin and smectites are extensively discussed below because they provide sites for a wide range of physico-chemical and chemical reactions especially with ions of heavy metals.

2.8.2.1 Quartz

The rocks at Selebi Phikwe are metamorphic rocks and it is likely that the different forms of silica minerals $n(SiO_2)$ may be found in the soil composition. The silica minerals: quartz, tridymite and cristobalite are three different silica minerals, $n(SiO_2)$, which exists in either the α- or β- form (Tan, 1998) depending on environmental temperature. Whereas the α- form of the minerals is prevalent in low temperature environments, the β- *form* exists in high temperature conditions as illustrated below, according to Tan (1998).

α- Quartz (trigonal) α- tridymite (hexagonal) α- cristobalite (tetragonal)

↑↓ 573 °C   ↑↓ 117 °C   ↑↓ 220-280 °C

β- Quartz (hexagonal) $\rightleftharpoons$ β- tridymite (hexagonal) $\rightleftharpoons$ β-cristobalite (cubic)

870 °C   1470 °C

Quartz inversion occurs quickly at 573 °C when α-quartz is inverted to β- quartz with a lattice expansion of 1 vol %. Cristobalite inversion occurs at 1220-1280 °C with a 2.5 vol % change (Tan 1998).

2.8.2.2 Micas and feldspars

Micas commonly found in soils of the Selebi Phikwe type include illite $K_{1-1.5}Al_4[Si_{7-6.5}Al_{1-1.5}O_{20}](OH)_4$; muscovite $K_2Al_4[Si_6Al_2O_{20}](OH,F)_4$ and probably biotite, $K_2(Mg, Fe^{+2})_{6-4}(Fe^{+3},Al,Ti)_{0-2}[Si_{6-5}Al_{2-3}O_{20}](OH,F)_4)$ (Gallon, 1986). Illite is a micaceous clay mineral with similar chemical and mineralogical composition as muscovite, but slightly smaller in particle size. These minerals occur in low to medium grade metamorphic and igneous rocks. Their layer charges result from isomorphous substitution taking place in the octahedral sheet of the unit cell. Biotite flakes may be found in low to high-grade metamorphic and igneous rocks (Dixon, 1989).

Ions of micas occupy two-thirds of the octahedral sheet of a unit cell, thereby creating sites for absorption of ions of heavy metals into their lattice structures. The CEC of micas are slightly higher than CEC of kaolin but lower than the values for smectites. Al^{3+} and Si^{4+} substitution reactions with micas are less compared to smectites (Murray and Keller, 1993). Soils rich in micas experience permanent and pH dependent charges, which result from isomorphous substitution at the time of argilisation and transformation from 2.1 to 1.1 clay minerals (Bailey, 1980).

The alkali feldspars, $(K,Na)[AlSi_3O_8]$ and plagioclase, $Na[AlSi_3O_8]$-$Ca[Al_2Si_2O_8]$ are likely present in soils of the Selebi Phikwe type (Dixon, 1989). Their significance is in their ability to transform into smectites and kaolins under favourable conditions. During the alteration processes, ions of heavy metals from the milieu of argilisation are entrapped into the lattice structure of the derived mineral (Dixon, 1989; Bailey, 1980).

2.8.2.3 Kaolins

Kaolin minerals (kaolinite, nacrite and dickite) are formed from the parent minerals feldspars and micas as illustrated in equation 1.3 below (Weaver, 1989):

$2KAlSi_3O_8 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2K(OH)$ (equation 1.3)

K-feldspar kaolinite

The alteration may be due to surface weathering, groundwater activity, or the action of hydrothermal fluids. Dickite and nacrite are normally restricted to hydrothermal occurrences. Halloysite is found in soils of hydrothermal and residual origin, but it is rare in soils of sedimentary origin (Murray and Keller, 1993).

The physico-chemical properties of kaolin are given in Table 2.3. Kaolins are usually fine (< 2 μm) in particle size and are white or cream in colour. The mineral contents and geology affect the quality of kaolin. Accessory minerals in most kaolins include quartz, muscovite, $K_2Al_4[Si_6Al_2O_{20}](OH,F)_4$; rutile, TiO_2; anatase, TiO_2; tourmaline, $Na(Mg,Fe,Mn,Li,Al)_3Al_6[Si_6O_{18}](BO_3)_3(OH,F)_4$; biotite, smectite, illite, $K_{1\text{-}1.5}Al_4[Si_{7\text{-}6.5}Al_{1\text{-}1.5}O_{20}](OH)_4$; goethite, α-FeO.OH; magnetite, $Fe.Fe_2O_4$ and ilmenite, $FeTiO_3$ (Bailey, 1980; Murray and Keller, 1993; Weaver, 1989)

The basic unit of a kaolin mineral is made of a tetrahedral sheet of silica (SiO_2) and an octahedral sheet of gibbsite ($Al(OH)_3$), both bonded by shared O atoms. It is classified as 1:1 dioctahedral kaolin because only two-thirds of the vacant sites in the octahedral sheet are filled. Kaolinite units are held by hydrogen bonds. Layer stacking of kaolinite is controlled by repulsion between highly charged Si and Al cations, which tend to avoid superposition (Dixon, 1989). Another controlling factor of layer stacking is the rotation of basal O atoms toward OH group in the adjacent layer so as to increase interlayer bonds (Bailey, 1980). Seventy five percent of the OH's within crystals occur in its inner-surface position of the crystal system. With a well-crystallized kaolinite, the (001) basal spacing is 7.14 Å listed in Table 2.4, and the second order spacing is at 3.57 Å. Both peaks disappear upon heating at 500 °C - 550 °C. At higher temperatures, it is transformed to metakaolinite and later to mullite, $Al_2O_3.2SiO_2$ and/or gamma alumina, γ-Al_2O_3.

Kaolinite particles are platy pseudo-hexagonal and form laths or vermicular books with irregular edges (Dixon, 1989). Its hexagonal shape persists even at higher temperatures close to 1000 °C (McConnel and Fleet, 1970). It has a triclinic crystal system but could also be monoclinic.

The chemical formula of the major kaolin mineral kaolinite is $Al_2Si_2O_5(OH)_4$ and its theoretical chemical composition is 39.8 % wt Al_2O_3, 46.3 % wt SiO_2, and

13.9 % wt H_2O. SiO_2/Al_2O_3 ratio for kaolinite is 1.2. Two-thirds of the atoms are shared by Si and Al, and then they become O instead of OH. Only two-thirds of possible substitution positions for Al in the octahedral sheet are filled. Al atoms are considered to be so placed that two of the Al are separated by an OH above and below, thus making a hexagonal distribution in a single plane in the centre of the octahedral sheet The OH groups are placed so that each OH is directly below the perforation of the hexagonal net of oxygens in the tetrahedral sheet (Bailey, 1980; Murray and Keller, 1993).

The lattice chemistry of kaolinite consists of tetrahedral and octahedral sheets in the *a* and *b* directions which are stacked one above another in the *c* direction. Charges within the structural formula units are balanced, and there is very little substitution within the lattice structure. It has regular stacking and close spacing of layers causing relatively strong H bonds between successive layers (Tan, 1998).

2.8.2.4 Smectites

Smectites are clay minerals with a high aluminium (Al) content (Weaver, 1989), and are rich in either calcium (Ca), or sodium (Na) regardless of their mode of origin (Christidis, 1998; Patterson and Murray, 1983) and occurrence (Grim, 1968). The Ca-smectite is calcium magnesium aluminium silicate hydroxide hydrate with the structural formula of $Ca_{0.2}$ $(Al,Mg)Si_4O_{10}(OH)_2.xH_2O$, and the Na-smectite is sodium aluminium silicate hydroxide hydrate with the structural formula of $Na_{0.3}$ $(Al,Mg)Si_4O_{10}(OH)_2.xH_2O$. They are formed from the alteration of volcanic ash, feldspars, micas, and various FeMg silicates (Weaver, 1989).

The physico-chemical properties of smectites are listed in Table 2.5 (Christidis, 1998) and include crystal shape and size, cation exchange capacity (CEC). Smectites are 2:1, structural type clay minerals of the dioctahedral layered subgroup (Bailey, 1980; Thorez, 1976), and their mineral associations include mica (mainly from muscovite, $K_2Al_4[Si_6Al_2O_{20}](OH,F)_4$ and biotite, $K_2(Mg,Fe^{+2})_{6\text{-}4}(Fe^{+3},Al,Ti)_{0\text{-}2}[Si_{6\text{-}5}Al_{2\text{-}3}O_{20}](OH,F)_4)$; calcite, $CaCO_3$; quartz, SiO_2; alkali feldspars, $(K,Na)[AlSi_3O_8]$ and plagioclase, $Na[AlSi_3O_8]\text{-}Ca[Al_2Si_2O_8]$; zeolites, $(Na_2,K_2,Ca,Ba)[Al,Si)O_2]_n.xH_2O$; gypsum, $CaSO_4.2H_2O$; cristobalite, $\alpha\text{-}SiO_2$; and volcanic ash. Whereas the Sodium Magnesium Aluminium Silicate Hydroxide Hydrate, $Na_{0.3}$ $(Al,Mg)Si_4O_{10}(OH)_2.xH_2O$, crystal exhibits a monoclinic crystal lattice system, the Calcium Magnesium Aluminium Silicate Hydroxide Hydrate, $Ca_{0.2}$ $(Al,Mg)Si_4O_{10}(OH)_2.xH_2O$, has an orthorhombic crystal system (see Table 2.6) (ICDD, 1986; Wilson, 1987).

Diagnostic peaks by XRPD of smectites are given in Table 2.6. The basal spacing of Na-smectite is 16.9 Å- 17.1 Åwhen treated with ethylene glycol and 17.8 Å when treatment is with glycerol (Wilson, 1987). Smectite loses its interlayer water at 150 °C and it contracts to 10 Å (Weaver, 1989). Na^+ adsorbs one layer of water and have a (001) spacing of about 12.5 Å Ca^{2+} contains two water layers and the (001) spacing is between 14 Åand 15.5 Å Dehydroxylation of smectite occurs between 600 °C and 700 °C (Brindley and Lemaitre, 1987). From X-ray powder diffraction, Mössbauer and infra-red (IR) spectroscopic studies of smectites, Heller-Kallai and Rozenson (1980), observed three stages of dehydroxylation: proton delocalisation, localized dehydroxylation, and loss of OH groups due to changes in cell dimension. Mineral rehydration may occur at temperatures less than 400°C.

The chemical formula of Na-smectite is $Na_{0.3}$ $(Al,Mg)Si_4O_{10}(OH)_2.xH_2O$, and theoretically, without any lattice substitution, it consists of 66.7 wt % SiO_2; 28.3 wt % of Al_2O_3 and 5 wt % of H_2O. Its lattice chemistry is composed of two silica tetrahedral sheets with a central alumina octahedral sheet All the tetrahedron tips are unidirectional. A common layer is formed by the tips of the tetrahedrons of each silica sheet and one of the hydroxyl layers of the octahedral sheet The atoms common to both octahedral and tetrahedral sheets become O atoms instead of OH groups forming layers that are continuous in the *a* and *b* directions and are stacked one above another in the *c* direction giving an orthorhombic geometry. Lattice expansion proceeds in the *c* direction. Only two-thirds of the possible positions in the octahedral sheet are filled; thus characterised as 2:1 dioctahedral smectite (Bailey, 1980). The chemical composition and structural characteristics of smectite affect its topactic reactions and influence the resulting high temperature mineral phases (Brindley and Lemaitre, 1987) such as β-quartz; cordierite, $Al_3(Mg,Fe)_2(Si_5Al)O_{18}$; cristobalite and mullite, $3Al_2O_3.2SiO_2$.

2.8.3 Particulate air matter

Particulate air matter (PAM) may consist of one or more of the following: dust, soot, smoke, and liquid droplets emitted directly into the atmosphere from sources such as factories, power plants, mines, transportation media, construction activity, fires, and windblown dust (USA-EPA, 1995). These particulate matter are known as primary PAM pollutants (PPAMP). Secondary PAM pollutants (SPAMP) result from the condensation or transformation of PPAMP into secondary gases and minerals. PAM refers to the solid or aerosol state at ambient conditions and the particulate should have an euhedral spherical diameter (esd) of $\leq 100\ \mu$m (USA-EPA, 1995).

According to USA-EPA (1995), PAM is classified based on its physical composition and particulate diameter into four main groups: deposited particulate air matter (DPAM), suspended particulate air matter (SPAM), visibility-reducing particulate air matter (VRPAM), and smoke.

- Deposited particulate air matter (DPAM) consists of particles having an esd of $\geq 20\ \mu$m $\leq 100\ \mu$m. They result from naturally occurring dust, and the larger particles from combustion processes.

- Suspended particulate air matter (SPAM) is comprised of particles with an esd within the range of $\geq 2.5\ \mu$m $\leq 20\ \mu$m. The particulates originate from combustion, naturally occurring dust, salt sprays, mining activities and a wide range of industrial processes.

- Visibility-reducing particulate air matter (VRPAM) is finer particulate having an esd of ≤ 2.5 μm. These particles have the tendency to scatter and absorb light causing visibility impairment. The finer particles react chemically and physically to produce larger particles that may be equally hazardous to the environment.

- Smoke is comprised of products of incomplete combustion, carbon, and volatile organic compounds (VOC). It may pose as a health hazard if it contains deposited or suspended particulate.

PAM may damage metal surfaces, fabrics, buildings, bridges and roads. PAM may damage crops, trees and shrubs. It may congest the leaves and make it difficult for photosynthesis to take place. The plants become distorted and eventually die through suffocation. Visual reduction is enhanced by finer particles causing haze, which may be dangerous to motorists, and diminish crop yield. Previous air pollution studies conducted (USA-EPA, 1995) show that PAM with an esd of ≤ 10 μm could be inhaled into the human respiratory system and could be deposited on the lungs. Acute exposure may lead to loss of lung function, aggravation of existing respiratory and cardiovascular diseases, loss of capacity to resist infection, carcinogenesis, and premature death. Population groups mostly affected are asthmatics, individuals with chronic obstructive pulmonary cardiovascular disease, individuals with influenza, children and the elderly. The Environment Protection Agency (US-EPA) has set a mean annual standard (MAS) of 50 $\mu g/m^3$ of PAM provided sampling is calculated on 24 hrs/day and only one day value in the whole year exceeds 150 $\mu g/m^3$. Figure 2.7 depicts PAM, fumes and gases being emitted from the smelter/concentrator plant at Selebi Phikwe.

2.8.4 Mopane Plant

The mopane Plant is a tree known as *Colophospermum mopane*. It is considered to be associated with hot dry valleys, and its distribution is correlated with the Karoo Sandstone, dating from Triassic Period, and it is found in a number of down-faulted troughs in Basement Complexes within Southern Africa. Its vegetation cover dominates the northern Botswana, Zimbabwe, and the Northern Province and lowveld of South Africa. Mopane vegetation grows on most soil types (Tietema *et al.*, 1991). Its glossy, rich-green leaves look like green butterflies as depicted in Figure 2.8. During the summer months, the leaves attract hundreds of brightly coloured caterpillars (2.8.5 below) that feed on them. Browsers such as elephants, giraffes and kudus also eat the leaves.

The mopane plant is also found in alkaline soils with high Na concentrations. The clay minerals swell on absorbing water, rapidly becoming impervious creating unfavourable conditions for the growth of other types of vegetation. The mopane plant has adapted itself to absorb water very rapidly for the short period that it is available (Tietema, 1993; Tietema *et al.*, 1991). The adaptation technique includes the superficial spreading of its root system, and suppression of perennial grass; a process, which promotes soil erosion and gulleying. Mopane can also grow in deep, well-drained soils, and most of the trees thrive on such soils. The wood of *Colophospermum mopane* shown in Figure 2.9 is very hard and durable. In the past, it was used for props in mineshafts and for bridges in the Okavango Delta Area in Botswana. It is useful as wood fuel for cooking and heating of homes during winter months.

2.8.5 Phane Caterpillar

The phane caterpillar as shown in Figure 2.10, also known in Botswana as phane worm, mopane worm and phane, derives its common name from its host plant, the *Colophospermum mopane.* The caterpillar is the larva stage of *Imbrasia belina,* which is commonly known as the Emperor Moth (Ditlhogo, 1996; Oberpreiler, 1995). The moth flies in the mopane veld from late December to early February, and could extend to March. Individual female moths lay single layered clusters of eggs on branches and leaf stalks of *Colophospermum mopane*. The quantity, which is laid per female at a laying period, accumulates from 30 to 355 eggs/egg mass (Ditlhogo, 1996). The eggs are hatched to larvae (the caterpillar stage of the moth's life cycle). Prior to the larvae pupating, they moult four times. At the fifth instar, the caterpillar burrows underground near the base of mopane trees and pupate.

Caterpillars usually grow for about forty days before pupating. During these days, the gregarious larvae feed on *Colophospermum mopane*, and sometimes defoliate entire trees. Their growth is strongly influenced by rainfall and leaf-water (Taylor and Moss, 1982; Scriber, 1977). Eclosion is from underground pupae. Both sexes of the moth fly at night with males coming into lights around midnight, which is the scenting time of the females. The ova are deposited in clusters and the larvae remain gregarious throughout their feeding cycle. The larvae are leathery yellow, have blackheads and extensive speckling.

Several local inhabitants in Botswana, Zimbabwe, Mozambique, South Africa and Namibia consider the larvae as a valuable protein source (De Foliart, 1989; Sekhwela, 1989), and also contain significant amounts of phosphorus (P), iron (Fe), and calcium (Ca) (Caterpillars and Campfires, 2000). Mopane caterpillars are easily harvested, dried, and have a long shelf life; an important factor to be considered in rural environments where refrigeration and modern day storage facilities might be lacking. Mopane worms can be exchanged for other food items such as sugar, tea, oil, maize meal and sorghum. Primate, birds and insects as well as human beings feed on the worms, whereas the buried mopane pupae are dug out from the ground and eaten by jackals, foxes, warthogs and ant bears (Caterpillars and Campfires, 2000).

Botswana is the largest producer of phane worm for open market (Allotey *et al.*, 1996). Until recently, before the exploitation of worms has been commercialised, it was done at subsistence level (Ditlhogo, 1996). In Botswana, it is harvested mostly in the north-eastern part of the country, and Selebi Phikwe is considered to be a high-density area of occurrence. Local women engage in the harvesting, processing, marketing and storage of phane. The worms are harvested in two periods: from late December/January for about three weeks, and small crops in March/April/May depending on the availability of rain (Allotey *et al.*, 1996).

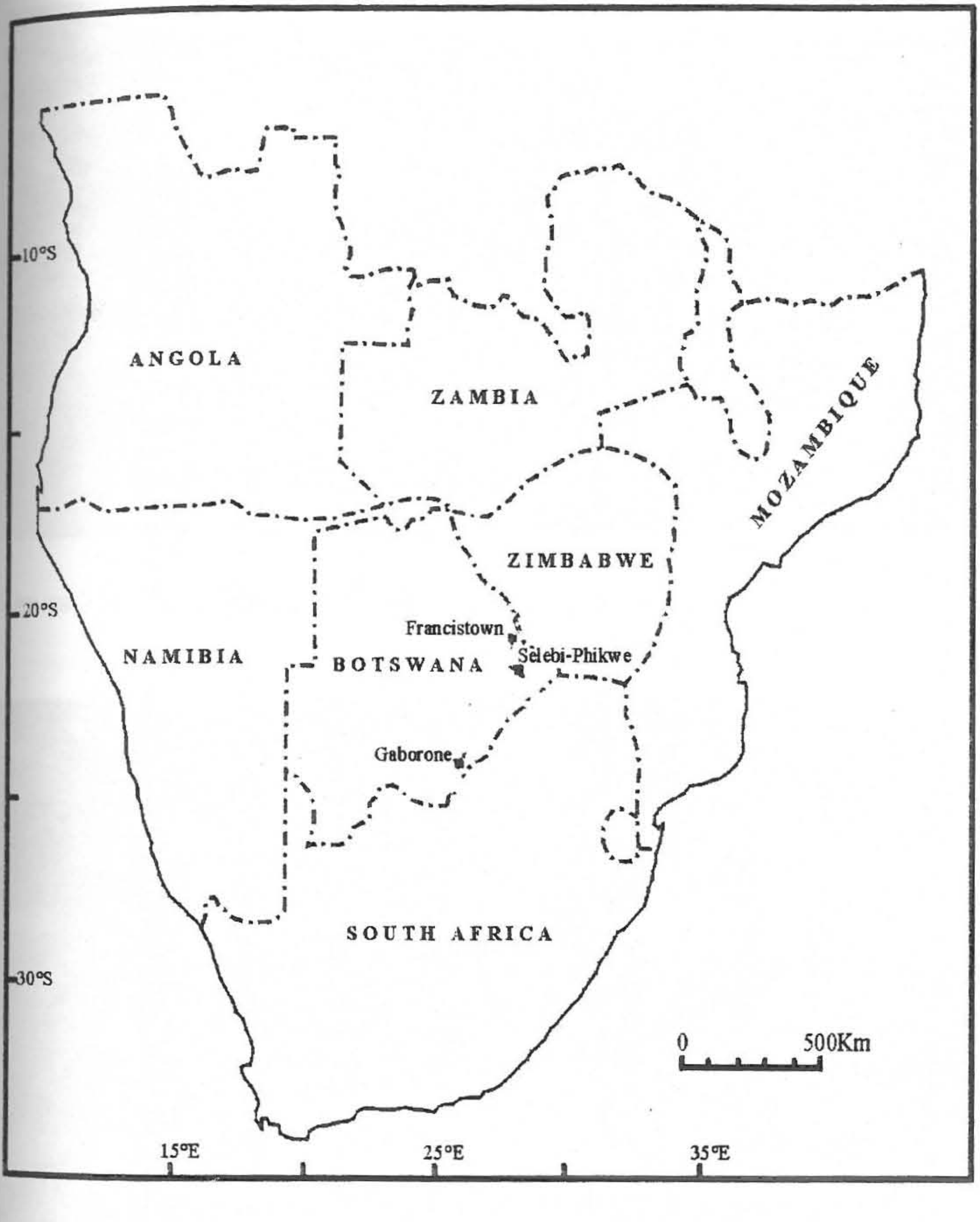

Figure 2.1: Location map of Selebi Phikwe in Botswana and southern Africa.

Figure 2.2: The urbanised business centre of Selebi Phikwe.

Figure 2.3: The shopping area of Selebi Phikwe with modern chain stores such as PEP, Woolworths and Dunns.

Figure 2.4: The Selebi Phikwe Concentrator and smelter plant.

Figure 2.5: Tailings dump pile at the smelter/concentrator plant, Selebi Phikwe.

Figure 2.6: Exposed Haplic Luvisol soil type around the smelter/concentrator plant, Selebi Phikwe.

Figure 2.7: Emission of PAM, fumes and gases from the smelter/concentrator plant into the atmosphere at Selebi Phikwe.

Figure 2.8: Glossy, rich-green, butterfly-like leaves of *Colophospermum mopane.*

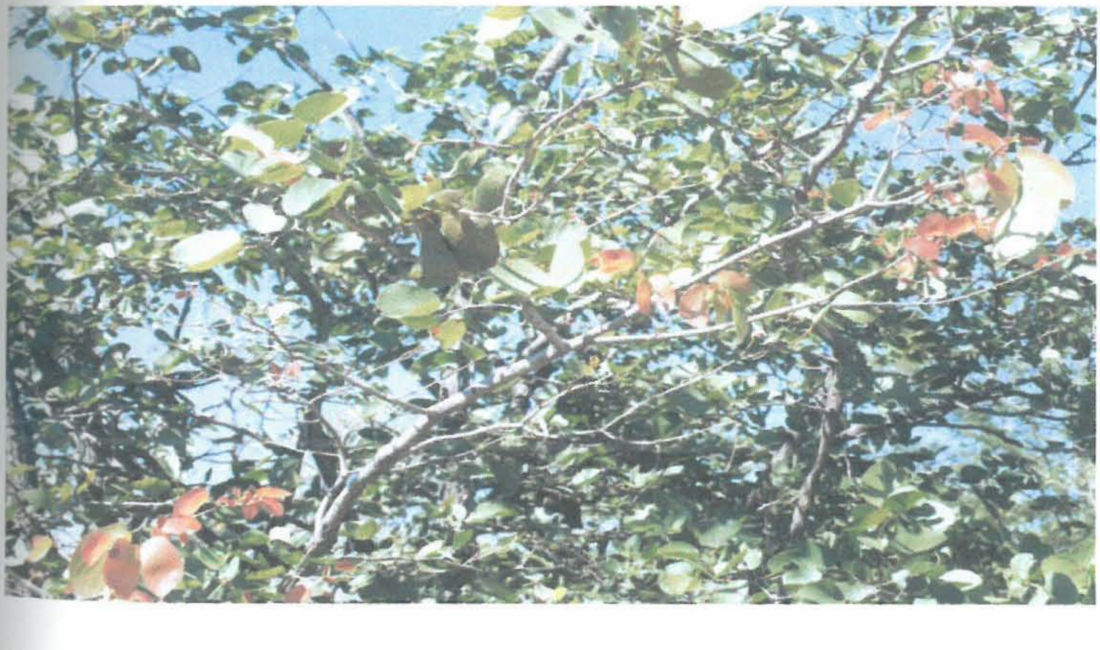

Figure 2.9: Hard stem of *Colophospermum mopane* commonly used as props for mineshafts and wood fuel.

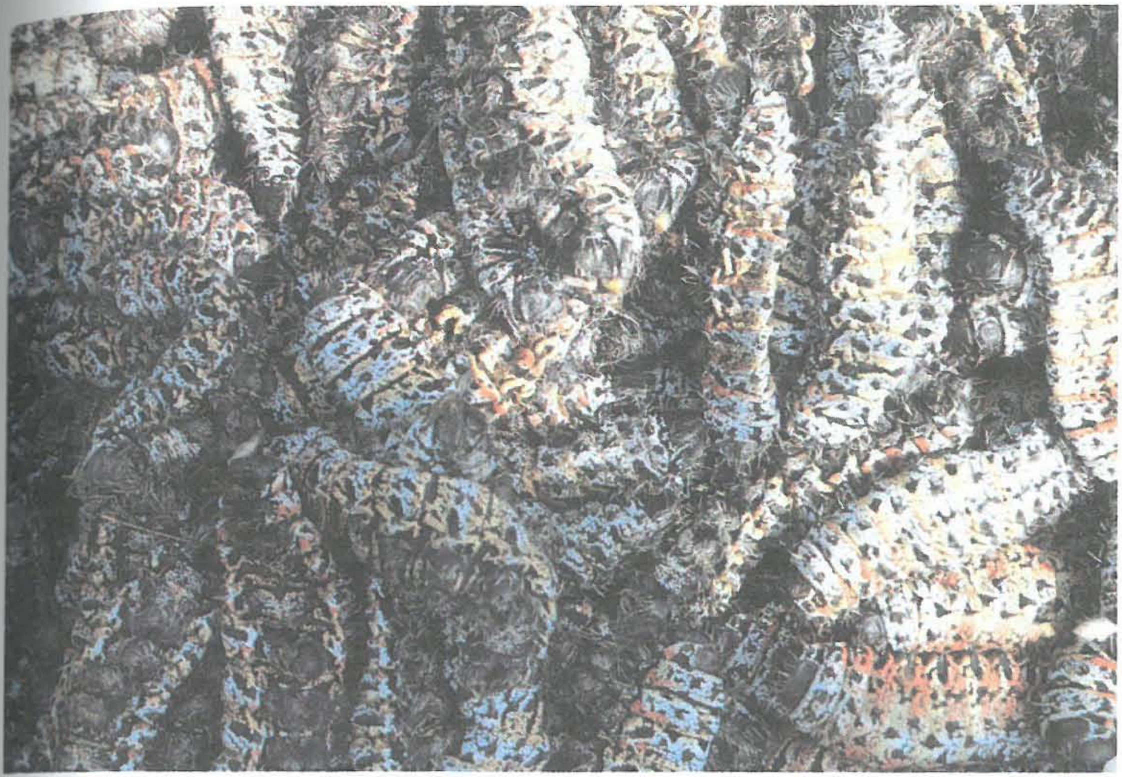

Figure 2.10: A collection of the mopane caterpillar, *Imbrasia belina* from Selebi Phikwe area.

Table 2.1: The stratigraphy of the Zimbabwe and Kaapvaal Cratons in Botswana (Carney *et al.*, 1994).

Age in Ma		**Complex**	**Group**	**Formation**
2500	ZIMBABWE CRATON	Motsetse	Matsitama Metasedimentary	Palamela Tsarutsaru Transitional
		Motloutse	Shashe Metasedimentary	
		Francistown Granite-Greenstone	Maitengwe Volcanic	Maitengwe Ultramafic Maitengwe Banded Ironstone
2600			Vumba Volcanic	Upper Vumba Mafic Upper Vumba Felsic Lower Vumba Mafic Lower Vumba Felsic Vumba Mixed Volcanic Sebina Ultramafic
2700			Tati Volcanic	Last Hope Selkiirk Penhalonga Lady Mary Old Tati Ultramafic Kgarimacheng
2783	KAAP-VAAL	Gaborone Granite Complex/Kanye Volcanic Formation/Lobatse Volcanic Formation		
		Modipe Gabbro		
3500	CRAT-ON		Kraaipan Group	

Table 2.2: Minerals found in the Ni-Cu orebodies at Selebi Phikwe (Nkoma and Ekosse, 1999).

Name of mineral	**Chemical formula**	**Elements contained in mineral**	**Remarks**
Chalcopyrite	$CuFeS_2$	Cu, Fe, S	Sulphide mineral
Pentlandite	$(Fe,Ni)_9S_8$	Fe, Ni, S	Sulphide mineral
Pyrrhotite	$Fe_{1-x}S$	Fe, S	Sulphide mineral
Bunsenite	NiO	Ni, O	Oxide mineral
Chalcocite	CuS	Cu, S	Sulphide mineral
Penroseite	$(Ni,Cu)Se_2$	Ni, Cu, Se	Selenide mineral
Magnetite	Fe_3O_4	Fe, O	Oxide mineral

Table 2.3: Physico-chemical properties of kaolin minerals (Murray and Keller, 1993).

Physico-chemical property	**Kaolin minerals**
pH value	6.8-7.3
Particle shape	Pseudo hexagonal crystalline plat or book
Particle size	60 wt % - 90 wt % >2 μm
Natural color	White or near white
Specific gravity	2.67
Melting point (^oC)	1850
Surface area (m^2/g)	10-18
CEC (meq/100g)	3-15

Table 2.4: Mineralogical data of diagnostic peaks used in identifying kaolinite by X-ray powder diffraction (XRPD) technique (ICDD, 1986).

ICDD Reference	**Radiation and filter**	**Crystal system**	**d-values (Å)**	**Intensity (%)**	***hkl* values**
29-1488	Cuk_{α}	Monoclinic	7.14	100	(001)
			4.41	60b	(110)
			3.57	100	(002)
14-164	Cuk_{α}	Triclinic	7.17	100	(001)
			4.47	35	(020)
			4.36	60	(110)
			3.84	40	(021)
			3.57	80	(002)

Table 2.5: Physico-chemical properties of smectites (Murray, 1986).

Physico-chemical property	**Smectite**
pH value	9.0-10.5
Particle shape	Very thin flakes, non-crystalline appearance
Particle size	90 wt % >1 μm
Natural colour	White, bluish-green, yellowish brown to black
Specific gravity	2.70
Melting point (^{o}C)	1250-1300
Surface area (m^2/g)	700-850
CEC (meq/100g)	50-150

Table 2.6: Mineralogical data of diagnostic peaks used in identifying smectite by X-ray powder diffraction (XRPD) technique (ICDD, 1986).

ICDD Reference	Radiation and filter	Crystal system	d-values (Å)	Intensity (%)	*hkl* values
29-1499	Cuk_{α}, Ni	Monoclinic	21.5	100	(001)
			4.45	55	(110) (020)
			3.15	40	
21-219	Fe k_{α},	Monoclinic	17.6	100	(001)
			9.0	50	(010)
			4.49	80	(102)
			3.38	40	(005)
			1.50	60	(330)
29-1498	Cuk_{α}, Ni	Monoclinic	13.6	100	
			4.46	65	(020)
			3.13	80	(122)
13-135		Orthorhombic	15.0	100	(001)
			5.01	60	(003)
			4.50	80	(020)
			3.02	60	(005)
13-259	Cuk_{α}, Ni		13.6	100	
			4.47	18	
			3.34	10	
			3.23	10	

Chapter 3

Methods and techniques

3.1 Fieldwork

The fieldwork focussed on observations and collecting of samples. Three investigatory field visits were carried out during the months of September and October in an attempt to understand the research problems and defining the study. A fourth field visit with the Project Supervisor was carried out on the weekend of 12 November 1999. After a number of field visits, on the weekend of the 12 May 2000, there was a comprehensive field visit by the Project Supervisor and Co-Supervisor, which focused on problems being encountered and giving academic guidance/direction.

3.1.1 General field observations

A hand lens was used at the field to have a closer look of hand specimens of tailings dump and soils. The shape and size of the tailings dump mount were visually observed as well as the colour of the mineral crystals. Exposed soils at the study area were observed in terms of soil colour and texture. The atmosphere was visually inspected for PAM, in order to note any significant quantity, as well as attempts for possible detection of gas smell emanating from the smelter/concentrator plant. The shape and length of the leaves as well as colour were observed. Where possible, the worms were observed as they fed on mopane leaves. Other observations included leaves sites where leaves were eaten, and how was the eating of the leaves by the phane done.

All the observations were carried out at the sampling sites on the same days and time that samples were obtained for laboratory analyses.

3.1.2 Sampling

There were 10 sampling areas, which included a chosen control site located close to the road juncture leading to Selebi Phikwe from the Gaborone-Francistown main road. This juncture is about 56 km from Selebi Phikwe. The soil lithology and vegetation cover of the control sampling site were very similar to those of Selebi Phikwe area. The only tailings dump at the Ni-Cu concentrator/smelter plant was also sampled at 3 points : the centre and at two sides.

Sampling was done twice monthly from January 2000 to July 2000 (Table 3.1). Nine sampling sites radiometrically distributed within the mine and smelter plant environments, and a control sampling site were identified. Samples of soil, PAM, mopane leaves and phane caterpillar were obtained as close to one another as possible from the sampling sites (Figure 3.1 and Table 3.2). Tailings dump samples were obtained from the tailings dump mount close to the concentrator/smelter plant.

Samples were collected from the tailings dump, soil, and mopane leaves on each of the fourteen field visits during sampling. The phane caterpillar was sampled only when available, namely on four visits because it is seasonal (Table 3.3). Samples of tailings dump, soils, mopane leaves and phane were obtained in the morning hours between 5.00 AM and 8.00 AM. Air samplers were placed at the same time in the early morning hours and removed in the evening, after twelve hours of PAM collection. Atmospheric conditions including temperature and wind direction at time of sampling were also recorded.

3.1.2.1 Tailings dump samples

Grab samples from the only tailings dump were collected for laboratory analyses. During each sampling trip, three representative samples were chosen. Two of the three samples were obtained close to the sides and one was taken from the centre of the tailings dump, thus a total of 42 tailings dump samples were collected for analyses. A hand shovel and a trowel were used to obtain the samples. Sampling was done at about 5 cm from the surface of the tailings dump mount, and at the sides taking into consideration the position of the dump. Each sample was put in a 14 cm x 12 cm Hubco Sentry environmental sample bag, and transported to Gaborone. The transported samples were put in an oven at the Geology Departmental Laboratories, University of Botswana, Gaborone where they were heated to allow surface moisture on them to escape. The oven was set at a temperature of 60 °C overnight.

3.1.2.2 Soil samples

Random techniques highlighted in Jewell *et al.,* (1993) and judgmental techniques described in Crépin and Johnson (1993) were used in obtaining soil samples from the ten sampling sites at each of the fourteen field visits. A total of 140 samples were collected for analyses. Grab soil sampling method as explained by Tan (1996) was used to obtain the samples with the aid of a machete, a trowel and/or a shovel. Soil samples were taken at a depth of between 0 cm and 20 cm. Each sample was placed in a 20 cm x 30 cm polythene bag and transported to the Geology Departmental Laboratories, University of Botswana, Gaborone where it was placed in an oven at 60 °C overnight for surface soil moisture to escape.

3.1.2.3 Particulate air matter samples

Samples of PAM were obtained from source and non-source emission points according to US NIOSH method 0500 for elemental analyses. Six Gilian Gilair - 3 personal air sampling system (SA version) for low flow and two Air con 2 constant medium flow samplers were used for sampling of PAM. Sampling equipment was obtained from the Department of Environmental Science, Technikon Free State. It was not possible to collect samples on a monthly basis due to unusually heavy rains during the wet season of the year.

The medium flow samplers were used to obtain samples over a period of three days at each of the sampling points. The samplers for low flow were placed at the various sampling points and allowed to run for 12 hours at a flow rate of 1,9 l/min, as specified by the NIOSH manual of analytical methods of 1995. At the Environmental Science Laboratories of Technikon Free State, Bloemfontein, South Africa, the cellulose acetate filters were acclimatised in an atmospheric stabilising cabinet for 24 hours in a clean laboratory environment where it was to be weighed. The balances were kept in a dust free room. Weighing of filters was done to an accuracy of 0.01 mg on the chemical balance. The weighed filters were kept in a filter container, sealed and transported to Gaborone by courier service. The filters with the open ends pointing upwards were linked to calibrated pumps at the sampling sites at Selebi Phikwe. After 12 hours, the open end of the filter system was sealed with a clip and later shipped to Bloemfontein where it was weighed and shipped back to Gaborone for possible mineralogical and chemical analyses.

After 35 samples (12 - hour sampling time) were obtained and weighed, the masses of sample concentrations obtained were very low; between 0.01 mg and 0.37 mg, with a mean average of 0.10 mg. The Department of Mines was therefore contacted to supply PAM samples. They supplied six samples, which could be analysed. Medium flow samplers were used to obtain the samples as mentioned in Department of Mines (1998).

3.1.2.4 Mopane samples

Mature dark green leaves with leaf diameter ranging from 4 cm to 8 cm of *Colophospermum mopane* around the Selebi Phikwe area were harvested at the sampling sites for laboratory analyses. Between 10 and 12 leaves depending on the leaf diameter, which constituted a sample set, were sampled per sampling area. A total of 140 sample sets were obtained during the sampling period. The samples were transported to the Geology

Departmental Laboratories, University of Botswana, Gaborone for processing and analyses. Samples were aerated for one week or more, until there was an escape of leaf moisture.

3.1.2.5 Phane samples

The matured phane worms, dark brown, with length ranging from 3 cm to 5 cm were harvested. Ten worms were sampled per sampling area. The worms were hand-picked from the mopane plants. Most of the harvested worms were those that were found to be either eating the leaves of the mopane tree or were found close to eaten leaves of the plant. The guts of the transported fresh phane samples were squeezed out, and the worms were later dried in the oven at 105 °C for 48 hours. After drying they were stored at room temperature of about 25 °C until analyses were carried out.

3.1.2.6 Coding of samples

Each sample was given a code, which facilitated its recognition during data interpretation. The details are reported in Appendix 1.

3.2 Meteorological parameters

Meteorological parameters were recorded at noonday on the days of sampling. These included ambient temperature and wind speed.

3.3 Analyses

3.3.1 Petrographic tests

3.3.1.1 Colour determination

Soil and tailings dump samples used for colour determination were aerated for 24 hours. Clayey aggregates were separated using a mortar and pestle. A spatula was used to mount samples on white cardboard sheets provided by the Munsell Colour Company Inc., MD 21218, USA. The colour descriptions, which comprised the hue, value/chroma and colour of the mounted samples, were obtained by visually comparing it to those of standard soils recorded in the Munsell Soil Colour Book (1992).

3.3.1.2 Granulometric analyses

The soil samples were characterised granulometrically (particle size and particle size distribution). The analyses were performed in two stages: the first stage was using a mechanical/electrical shaker with a nest of sieves, and the second stage was using an automatic particle size analyser (PSA). The principle of operation was based on Stoke's law of sedimentation of individual spherical particles falling freely at a steady velocity under the influence of gravity, resisted only by the viscous drag of the medium (Gaspe *et al.*, 1994), and was mathematically expressed as:

$$V = [2r^2(d_p - d_w)g]/9\eta \qquad \text{(equation 3.1)}$$

Where V = rate of settling of particles (cm/s), r = radius of particles (cm), d_p = density of particles (g/cm^3), d_w = density of water (g/cm^3), η = poise (g/cm/s) and g = acceleration due to gravity (981cm/s^2).

The mechanical/electrical shaker was set at 60 strokes per minute (spm), and the nest of sieves consisted of the following particle size ranges in μm: 500, 425, 355, 300, 250, 180, 150, 125, 106, and 53. The < 53 μm size fraction of soil samples were analysed using a 1993 model Shimadzu SA-CP4 automatic particle size analyser (PSA) which was at the Environmental Science Laboratory, Department of Environmental Science, University of Botswana. The analyser was set at 240 revolutions per minute (rpm). The particle sizes were automatically measured by the PSA.

3.3.1.3 Descriptive petrography

Optical microscopy technique was used for descriptive analyses of samples of the non-clay fraction of the soil and tailings dump. The identification process involved testing for hardness, cleavage, fracture, colour, streak, lustre and crystal appearance. A Leitz Ortholux II Pol-BK petrographic microscope available at the Petrography Laboratory of the Department of Geology, University of Botswana, was used for descriptive analyses of the non-clay fraction of the samples.

3.3.2 Physico-chemical characterisation

3.3.2.1 pH determination

Barnard *et al.* (1990) and Van Reeuwijk (1993) described the method for pH analysis of soil samples. Finely ground/pulverised samples of tailings dump and soil were used for pH determination. Two and a half gram aliquots of sample were placed in three centrifuge tubes and suspended in 25 ml of distilled H_2O. After the samples were shaken on a horizontal shaker for about 30 minutes, the tubes containing the samples were centrifuged for 5 minutes. Average values were calculated and recorded for each sample analysed. The pH of the sample supernatant was analysed with a Jenway 3020 pH meter available in the Geochemistry Laboratory, Department of Geology, University of Botswana. Temperatures of samples at the time of analyses were recorded.

3.3.2.2 Electrical conductivity determination

The amount of total dissolved solids (TDS) in the soil samples could be estimated from their electrical conductivity (EC) values. The EC is used to estimate the presence of dissolved salts such as sulphates, carbonates, phosphates and chlorides. The TDS of given sample might not be reflected by its pH because the salts are generally neutral. Finely ground/pulverised samples of tailings dump and soil were used for EC determination. Sample preparation was similar to that of pH analyses in section 3.3.2.1 (Barnard *et al.*, 1990; Okalebo *et al.*, 1993; Van Reeuwijk 1993). The EC of the supernatant of the samples were analysed with a Jenway 4020 EC meter available at the Soils Laboratory, Department of Environmental Science, University of Botswana. Average values were calculated and recorded for each sample analysed. The temperatures of the samples at the time of analyses were recorded.

3.3.2.3 Analysis of exchangeable cations

The cation exchange capacity (CEC) of the bulk soil was determined using the barium chloride-triethanolamine ($BaCl_2$ - CH_3-$CH_2OH)_3N$ method which has been mentioned in Inglethorpe *et al.* (1993), and also described in Ma and Eggleton (1999). Five gram of the soil sample was put in 100 ml centrifuge and buffered with $BaCl_2$ for an hour with four or five stirrings periodically. The centrifuge was set to make 30 000 rounds at 2000 rpm. After centrifuging, the supernatant was decanted and an additional 100 ml of $BaCl_2$ added. All the unabsorbed ions of Ba were washed off using deionised water. One hundred millilitres of 0.05 M $MgSO_4.7H_2O$ was added to each of the weighed contents in the tube and the mixture was allowed to react for at least 2 hours. Centrifuging of the mixture was done for another hour, and 10 ml of the supernatant was collected into a 100 ml conical flask. Twelve drops of 1M NH_3 of specific gravity (SG) 0.91 and 6 drops of catechol violet indicator were added to the suspension, which was titrated with 0.02 M Di-Na EDTA. The CEC was calculated from the titrant values.

3.3.3 Mineralogical analyses

The mineral phases in the tailings dump, clay fraction of soil and whole soil, and PAM, were identified using X-ray powder diffraction (XRPD) techniques.

The mopane leaves and phane worms could not be analysed by XRPD techniques because they are non-crystalline amorphous substances. In XRPD, diffraction peaks occur when the path of the diffracted X-rays is equal to an integer multiple of the path difference expressed by Bragg's equation which is given by

$$n\lambda = 2d\sin\theta \qquad \text{(equation 3.2)}$$

where n is an integer, λ is the wavelength, d is the interatomic spacing, and θ is the diffraction angle (Bailey, 1980).

The XRPD studies for soil samples and the < 2 μm fraction, and the tailings dump samples were carried out using a Philips PW 3710 XRPD system located at the Department of Geology, University of Botswana. Samples of tailings dump, untreated soil and < 2 μm clay fraction were examined by XRPD. Samples were scanned from 2° to 70° 2θ for tailings dump and whole soil samples, and from 2 ° 2θ to 35 ° 2θ for < 2 μm fraction. The corresponding diffractograms were recorded for scanned samples.

In this study, the analytical system operated at 40kV and 45 mA, with a Cu-K_a radiation. The data was obtained with the aid of a graphite monochromator PW 1877 Automated Powder Diffraction, and an X'PERT Data Collector software package. The collected data was processed for qualitative identification of the minerals from both the data and patterns obtained by scanning using a 1999 Philips X'PERT Graphics & Identify software package. The interpreted results were compared with data and patterns available in the Mineral Powder Diffraction File, data book and the search manual issued by the International Centre for Powder Diffraction Data, 1986, for confirmation purposes.

The heavy minerals of the soil fraction were separated from the bulk soil by placing the soil sample in a separation funnel, and adding 300 ml bromoethane to it. After 24 hours, the heavy fraction was settled at the bottom of the funnel, and was collected in a small beaker. The fraction was allowed to dry overnight and then pulverised in the Sieb Mill for mineralogical analyses. Heavy minerals separation was limited to 10 samples (a sample from each site) because of the very high cost of chemicals involved.

The clay fraction of soil samples were mixed with a few drops of epoxy glue and allowed to dry overnight in an oven. The dried samples were gently crushed in an agate mortar to a fine texture. The powder samples were mounted on the sample holder with very little pressure, using a blade to minimise preferred orientation of the kaolinite particles (Hughes and Brown, 1979), and later scanned in the XRPD system.

Samples of oriented clay fraction for confirmation of kaolinite were prepared by sedimentation (according to Stoke's Law on the settling of different particles sizes in a liquid medium), and drying of the clay suspension on spherical glass plates. Some of the samples were solvated with dimethylsulphoxide (DMSO) in a saturated environment at 50 °C for 4 hours (Delgado *et al.*, 1994; Gonzlez and Camazano, 1968). The hypothetical kaolinite crystallinity index in the clay fraction (the DMSO Solvation Index, DSI) was calculated, provided no chlorite was detected in the clay fraction of the samples. The DSI was calculated as followsin equation 3.3:

DSI (%) = 100 X (I at 7.2 Å untreated - I at 7.2 Å DMSO)/I at 7.2 Å untreated

(equation 3.3)

Other samples were prepared by pressing the powder in a round aluminium sample holder on a flat Al surface using an Al stump. Smectites were distinguished from chlorite and vermiculite groups by rendering the clay homoionic with preferably Mg^{2+}, solvating with glycerol (under-estimates smectite content) and ethylene glycol (over-estimates smectite content) and observing shifts in the 001 spacing.

3.3.4 Chemical analyses

The methods for the analysis of the different chemical parameters for soil have been mentioned in Van Reeuwijk (1993), and for vegetation in Okalebo *et al.* (1993) but no literature was found for chemical analyses of phane worms. Chemical analyses were carried out on the tailings dump, different fractions of soils, PAM, mopane leaves and phane worms. Elements associated with Ni-Cu mining and smelting included Cd, Cr, Co, Cu, Fe, Ni, Se and Zn, which were likely to be found in Ni-Cu orebodies and released into the physical environment through mining and smelting activities.

The graphite furnace technique was quite useful where the concentrations of elements were very low, and also for extremely small sample volumes (Beach, 1989). Ionic concentrations of Cd, Cr, Co, Ni and Se present in extracts of samples of soil, vegetation and worms were determined using a Varian Spectra AA 400 plus Atomic Absorption spectrometer with a Zeeman Graphite Tube Atomizer (GTA) 96 model at the Department of Geological Sciences, University of Botswana, Gaborone, Botswana. Ionic concentrations of Cu, Fe and Zn were measured with a Varian Spectra AA 10 Flame Atomic Absorption Spectrometer (FAAS) available at the Department of Agricultural Research (DAR), Sebele, Botswana.

The atomic absorption spectrometer (AAS) caused a bright source cathode lamp, containing the element to be analysed, to pass through a cloud of non-excited ground-state atoms from the sample where it was absorbed. The degree of absorption was proportional to the amount of the element present in the cloud. The light then proceeded to a monochromator that separated the energy wavelength of interest. The wavelength was then converted into an electrical current, amplified and rectified. A computer software package was used to calculate the quantity of the element in the samples and was reported in weight percentage (wt %), parts per million (ppm) or parts per billion (ppb).

The procedure for the determination of the concentrations of heavy metals described below was adapted from both Beach (1989) for the Zeeman GFAAS and NIOSH (1995) manual of analytical methods for FAAS depending on the analyte being analysed. Analytical grade reagents were used in all the chemical analyses. Samples were homogenised and 0.5 g of sample was weighed into a 30 ml Teflon beaker. The sample solution was heated slowly at low temperature to dry. Then it was the ashing stage, which took place at a high temperature, and thirdly by atomisation. Samples were treated with HNO_3 digestion at a temperature not exceeding 500 °C. Zero point one gram of sample was weighed into a Pt crucible wetted with water. Each sample was digested with 0.5 ml of 72 % perchloric acid and 5 ml of 48 % hydrofluoric acid on a sand bath at 200 °C - 225 °C in a partially closed Pt crucible with lid. The residue was collected by boiling the sample with 5 ml of 60 % HCl and 10 to 15 ml of water. The contents of the crucible together with its lid were washed into a 100 ml volumetric flask filled to mark with ultra pure water, from which very small aliquots were aspirated into the graphite furnace for atomisation and analysis of the heavy metal concentrations in the samples.

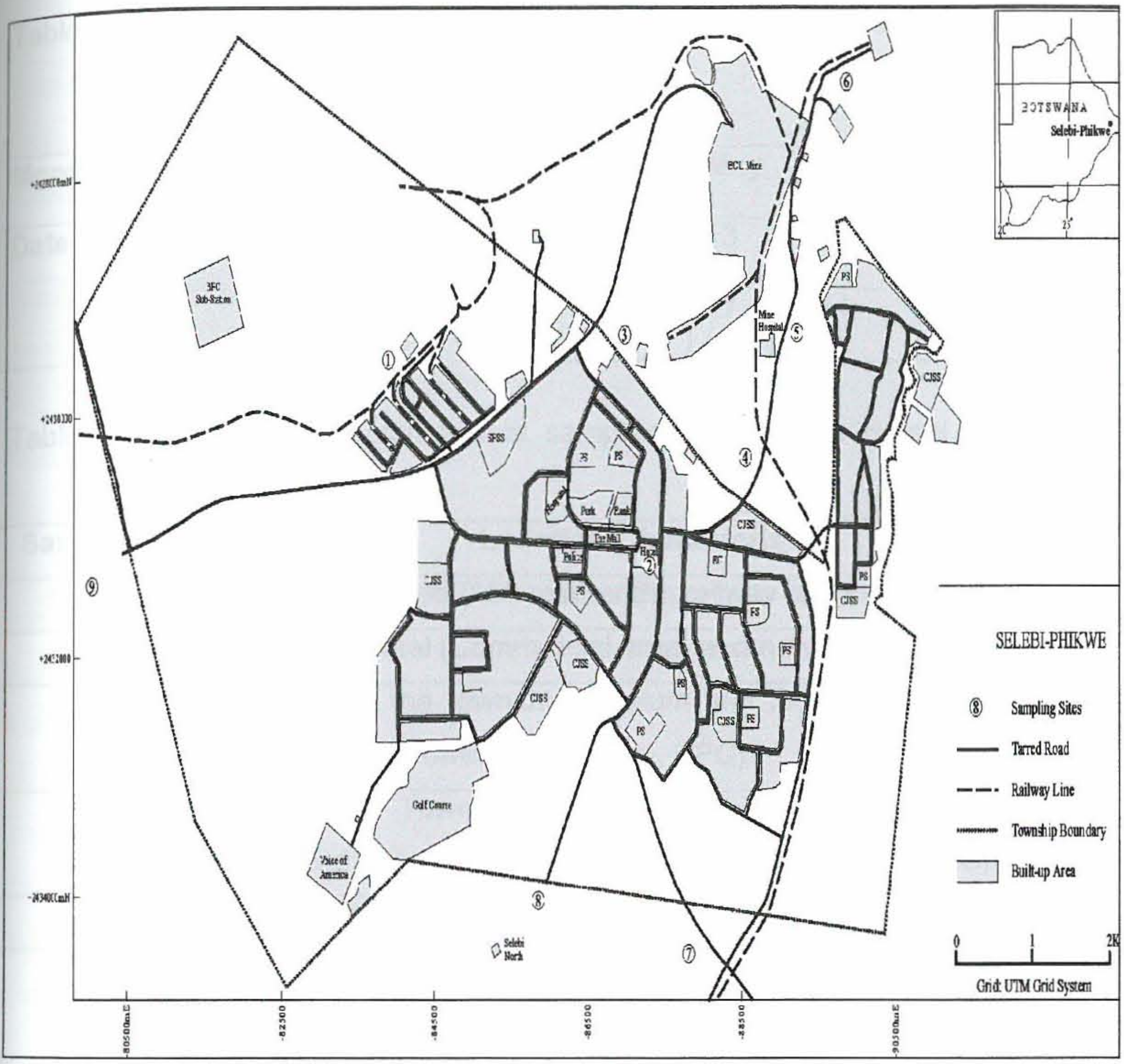

Figure 3.1: Map of the study area showing sampling points.

Table 3.1: Dates during 2000 when samples were obtained at the study site area.

Month	**January**	**February**	**March**	**April**	**May**	**June**	**July**
Date	15	12	11	15	13	10	15
	29	26	25	29	27	24	29

Table 3.2: Location/characteristics of sampling sites at the Selebi Phikwe study site area.

Sampling site	**Location/Characteristics**
1	Industrial area (150 m after the railway crossing)
2	Bosele Hotel (Commercial area) and new township
3	Between the township stadium and the mine (behind the Botswana Power Corporation, BPC)
4	Between Township boundary and the railway line (directly behind a Community Junior Secondary School, CJSS)
5	Opposite the Mine hospital, close to old township
6	Between the mine and explosive storage facilities (close to old township)
7	Towards the airport (about 250 m from the Airport-Sefophe-Selebi Phikwe Road juncture)
8	Off untarred road leading to the Selebi North mine (100 m out of township boundary, adjacent to the new township)
9	Close to the second bridge before entering into the Selebi Phikwe township
10	Control site located close to the road juncture leading to Selebi Phikwe from the Gaborone-Francistown main road

Table 3.3: Dates with corresponding types of study material sampled

Date of Sampling	Type of Study Material Sampled				
	Tailings dump	Soil	Mopane	Phane	PAM
January 15	√	√	√	√	√
January 29	√	√	√	√	√
February 12	√	√	√	√	√
February 26	√	√	√	√	∩
March 11	√	√	√	∩	∩
March 25	√	√	√	∩	∩
April 15	√	√	√	∩	∩
April 29	√	√	√	∩	∩
May 13	√	√	√	∩	∩
May 27	√	√	√	∩	√
June 10	√	√	√	∩	√
June 24	√	√	√	∩	√
July 15	√	√	√	∩	√
July 29	√	√	√	∩	√

Note symbols indicate as follows: √ = was sampled; ∩ = was not sampled

Chapter 4

Results

4.1 Fieldwork

The results obtained during the fieldwork period are reported in sections 4.1.1 and 4.1.2 below; these thus include general field observations and sampling method.

4.1.1 General field observations

The observations of the tailings dump, soils, PAM, mopane leaves and phane caterpillars are reported below.

4.1.1.1 Tailings dump

The tailings dump mount was continuously built from waste products of the mining and from the processing of the ore minerals, continuously as waste was deposited there. The surface of the tailings dump mount was exposed to wind erosion. Small, dark and brassy yellow pseudo-tetragonal crystals of chalcopyrite and acircular green films of malachite could visibly be detected as constituents of the tailings dump. Hand specimen of the tailings dump samples, observed by using a hand lens, showed sub-angular quartz grains and crystals of grayish green amphiboles.

4.1.1.2 Soils

The colour of the soil was predominantly between reddish yellow, golden yellow to yellow. At sites one, two and eight, the colour was strong brown to reddish brown, and at sites three and four the soil colour was very dark brown. At the control site, the colour of the soil was light reddish brown. Whitish gray to reddish gray precipitates as reflected in Figure 4.1, were found on soils close to the smelter/concentrator plant. In areas where the surface soil was tinted with whitish gray precipitates, the strong smell of sulphur was detected, and there was no vegetation cover (Figure 4.1).

4.1.1.3 Particulate air matter

During the sampling period, the atmosphere was generally very clear, to the extent that no PAM could be detected with the naked human eye. At sites one, two, three and eight the smell of sulphur rich gases (SO_2, H_2S) was very strong during most of the sampling periods. At the other sites (four, five, six, seven, nine and ten), sulphur smell could not easily be discerned.

4.1.1.4 Mopane leaves

It was also observed that the plant leaves changed in colour probable due to deposition of sulphate particles on them as depicted in Figure 4.2. It was noticed that leaves located at the periphery of the plant were more affected by the deposition of PAM than others. The peripheral leaves were the first to alter in colour as shown in Figure 4.3. The coloration on leaves varied with location and with season. At the beginning of the field season, most of the leaves at the area were generally green as shown in Figure 4.4 below. Where discoloration occurred, the leaves were initially green in the months of January, February and March, and they turned to pale yellow and later golden yellow in the subsequent months of the field season. Both the leaves and the stems of the mopane plants at site one were stunted. At site two, the leaves were initially green and changed to brownish green and eventually golden yellow. At site three the mature leaves were very short, between 2 cm and 2.5 cm in length. At site four, the leaves were constantly very broad and they exhibited full growths both in colour (rich green) and length (6 cm to 7 cm). At sites seven, nine and ten, the leaves were constantly green and of full length between 4 cm and 6 cm.

4.1.1.5 Phane caterpillar

Fresh, full length, gregarious phanes were seen at sites four, five, six, seven, nine and ten. The phanes at sites one, two, three and eight were thin and very short. The fresh phanes were observed where the mopane leaves were a very rich green. They fed on the juicy leaves, eating from the edges to the centre of the leaves as shown on the eaten leaves in Figure 4.5. Only some of the leaves of the mopane plants (at sites one, two, three, and eight) were discoloured. Quite interestingly, the worms fed only on the green leaves and avoided the discoloured ones (Figure 4.6).

At sites four, five, six, seven, nine and ten there were not many worms, although it was seen that these colonies of worms were very fresh and fat. The phanes were harvested from these sites. At other sites where harvesting was not done, there were many worms, but they were quite small in size.

4.1.2 Sampling

The tailings dump, soils and mopane leaves were sampled during fourteen field visits. The phane was sampled during four visits because these worms are seasonal. The PAM was sampled during eight visits. Problems were encountered using the flow pumps and with the collection of the PAM samples. These problems included the Ni batteries of the flow pumps failing to be recharged and the unusually clear atmosphere during sampling periods.

4.2 Meteorological parameters

The ambient temperature and wind speed on the days of sampling for the Selebi Phikwe area are given in Table 4.1. The winds prevailed from the East and North-Eastern directions, through Selebi Phikwe in an East-south-east direction towards Mmadinare, a village located 15 km SE of Selebi Phikwe.

Between January and July, daily average temperatures on days of sampling decreased from a maximum of 28 °C in February to 14 °C in July, whereas the wind speed increased from 2 m/s in January to 6 m/s in July. During the winter months, ambient temperature values in the mornings were as low as 6 °C, but quickly rose to between 14 °C and 20 °C by noonday. High temperatures decreased from noonday to low temperatures in the winter evenings with remarkably cold weather. Although the month of July is characterised with irregular short-lived dust storms, it should be noted that no storms were observed on the days of sampling.

4.3 Analytical results

The types of analyses performed on the samples are reported in Table 4.2. The analyses conducted depended on the physical state of the sample, type and objective of experiment, and the available quantity of the given sample. All tests were performed for soil samples. Only chemical analyses were conducted on the mopane and phane samples. Mineralogical tests were carried out for samples of the tailings dump, soils and PAM. Physico-chemical tests were performed only on soil samples except for descriptive petrography which was done on both the tailings dump and soil samples. Quantitative analyses for heavy metals were performed on all samples.

4.3.1 Petrographic tests

4.3.1.1 Colour

The colour of the tailings dump was reported in section 4.1.1.1 above, as part of the results of field observations. Only the colour of soils is reported in this section. The colour of the soils at the study area showed varied colour distribution patterns, ranging from pale yellow, reddish yellow to dark reddish brown. A summary of the soil colour according to the study sites is given in Table 4.3. The soil samples from sites four, five, six and seven were light coloured compared to those from the other sites. At sites nine and ten, the soil was dark reddish brown and very dark gray; dark colour being influenced from organic matter deposition resulting from decayed plants and fluvial activities. Cement, sand and concrete formed an integral part of the soil at the control site.

4.3.1.2 Granulometric analyses

Based on the classification scheme of particle sizes for United States Department of Agriculture (USDA) and the *Association Internationale Pour Les Etudes d'Argiles* (AIEA) (International Association for Study of Clay Minerals), particles that are ≤ 2 μm in euhedral spherical diameter (esd) are classified as clay, particles that are > 2 μm esd ≤ 50 μm esd are taken to be silt, and particles $> 50\mu$m esd ≤ 250 μm esd are considered to be sand. Particles $> 250\mu$m esd were discarded because their mineralogy is mainly grain quartz. Grain quartz does not affect the chemistry of the surface environment as explained by Kralik, 1999 and Gaspe *et al.*, 1994.

Average trend of distribution of particles revealed clay fraction to be between 3 wt % and 9 wt % with a mean of 7 wt %, silt portion to be between 34 wt % and 44 wt % with a mean of 39 wt %, and the sand portion to be between 47 wt % and 63 wt % with a mean of 51 wt %. The wt % of the clay size fraction along study sites was almost uniformly distributed as revealed in Figure 4.7. Sites two, four and nine were the most clayey sites with mean average of 9 wt %. These sites were close to water runways and a stream (site nine) where leaching of ions for clay mineral formation could take place. Clay contents in sites six, seven, and eight were less than the mean wt % of clay at the study area. The 7 wt % of clay in soil samples from sites three, five and ten corresponded to the mean wt % of clay fraction at the study area.

The siltiest samples were from sites two, seven and eight with values which approached 44 wt %, whereas the least silty samples were from site five with 35 wt % as indicated in Figure 4.8. The sites where the siltiest samples were found were located near gravelled motorways where particle reworking had been promoted by traffic as well as other factors, such as wind, rain and topography. The silt fraction obtained from soils at sites one, four, nine and ten were consistent and approximated at 40 wt %. The values for the silt fraction from sites three and six exceeded 35 wt % but were below 40 wt %.

Site one, as shown in Figure 4.9, was the most sandy with a value of 63 wt % and site two was the least sandy, with a value of 47 wt %. All other sites had mean values of their sand fraction to between 48 wt % and 58 wt %. Trends in sandiness of soil samples deviated slightly from trends for silt and clay fractions of the samples.

The mean particle size distribution curves for the ten study sites are reported in Figures 4.10 to 4.19. The distibution pattern showed homogeneity within the study area. Slight variations were detected at differences in particle sizes with the mean wt %. The mean wt % for the soil samples occurred at between 100 μm esd and 120 μm esd.

4.3.1.3 Descriptive petrography

4.3.1.3.1 Tailings dump

Mineral constituents of hand specimens of the tailings dump and soil samples were viewed with a microscope. Table 4.3 depicts the minerals, which were identified. Actinolite, $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$; albite, $NaAlSi_3O_8$; cristobalite, α-SiO_2; chalcopyrite, $CuFeS_2$; malachite, $Cu_2(CO_3)(OH)_2$; pyrite, FeS_2; pyrrhotite, $Fe_{(1-X)}S$; tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$; and pentlandite $(Fe,Ni)_9S_8$ were identified and have been described as observed petrographically in Table 4.4.

4.3.1.3.2 Soils

The quartz grains were poorly sorted, and were subangular at the sites close to the smelter/concentrator plant. Further away from the plant, where wind-blown fluvially deposited particles were found, the grains were well sorted, semi-rounded to round. Other mineral assemblages associated with the soils have been discussed in the section above, which dealt with the descriptive petrography of tailings dump.

The clay size fraction of particles could not be identified and described using optical microscopy. When observed with a microscope, the soil particles were generally semi-rounded to rounded with low to high sphericity in shape. The quartz grains, which constituted part of the soil, were angular to subangular with high sphericity.

4.3.2 Physico-chemical characterisation

4.3.2.1 Soil pH

The average pH values for all the sampling sites are given in Figure 4.20. The pH was generally acidic, with values that ranged from 3.5 to 6.0. Slightly acidic to basic pH values were obtained from soil samples from sites seven, eight, nine and ten. The pH values obtained for samples from sites three, four five and six were prominently lower than those for samples from other sites of the study area.

4.3.2.2 Electrical conductivity of soil

The average EC results of the samples obtained from the 10 sites of the study area is given in Figure 4.21. The samples obtained from the ten sites of the study area were grouped into three based on their EC values. Samples from sites four and five have EC values which are < 50 μS/cm. Samples obtained from sites one, two, seven, eight and nine had EC values ≥ 50 μS/cm ≤ 150 μS/cm. The third group of samples was obtained from sites three, six and ten and had EC values ≥ 100 μS/cm ≤ 250 μS/cm.

4.3.2.3 Cation exchange capacitance of soils

The CEC values of the soil samples were between 2 meq/100 g and 20 meq/100 g (Figure 4.22), which is typical of 1:1 clay minerals that are found dominantly in kaolinitic soils. The soil mineral content could have included minor/trace quantities of 2.1 clay minerals such as smectite and illite. It should be pointed out that the soil samples from site 8 had a remarkably low CEC; with an average value of ≤ 2 meq/100 g. Soils from sites one, three and six had CEC values slightly higher than 15 meq/100 g.

The average CEC value for site one was 20 meq/100 g, site three was 16 meq/100 g and site six was 17 meq/100g. With low pH values and high CEC values for soil samples from site six, it was likely that chemical reactions and soil acidification could have taken place compared to other sites of the study area.

4.3.3 Mineralogy

There were no changes in the mineral contents of samples obtained from a given site during the period this study was conducted. Different mineralogical aspects are reported in corresponding sections below.

4.3.3.1 Mineralogy of tailings dump

The following minerals were found to be unevenly distributed in the samples of the tailings dump: nickelblodite, pyrrhotite, quartz, pentlandite, malachite $Cu_2(CO_3)(OH)_2$, chalcopyrite, actinolite $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$, cristobalite, tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$, kaolinite, mica and albite $NaAlSi_3O_8$ as shown in Figures 4.23, 4.24 and 4.25. Samples from the older part of the tailings dump were deprived of pyrrhotite, pentlandite and chalcopyrite. The samples mainly malachite, cristobalite and nickelblodite as reflected in the diffractogram of Figure 4.25. The XRPD analyses revealed the following mineral phases in the mineral content of the more recent part of the tailings dump: pyrrhotite, pentlandite, actinolite, malachite and chalcopyrite as indicated from the diffractogram in Figure 4.25. Samples of the tailings dump obtained from the sides of the tailings mount were found to contain traces of phyllosilicate minerals such as kaolinite and mica, as well as tremolite, albite and actinolite as exemplified in Figure 4.23.

4.3..3.2 Mineralogy of the bulk soil

A typical X-ray diffractogram of the samples from site one is illustrated in Figure 4.26. Silicon sulphide, quartz, and actinolite were the dominant minerals, whereas microcline occurred as a minor mineral component. Albite, pyrrhotite, cuprite and cobalt oxide occurred as trace minerals. From the diffractogram, pyrrhotite was both poorly crystallised and the least representative mineral in the soil at the site. Secondary mineralisation of Cu, Co and Si led to the formation of cuprite, cobalt oxide and silicon sulphide. The mineralogy of soil samples from site one (Figure 4.26) was qualitatively similar to that of site three (Figure 4.28) except for the slight variation of their mineral wt % in the different samples from the two sites.

Soil samples obtained from sites two, four, five, six, seven and eight had similar qualitative mineralogical patterns as shown in Figures 4.27, 4.29, 4.30, 4.31,4.32 and 4.33. The dominant mineral phase at these sites was quartz followed by silicon sulphide. Albite, microcline, cobalt oxide and cuprite occur as minor components. Pyrrhotite was found in trace quantities and albite and microcline had equal wt % and uniform distribution at these five sites.

Sites four, five and six, had more silicon sulphide coupled with a corresponding decrease of quartz by wt % than sites two and seven of the study area.

Approximated equal quantities of cobalt oxide and cuprite were present at five sites (two, four, five, six and seven). Occurrence of the secondary soil components, namely cobalt oxide, silicon sulphide and cuprite, at these sites was an indicative effect of environmental chemical alteration.

The soils from sites nine and ten, as revealed by XRPD shown in Figures 4.34 and 4.35, both contained albite, quartz and microcline as gangue minerals of orebodies and mineral constituents of hostrock and country rocks. These soils were contaminated with silicon sulphide, which may have been formed from the migration of sulphide particles by both wind and water to the sites.

The mineralogy of the bulk soil samples as revealed by XRPD was consistent in samples taken from the same site. It indicated that the soils comprised of primary minerals, which were contained in the orebodies and country rocks, and secondary minerals, considered to have derived from the mining and smelting activities, and alteration of country rocks. Actinolite, albite, quartz, microcline and pyrrhotite were the primary minerals in the bulk soil samples.

Silicon sulphide and cobalt oxide, although not minerals, were part of the soil chemistry and material components at the Selebi Phikwe area and as such are discussed as minerals in this study. The former two substances and cuprite were the secondary minerals contained in the soil samples. Quartz was a very dominant mineral in the soils constituting at least 60 wt % of the samples. Whereas quartz is very dominant as a principal mineral component in the soil, the next dominant mineral varies from site to site depending on the closeness of the site to where mining and ore processing activities were conducted, as well as on the environmental chemistry.

4.3.3.3 Mineralogy of heavy minerals fraction of soil

The results of the heavy minerals fraction in soils are presented in Figure 4.36. Forty three wt % of samples from site one and 39 wt % of samples from site three constituted the heavy minerals fraction of the soil. Samples from site two contained 15 wt % of heavy minerals whereas those from sites five, seven and eight contained 20 wt % of heavy minerals. Samples from sites four and six contained 25 wt % of heavy minerals. Samples from site nine contained 7 wt % of heavy minerals, and samples from site ten contained 5 wt % of heavy minerals.

The heavy minerals identified in samples from sites one and three were actinolite, pyrrhotite, and cuprite. Samples from sites two, five, seven as well as eight contained pyrrhotite and cuprite. Samples from sites four and six contained pyrrhotite and cuprite as the major heavy minerals and actinolite as minor heavy mineral. Samples obtained from sites nine and ten contained mainly pyrrhotite and traces of cuprite. Actinolite was not detected as a trace component of heavy minerals fractions in soil samples from sites nine and ten.

4.3.3.4 Mineralogy of < 2 μm fraction of soil

The X-ray diffractograms as illustrated in Figures 4.37 to 4.46 revealed kaolinite, smectite, and illite to be the types of clay minerals present in the < 2 μm fraction of the soil around Selebi Phikwe area. The clay size fraction also contained both anorthite and very fine-grained quartz in trace quantities. The clay-size fraction of soil samples from sites one (see Figure 4.37) and ten (see Figure 4.46) constituted smectite, illite, kaolinite and quartz, none being more dominant. Kaolinite was very poorly crystallised, and it was not possible to determine its Hinckley's Crystallinity Index (HI) value. At site two, kaolinite was the only clay mineral contained in the clay-size fraction of the soil as illustrated in Figure 4.38. Low mean HI value (0.24) of kaolinite at this site was attributed to poor crystallinity, which may have been indicative of early stages of kaolinitisation. Less than 10 wt % of the < 2 μm fraction of the soil samples at site two consisted of quartz.

The mineralogy of the < 2 μm fraction of the samples from sites three and six was similar, as shown in Figures 4.39 and 4.42. Whereas quartz was a dominant mineral phase, kaolinite occurred as a minor phase and smectite in a trace quantity. The mean HI value of 0.29 of kaolinite at the two sites was slightly higher than that at site two. The quantity of smectite contained in the clay-size fraction at the two sites was the same, and similar to the mineral present at sites one and ten. Kaolinite was the only clay mineral contained in the clay-size fraction of soils from site four as shown in Figure 4.40. With a mean HI of 0.30, kaolinite crystallinity at site four was slightly more when compared to its similar mineral characteristic in soils obtained from sites one, two, three, six and ten. The clay-size fraction of soils from sites five and nine, as reflected in Figures 4.41 and 4.45, were about 80 wt % kaoilinitic, and they had a mean HI of 0.68. The HI value was significantly higher than for the soil samples from all the other sites, which was indicative of crystal maturity.

Anorthite, $(Na,Ca)AlSi_3O_8$, a plagioclase that alters to either Na-smectite or Ca-smectite depending on the mineral chemistry of the environment, was found to be present in the clay-size fraction of soils from both sites seven and eight as shown in Figures 4.43 and 4.44. At both sites, kaolinite was the only clay mineral. Anorthite was the dominant component in the clay-size fraction at site eight. At site seven, quartz was dominant with kaolinite as a minor component and anorthite as a trace component.

4.3.3.5 Mineralogy of particulate air matter

XRPD analysis of the composite PAM sample indicated that it was mainly composed of very fine quartz, pyrrhotite, chalcopyrite, albite and djurleite, $Cu_{31}S_{16}$ as shown in Figure 4.47.

4.3.4 Chemical analyses

Results obtained from chemical analyses of the tailings dump, soils, mopane leaves and phane worms were indicative of an increase in concentration of heavy metals at the study sites close to the smelter/concentrator plant compared to sites further away from the plant.

4.3.4.1 Tailings dump

The analytical results for heavy metals in the tailings dump are reported in Appendix 2. Concentration values obtained for analysed heavy metals in soil samples were as follows: Cd was between 9 ppm and 16 ppm, Co was between 66 ppm and 89 ppm, Cr was between 312 ppm and 431 ppm, Cu was between 779 ppm and 896 ppm, Fe was between 3100 ppm and 3555 ppm, Ni was between 328 ppm and 389 ppm, Se was between 1.7 ppm and 2.2 ppm, and Zn was between 46 ppm and 77 ppm. The correlation coefficients are depicted in Table 4.5.

The mean concentration values, as reflected in Figure 4.48 indicated lower concentration values at the centre of the tailings dump compared to higher concentration values at the sides of the waste mount. Most correlations between heavy metals in the tailings dump were very strong with a few exceptions. Very strong correlations included Cr/Cd, Fe/Cu, Ni/Cd, Ni/Co, Ni/Cu, Se/Cd, Se/Co, Se/Cr, Se/Fe, Zn/Cd, Zn/Cr, Zn/Ni and Zn/Se. Very insignificant associations occurred for Cr/Co and Cu/Cr with a correlation coefficient value of 0.06.

4.3.4.2 Soils

The analytical results for heavy metals in soil are reported in Appendix 3. Concentration values obtained for analysed heavy metals in tailings dump samples were as follows: Cd was between 0.01 ppm and 0.05 ppm, Co was between 1 ppm and 28 ppm, Cr was between 0.03 ppm and 14 ppm, Cu was between 11 ppm and 116 ppm, Fe was between 31 ppm and 430 ppm, Ni was between 19 ppm and 120 ppm, Se was between 0.01 ppm and 0.03 ppm, and Zn was between 17 ppm and 68 ppm. The correlation coefficients are shown in Table 4.6.

The mean concentration values as reflected in Figure 4.49 indicated that the lowest concentration values occurred at the control site. Other low concentration values of the different heavy metals were further away from the smelter/concentrator plant (sites eight, nine and ten). The soils close to the plant, more specifically site four, five and six were the most contaminated.

The correlation coefficients between heavy metals in soil samples depicted very good associations for more than 50 % of the relationships. Very strong correlations included Co/Cd, Cr/Cd, Cr/Co, Fe/Cr, Fe/Cu, Ni/Cu, and Se/Cu. The lowest correlation coefficient was at 0.2 with Zn/Co and may not be considered insignificant. The other associations occurred with average correlation coefficient values.

4.3.4.3 Particulate air matter

Only one composite sample was chemically analysed. The concentration values were given in Table 4.7. The concentrations of the heavy metals in PAM were parallel to those in the soil samples and the tailings dump. Concentration values for Co, Cr, Cu, Fe, Ni and Zn in PAM were higher than usual for residential areas.

4.3.4.4 Mopane leaves

The analytical results for heavy metals in mopane leaves are reported in Appendix 4. Concentration values obtained for analysed mopane leaves were as follows: Cd was between 0.01 ppm and 0.05 ppm, Co was between 1 ppm and 28 ppm, Cr was between 0.03 ppm and 11 ppm, Cu was between 4 ppm and 116 ppm, Fe was between 31 ppm and 430 ppm, Ni was between 19 ppm and 120 ppm, Se was between 0.01 ppm and 0.03 ppm, and Zn was between 17 ppm and 79 ppm. The correlation coefficients are shown in Table 4.8.

The mean concentration values of heavy metals in leaves as reflected in Figure 4.50, indicated that the lowest concentration values occurred at the control site. Other low concentration values of the different heavy metals were further away from the smelter/concentrator plant (sites seven, eight, nine and ten). The leaves close to the smelter/concentrator plant; more specifically sites four, five and six were the most contaminated.

The correlation coefficients between heavy metals in plants reflected very good associations for more than 75 % of the relationships. Very strong correlations included Cr/Cd, Cr/Co, Cu/Cd, Cu/Co, Cu/Cr, Fe/Cd, Fe/Co, Fe/Cr, Fe/Cu, Ni/Cu, Ni/Fe, Zn/Cu and Zn/Ni. The lowest correlation coefficient was at 0.1 with Zn/Se. The correlation coefficient values for Se/Co, Zn/Cd and zn/Cr were the same.

4.3.4.5 Phane caterpillars

The analytical results for heavy metals in phane caterpillars are reported in Appendix 4. Concentration values obtained for heavy metals in phane caterpillars were as follows: Cd was between 0.01 ppm and 0.05 ppm, Co was between 0.01 ppm and 0.6 ppm, Cr was between 0.03 ppm and 1.03 ppm, Cu was between 1.3 ppm and 9.79 ppm, Fe was between 1 ppm and 13.5 ppm, Ni was between 1.2 ppm and 4.20 ppm, Se was between 0.01 ppm and 0.03 ppm, and Zn was between 0.6 ppm and 5.79 ppm. The correlation coefficients are shown in Table 4.9.

The mean concentration values of heavy metals in leaves, as reflected in Figure 4.51, indicated the lowest concentration values occurring at the control site. Other lower concentration values of the different heavy metals were further away from the smelter/concentrator plant (sites seven, eight, nine and ten). The worms close to the plant; more specifically sites four, five and six were the most contaminated.

The correlation coefficients between heavy metals in phane caterpillar reflected very good associations. Strong correlations included Fe/Cu, Ni/Cr, Se/Co, Zn/Cu and Zn/Ni. The lowest correlation coefficient was at 0.03 with Ni/Fe.

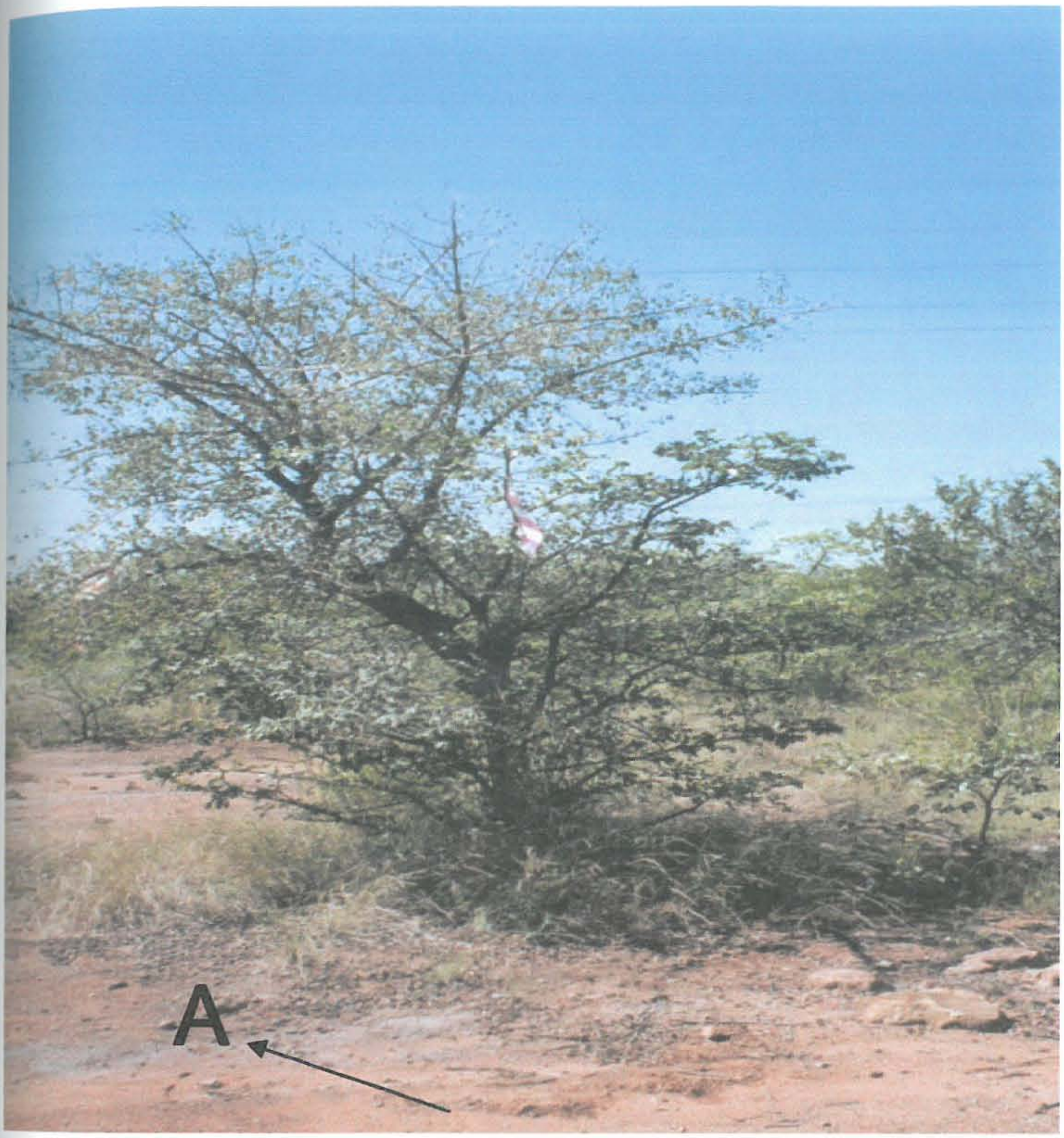

Figure 4.1: Soil that developed into a dead zone close to site three.

(Note the absence of vegetation where whitish gray precipitates (A) occurred).

Figure 4.2: Mopane leaves coated with layers of particulate air matter and dust. (Note the yellow colouring (A) of the leaves).

Figure 4.3: Mopane trees demonstrating peripheral yellow (A) and orange (B) discolouring of leaves.

Figure 4.4: Fresh, glossy green leaves of the mopane plant.

Figure 4.5: Partially eaten green glossy leaves of a mopane tree.

Figure 4.6: Photograph of a mopane tree demonstrating both green (A) and yellow (B) leaves on the same tree (the green ones being on the leeward side of the prevailing wind).

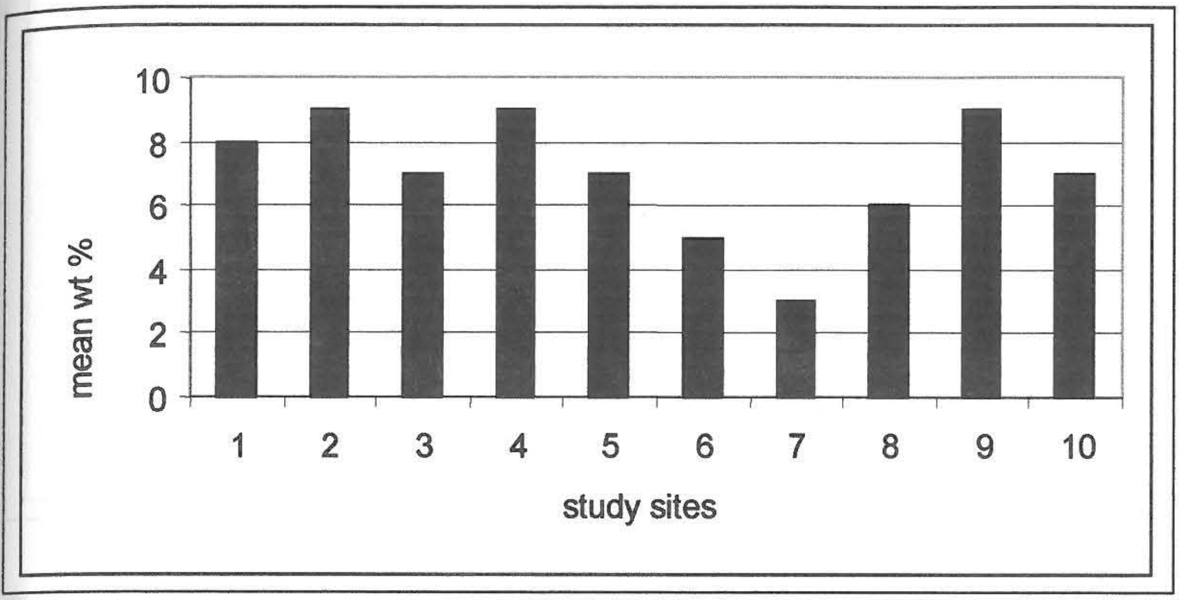

Figure 4.7: Mean weight percent of clay fraction of soil from the study sites.

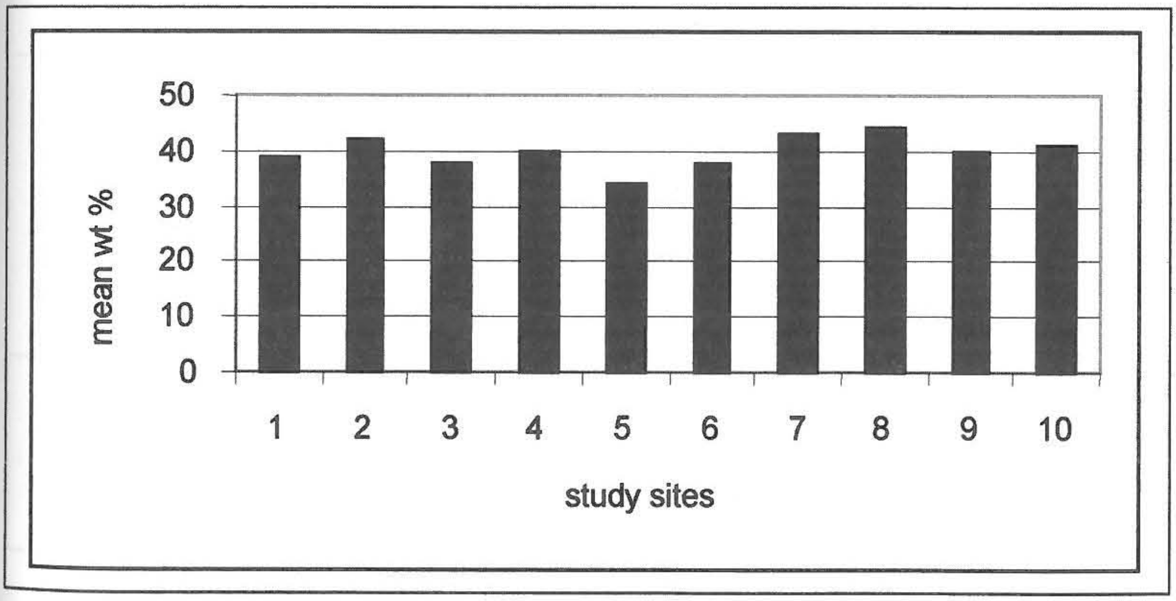

Figure 4.8: Mean weight percent of silt fraction of soil from the study sites.

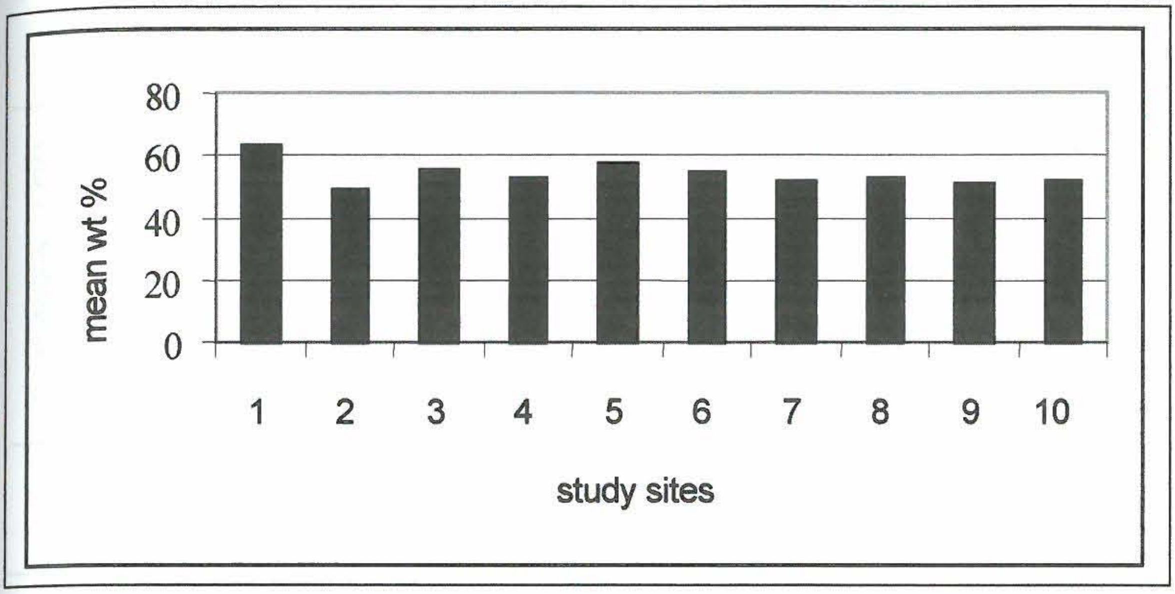

Figure 4.9: Mean weight percent of sand fraction of soil from the study sites

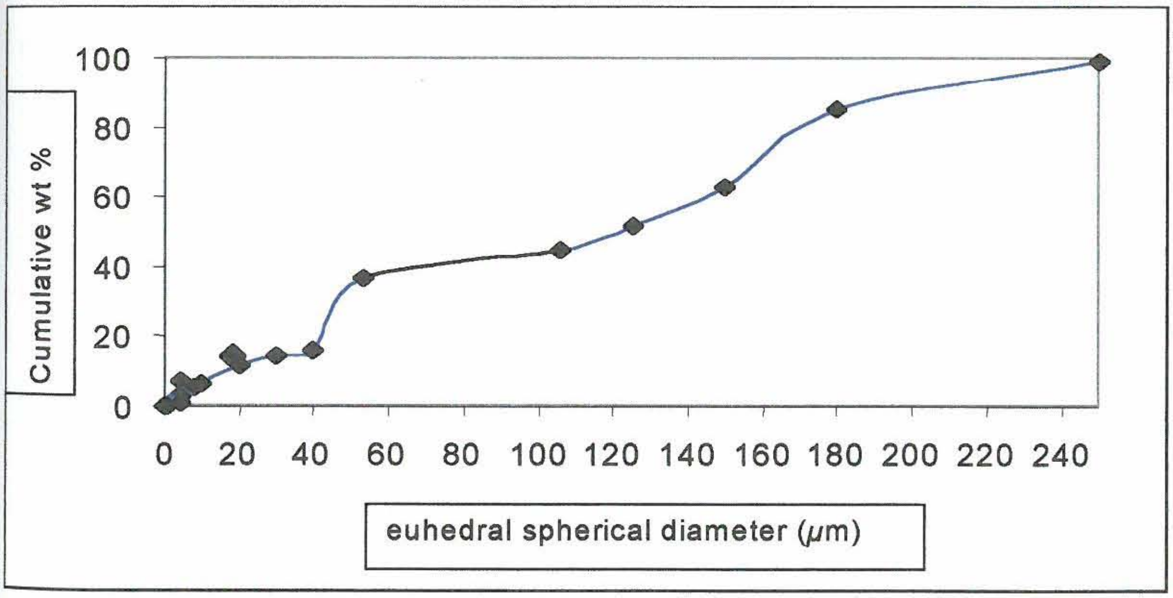

Figure 4.10: Mean cumulative frequency distribution of representative soil samples from site one.

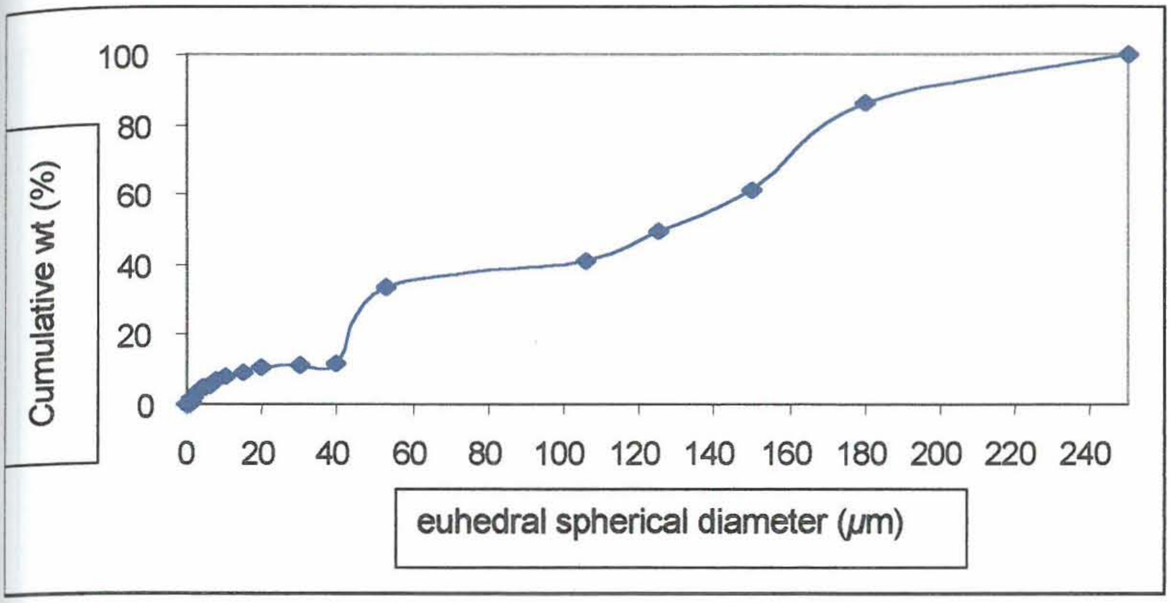

Figure 4.11: Mean cumulative frequency distribution of representative soil samples from site two.

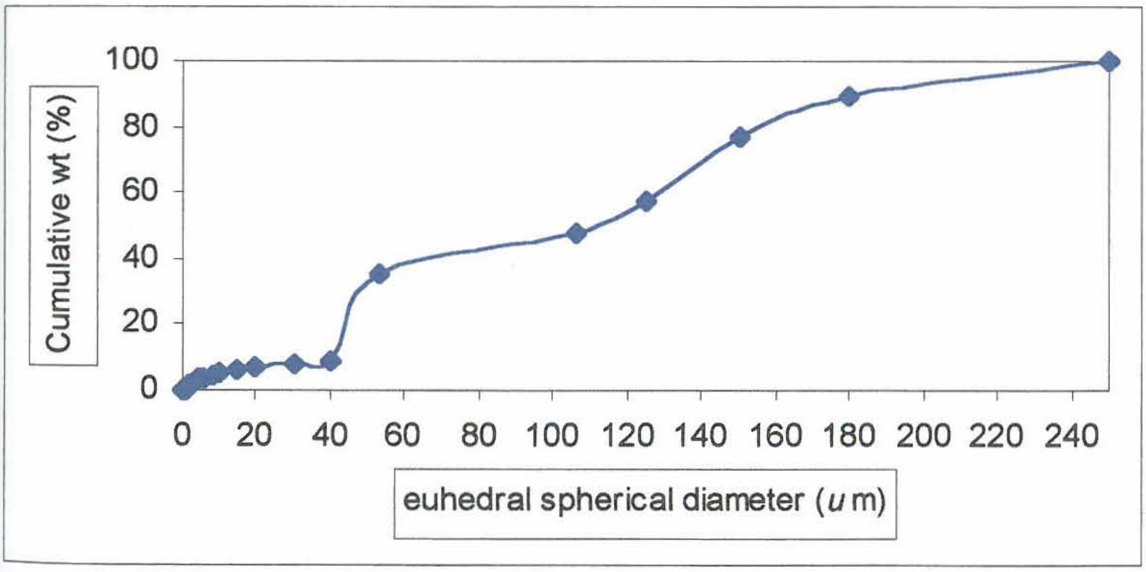

Figure 4.12: Mean cumulative frequency distribution of representative soil samples from site three.

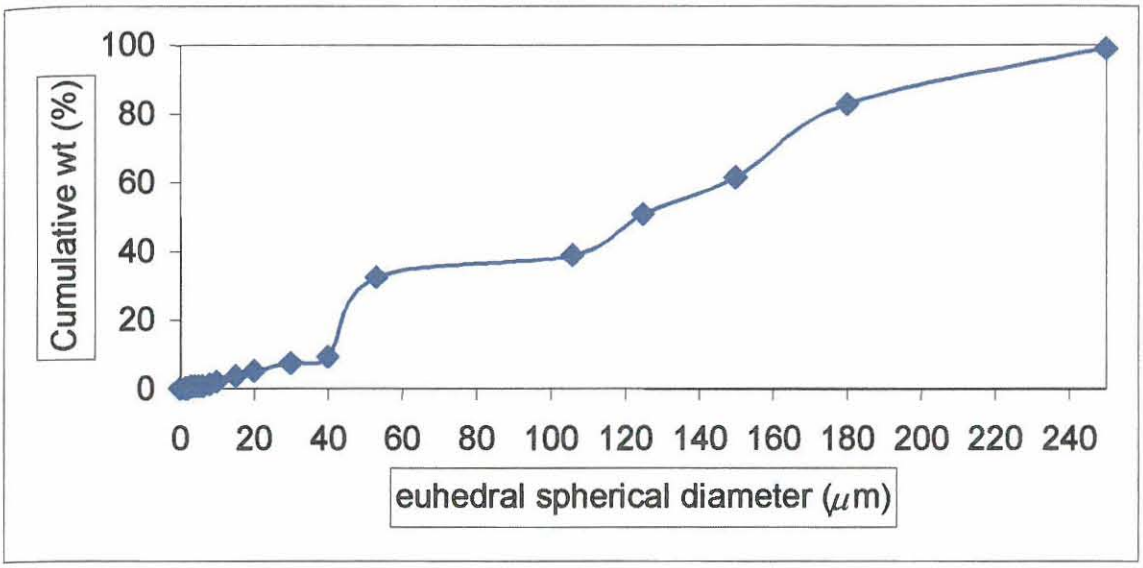

Figure 4.13: Mean cumulative frequency distribution of representative soil samples from site four.

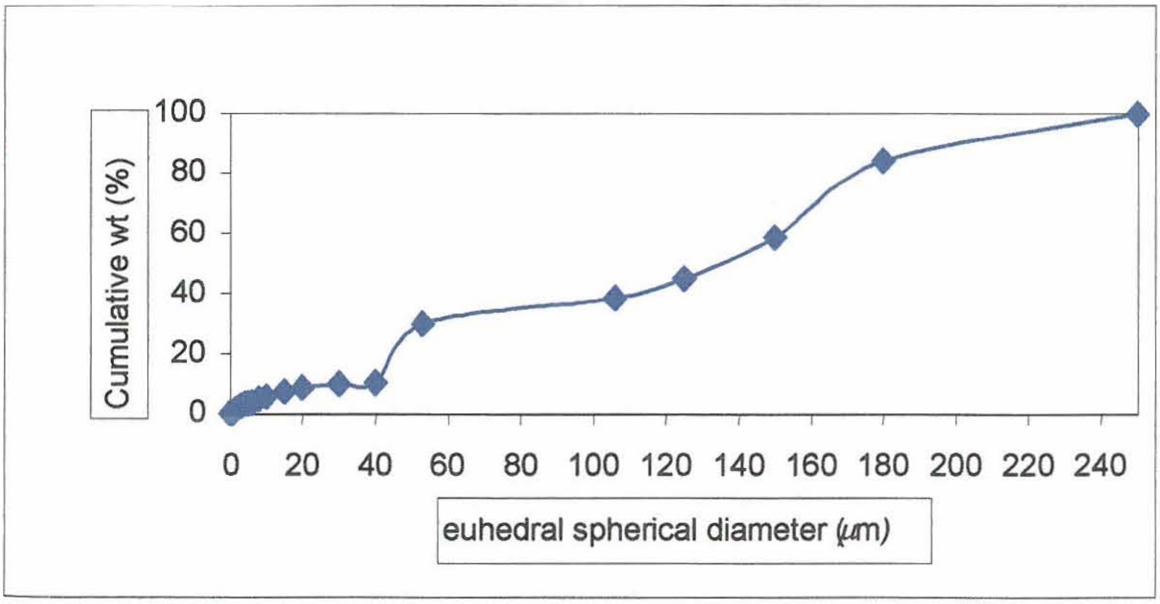

Figure 4.14: Mean cumulative frequency distribution of representative soil samples from site five.

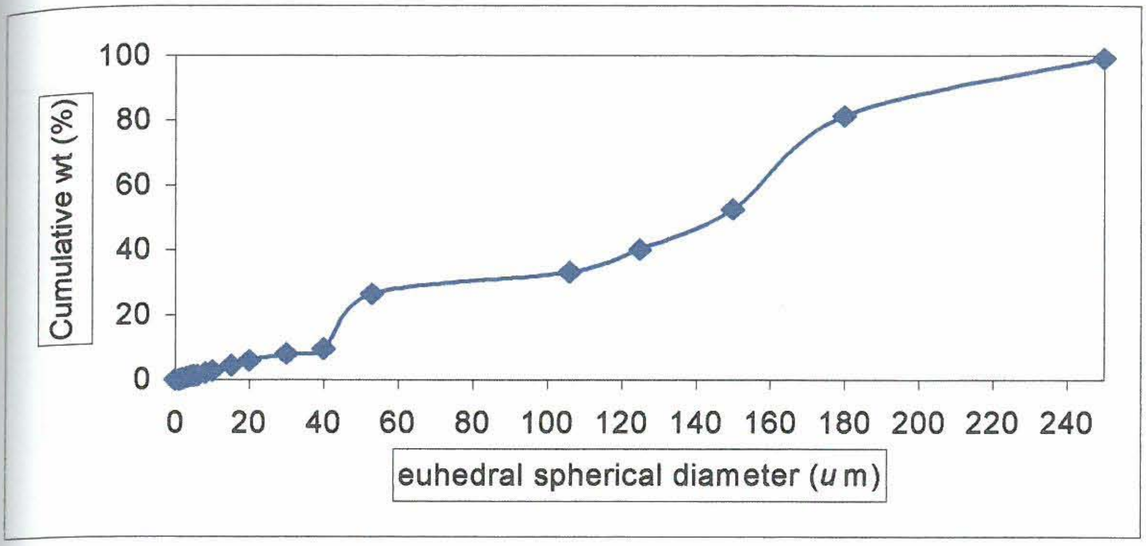

Figure 4.15: Mean cumulative frequency distribution of representative soil samples from site six.

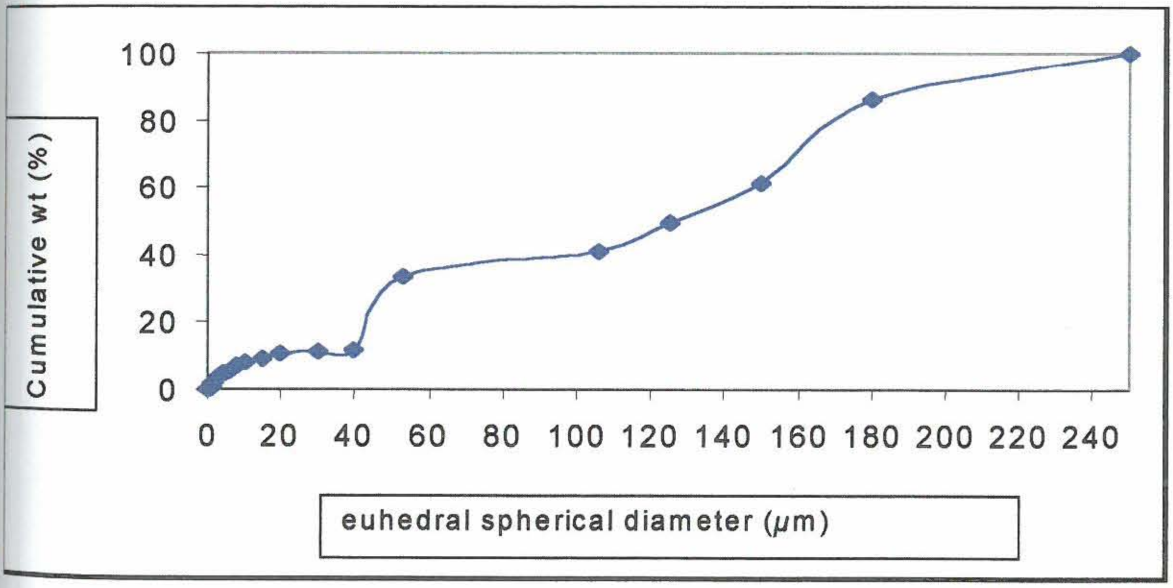

Figure 4.16: Mean cumulative frequency distribution of representative soil samples from site seven.

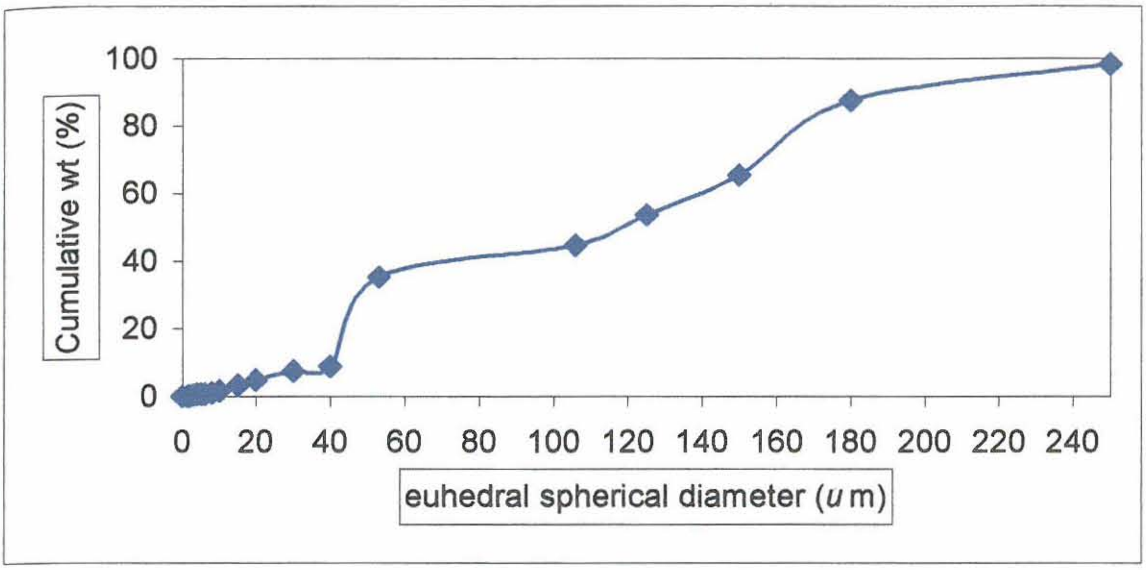

Figure 4.17: Mean cumulative frequency distribution of representative soil samples from site eight.

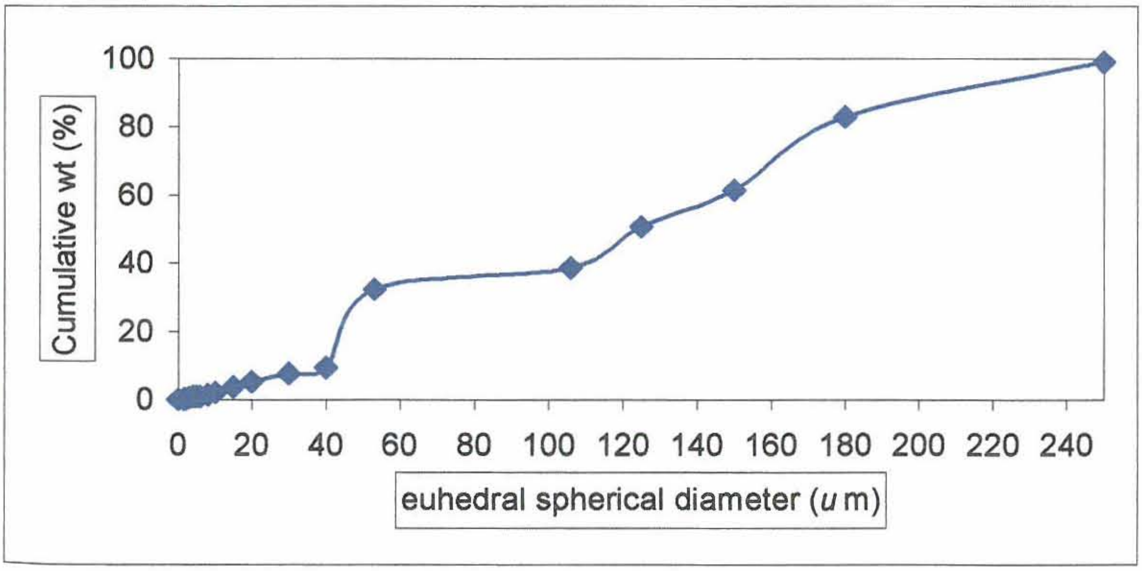

Figure 4.18: Mean cumulative frequency distribution of representative soil samples from site nine.

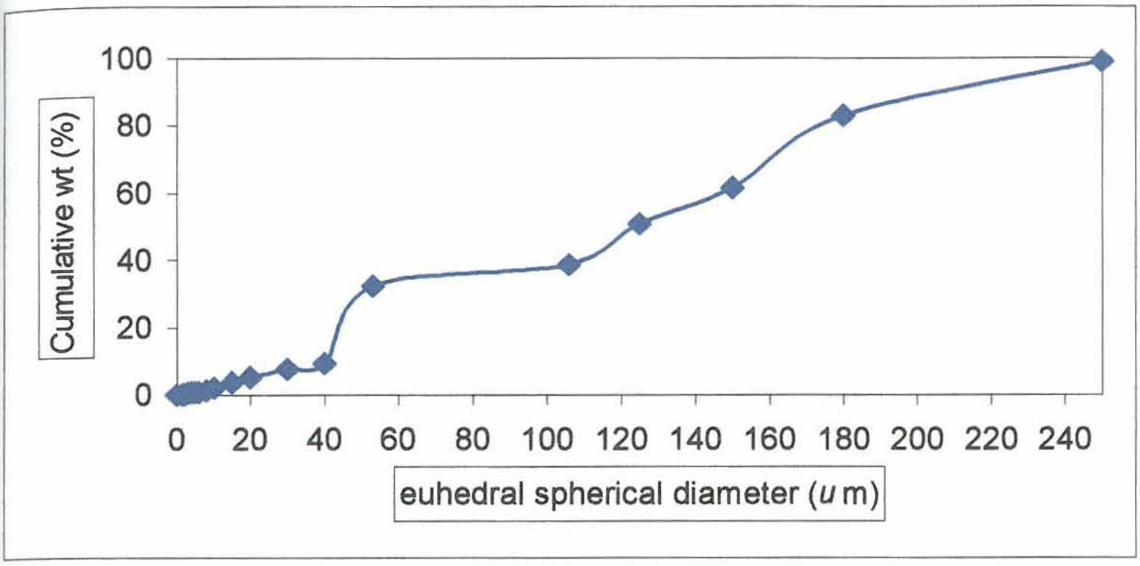

Figure 4.19: Mean cumulative frequency distribution of representative soil samples from site ten.

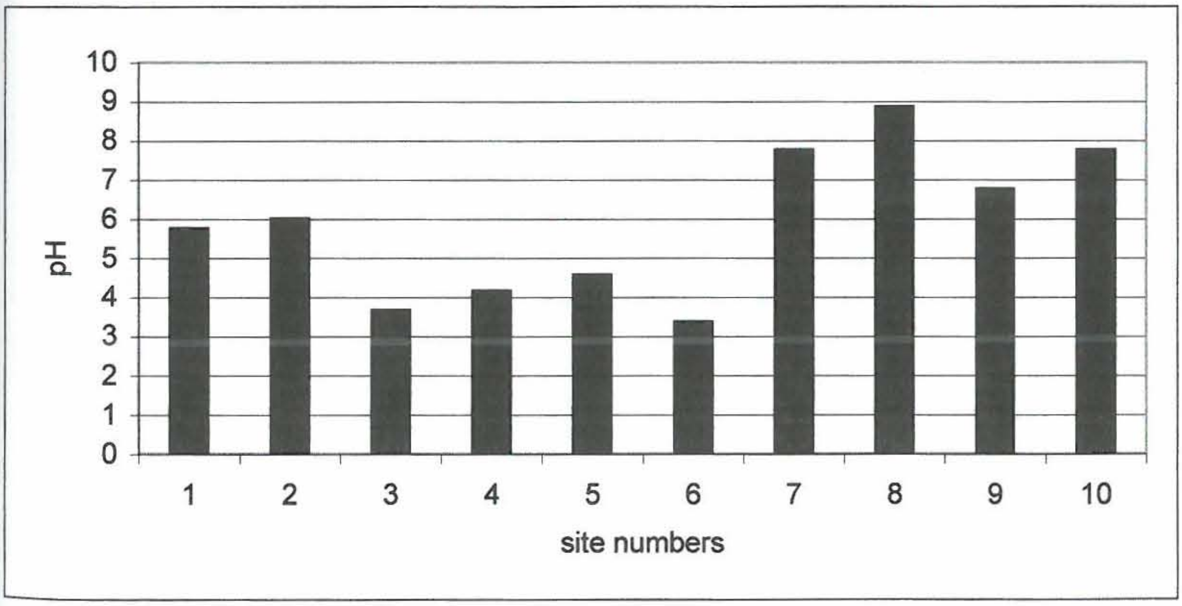

Figure 4.20: Average pH values of whole soil samples from the different sampling

sites at the Selebi Phikwe area.

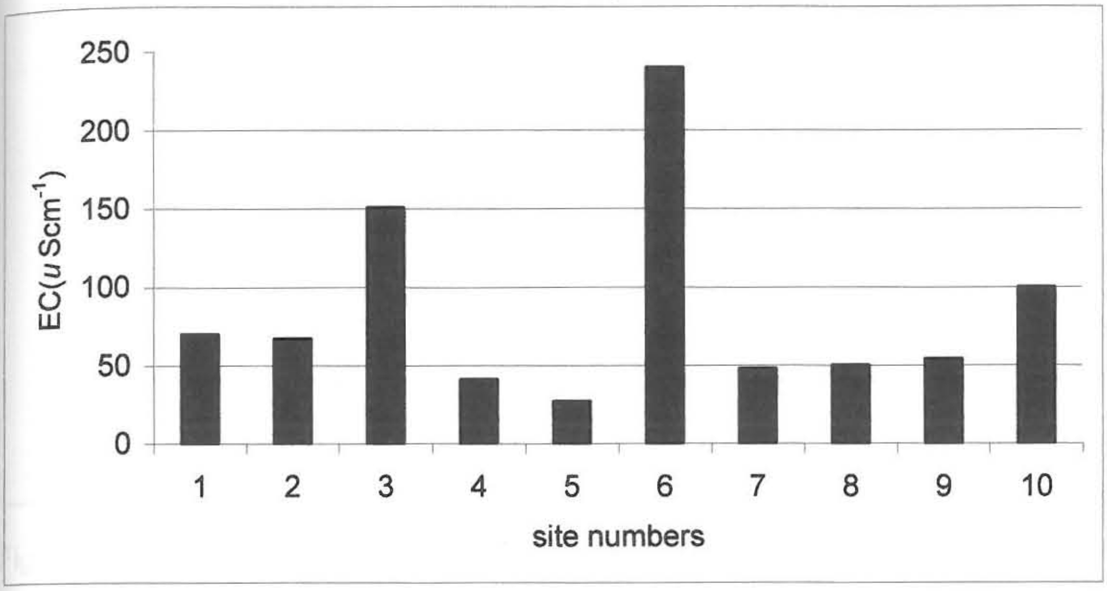

Figure 4.21: Average values of electrical conductivity of whole soil samples from the different sampling sites at the Selebi Phikwe area.

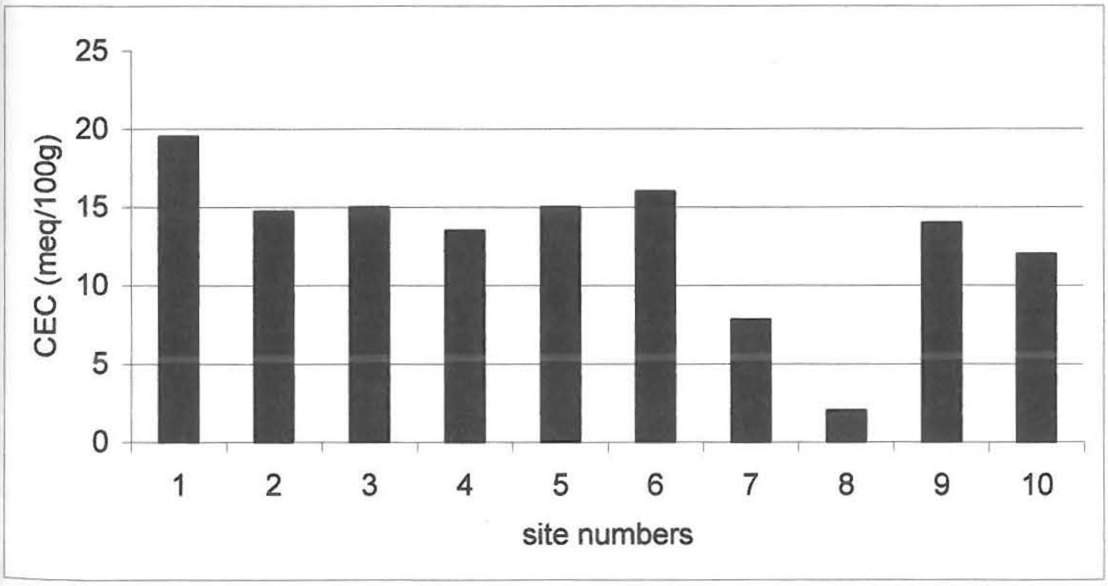

Figure 4.22: Average values of cation exchange capacity of whole soil samples from the different sampling sites at the Selebi Phikwe area.

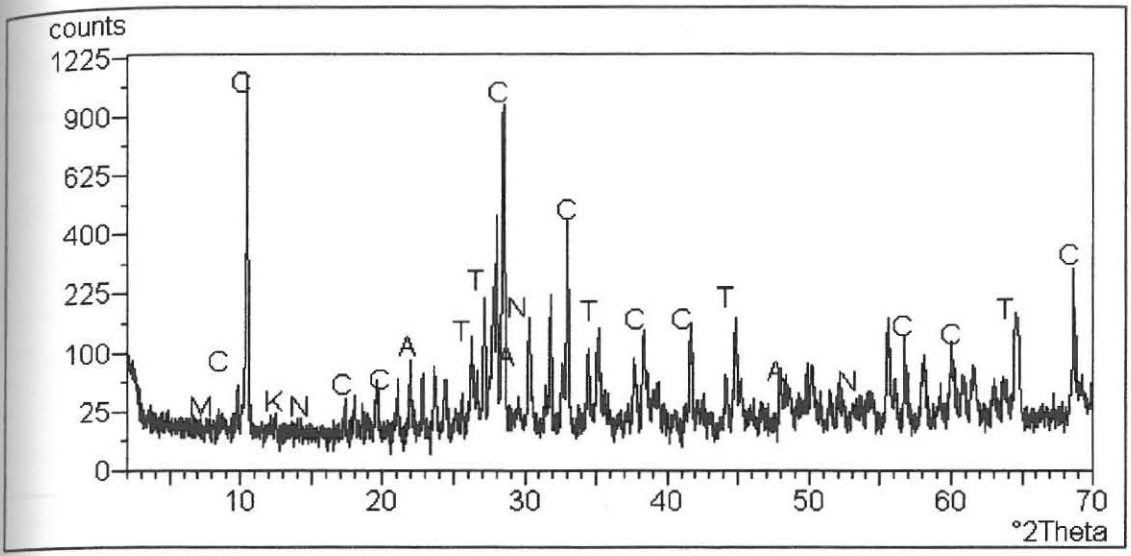

Figure 4.23: X-ray powder diffractogram of representative tailings dump sample obtained from site one of tailings dump (K is kaolinite, N is albite, C is actinolite, T is tremolite and M is mica). Sample represented is T1H.

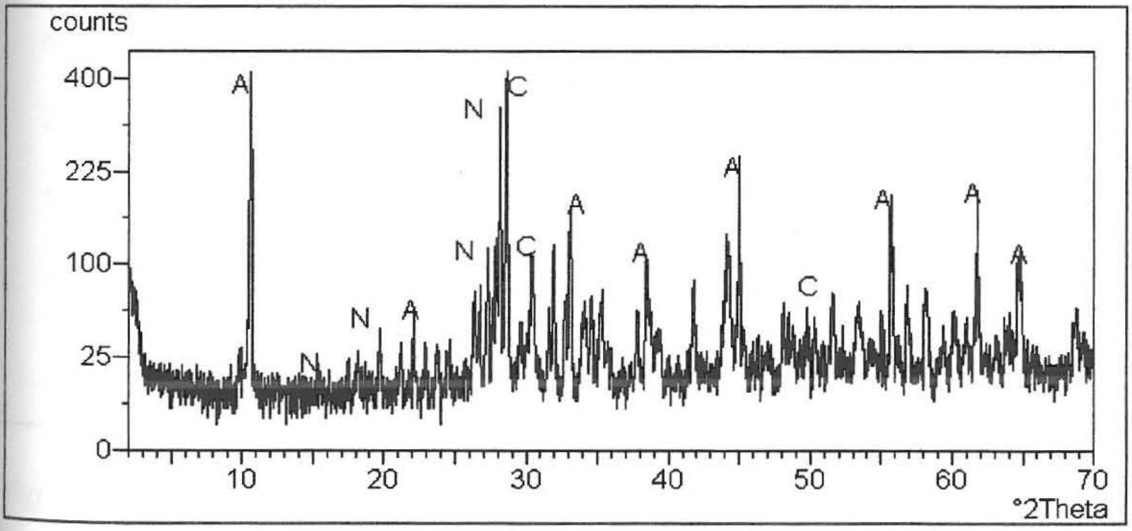

Figure 4.24: X-ray powder diffractogram of representative tailings dump sample obtained from site two of tailings dump (A is actinolite, C is cristobalite and N is nickelblodite). Sample represented is T2H.

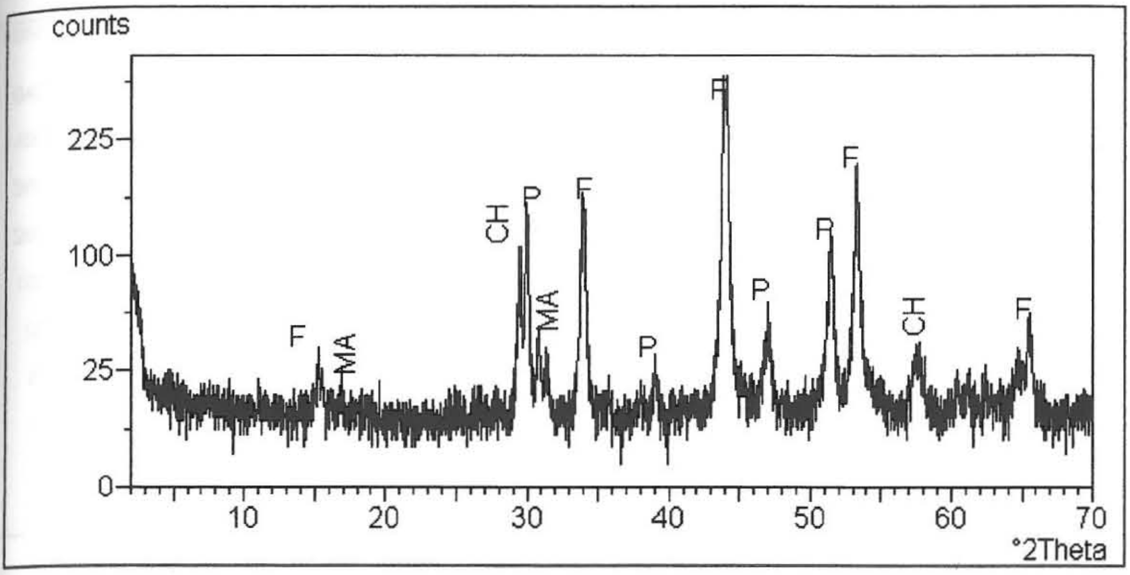

Figure 4.25: X-ray powder diffractogram of representative tailings dump sample obtained from site three of tailings dump (F is pyrrhotite, P is pentlandite, MA is malachite and CH is chalcopyrite). Sample represented is T3H.

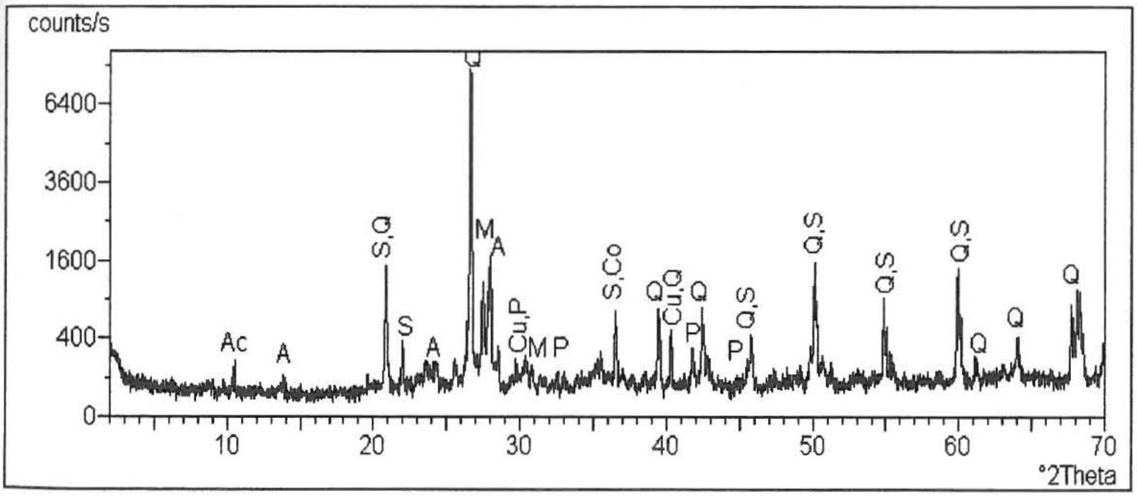

Figure 4.26: X-ray powder diffractogram of representative bulk soil sample obtained from site one (Ac is actinolite, A is albite, S is silicon sulphide, Q is quartz, M is microcline, Cu is cuprite, P is pyrrhotite and Co is cobalt oxide). Sample represented is S1A.

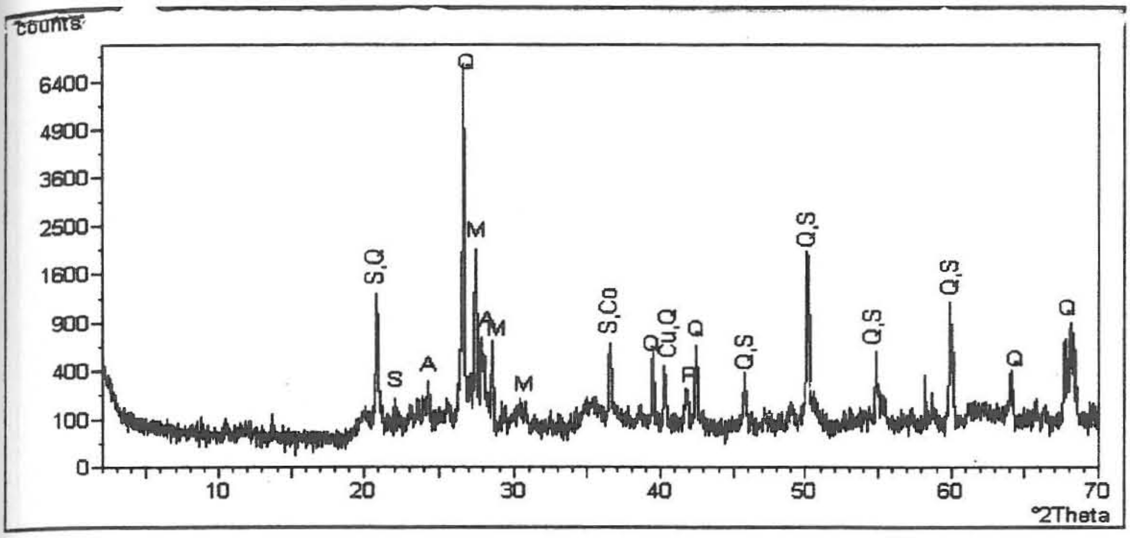

Figure 4.27: X-ray powder diffractogram of representative bulk soil sample obtained from site two (S is silicon sulphide, Q is quartz, A is albite, M is microcline, Co is cobalt oxide, Cu is cuprite and P is pyrrhotite). Sample represented is S2A.

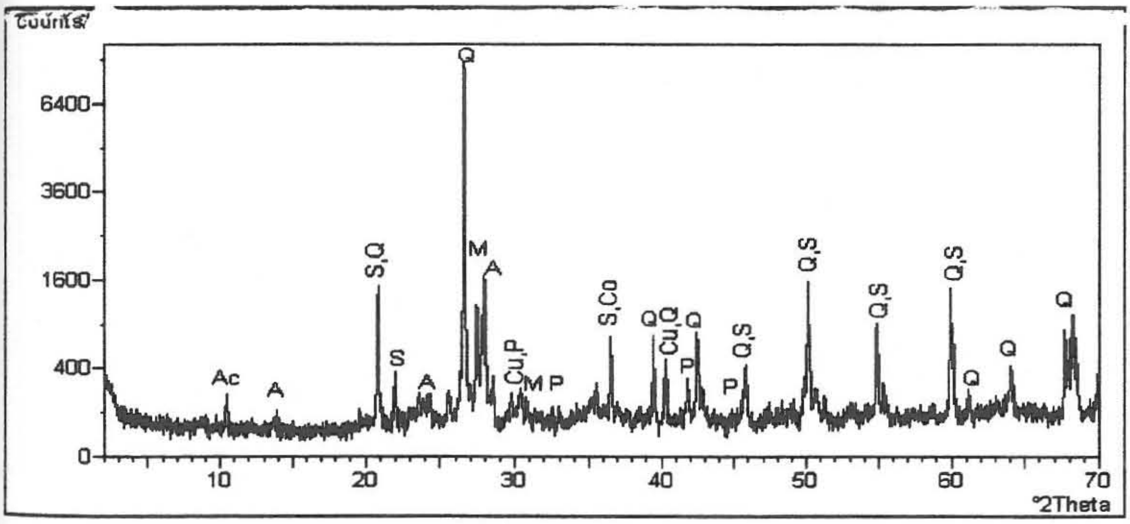

Figure 4.28: X-ray powder diffractogram of representative bulk soil sample obtained from site three (Ac is actinolite, A is albite, S is silicon sulphide, Q is quartz, M is microcline, Cu is cuprite, P is pyrrhotite and Co is cobalt oxide). Sample represented is S3A.

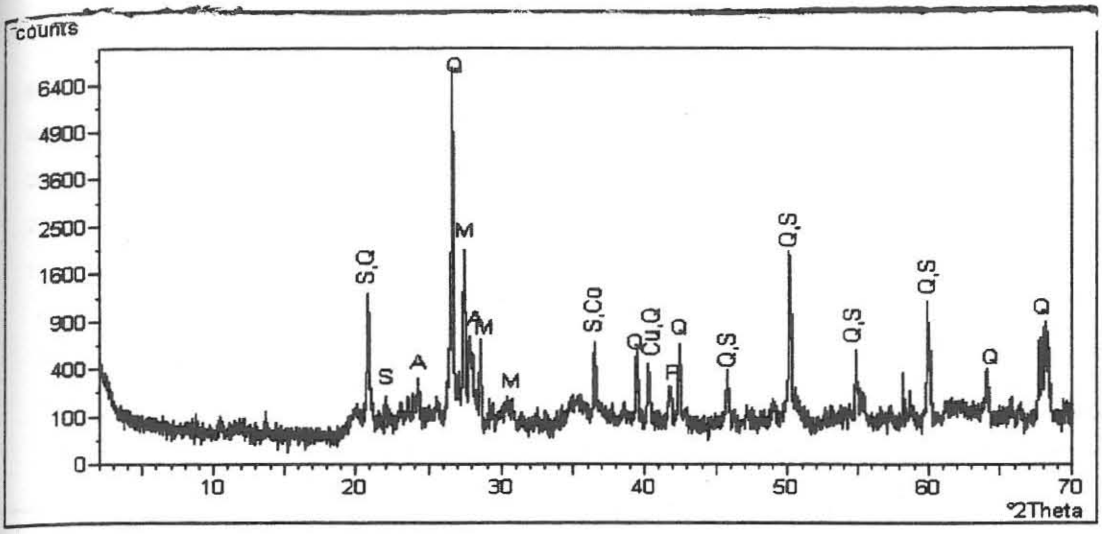

Figure 4.29: X-ray powder diffractogram of representative bulk soil sample obtained from site four (S is silicon sulphide, Q is quartz, A is albite, M is microcline, Co is cobalt oxide, Cu is cuprite and P is pyrrhotite). Sample represented is S4A.

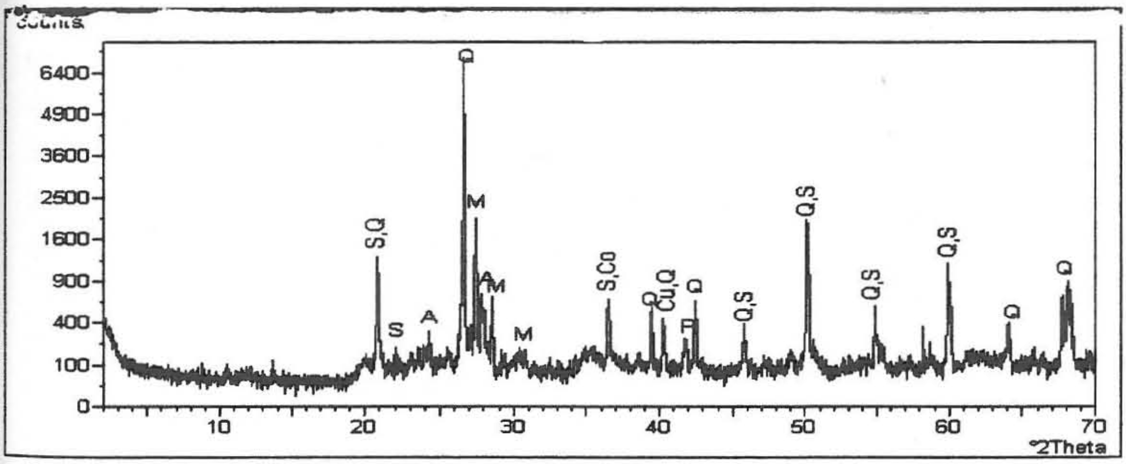

Figure 4.30: X-ray powder diffractogram of representative bulk soil sample obtained from site five (S is silicon sulphide, Q is quartz, A is albite, M is microcline, Co is cobalt oxide, Cu is cuprite and P is pyrrhotite). Sample represented is S5A.

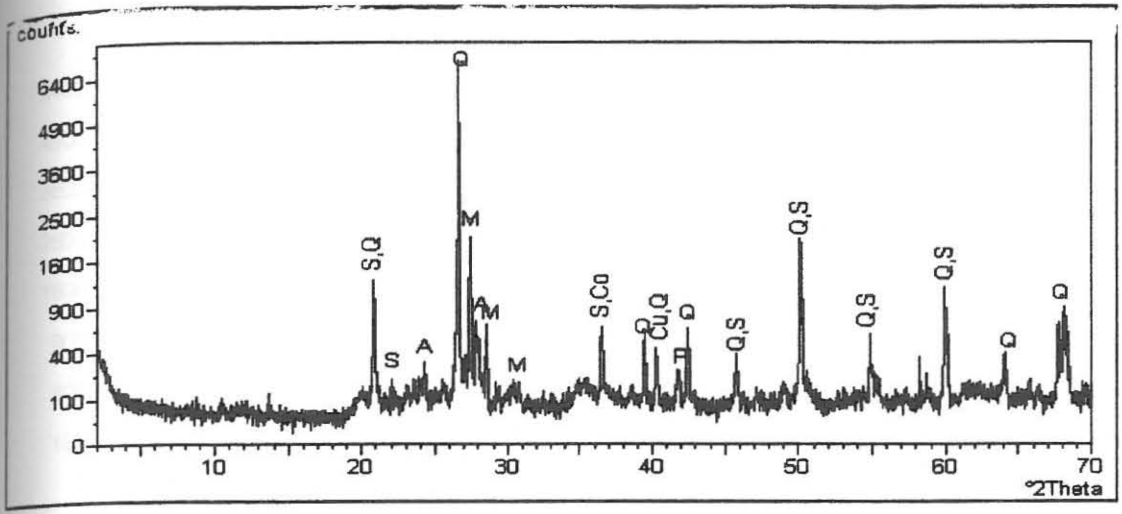

Figure 4.31: X-ray powder diffractogram of representative bulk soil sample obtained from site six (S is silicon sulphide, Q is quartz, A is albite, M is microcline, Co is cobalt oxide, Cu is cuprite and P is pyrrhotite). Sample represented is S6A.

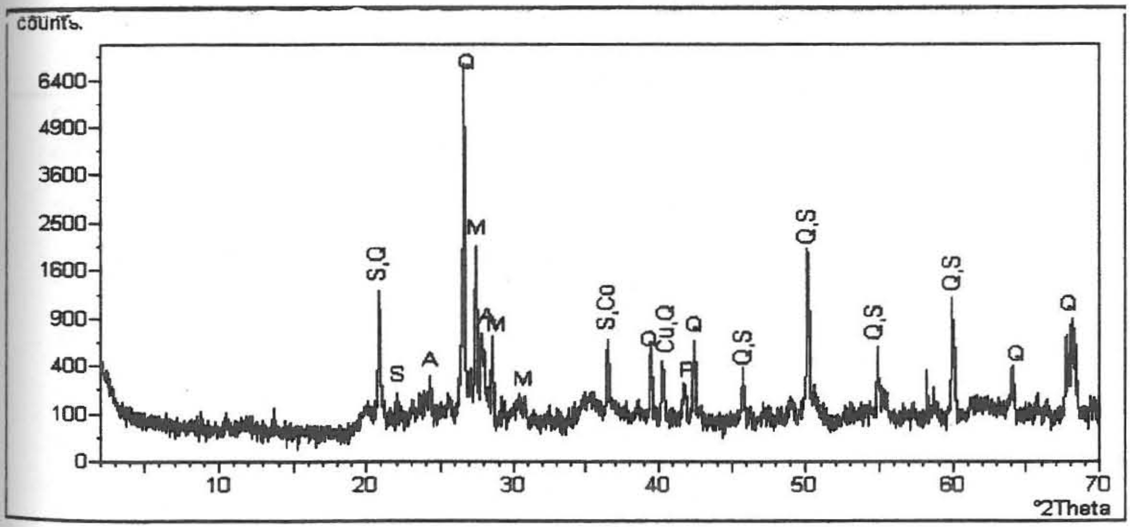

Figure 4.32: X-ray powder diffractogram of representative bulk soil sample obtained from site seven (S is silicon sulphide, Q is quartz, A is albite, M is microcline, Co is cobalt oxide, Cu is cuprite and P is pyrrhotite). Sample represented is S7A.

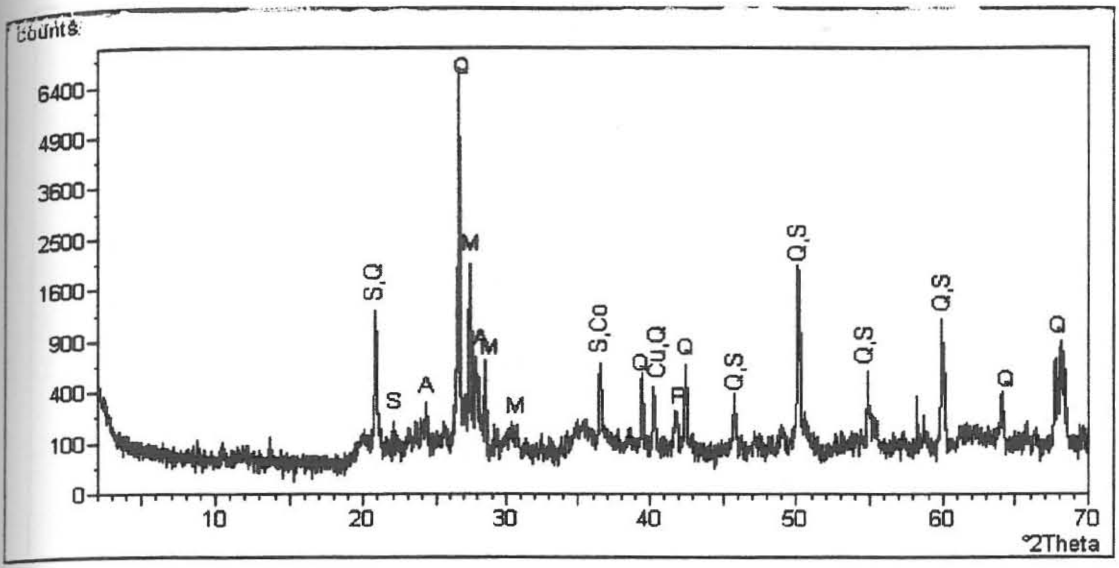

Figure 4.33: X-ray powder diffractogram of representative bulk soil sample obtained from site eight (S is silicon sulphide, Q is quartz, A is albite, M is microcline, Co is cobalt oxide, Cu is cuprite and P is pyrrhotite). Sample represented is S8A.

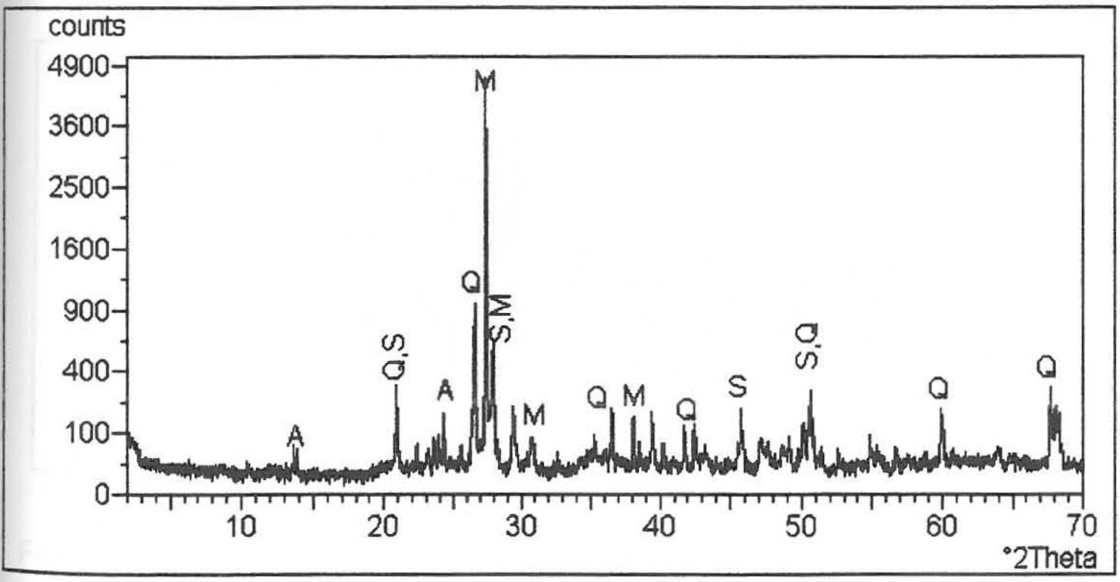

Figure 4.34: X-ray powder diffractogram of representative bulk soil sample obtained from site nine (A is albite, Q is quartz, S is silicon sulphide and M is microcline). Sample represented is S9E.

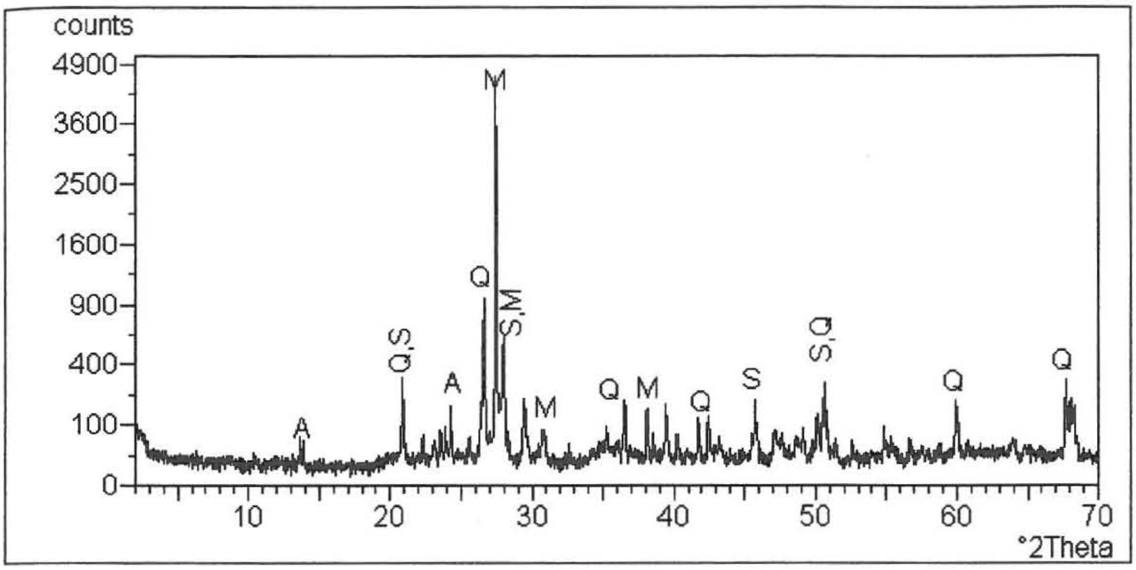

Figure 4.35: X-ray powder diffractogram of representative bulk soil sample obtained from site ten (A is albite, Q is quartz, S is silicon sulphide and M is microcline). Sample represented is S10E.

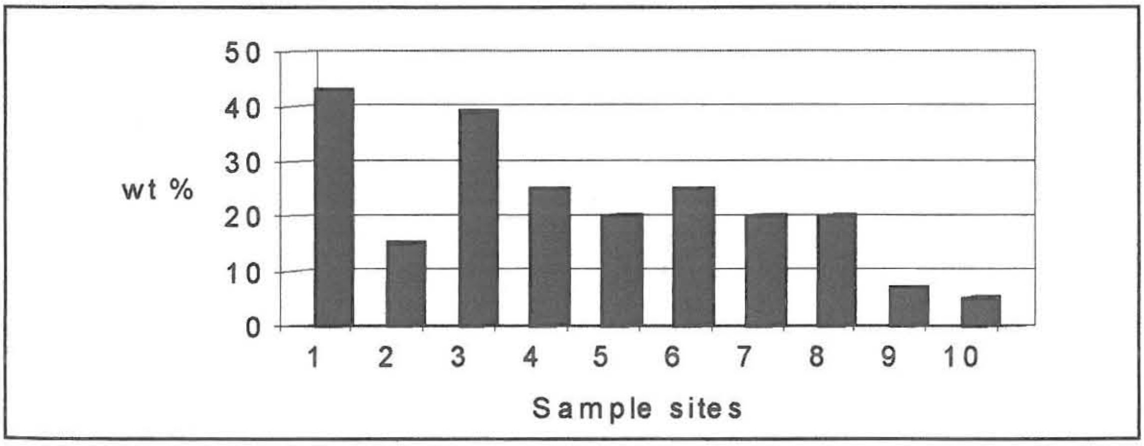

Figure 4.36: Mean cumulative weight percent distribution of the heavy minerals fraction of soil samples from the Selebi Phikwe study area.

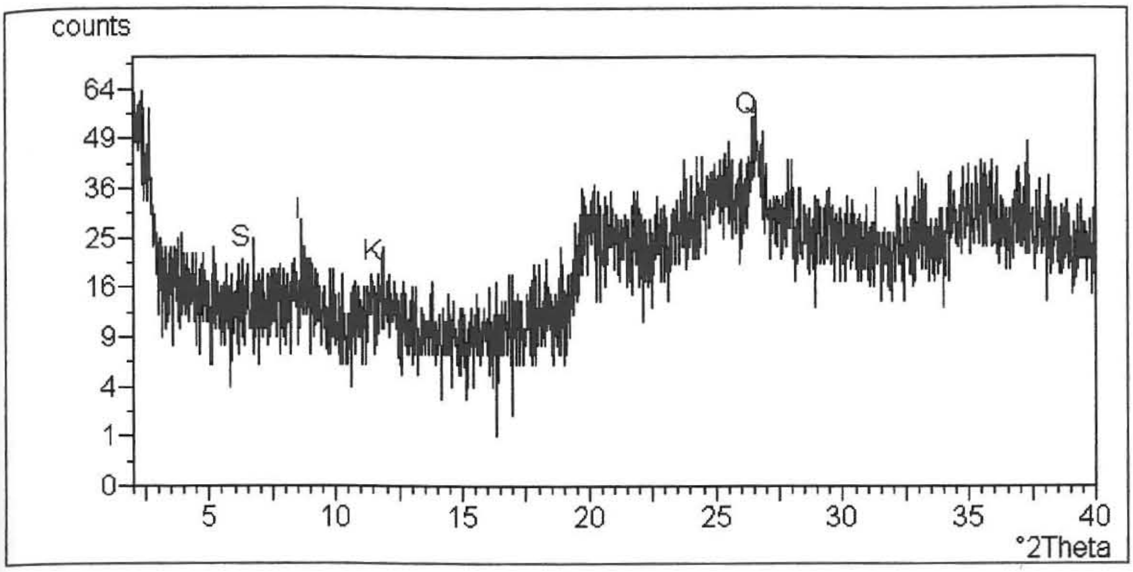

Figure 4.37: X-ray powder diffractogram of the < 2 μm fraction of representative soil sample from site one (S is smectite, I is illite, K is kaolinite, and Q is quartz).

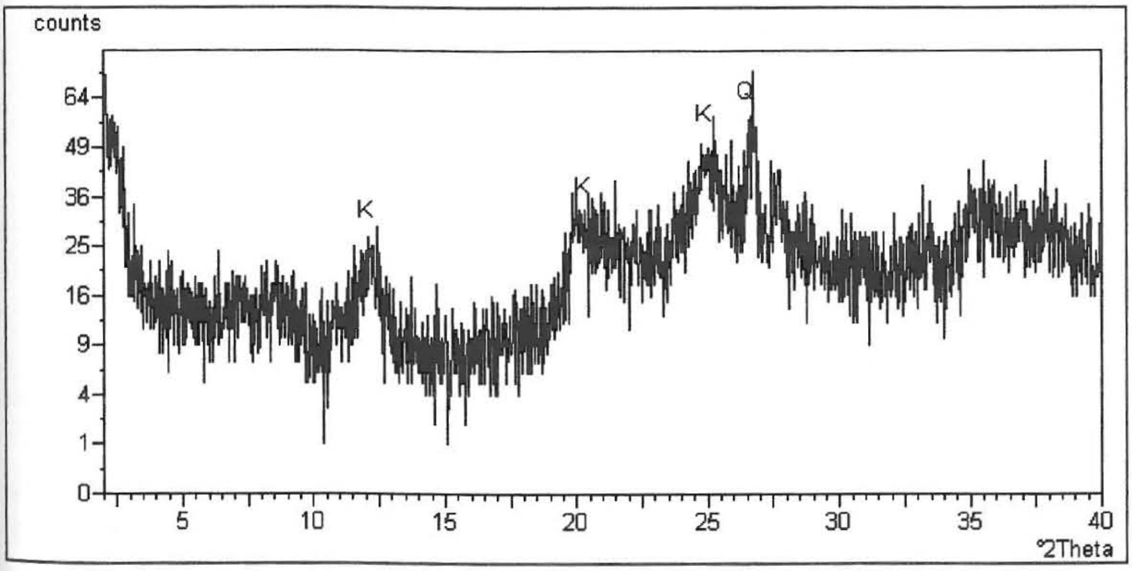

Figure 4.38: X-ray powder diffractogram of the < 2 μm fraction of representative soil sample from site two (K is kaolinite and Q is quartz).

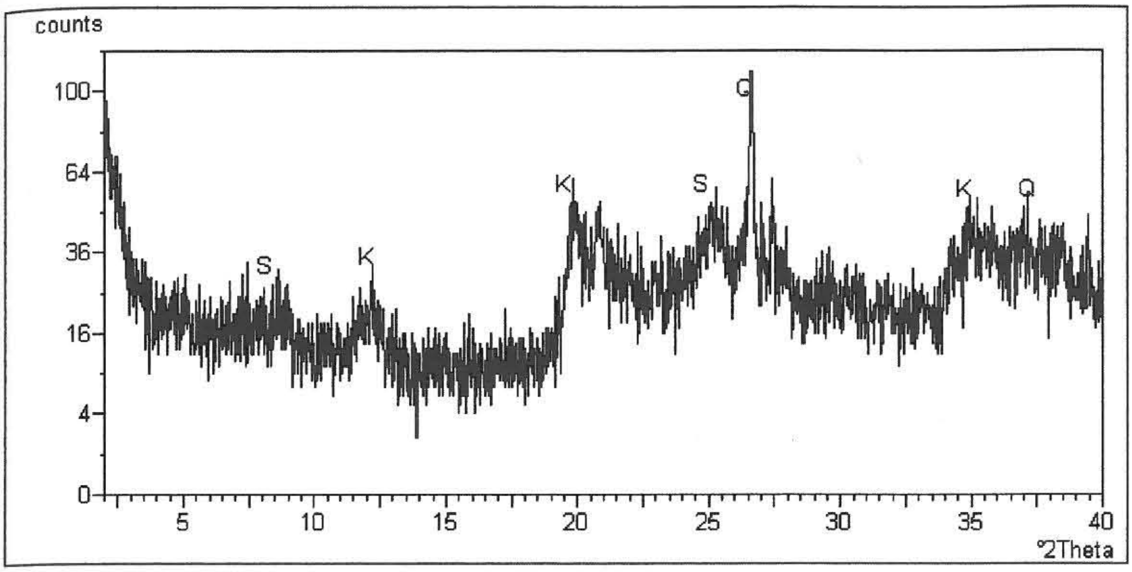

Figure 4.39: X-ray powder diffractogram of the < 2 μm fraction of representative soil sample from site three (S is smectite, K is kaolinite, and Q is quartz).

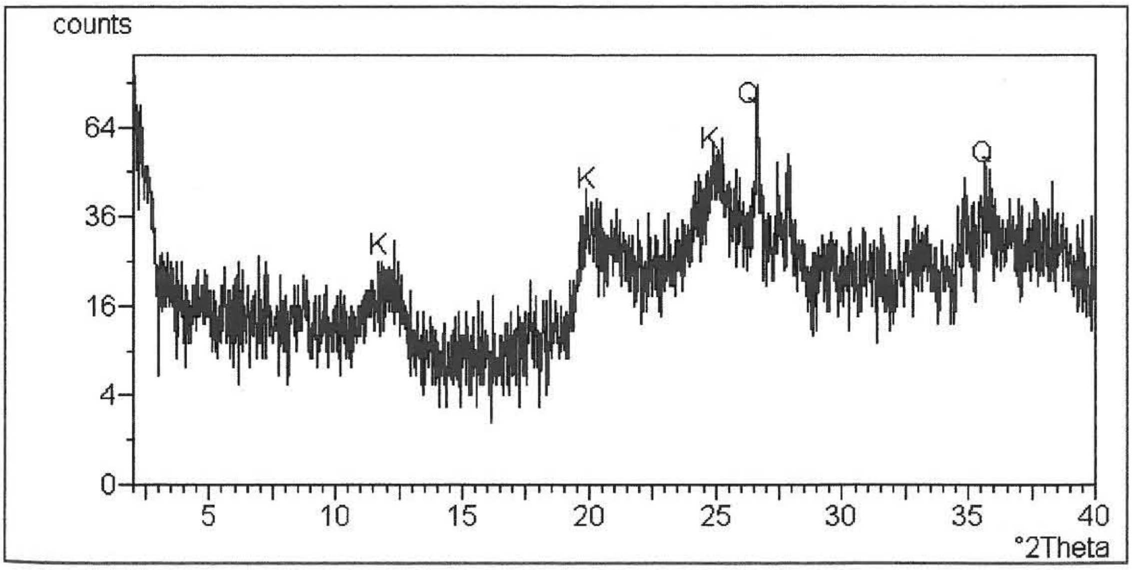

Figure 4.40: X-ray powder diffractogram of the < 2 μm fraction of representative soil sample from site four (K is kaolinite and Q is quartz).

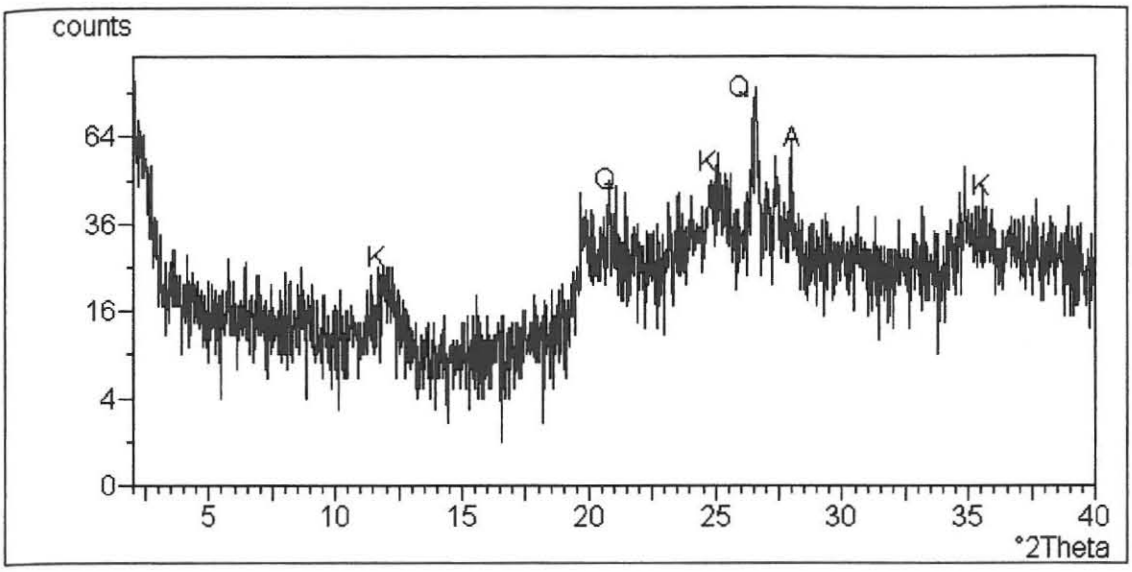

Figure 4.41: X-ray powder diffractogram of the < 2 μm fraction of representative soil sample from site five (K is kaolinite, A is anorthite, and Q is quartz).

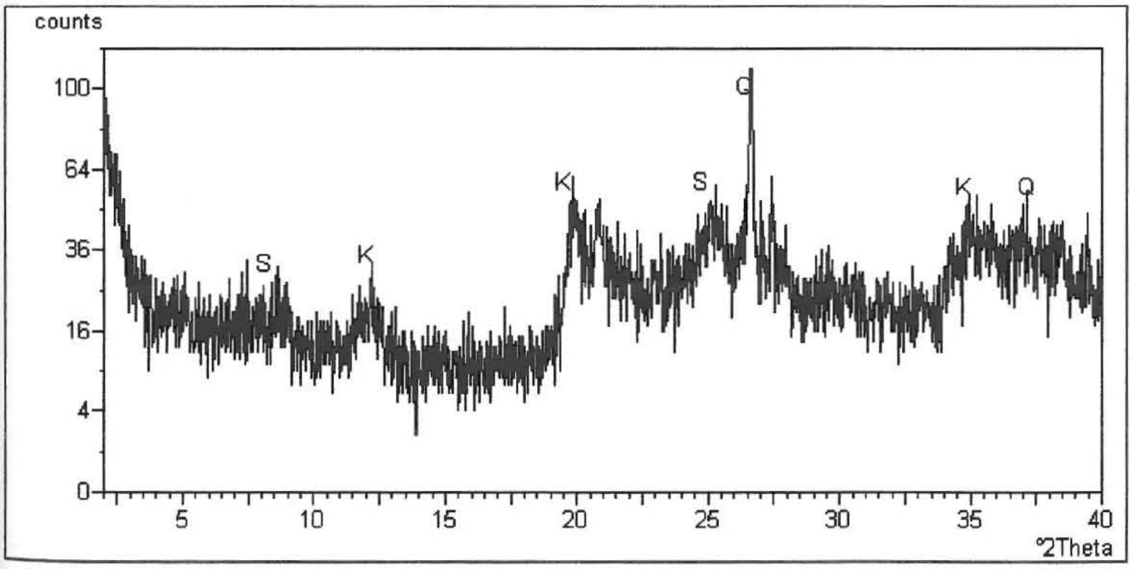

Figure 4.42: X-ray powder diffractogram of the < 2 μm fraction of representative soil sample from site six (S is smectite, K is kaolinite, and Q is quartz).

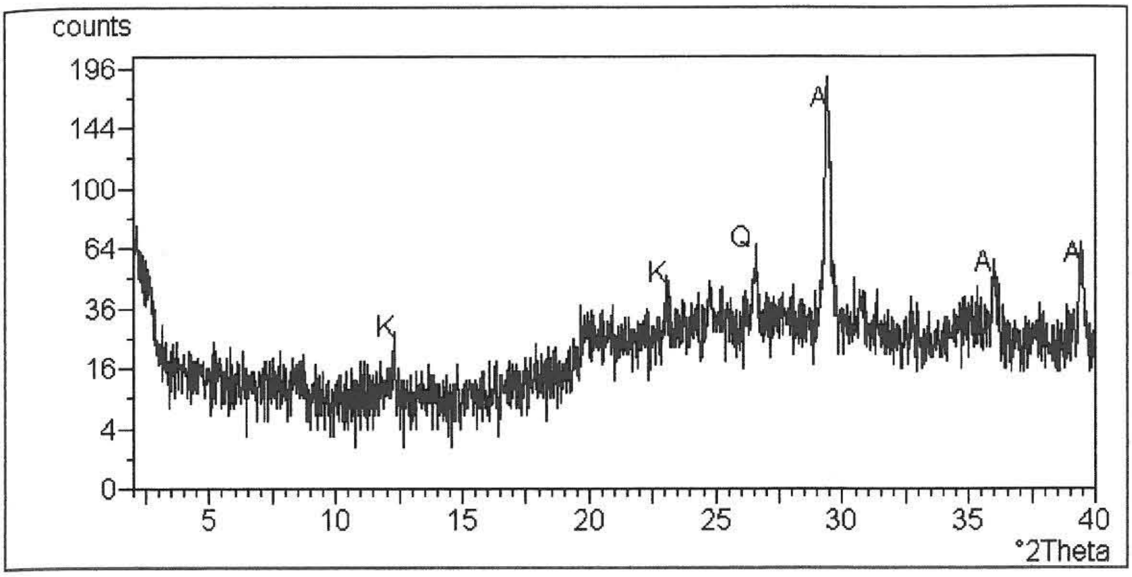

Figure 4.43: X-ray powder diffractogram of the < 2 μm fraction of representative soil sample from site seven (A is anorthite, K is kaolinite, and Q is quartz).

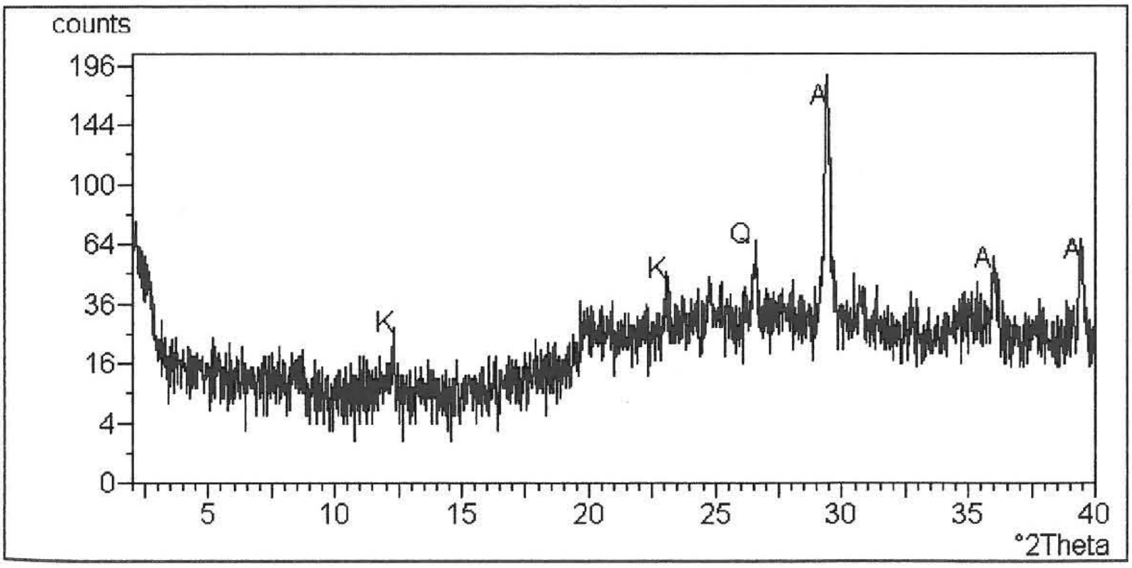

Figure 4.44: X-ray powder diffractogram of the < 2 μm fraction of representative soil sample from site eight (K is kaolinite, Q is quartz and A is anorthite).

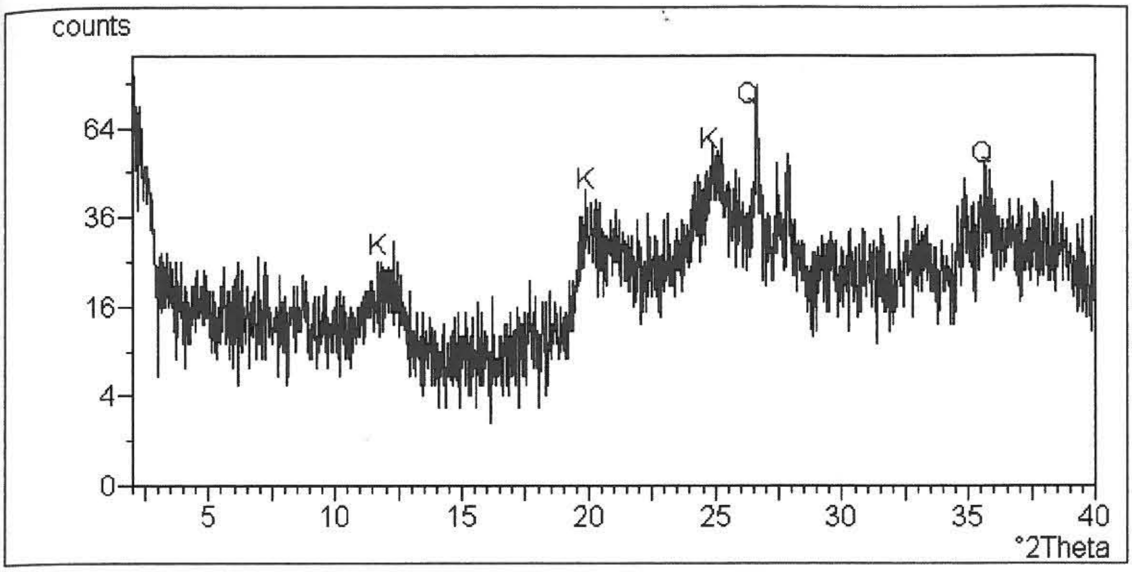

Figure 4.45: X-ray powder diffractogram of the < 2 μm fraction of representative soil sample from site nine (K is kaolinite, and Q is quartz).

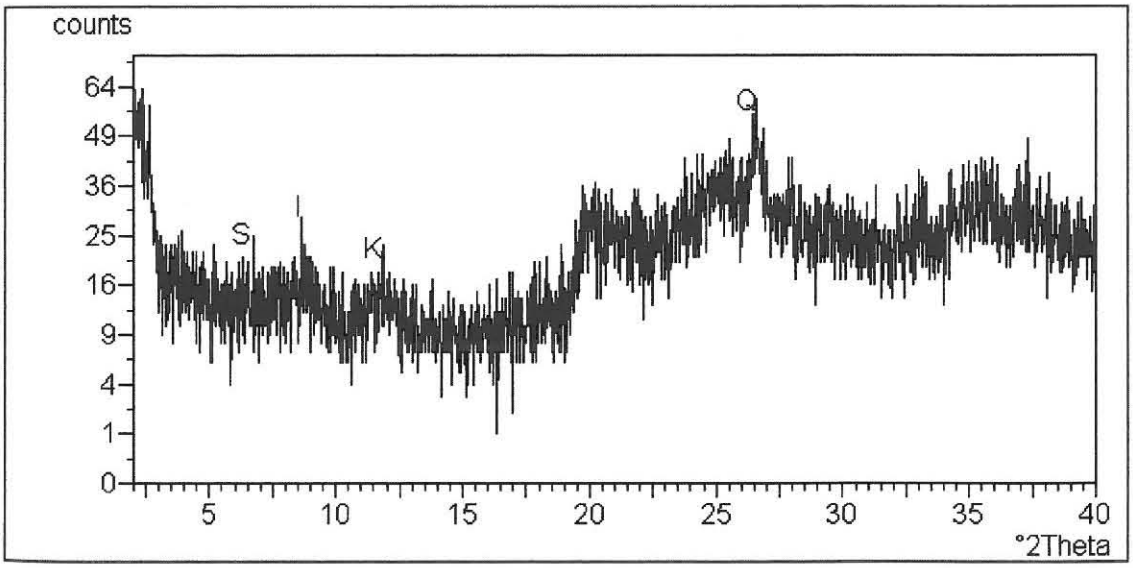

Figure 4.46: X-ray powder diffractogram of the < 2 μm fraction of representative soil sample from site ten (S is smectite, I is illite, K is kaolinite, and Q is quartz).

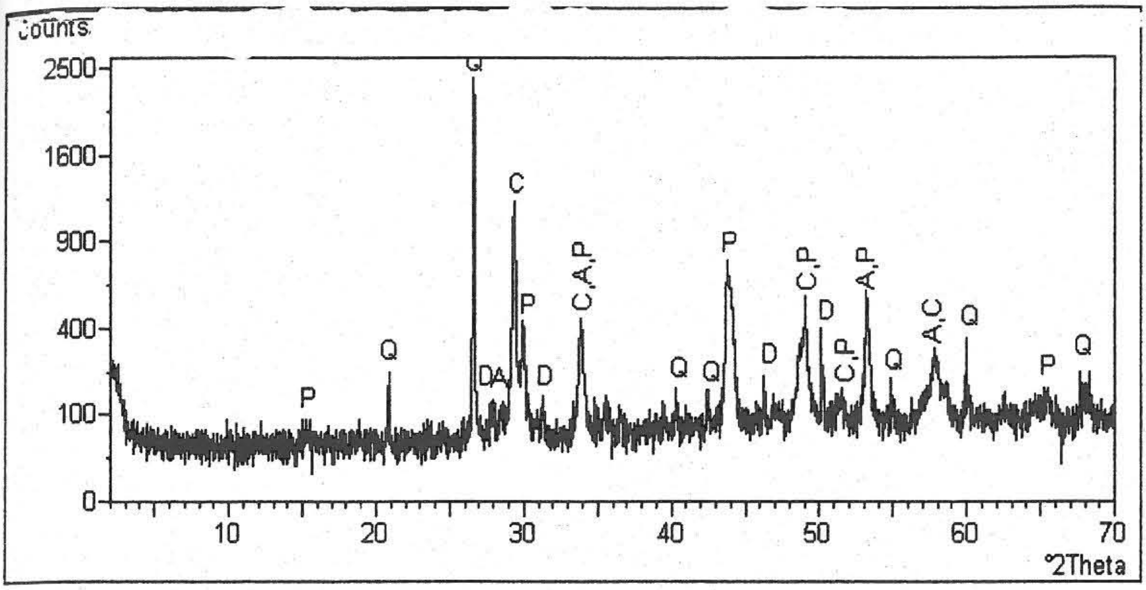

Figure 4.47: X-ray powder diffractogram of the representative composite particulate air matter sample (Q is quartz, P is pyrrhotite, C is chalcopyrite, A is albite and D is djurleite).

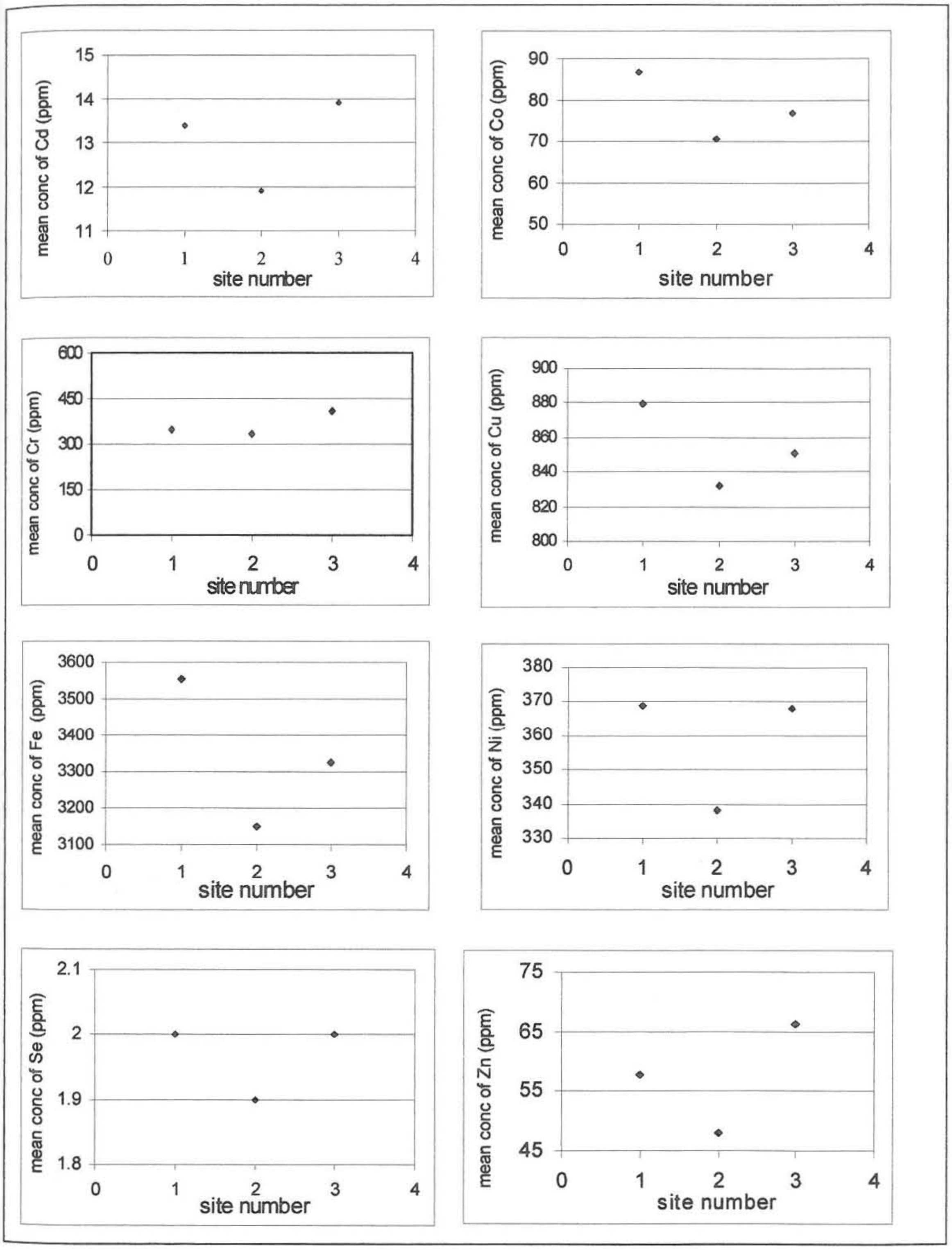

Figure 4.48: Mean concentrations of heavy metals in tailings dump around the Selebi Phikwe study area.

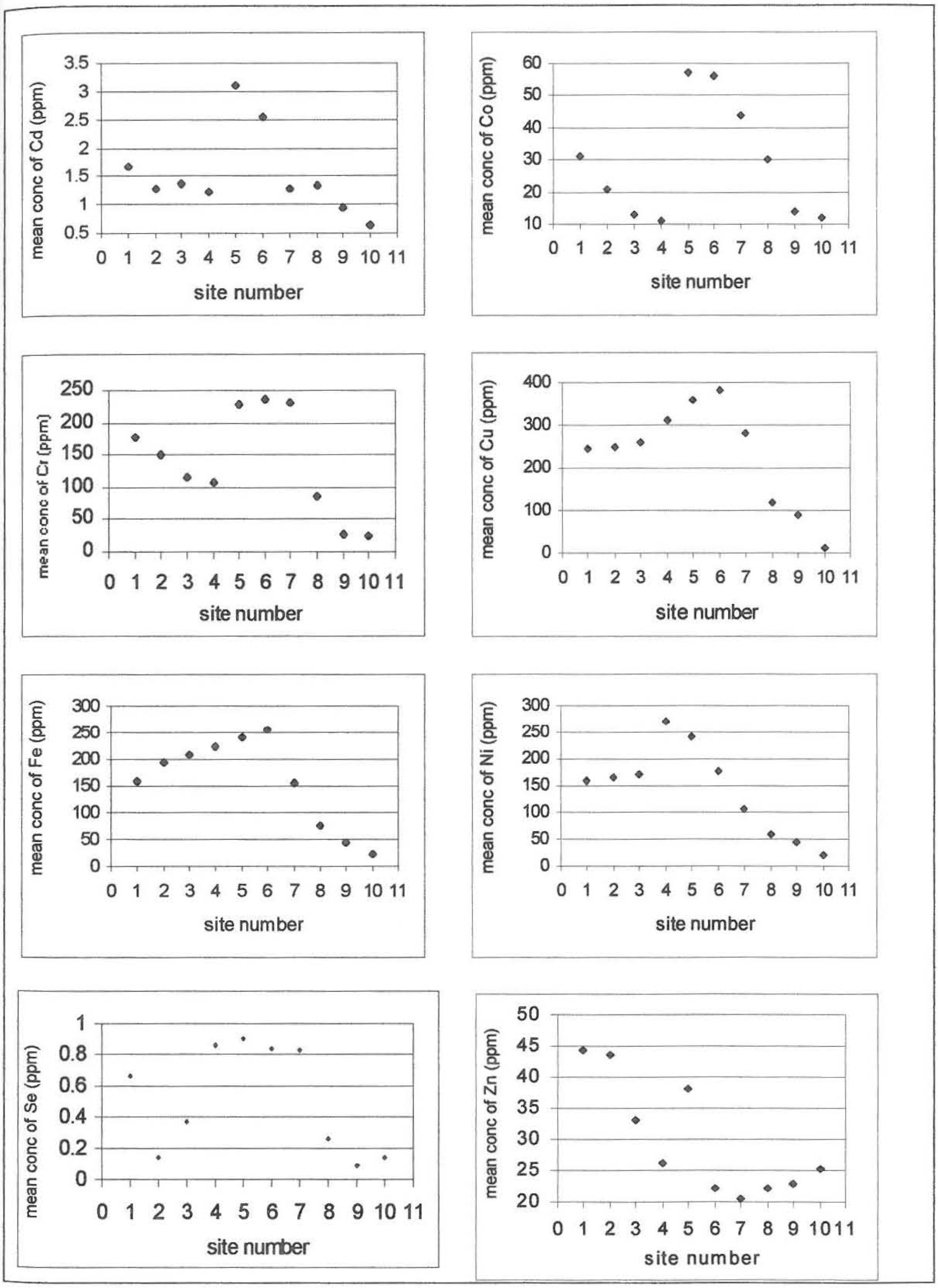

Figure 4.49: Mean concentrations of heavy metals in soil around the Selebi Phikwe study area.

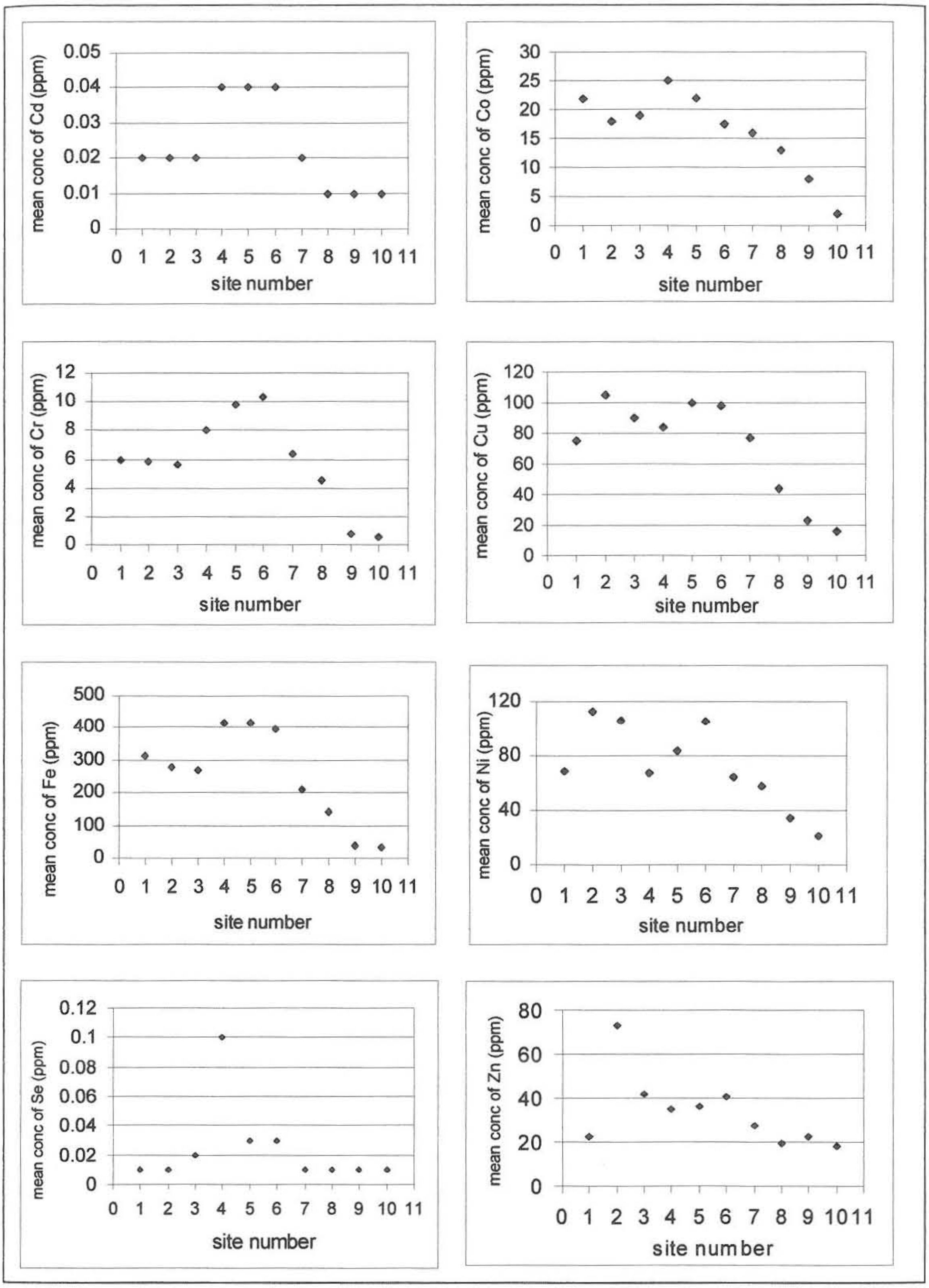

Figure 4.50: Mean concentrations of heavy metals in Mopane leaves around the Selebi Phikwe study area.

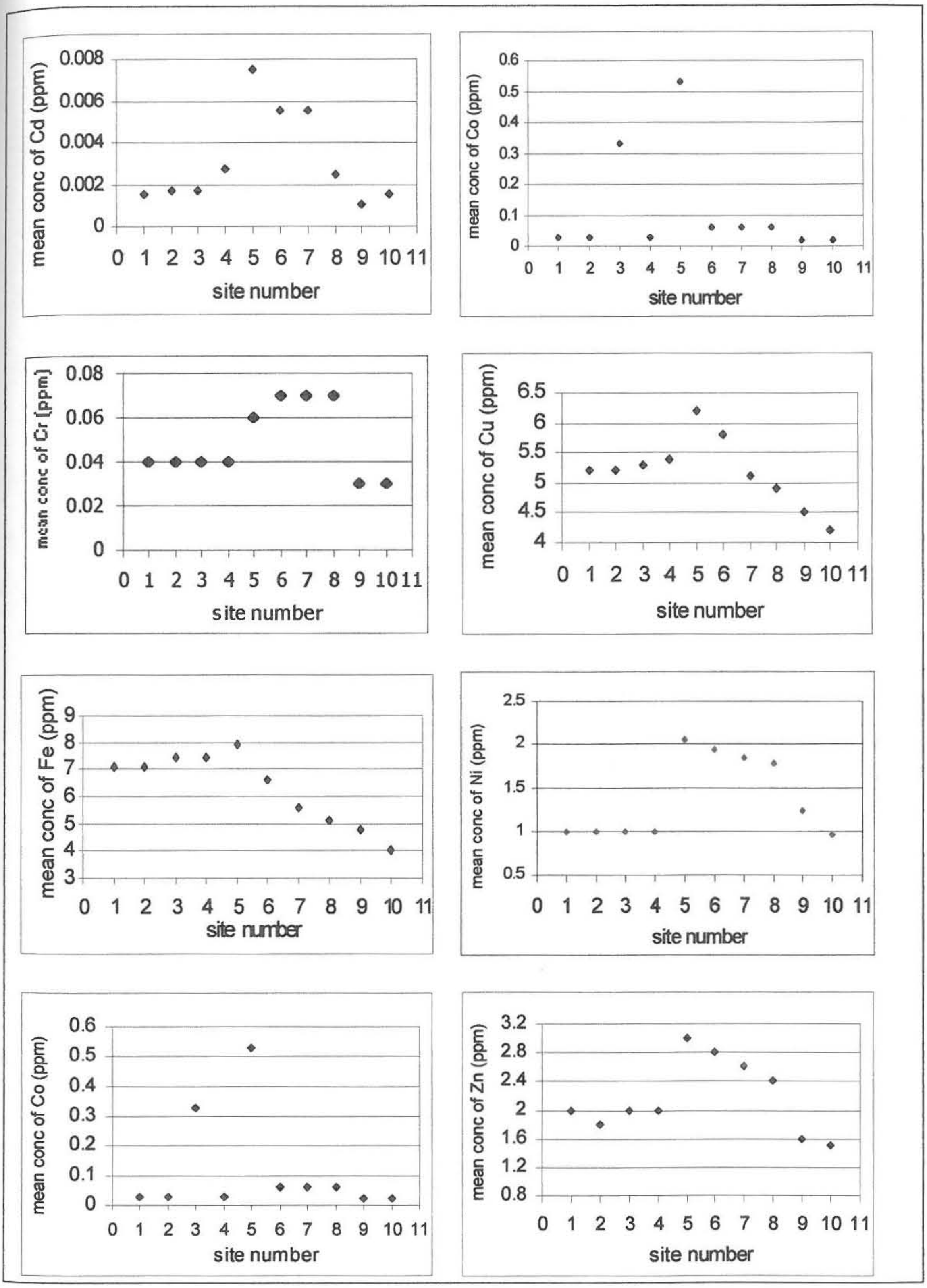

Figure 4.51: Mean concentrations of heavy metals in phane caterpillar around the Selebi Phikwe study area.

Table 4.1: Meteorological parameters recorded at Selebi Phikwe, near site two of study area.

Date of Sampling	Average ambient temperature (°C)	Wind speed (m/s)	Wind direction
January 15	25	2	ESE
January 29	27	4	ESE
February 12	25	3	ESE
February 26	28	3	ESE
March 11	23	4	ESE
March 25	22	2	ESE
April 15	20	2	ESE
April 29	22	3	ESE
May 13	18	4	SE
May 27	17	4	SE
June 10	16	5	SE
June 24	18	5	SE
July 15	14	6	SE
July 29	16	5	SE

Table 4.2: Types of analyses performed on various categories of samples obtained from the Selebi Phikwe Ni-Cu mine, and smelter and concentrator area.

Type of experiment	**Tailings dump**	**Soils**	**PAM**	**Mopane**	**Phane**
Physico-chemical tests					
PSD	∅	√	∅	∅	∅
CEC	∅	√	∅	∅	∅
PH	∅	√	∅	∅	∅
EC	∅	√	∅	∅	∅
Descriptive petrography	√	√	∅	∅	∅
Mineralogical	√	√	√	∅	∅
Chemical	√	√	√	√	√

Note: √ indicates analysis was performed and ∅ indicates analysis was not performed.

Table 4.3: Colour distribution pattern of representative soil samples from the sites of the Selebi Phikwe study area.

Site Number	Hue (YR)	Value/Chroma	Colour
1	7.5	5/8	Strong brown
2	5	¾	Dark reddish brown
3	10	6/3	Pale red
4	7.5	7/6	Reddish yellow
5	10	7/6	Yellow
6	10	8/3	Very pale brown
7	7	7/6	Reddish yellow
8	10	8/4	Very pale brown
9	10	¾	Dark reddish brown
10	10	3/1	Very dark gray

Table 4.4: Descriptive petrography of minerals contained in tailings dump from the Selebi Phikwe Ni-Cu orebodies.

Mineral	**Hardness (Mohr scale)**	**Cleavage**	**Fracture**	**Colour**	**Streak**	**Lustre**	**Crystal appearance**
Actinolite	5 - 6	Good	Uneven to subconchoid	Light to blackish green	White	Vitreous	Monoclinic
Albite	6 - 6.5	Distinct	Uneven	White to colourless	White	Vitreous to pearly	Triclinic
Cristobalite	7	None	Conchoidal	Colourless to gray	White	Vitreous	Tetragonal
Chalcopyrite	3.5 - 4	Poor	Uneven to conchoidal	Brassy yellow	Green to black	Metallic	Tetragonal
Malachite	3.5 - 4	Good	Uneven	Emerald green	Light green	Vitreous to silky	Monoclinic
Pyrite	6 - 6.5	None distinct	Conchoidal to uneven	Pale yellow	Green to black	Metallic	Cubic
Pyrrhotite	3.5 - 4.5	None	Uneven to subconchoidal	Bronze yellow	Dark gray to black	Metallic	Hexagonal
Tremolite	5 - 6	Good	Uneven to subconchoidal	Colourless white	White	Vitreous	Monoclinic
Pentlandite	3.5 - 4	None	Uneven to conchoidal	Light bronze yellow	Bronze to brown	Metallic	Isometric

Table 4.5: Correlation coefficients between heavy metals in the tailings dump.

	Cd	**Co**	**Cr**	**Cu**	**Fe**	**Ni**	**Se**	**Zn**
Cd	1							
Co	0.59	1						
Cr	0.84	0.05	1					
Cu	0.60	1.00	0.06	1				
Fe	0.63	1.00	0.11	0.84	1			
Ni	0.95	0.81	0.62	0.82	0.84	1		
Se	0.90	0.88	0.97	0.92	0.91	0.10	1	
Zn	0.98	0.43	0.93	0.44	0.48	0.87	0.80	1

Table 4.6: Correlation coefficients between heavy metals in soil.

	Cd	**Co**	**Cr**	**Cu**	**Fe**	**Ni**	**Se**	**Zn**
Cd	1							
Co	0.85	1						
Cr	0.78	0.85	1					
Cu	0.77	0.48	0.87	1				
Fe	0.09	0.47	0.77	0.97	1			
Ni	0.61	0.25	-0.14	0.87	0.87	1		
Se	0.60	0.58	0.65	0.75	0.66	0.46	1	
Zn	0.26	-0.20	0.24	0.26	0.36	0.42	-0.28	1

Table 4.7: Concentrations of heavy metals contained in particulate air matter.

Element	Concentration in ppm
Cd	0.03
Co	12
Cr	19
Cu	87
Fe	91
Ni	41
Se	0.01
Zn	4

Table 4.8: Correlation coefficients between heavy metals in the leaves of mopane plants.

	Cd	**Co**	**Cr**	**Cu**	**Fe**	**Ni**	**Se**	**Zn**
Cd	1							
Co	0.68	1						
Cr	0.90	0.78	1					
Cu	0.71	0.82	0.85	1				
Fe	0.92	0.88	0.94	0.88	1			
Ni	0.45	0.66	0.72	0.93	0.72	1		
Se	0.68	0.26	0.67	0.49	0.58	0.53	1	
Zn	0.3	0.40	0.39	0.74	0.63	0.81	0.10	1

Table 4.9: Correlation coefficients between normalised heavy metals in the phane caterpillars.

	Cd	**Co**	**Cr**	**Cu**	**Fe**	**Ni**	**Se**	**Zn**
Cd	1							
Co	0.54	1						
Cr	0.51	0.33	1					
Cu	0.66	0.63	0.54	1				
Fe	0.17	0.54	0.11	0.85	1			
Ni	0.65	0.38	0.89	0.53	003	1		
Se	0.67	0.84	0.68	0.61	0.60	0.51	1	
Zn	0.64	0.50	0.87	0.81	0.40	0.92	0.58	1

Chapter 5

Discussion

5.1 Problem statement

This study has focused on appraising the physical environmental quality at Selebi Phikwe. Mining and smelting activities at Selebi Phikwe have the tendency of introducing contaminants into the physical environment. Previous studies carried out by Nkoma and Ekosse (1999; 2000) identified and characterised the sulphide minerals at Selebi Phikwe but did not link the findings to the physical environment.

Research efforts in this study attempted to answer questions posed in the introductory chapter (section 1.2). The results obtained were examined contextually in order to ascertain whether mining and smelting activities had affected the quality of the physical environment. Discussions concentrated on analysing results obtained for tailings dump, soils, PAM, mopane leaves and phane caterpillar in the light of prevailing circumstances at Selebi Phikwe.

5.2 General field observations

Figure 5.1 is a schematic diagram explaining the processes and relationships of the environmental constituents taking place at Selebi Phikwe. Orebodies rich in Ni-Cu minerals are mined. In the process of mining and transporting the orebodies to the smelter/concentrator plant, dust particles are released into the atmosphere and water erosion also occurs.

The tailings dump, the principal waste from the concentration and smelting processes is dumped at a site close to the plant, and the mount has continued to build up. Through leaching and other related chemical processes, ions are released to the soil. The ion-rich soils provide a milieu for plants including mopane to become enriched in heavy metals through uptake. The phane worms feed from the contaminated leaves, and man in turn ingests the worms.

5.2.1 Tailings dump

Only one mount of tailings dump was present at Selebi Phikwe Ni-Cu smelter/concentrator plant. When asked why there was only one mount for tailings dump, the Environmental Engineer (Modisanyane, 1997) said it was easier to contain waste and limit transportation of contaminants from the mount to the environment. The grains of tailings dump observed at Selebi Phikwe were subangular, depicting limited transportation from source (Bain *et al.*, 1995), and also indicative of less aggressive leaching activities taking place (Singh *et al.*, 1999).

Mineral ore bodies and tailings dump release particles to the atmosphere through convectional forces with wind energy as vector agent (Buseck and Posfai, 1999).

Smelting processes release gases. Most significant are wastes released from tailings dump into the soils, which eventually influence the concentrations of heavy metals (Kozák *et al.*, 1995) contained in living organisms. Due to the fact that tailings dump are main sources of AMD (Galan *et al.*, 1999), adequate control measures are necessary in limiting the spread of contaminants in the surrounding environments. The steps obviously taken by the BCL authorities in containing their tailings dump are in conformity to basic principles of environmental management of tailings dump as referred to by Galan *et al.* (1999), and Jambor and Bowles (1998).

5.2.2 Soils

The colour of soils as observed in Table 4.3 is indicative of Fe contents in soils (Dixon, 1989). The soil texture revealed kaolinite content (Weaver, 1989), and this was confirmed by XRPD results obtained for the < 2 μm fraction at most of the sites. The field observations at Selebi Phikwe study area showed that whitish grey sediments in some soils was due to precipitation from saturated ions of dissolved salts rich in heavy metals (Robertson *et al.*, 1997; and Shaw *et al.*, 1998). In these environments, the soils were deprived of vegetation cover and dead zones formed.

5.2.3 Particulate air matter

The atmosphere at Selebi Phikwe was generally clear, and this might partly explain why very low wt % of PAM was obtained using the air samplers during the study. The sampling of PAM may only be effectively carried out if the pumps and batteries are working properly, and the environment is found to be particle-contaminated. Unfortunately, PAM of environmental concern generally has a size fraction of $< 2\ \mu m$ (USA–EPA, 1995). The particles having this size are not visible with the naked human eye. At the Selebi Phikwe, on most of the sampling days, pungent odour of gases hovered in the atmosphere, specifically on sites one, two, three and eight. The smell was characteristic of H_2S and SO_2.

5.2.4 Mopane plant

At sites five and six, of the Selebi Phikwe study area, the *Colophospermum mopane* (mopane tree) and *Imbrasia belina* (phane caterpillar) were stunted. It might be that their growth patterns were influenced by high concentrations of heavy metals in their organic systems (Traina and Laperche, 1999). Whereby soil acidity increases, plants are adversely affected.

5.2.5 Phane caterpillar

Small phane worms were not harvested for consumption. It was suggested that the reason why the smaller phanes were not harvested be because they taste very bitter; this statement could however not be substantiated.

5.3 Sampling

The sampling techniques used for the collection of tailings dump and soil samples were the most appropriate for this type of study (Kralik, 1999). Problems of unusual heavy rainfall, apparently clean atmosphere with very good visibility due to rainfall, low pump pressure and low charge of Ni batteries affected the sampling of PAM. Seasonal variation affected the availability of living phane worms. Consequently, they were not sampled during all the field visits. Leaves obtained were green to dark green in colour. Discoloured leaves were not sampled for laboratory analyses.

5.4 Meteorological aspects

In the mornings, during sampling days, the temperatures were low and created a conducive environment for fieldwork. The wind speed was also appropriate in the mornings and during the day. Annual Report from the Department of Mines (1998) indicate that winds prevail from the North-East 40 % of the time. Prevailing winds carry PAM and at times affect certain parts of plants as shown in Figure 4.6. The velocity of the prevailing winds during sampling periods was low, consequently reflected in very low concentrations of PAM which was sampled.

5.5 Analytical results

5.5.1 Petrographic aspects

5.5.1.1 Colour

Soil colour varied from pale yellow, reddish yellow to dark reddish brown. The soil colour reflects Fe content which is contained in pyrite and pyrrhotite (Nkoma and Ekosse, 1999). Colour variation is an influence of variation in mineral and chemical compositions of the soil (Tan, 1996). The remaining aggregates used during road construction were not removed from the area. The weathering of these aggregates may also have influenced soil colour at the control site.

5.5.1.2 Granulometric analyses

The PSD of soil samples revealed the < 2 μm fraction (clay fraction) to be in the range of 3 wt % and 9 wt %, the > 2 μm to < 50 μm fraction (silt fraction) was between 34 wt % and 44 wt %, and the > 50 μm to < 250 μm fraction (sand fraction) was between 47 wt % and 63 wt %. This observed uniformity of particle size distribution created equal opportunity for ions of heavy metals to migrate and to adhere to the clay fraction; thereby promoted similar soil contamination trends. Distance of source of contaminants may have played a major role at determining the quantitative aspects of the contaminants in the soil.

5.5.1.3 Descriptive petrography

Hand specimens viewed with a microscope and physical tests performed on the samples for hardness, cleavage, fracture, colour, streak, lustre, and crystal appearance depicted albite, cristobalite, chalcopyrite, pyrrhotite, tremolite, and pentlandite in the samples. Grains were poorly sorted, with subangular grains located further from the plant, which is indicative of windblown particles transported at a short distance (Ringrose *et al.*, 1995).

5.5.2 Physico-chemical aspects

5.5.2.1 Soil pH

Soil pH ranged from 3.5 to 6.0 (Figure 4.20) with very acidic soils located close to the smelter/concentrator plant. The low pH values at these sites (three, four, five and six), could be attributed to their closeness to the smelter/concentrator plant, the tailings pond and the tailings dump where water concentrations of SO_4^{2-}, Cd, Co, Cr, Cu, Fe^{2+}, Ni, Se, and Zn as mentioned by Bowles *et. al*, (1992), remain very high. Very high concentrations of Fe^{2+} and SO_4^{2-} increase acidity in the environment, and there is the tendency of acid expansion due to probable depletion of the acid-neutralising capacity of the soils (Shaw *et al.*, 1998). Eventually, the pH values at sites seven, eight, nine and ten could drop as the surrounding soil acidity increases within the environment.

The high acidity could favour the leaching of heavy ions from the tailings dump and related mining waste to the soils. High acidity of soils is reflected by on-going acid mine drainage (AMD) activity which is depicted by the formation areas referred to as dead zones. A similar phenomenon occurred at the Ni mine area, near Sudbury, Ontario, Canada (Hanton-Fong *et al.*, 1997).

The low soil pH, furthermore, could promote the leaching and precipitation of ions including those of heavy metals namely Cd, Co, Cr, Cu, Fe, Ni, Se and Zn. The pyrrhotite (Fe_7S_8-FeS) and pyrite (FeS_2) in the tailings dump are oxidised on exposure to water to form sulphate and sulphuric acid (Holmström and Öhlander ,1999; and Holmström *et al.*, 1999).

5.5.2.2 Electrical conductivity of soil

The EC values obtained were significantly low, and ranged from 50 μS/cm to 250 μS/cm (Figure 4.21). Soils with low pH correspondingly had low EC. Total dissolved salts may not be reflected in the soil pH because salts are neutral. Dissolved salts of SO_4^{2-}, CO_3^{2-}, Cl^-, NO_3^- and PO_4^{2-}, which may be present in solution, are contributory to high EC values (Murray, 1986), at certain localities within the study area. The ions of the heavy metals of Cd, Co, Cr, Cu, Fe, Ni, Se, and Zn constituted the anionic portion of the salts.

5.5.2.3 Soil cation exchange capacity

The CEC values for soil samples obtained were between 2 meq/100g and meq/100g (Figure 4.22). These values are typical for kaolin minerals intercalated with smectites in soils (Dixon, 1989). Samples with high EC also contained illite. Finer clayey particles tend to adsorb heavy ions of elements on their surfaces as demonstrated by Song *et al.* (1999). In the soil samples, fewer exchange sites resulted in a low CEC for ions adsorbed on the sediment surfaces, consequently they remained in solution and are bioavailabe for plant uptake.

Values obtained for CEC at the study area reflected cation exchange sites for ions of heavy metals to either have been adsorbed on the surface of clay mineral structure, or absorbed by isomorphous substitution. Whereby heavy metal ions are either adhered on or absorbed into the clay mineral structure, the soils were contaminated with the corresponding heavy metals, and eventually got polluted.

5.5.3 Mineralogical aspects

5.5.3.1 Tailings dump

The tailings dump comprised nickelbloedite, $Na_2(Ni(SO_4)_2.4H_2O$; pyrrhotite, quartz, pentlandite, $(Fe,Ni)_9S_8$; malachite,$Cu_2CO_3(OH)_2$; chalcopyrite, actinolite, $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$; cristobalite, SiO_2; tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$; kaolinite, $Al_2Si_2O_5(OH)_4$; mica and albite as shown in Figure 5.2. Bulk soil samples consisted of actinolite, albite, quartz, microcline, $KAlSi_3O_8$; pyrrhotite, silicon sulphide and cobalt oxide, whereas the < 2 μm fraction is made of kaolinite, illite, $KAl_2(Si_3AlO_{10})(OH)_2$; smectite, $Na_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.xH_2O$; anorthite, $CaAl_2Si_2O_8$ and quartz.

Similar mineralogical trends have been observed by other researchers at other mining sites including Al and Bowles (1999); Al *et al.* (1994) and Benner *et al* .(1999). The tailings contained metals as well as pyrite and other sulphur minerals. These could, when associated with other weathering products, dissolve and could be washed away both vertically and horizontally into soils. The slopes of the tailings dump served as migratory pathways for ions of SO_4^{2-}, CO_3^{2-}, Cl^-, NO_3^-, PO_4^{2-}, Cd, Co, Cr, Cu, Fe, Ni, Se, and Zn to have been leached through labile corridors to the subsurface environments where applicable.

5.5.3.2 Soils

The Selebi Phikwe soils were secondarily enriched by heavy metals concentrations as a result of a number of geochemical and mineralogical processes taking place which were similar to those occurring in the tailings dump, resulting from the mining and smelting activities. High acidity in soils could be attributed to bacterially catalysed oxidation of pyrite (FeS_2) and chalcopyrite ($CuFeS_2$), leading to the dissolution of many other sulphide minerals (Bowles *et. al.*, 1992).

Dissolved heavy metals have the tendency of contaminating the surrounding soils mainly by oxidation (De Vos *et. al.*, 1995). Oxidisable heavy metals are associated with mineral sulphides. Sulphide -oxidation reactions from pyrrhotite oxidation are as follows, according to Benner *et al.* (1999) and Bowles and Jambor (1994):

$$Fe_{(1-x)}S + 2O_2 \rightarrow (1-x)\ Fe^{2+} + SO_4^{2-} \qquad \text{(equation 5.1)}$$

The Fe^{2+} shown in equation 5.1 is further oxidised to Fe^{3+} as follows:

$$4Fe^{2+} + O_2 + 4H^+ \rightleftharpoons 4Fe^{3+} + 2H_2O \qquad \text{(equation 5.2)}$$

Further oxidation and hydrolysis of pyrrhotite results in goethite precipitation as indicated in the equations of reaction below:

$$Fe_{(1-x)}S + (8-2x)\ Fe^{3+} + 4H_2O \rightleftharpoons (9-3x)\ Fe^{2+} + SO_4^{2-} + 8H^+ \qquad \text{(equation 5.3)}$$

$$Fe_{(1-x)}S + (2-2x)\ Fe^{3+} \rightleftharpoons (3-3x)\ Fe^{2+} + S \qquad \text{(equation 5.4)}$$

$$4Fe^{3+} + O_2 + 6\ H_2O \rightleftharpoons 4FeOOH + 8H^+ \qquad \text{(equation 5.5)}$$

At the Selebi Phikwe area, both nickelblodite and malachite occurred as secondary minerals, which could have been formed from primary ore minerals such as pentlandite, chalcopyrite and pyrrhotite under room temperature and in an acidic environment.

The clay minerals may have been formed from the alteration of feldspars and micas contained in the country rocks. Soils rich in clay minerals created competitive exchange sites for both plant nutrients and heavy metals, released from mining activities.

5.5.3.3. Particulate air matter

The PAM consisted of quartz, SiO_2; pyrrhotite, $Fe_{1-x}S$; chalcopyrite, $CuFeS_2$; albite, $NaAlSi_3O_8$; and djurleite, $Cu_{31}S_{16}$. Djurleite polymorphs ($Cu_{31}S_{16}$ and $Cu_{1.93}S$) were formed from secondary mineralisation of chalcopyrite and the SO_2 released from concentration/smelting processes. Djurleite could not be detected in soil samples possibly because it may have been easily altered to pyrrhotite as a result of excess Fe ions in solution.

The minerals reflected by the XRPD could not be the only minerals present in the atmosphere as a result of the mining and smelting of Ni-Cu orebodies. It is possible for PAM to have consisted of other mineral phases such as pentlandite, actinolite and tremolite but they were not demonstrated because of detection limit of the instrument.

Djurleite polymorphs $Cu_{31}S_{16}$ and $Cu_{1.93}S$ are closely related to chalcocite polymorphs Cu_2S and $Cu_{1.96}S$. Its formation could possibly have been as a reaction of SO_2 gas with the Cu minerals such as chalcopyrite.

5.5.4 Chemical aspects

5.5.4.1 Tailings dump

The low values obtained for heavy metals at the centre of the dump (see 4.3.4.1) suggested leaching of ions occurring more vigorously, and high concentration values at the sides was as a result of enrichment of ions which were displaced from the top of the dump. In the tailings dump and soils the mobility of the ions depended on the pH, which in turn was controlled by precipitation, dissolution, solid-solution substitution, and adsorption/desorption reactions (Coggans *et al.*, 1999). The relative mobilities of the heavy metals were as follows: Fe = Ni = Co > Cu.

The high concentration levels of heavy ions in the tailings dump were indicative of the mount being a major source for the introduction of contaminants into the physical environment. Bertsch and Seaman (1999), Bowles and Jambor (1990), Bowles *et al.* (1992) Bowles *et al.* (1995), and De Vos *et al.* (1995) have demonstrated that the tailings dump of sulphide mines promote AMD and introduce heavy metals into the environment.

5.5.4.2 Soils

The pH, and EC of the pore water influence the geochemical pathways (Al *et al.*, 1994), and is a determinant factor in the dissolution of heavy ions. Accumulation of heavy ions is more rapid in clear terrains than where vegetation cover is available (Berthelsen and Steinnes, 1995). The precipitates accumulated from constant leaching of ions of heavy metals emanating from tailings dump caused the soils to be over saturated with heavy metals.

In this regard, as vegetation was depleted due to the formation of dead zones, heavy metals concentrations in soils increased correspondingly. On the other hand, transportation and migration mechanisms of heavy ions favoured sandy soils compared to silty and clayey soils. The soils at Selebi Phikwe being predominantly silty with an average migration rate, heavy metals contamination could be detected as far as the control site (site ten) though at lower concentration levels.

The soils close to the smelter/concentrator plant were enriched from wash-offs, PAM and other wastes due to mining and smelting activities. The soils around the mining sites, and the smelter/concentrator plant at Selebi Phikwe presented a large and higher range of heavy metal contents with decreasing proportionality as distance increased from the sources. This chemical phenomenon was documented by Bowles *et al.* (1998), for similar mines and smelter settings in the world, namely at Sandbury, Ontario, Canada. The nature of some of the polluting elements depended on how the ore was processed, the concentration of the noxious elements and how residual materials were disposed.

5.5.4.3 Particulate air matter

The PAM depicted levels of contamination as a result of mining and smelting activities.

5.5.4.4 Mopane leaves

Moane leaves were enriched from wash-offs, PAM, plant uptake from soils, and other wastes due to mining and smelting activities.

5.5.4.5 Phane caterpillar

The concentrated heavy metal content in the phane caterpillars at these sites was attributed to the fact that the leaves they fed on were heavily contaminated.

5.6 General environmental implications

The mining of and processing of sulphide minerals at Selebi Phikwe is accompanied by mine waste. These wastes led to the formation of different gas and PAM contents, deposition of tailings dump, and contamination of surrounding soils, vegetation and animals. A schematic presentation of the likely environmental implications at different stages is depicted in Figure 5.3. Fumes rich in sulphur, nitrous oxides (NO_x) and other associated gases were found to be deleterious to human life as well as cattle and game (Prospero, 1999). The emissions of SO_2, CO, CO_2, and other gases from concentrator and smelter plants affect people, plants, wildlife, rocks and soils, buildings and landscape topography (Buseck and Posfai, 1999).

Air pollution resulting from particulate matter of SO_x gases, metals and minerals has led to deposition and increasing acidity of soils. This might cause an increased bioavailability of metal ions in soils and more uptake by plants as suggested by Tagami and Uchida (1997). Concentration levels of plant nutrients in the surrounding mining environment increased due to the introduction of contaminants; a condition that might eventually lead to certain vegetation type becoming either endangered or locally extinct (Chaney *et al.*, 1995).

5.6.1 Effect on soil

Parent materials on the earth's crust from which soils are derived have different levels of concentrations of heavy metals as depicted in Table 5.1, and exert a direct influence on the concentrations of heavy metals found in soils. Cadmium is usually found in the soil as cadmium oxide, cadmium chloride and cadmium sulphide. At Selebi Phikwe the sulphide form is most likely to occur. Cadmium is quite soluble, and mobile. Cadmium poisoning in Japan led to the *itai-itai* disease, which was manifested, with deformed bones accompanied by pains (Alloway and Ayres, 1993). The concentration values of Cd obtained in this study are considerably lower than those recorded in Japan which eventually led to *itai-itai* disease. Cadmium in soils is readily bioavailable for plant uptake, and also exists in soluble forms in water. Research carried out indicated that Cd mobility is a greater threat to the human food chain than any of the other heavy metal (Alloway and Ayres, 1993).

Cobalt occurs in different ionic species in soils. The high levels of Co in Selebi Phikwe soils, except if compared with Ultramafic and Mafic rocks, (Table 5.1) provide contaminant trends for mineral uptake of plants. Cobalt migrates quite slowly, therefore it has the tendency to be retained in soils for longer periods compared to several other heavy metals.

Chromium is a naturally occurring element present in rocks and soils in several species. It is commonly found in the forms of either Cr(VI) or Cr(III) of which the hexavalent form is more phytotoxic than the trivalent form. Cr levels in soils increase mainly from disposal of commercial products, and Cr waste from industry and mining activities. The migration of Cr in soils depends on soil type, and other physical parameters. With concentration levels of Cr in the soils around Selebi Phikwe as shown in Table 5.1, being higher than the acceptable level of 0.5 $\mu g/ml$ (Alloway and Ayres, 1993), the soils can be considered to be both Cr-enriched geochemically and polluted from mining activities.

The level of Cu in soils is the primary controlling factor to prevent its toxicity of water, plants and animals. Cu enrichment and retention in soils is dependent on soil pH, soil texture, and soil sorption properties. Cu is not easily adsorbed at low pH due to competition with Mg^{2+}, Fe^{3+}, H^+ and Al^{3+} for sorption sites, but its content in soils increase with increasing pH. Soil Cu content is between 2-100 ppm with an average of 30 ppm, and a recommended accumulation of 250 ppm in the upper 15 cm of soil (Alloway and Ayres, 1993). The levels obtained for Selebi Phikwe were higher. The Cu^{2+} was sorbed by clay minerals in the order kaolinite > illite > smectites.

Iron is commonly found in most soils as oxides. At Selebi Phikwe, it exists mainly in the form of sulphides. Iron content in soils affects plant growth, and promotes soil acidity (Ptacek and Bowles, 1992). Unfortunately, Fe is a major accessory element present in the Ni-Cu ore, which is being mined at Selebi Phikwe. Without doubt, the Selebi Phikwe soils are Fe-contaminated, as depicted in the XRPD analyses which reflected pyrite and pyrrhotite.

Nickel occurs in soils as sulphides and oxides of which the sulphides were more prevalent in the Selebi Phikwe soils. Ni found in soils is usually embedded with minerals and is not readily bioavailable for plant uptake. Tolerant levels for Ni in soils are between 4 ppm and 80 ppm (Alloway and Ayres, 1993; Suschka and Zielonka, 1995), although values can reach 9000 ppm where Ni is extracted from ore. Concentration values obtained for the Selebi Phikwe soils implied that the soils were Ni-contaminated.

Nickel (Ni) is ubiquitous and is a contaminant of soils and water. Its ore occurs in the form of sulphide minerals, and at Selebi Phikwe the minerals were pentlandite, bunsenite and penroseite. Ni is extracted in concentrators and smelters creating serious environmental contamination. Ni in air is generally $< 0.5\ \mu g/m^3$ but levels can rise to $400\ \mu g/m^3$ in industrial and mining areas (Alloway and Ayres, 1993). Average Ni content on the earth's crust is 80 ppm, and in soils the range is 5-500 ppm (Alloway and Ayres, 1993; Suschka and Zielonka, 1995). Ni in soils is precipitated as Ni hydroxyoxides at alkaline pH. In lower oxidation states, Ni precipitates as Ni carbonate and Ni sulphide. The quantity and type of clay, and the soil CEC do not have any direct influence on Ni retention in soils. Fe and Mn oxides are positively correlated to Ni sorption. Organic matter can hold Ni at levels up to 2000 ppm. Soil accumulation of 100 ppm Ni appears to be acceptable based on phytotoxicity and microbial toxicity (Li *et al.*, 2000; Wang and Chen, 1998).

Selenium occurs naturally, and is both widely and unevenly distributed in rocks and soils. The Se in soils occurs as selenite, selenate and selenide compounds. In China, high Se levels in soils led to correspondingly high Se levels in vegetables and plants; thereby introducing toxic levels to the human food chain (Li *et al.*, 2000). Selenium can be washed easily from soils to surface water, and it can also contaminate subsurface water bodies (Wang and Chen, 1998). Although concentration values obtained for selenium in the soils at Selebi Phikwe study area were quite high, control measures should be put in place due to its high toxicity.

Zn is found in soils in the forms of oxides and sulphides, of which the latter might be prevalent at Selebi Phikwe. Zn content in soils range from 10-300 ppm with an average of 50 ppm. Selebi Phikwe soils may be considered as not being Zn-contaminated due to the low concentration levels of its occurrence. Where sulphides occur as parent material, Zn is abundant. Zn in soils is bound and does not easily dissolve in water except where the pH is acidic as at Selebi Phikwe.

Dead zones and waste lands at Selebi Phikwe have been discussed in earlier chapters of this work. AMD is a proponent factor for the development of dead zone (Benner *et al.*, 1997; Bowles *et al.*, 1991; 1994; 1995; 1998). Estimates show that the area of contaminated land in the world range from 50 000 to 200 000 hectares, which may be over 100 000 sites consumption. Some soils contaminated by heavy metals could produce apparently normal crops that can be unsafe for both human and animal consumption (Benner *et al.,* 1997). Contamination of land due to industrial pollution, fall out from smelters and mine spoil are of increasing concern because the inorganic contaminants have the potential of entering food chains.

5.6.2 Effect on atmosphere

Gaseous pollutants such as sulphur dioxide (SO_2), nitrogen dioxide (NO_2), carbon monoxide (CO) and ozone (O_3) are excluded from the definition of PAM (USA – EPA, 1995). Minerals make up between 14.6 % and 69.9 % of the major constituent of particles (Air Quality Criteria, 2000). Mineral dust at Selebi Phikwe consisted of particulate released into the atmosphere from mining and smelting activities, as well as spatially transported aoelian particulate. Regional climatic and geomorphic factors such as draught and desertification encroachment tended to increase the quantity of mineral dust that enters into both the atmosphere and troposphere (Ringrose *et al.*, 1995). This phenomenon might dilute the proportions of heavy metals contained in mineral dust (PAM).

Secondary PAM is formed by atmospheric chemistry, by reactions of primary PAM with atmospheric gases and fluids. Mineral dust can force both cooling and warming effects on its environment locally, regionally and globally depending on the quantity contained in air as explained by Prospero (1999) and discussed by Buseck and Posfai (1999). Mineral particles absorb light creating a heating effect as explained by Buseck and Posfai, (1999).

The surfaces of mineral dust particles are used as reactive milieus for a wide variety of chemical reactions in the atmosphere, which significantly influence the cycles of N, S, and oxidants in the air. When mineral particles are associated with hygroscopic S compounds, they act as cloud condensation nuclei (CCN) and modify the cloud radiative properties as mentioned in Buseck and Posfai (1999). In this regard, they promote precipitation and concentration of ice. This phenomenon may explain why Selebi Phikwe has slightly more rain than its neighboring areas even though they are classified within the same climate type.

In a recent report by the Department of Mines (1998), they indicated that 46 850 kg/h of SO_2 and 190 kg/h of PAM were emitted from the BCL smelter complex. Average particulate in the air remain at $1\mu g/m^3$. The gas emissions are discharged at a chimney height of 153 m through the main stack of the plant. It is assumed that at this elevation, the smelter waste gases would have dispersed and diluted before reaching ground level. Other gases (mainly from the drying plant and steam super heater) are released into the atmosphere at 73 m through plant stack. The Government of Botswana set a mean annual guideline of 80 $\mu g/m^3$ for residential areas of Selebi Phikwe, which has a direct bearing on future expansion for residential purposes. This study suggests that residential properties be developed on the north-eastern section of the township. This view is also recommended by the Department of Mines (Department of Mines, 1998).

There are grave concerns for the health of people living close to mining and smelting environments such as Selebi Phikwe, and these include effects on breathing and respiratory systems, damage to lung tissue, cancer and premature death. Other related effects observed in the United States of America are reflected on the elderly, children and people with chronic lung disease, influenza, or asthma, who are especially sensitive and the most affected as shown in the National Air Quality Trends Brochure of 1995. Acidic PAM deteriorates paint quality, marble buildings and bridges, and vehicles within the vicinity of its influence. The health effects resulting from emission of finer particulate matter are very adverse.

5.6.3 Effect of particulate air matter on human beings and animals

Particle rejection by the pulmonary system is proportional to its size as shown in Figure 5.4. PAM of size > 10 μm can easily be removed from the nasal chamber; consequently it has little chances of penetrating the lungs (USA-EPA, 1995). Results from the composite PAM sample obtained at Selebi Phikwe area, showed that the particles were very fine in appearance and could likely be composed of 80 wt % being < 5 μm. It thus implied that > 80 wt % of the PAM might be inhaled into the respiratory system of human beings living within the vicinity of the study area. The wt % of inhaled particles deposited in the pulmonary airspace of lungs, with a particle diameter of <2 μm is 20 wt % (USA-EPA, 1995). The relative amount of PAM deposited is controlled by a number of other factors including the tidal volume, the breathing frequency, particle morphology, particle chemistry and particle mineralogy (USA-EPA, 1995). Animals within the environment are likely to suffer from respiratory problems associated with PAM. Mammals especially sheep and cows could be more affected than birds, which migrate due to, forced changes in climatic conditions.

5.6.4 Effect on plants

The mean concentration levels of heavy metals in mopane leaves are compared to the EPA general trend and toxic levels as shown in Table 5.2. Cadmium, Cr, Se and Zn in mopane leaves occurred in levels, which bear general trends, although concentration levels of Cr were higher. The Co, Cu, Fe and Ni in mopane leaves at Selebi Phikwe were quite high and levels are indicative of phytotoxicity. The concentration levels for Ni were at an early stage of phytotoxicity. Plants are intermediate reservoirs for heavy metals, whereby they migrate from soils to animals and human beings. The availability of heavy metals to plants depends on the metal species, among several other plant and soil conditions. Only part of the total amount of heavy metals in soils is bioavailable for plant uptake. Certain plant species are hyperaccumulators of specific heavy metals, and serve as geobotanical-biochemical indicators (Chaney *et al.*, 1995). High concentrations of heavy metals with values exceeding plant tolerant levels are indicative channels of potential phytotoxicity.

Excessive concentrations of heavy metals affect biochemical processes in plants as revealed in Table 5.3 below. Cadmium, Co and Se affect plant metabolism more than other heavy metals. From this study, it is shown that Co, Cr, Cu, Fe and Ni occured at toxic concentration levels in the sampled mopane leaves. High Co causes plant chlorosis and together with Cr, Fe and Ni, they affect phosphate affinity (Table 5.3). Copper and Fe result in plants dark green leaves. Copper also affects permeability of cell membranes. The concentrated levels of Cu and Fe thus resulted in the mopane plants with dark green leaves and stunted growth.

The copper concentrations in plants are 4 -15 ppm. Soil Cu content as mentioned by Alloway and Ayres (1993) is the most important level in controlling the Cu content in plant leaves. Cu is toxic to plants and animals. At 20 ppm and above, Cu content in the leaves of plants is considered to be toxic. Other investigators suggest soil Cu concentration to be > 80 ppm for plant growth to be adversely affected (Rauta *et al*., 1995). It has also been proved that large amounts of organic matter reduce soil Cu concentrations. Small quantities of Cu activate certain enzymes required for respiration, redox reactions and protein synthesis (Tan, 1998).

Nickel is not essential to plants and in many species it is toxic. Early stages of Ni toxicity are expressed by stunting of the affected plant. Fifty ppm in plant tissue is considered to be toxic (Table 5.2). Ni uptake and toxicity was found to be much greater in acidic soils (Jaffré and Schmid, 1974). Symptoms of Ni phytotoxicity include intervenial chlorosis in new leaves, grey-green leaves and brown stunted roots. These observations were noted at the Selebi Phikwe study area on sites with high concentrations of Ni (Table 5.2). At these sites, (particularly sites five and six), the plants were stunted.

5.7 Related aspects of phane consumption

Investigations on the dimensions of phane trade carried out by Moruakgomo (1996), revealed that the population at Selebi Phikwe feed on phane quite often, and also export the worm to other parts of the country, South Africa, Zimbabwe, Europe and the United States of America. Phane is regularly eaten and considered as a cheaper source of protein compared to beef. Quite interesting, this study showed contamination levels of heavy metals in phane to be high. The direct sources of heavy metals in the organisms were most probably the mopane leaves and the settled PAM.

Contaminant levels of heavy metals obtained by analyses after having dried and pulverised ten phane caterpillars showed a linear relationship with the leaves and the soil. The worms were generally more contaminated than the soils, which supply plant nutrient and the mopane leaves, which serve as the principal food source for phane. The regular consumption of phane might lead to the accumulation of heavy metals in vital organs such as kidneys and liver of both mammals and human beings. Results from the analyses of phane showed that heavy metals accumulated in the organic system of the worms. Consequently, through the food chain, these metals could also accumulate in the systems of human beings over time.

5.8 Aspects related to aquatic systems

Mine drainage water has been known to affect the quality of aquatic organisms and the quality of water received by downstream communities (Al *et al.*, 1994a; and Egbu, 2000). Although water analyses and characterisation were not conducted as part of the study, it is worthwhile to mention some possible effects of high levels of concentrations of heavy metals on aquatic systems. Heavy metals pose serious water quality concerns because of their toxicity, persistence, and potency to living organisms.

Studies on effluent quality conducted by the Department of Mines, Botswana revealed concentrations of Cu, Co, Pb, Cd to be within acceptable levels as compared to the World Health Organization recommended standards for drinking water and the values set by the Department of Water Affairs, Botswana Department of Mines (1998). Ni, Fe and Mn exceed the recommended values. High concentrations of heavy metals in effluent may be as a result of seepage from mine tailings into water bodies. On days of rainstorms, leaching activities are greatly intensified (Adelekan, 2000; Al and Bowles, 1995; Allan, 1995), and consequent increase in concentration levels of heavy metals in aquatic systems is obvious.

Toxic components of heavy metals pose as a threat to all living organisms in aquatic systems. Surface waters and runoffs during wet weather storms, or water from other sources such as vehicle brake pad dust, exhaust, oil, grease, tyre and fuel discharges, solid waste disposal areas (the Selebi Phikwe landfill), pesticide residues, and illegal and inappropriate disposal practices may contain ions of heavy metals. The ions of heavy metals resulting from commercial, industrial, agricultural and domestic activities are conveyed in the water bodies within the environment (Egbu, 2000; Hudson-Edwards *et al.*, 1999).

5.9 Heavy metals and their associated human diseases

Although this study did not cover experiments to establish diseases and sicknesses caused as a result of exposure to mining and ore processing activities, it is necessary to discuss some of the likely health hazards that could occur based on the results obtained for heavy metal concentrations and mineral associations within the Selebi Phikwe study area.

Cadmium (Cd) contamination has been found in water, soils, vegetation (WHO, 1993) and possibly animals. It is associated with the sulphides of Zn, nickel (Ni) and copper (Cu) and their ore minerals. It has a long biological half time in the body and accumulates with age. At high levels above 60 μg/day, Cd is known to affect the renal, skeletal and respiratory systems, and causes itai-itai disease (Alloway and Ayres, 1993; WHO, 1993). The effects of Cd contamination in humans usually involve the kidneys and lungs (Langer, 1999)

Chromium (Cr) is associated with Ni ore minerals, and is an impurity in pentlandite, bunsenite and penroseite (Nkoma and Ekosse, 2000). In its naturally occurring state, Cr is highly insoluble, but weathering, oxidation and bacterial action can alter its physical state to a soluble form such as the hexavalent Cr

(McGregor *et al.*, 1995). The mean values of Cr in the air is usually 0.02 $\mu g/m^3$ but the figure may rise to 0.40 $\mu g/m^3$ in heavily industrialised and mining areas. The concentration levels of airborne Cr due to occupational exposure can rise to hundreds of $\mu g/m^3$ (Prospero, 1999). In air, Cr exists in the form of very fine particles. Although Cr is a micronutrient essential for carbohydrate metabolism in animals, it is carcinogenic and can cause cancer of the respiratory organs and chlorosis. Hexavalent Cr can also produce cutaneous and nasal mucous-membrane ulcers and dermatitis. It is reported by Langer (1999) that workers who process ore rich in Cr have the tendency of developing lung cancer.

Cobalt (Co) is an economic bye product in the mining and smelting of Ni-Cu. It is one of the constituents of the penroseite pseudomorph $(Ni,Co,Cu)(Se,S)_2$ and is also an impurity in other Ni-Cu ore minerals. An intake of > 500 mg/day is considered to be toxic (Alloway and Ayres, 1993). Excess incidence of cancer is reported among ore processors. It causes lung cancer and cancer of the main bronchus. Langer (1999), mentioned Co to be the cause of what is known as 'hard metal disease".

Copper (Cu), as Ni is ubiquitous and is found in water, soils, plants and living organisms. Copper is mined from its sulphide ores and smelted with the release of oxides of sulfur into the atmosphere. Toxicity problems may occur in crops and livestock growing in contaminated areas. Copper is essential for human metabolism. However, excessive intake by man leads to severe mucosal irritation and corrosion, capillary damage, hepatic and renal damage, gastrointestinal and nerval disturbances (WHO, 1993).

Iron (Fe) occurs as an integral element in Ni and Cu minerals ore bodies and is a by-product in their extraction metallurgy. Although it is a very essential component of blood, it may also have some adverse effects. In the oxidation of sulphides of Fe, acidic solutions are created which tend to decrease adsorption and promote mobility of metals in soils, water and sediments. Iron is known to cause siderosis, and scarring of the lungs depending on the quartz content. Experimental work conducted on ore miners in Newfoundland indicated that Fe is carcinogenic (Langer, 1999).

Nickel can be carcinogenic, and causes dermatitis, eczema, vertigo and dyspnoea to exposed human population (WHO, 1993). Ni causes pneumoconiosis to workers exposed to it during mining and processing (Langer, 1999). A higher than normal rate of occurrences of lung cancer is common among miners of Ni found in hard rock areas. Workers at concentration and smelter plants have been reported to suffer from very high incidences of lung and nasopharynx cancer. Nickel in trace amounts may have a role in human nutrition. Studies have shown Ni to be carcinogenic to humans through intravenous, intramuscular and respiratory routes of administration.

At the Selebi Phikwe Ni-Cu ore deposit, selenium (Se) occurred as a constituent element in penroseite (Nkoma and Ekosse, 1999). It causes pneumoconiosis, which may be as a result of the associated gangue minerals within the ore body (Langer, 1999). The humans are exposed to the health hazards during ore processing. Langer (1999) reported that workers exposed to Se, suffer from severe irritation of the nose and eyes, gastro-intestinal disorders, and dental caries.

Zinc (Zn) minerals usually occur with cadmium (Cd) and lead (Pb). Zn pollution is associated with mining and smelting and may occur in tailings dump from nickel (Ni) and copper (Cu) mine workings. Its association with Cd may cause an increase in Cd levels in soils, water, and living organisms. Although generally considered to be non-toxic, it can cause vomiting, dehydration, electrolyte imbalance, abdominal pain, nausea, dizziness, lack of muscular coordination, and renal failure (WHO, 1993). Zn causes shortness of breath, minor lung changes and pneumoconiosis (Langer, 1999).

5.10 Aspects of pollution management

5.10.1 Environmental time bomb

Environmental time bombs predicted in 2000, 1998 and 1997 (Bowles and Jambor, 1990) are in existence all over the world where there are abandoned and exploited mines that have manifested the phenomenon of AMD due primarily to the oxidation of sulphudic mining waste after ore removal (Bowles *et al.*, 1995). Potential contamination of vulnerable environmental systems poses as a liability for mining industry (Bowles and Jambor, 1990). In the past short term solutions were applied to abandoned mines because there were no legislation regulating the rehabilitation of mines and mining industry was oriented at maximizing benefit (Ernst, 1995). An example of such short term measures utilised at abandoned mines involved capping with three layers of earth material: clay, sandy loam and gravel sand, to attenuate possible hazards by reducing oxygen and water penetration in the tailings dump (Holmström *et al.*, 1997).

Miners, legislature, government regulatory bodies and the public now know the catastrophic effects of AMD. Degradation of water quality in surface and ground waters in contact with acid producing tailings dump poses as a major environmental problem associated with AMD. The water pH is lowered by the alteration of sulphide minerals and release of heavy ions such as Cd, Co, Cr, Cu, Fe, Ni, Se and Zn. The residual sulphides contained in tailings dump have to be addressed in order to alleviate possible contamination of surface and ground water bodies Mayer *et al.* (1999). The discharge run-offs from S-rich tailings dump are very unsuitable for irrigation, stock weathering, drinking water, or recreational use.

5.10.2 Phytoremediation and phytomining

Heavy metals contribute very significantly to the pollution of the environment at Selebi Phikwe. The metals have very strong toxic effects to soils, vegetation and animal life. One of the suggested ways of reducing the amounts of heavy metals in soils and plants within the area is phytoremediation and phytomining. Phytoremediation of metal contaminated soil as explained by Chaney *et al.* (1995), offer a lower cost method of soil remediation and some of the extracted metals may be recycled for value. Phytoremediation as experimented and discussed by Chaney *et al.* (1995); Cunningham *et al.* (1995) and Salt *et al.* (1996), is a potential practical and more cost effective technology than a number of the presently used soil amelioration techniques such as soil replacement, solidification, and washing strategies.

Phytoremediation as explained by Nedelkoska and Doran (2000), is the process whereby plant heavy metals hyperaccumulators (PHMH) are applied to clean up soils and/or water bodies. The objective of phytoremediation [also referred to as bioremediation, botanical-bioremediation, and green remediation by Chaney *et al.* (1995), is to use plants to make soil contaminants non-toxic. The rate of uptake of heavy metals in soils by PHMH depends on variable soil type and texture, production of undesirable metabolic products, site destruction or long-term destabilisation, and the potential for increased contaminant mobilisation.

Studies conducted by Brooks *et al.* (1998) identified more than 400 plant species known to hyperaccumulate heavy metals. These plants have the advantages of accumulating heavy metals in their system. Other related advantages named by Cunningham and Berti (1993) and Nedelkoska and Doran (2000) are:

- The site is neither destroyed nor destabilized,
- Low environmental impact
- Favourable aesthetics
- Continuous *in situ* generation of biomass
- Ability of living plant cells to supplement passive sorption of metals
- Metabolic mechanism of metal uptake and detoxification

5.10.3 Environmental desulphurisation

Mining processes at Selebi Phikwe generated substantial tonnage of mine tailings that contain sulphides of which pyrite and chalcopyrite are major components. The sulphides are oxidised with the aid of *Thiobacilli ferroxidans* under favourable geochemical conditions, with the resultant effect on the environment being AMD (Chai *et al.*, 2000). In an effort of reducing AMD, which is a problem of grave environmental concern at Selebi Phikwe, desulphurisation is suggested.

Environmental desulphurisation has been recommended by Benzaazoua *et al.* (2000) as an alternative for management of acid generating tailings. The process of desulphurisation occurs at the end of the primary treatment of sulphide minerals. It reduces a large amount of problematic tailings by concentrating the sulphide fraction. The process depends on the amounts of sulphur in the tailings and their neutralization potential (NP). The desulphurised tailings can be used as cover material, thereby reducing rehabilitation costs by a factor of between 10 % and 35 % (Bussiere *et al.*, 1997; 1998).

5.10.4 Phytostabilisation

Phytostabilisation is a recently developed technique aimed at rendering heavy ions to species that are "environmentally friendly". An example that could be applicable in reducing available Cr^{6+} at Selebi Phikwe is to render Cr into the insoluble Cr^{3+} form. The Cr^{6+} constitutes as much as 40 wt % to 66 wt % of total Cr released into the environment as indicated by WHO (1993) and discussed by Van den Heever and Frey (1996). Deep-rooted plants are used to accumulate Cr^{6+} and convert it to Cr^{3+} in plant systems. Studies conducted by James (1996) indicated that chromate reduction (chromate, an environmental risk species of Cr) to Cr^{3+} by chemical or biological method offers inertness and insolubility of Cr^{3+} oxides in soils, which limit formation of the Cr^{6+}. Phytostabilisation offers the ability of reducing Cr^{6+} to Cr^{3+} below the tilled soil layer that is generally regarded as the heavy metals sink. In doing so the amount of bioavailable Cr to other plants will be extremely very low.

5.10.5 Biotechnology

In relation to the above techniques of environmental management, there are on going research endeavours as mentioned by Chaney *et al.* (1995) and Salt *et al.* (1996), geared at developing synthetic plants, clones and resins with very high capabilities for heavy metals extraction from soils, atmosphere and water. Fundamental characterisation of mechanisms and cloning of genes as mentioned by Chaney *et al.* (1995, 1997), for phytoremediation in higher plants is expected soon. The development of specialised plant hyperaccumulators of heavy metals and their possible use as metallophores to aid in phytoextracting heavy metals in soil, and aquatic systems is being researched. Phytosiderophores have been developed for the uptake of Fe in soils, and these plants consume nearly only Fe as demonstrated by Yehuda *et al.* (1996). Nickel-hyperaccumulators, (also known as hypernickelophores), have been used in soils close to Ni-mining areas (Jaffré and Schmid, 1974). Cadmium uptake by "hypercadmiumophores" has been studied by several researchers including Ortiz *et al.* (1995) and Vogeli-Lange and Wagner (1990). Currently, the use of Se hyperaccumulator plants coined as "hyperselenuimophore" in phytovolatilisation is being applied to solve problems of Se-contaminated soils.

Research is directed at phytoextracting all heavy metals with specific "metallophores". The plants are expected to manifest very high biomass with sustainable biochemical pathways for extraordinary uptake of metals and hypertolerance. The hypertolerance results from vacuolar compartmentalisation and chelation (Ortiz *et al.* 1995; Vogeli-Lange and Wagner, 1990). "Metallophores" must be able to translocate the heavy metals from roots to shoots at high rates, and they must also have the ability of maintaining a very rapid uptake rate of the elements at levels that occur in soil solution (Chaney *et al.*, 1997). Commercial firms are increasingly investing in the area of phytoremediation biotechnologies, and without doubt, environmental clean-up activities in future shall abide to this novel trend currently being perfected.

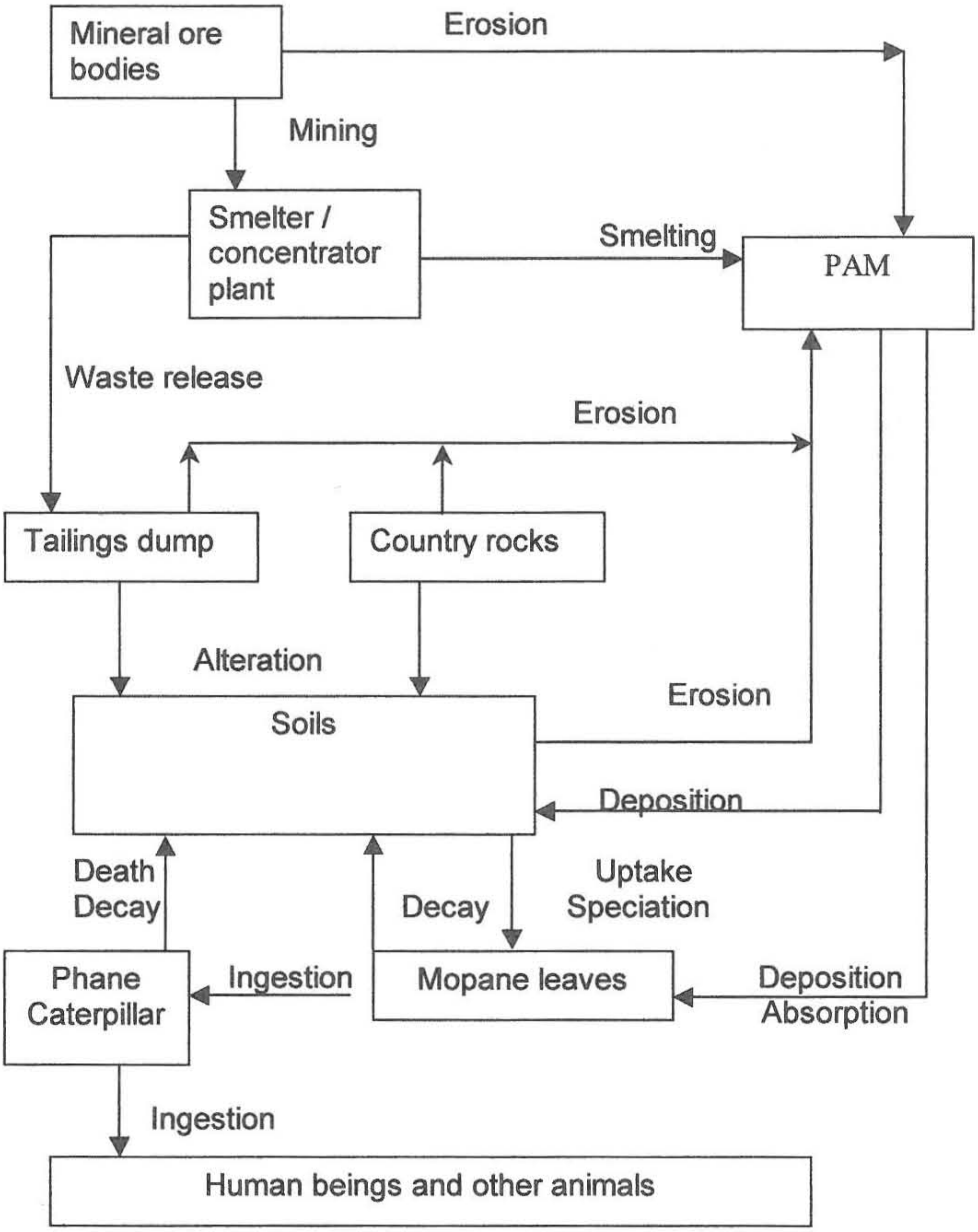

Figure 5.1: Schematic diagram showing physico-chemical processes and relationships of environmental constituents at the Selebi Phikwe study area.

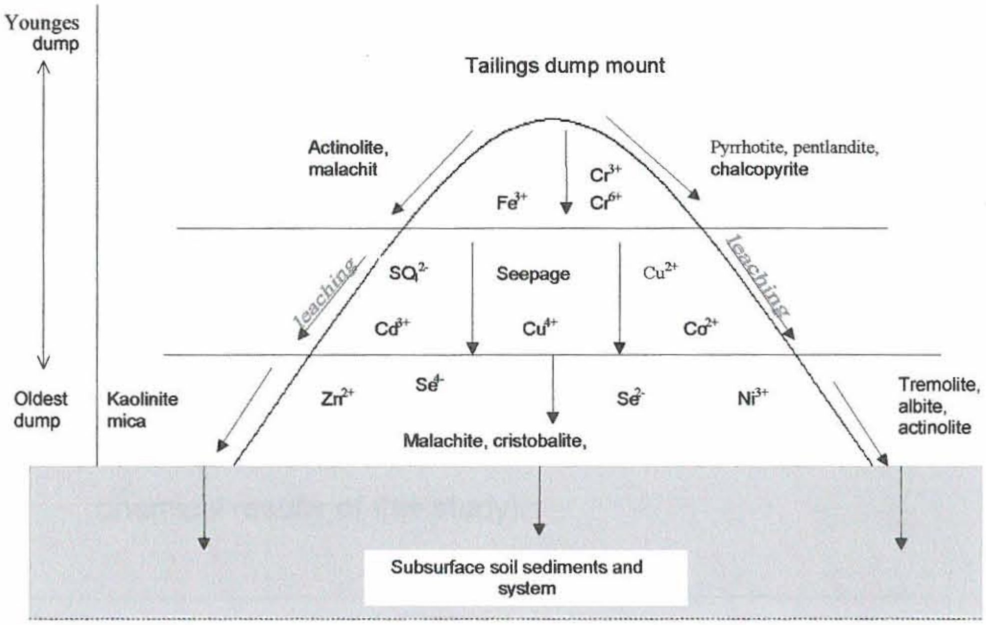

Figure 5.2: Location of minerals and heavy ions on tailings dump at Selebi Phikwe. (Compiled from mineralogical and chemical results of this study).

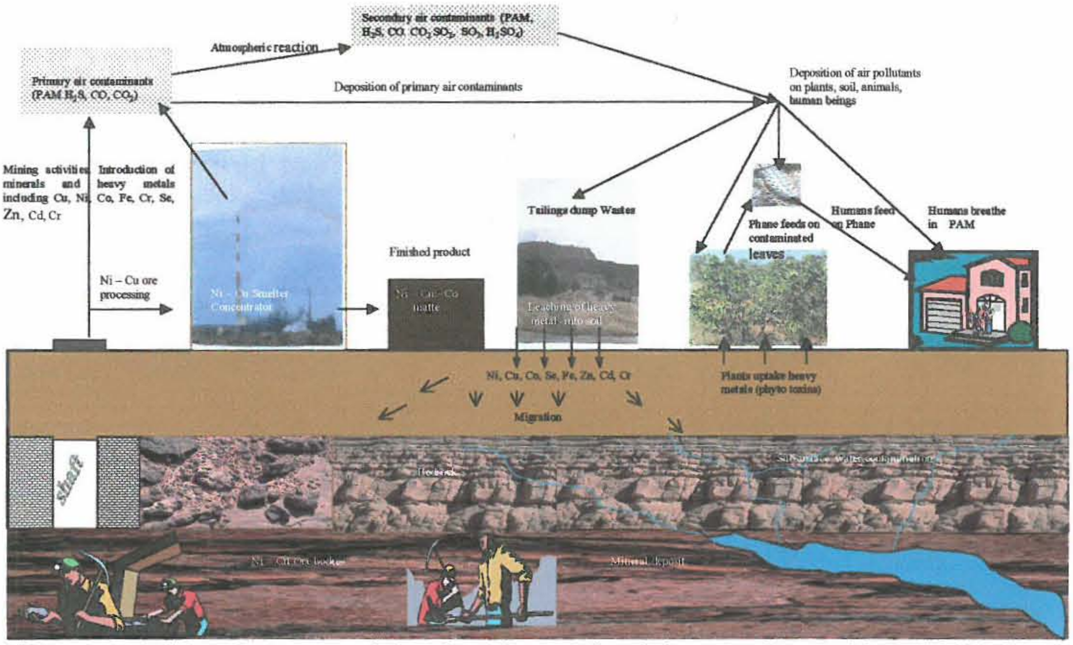

Figure 5.3: Environmental implications of mining and smelting of Ni-Cu minerals at Selebi Phikwe. (Compiled from mineralogical and chemical results of this study).

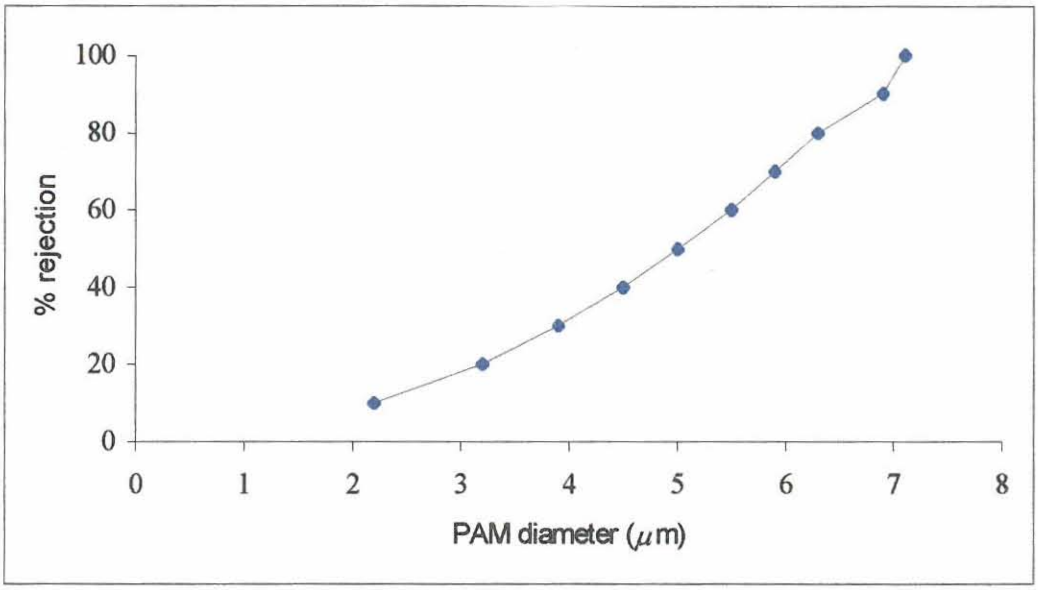

Figure 5.4: Percentage particle rejection by pulmonary system of human beings based on particulate air matter diameter. (Based on USA-EPA, 1995).

Table 5.1: Concentrations of heavy metals in earth's crust, selected metamorphic and sedimentary rocks (Alloway and Ayres, 1993) compared to mean concentrations of tailings dump and soil at the Selebi Phikwe study area.

Heavy metal	**Earth's crust**	**Ultramafic rock**	**Mafic rock**	**Shales / clays**	**Tailings dump (Selebi Phikwe)**	**Soil (Selebi Phikwe)**
Cd	0.1	0.12	0.13	0.22	12.79	1.54
Co	20	110	35	19	78.05	28.77
Cr	100	2980	200	39	363.31	138.32
Cu	50	42	90		854.26	229.12
Fe					3342.38	131.99
Ni	80	2000	150		358.47	139.90
Se	0.05	0.13	0.05		1.93	0.45
Zn	75	58	100		57.43	29.84

Table 5.2: Concentration levels of heavy metals in leaves

Element	**Mopane leaves at Selebi Phikwe**	**General trend in leaves (EPA) (ppm)**	**Toxic level (ppm)**	**Toxic level (Vardaki and Kelepertsis,1999) (ppm)**
Cd	0.02	0.2-0.8	5-7000	
Co	16.54	0.01-0.30	200	
Cr	5.72	0.1-1.0	10-20	75-100
Cu	71.40	4-15	> 20	60-125
Fe	252.10	20-300	-	
Ni	72.15	0.1-1.0	50-200	100
Se	0.02	0.02-2.0	50-100	
Zn	33.68	15-150	500	70-400

Note, the concentrations of heavy ions in plant leaves (ppm dry weight)

Table 5.2: Concentration levels of heavy metals in leaves

Element	Mopane leaves at Selebi Phikwe	General trend in leaves (EPA) (ppm)	Toxic level (ppm)	Toxic level (Vardaki and Kelepertsis,1999) (ppm)
Cd	0.02	0.2-0.8	5-7000	
Co	16.54	0.01-0.30	200	
Cr	5.72	0.1-1.0	10-20	75-100
Cu	71.40	4-15	> 20	60-125
Fe	252.10	20-300	-	
Ni	72.15	0.1-1.0	50-200	100
Se	0.02	0.02-2.0	50-100	
Zn	33.68	15-150	500	70-400

Note, the concentrations of heavy ions in plant leaves (ppm dry weight)

Table 5.2: Concentration levels of heavy metals in leaves

Element	Mopane leaves at Selebi Phikwe	General trend in leaves (EPA) (ppm)	Toxic level (ppm)	Toxic level (Vardaki and Kelepertsis,1999) (ppm)
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Co	16.54	0.01-0.30	200	
Cr	5.72	0.1-1.0	10-20	75-100
Cu	71.40	4-15	> 20	60-125
Fe	252.10	20-300	-	
Ni	72.15	0.1-1.0	50-200	100
Se	0.02	0.02-2.0	50-100	
Zn	33.68	15-150	500	70-400

Note, the concentrations of heavy ions in plant leaves (ppm dry weight)

Table 5.3: Biochemical effects of excessive concentrations of heavy metals on plants (Alloway and Ayres, 1997).

Biochemical effect	**Heavy metals**
Changes in permeability of cell membranes	Cd, Cu
Bonding of sulfydryl groups	Cd
Site competition with essential metabolites	Se
Affinity for phosphate, ADP and ATP groups	Cd, Cr, Cu, Co, Fe, Se, Ni, Zn
Replacement of essential atoms	Se
Occupation of sites for essential groups	Se
Enzyme inhibition	Cd
Respiration	Cd
Photosynthesis	Cd, Zn
Transpiration	Cd
Chlorosis	Cd, Co, Cr, Ni, Se, Zn
Dark green leaves	Cu, Fe

Chapter 6

Conclusions and recommendations

The Selebi Phikwe area, Botswana has underground mines from which Ni-Cu ore is being mined as well as a concentrator/smelter plant for the processing of the ore to Ni-Cu matte. Exploitation of Ni-Cu ore bodies at Selebi Phikwe has been active for more than twenty years. Growing concerns that mining and smelting activities are having a direct influence on the environment were investigated in this study. Its aim was to achieve a better understanding of the environmental physico-chemistry, environmental mineralogy, and environmental chemistry of the Selebi Phikwe Ni-Cu mine area in south-eastern Botswana.

6.1 Physico-chemical aspects

The PSD of soil samples revealed the average wt % of the three soil fractions as follows:

- the $< 2\ \mu m$ fraction (clay fraction) was between 3 wt % and 9 wt %,
- the $> 2\ \mu m$ to $< 50\ \mu m$ fraction (silt fraction) was between 34 wt % and 44 wt %,
- the $> 50\ \mu m$ to $\leq 250\ \mu m$ fraction (sand fraction) was between 47 wt % and 63 wt %.

Soil pH ranged from 3.5 to 6.0 with very acidic soils located close to the smelter/concentrator plant. Electrical conductivity values were significantly low, and the range was from 50 $\mu S/cm$ to 250 $\mu S/cm$. Soils with low pH correspondingly had low EC. The CEC values occurred between 2 meq/100 g and 20 meq/100 g. The results are indicative of increase in soil acidity due to mining and smelting of Ni-Cu at Selebi Phikwe area. Correspondingly, soils of higher EC were closer to the mine compared to those with lower EC values which were further away from the mine. The kaolinitic soils had lower CEC compared to soils rich in smectites. High acidity favoured the leaching of heavy ions from tailings dump and related mining waste to the soils. Fewer exchange sites have resulted in a low CEC for ions adsorbed on the sediment surfaces, consequently they remain in solution and are bioavailabe for plant uptake.

Hand specimens of tailings dump viewed with a microscope and physical tests performed on the samples for hardness, cleavage, fracture, colour, streak, lustre, and crystal appearance depict albite, cristobalite, chalcopyrite, pyrrhotite, tremolite, and pentlandite to be contained in them. Soil colour varied from pale yellow, reddish yellow to dark reddish brown. Grains were poorly sorted, with subangular grains located further from the plant, which is indicative of windblown particles transported at a short distance. Reddish brown soils were closer to the tailings dump, mining areas and the smelter/concentrator plant. The observation is indicative of both Fe and Cu containing minerals enriching the soils of the study area.

6.2 Mineralogical aspects

The PAM consisted of quartz, SiO_2; pyrrhotite, $Fe_{1-x}S$; chalcopyrite, $CuFeS_2$; albite, $NaAlSi_3O_8$; and djurleite, $Cu_{31}S_{16}$. The tailings dump comprised nickelbloedite, $Na_2(Ni(SO_4)_2.4H_2O$; pyrrhotite, quartz, pentlandite, $(Fe,Ni)_9S_8$; malachite,$Cu_2CO_3(OH)_2$; chalcopyrite, actinolite, $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$; cristobalite, SiO_2; tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$; kaolinite, $Al_2Si_2O_5(OH)_4$; mica and albite. Bulk soil samples consisted of actinolite, albite, quartz, microcline, $KAlSi_3O_8$; pyrrhotite, silicon sulfide and cobalt oxide, whereas the < 2 μm fraction was made of kaolinite, illite, $KAl_2(Si_3AlO_{10})(OH)_2$; smectite, $Na_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.xH_2O$; anorthite, $CaAl_2Si_2O_8$ and quartz.

Djurleite polymorphs ($Cu_{31}S_{16}$ and $Cu_{1.93}S$) identified in PAM were formed from secondary mineralisation of chalcopyrite and the SO_2 released from concentration/smelting processes. Ambient temperature and an acidic milieu created favourable conditions for the formation of nickelblodite and malachite from the primary ore minerals: pentlandite, chalcopyrite and pyrrhotite in tailings dump. Cobalt oxide and silicon sulphide identified in surface soils are indicative of chemical alteration of mining waste deposited on surface soils. The occurrence of ferruginous minerals at all the sampling sites demonstrated soil contamination due to mining activities.

6.3 Aspects of heavy metals chemistry

Levels of concentrations obtained for analysed heavy metals in tailings dump samples were as follows: Cd was between 9 ppm and 16 ppm, Co was between 66 ppm and 89 ppm, Cr was between 312 ppm and 431 ppm, Cu was between 779 ppm and 896 ppm, Fe was between 3100 ppm and 3555 ppm, Ni was between 328 ppm and 389 ppm, Se was between 1.7 ppm and 2.2 ppm, and Zn was between 46 ppm and 77 ppm.

Concentration levels obtained for analysed heavy metals in soil samples were as follows: Cd was between 0.01 ppm and 0.05 ppm, Co was between 1 ppm and 28 ppm, Cr was between 0.03 ppm and 14 ppm, Cu was between 11 ppm and 116 ppm, Fe was between 31 ppm and 430 ppm, Ni was between 19 ppm and 120 ppm, Se was between 0.01 ppm and 0.03 ppm, and Zn was between 17 ppm and 68 ppm.

Levels of concentrations of heavy metals analysed for composite sample of PAM were as follows: Cd was 0.03 ppm, Co was 12 ppm, Cr was 19 ppm, Cu was 87 ppm, Fe was 91 ppm, Ni was 41 ppm, Se was 0.01 ppm and Zn was 4 ppm.

Concentration values of heavy metals obtained for analysed mopane leaves were as follows: Cd was between 0.01 ppm and 0.05 ppm, Co was between 1 ppm and 28 ppm, Cr was between 0.03 ppm and 11 ppm, Cu was between 4 ppm and 116 ppm, Fe was between 31 ppm and 430 ppm, Ni was between 19 ppm and 120 ppm, Se was between 0.01 ppm and 0.03 ppm, and Zn was between 17 ppm and 79 ppm.

Concentration values obtained for heavy metals in phane caterpillars were as follows: Cd was between 0.01 ppm and 0.05 ppm, Co was between 0.01 ppm and 0.6 ppm, Cr was between 0.03 ppm and 1.03 ppm, Cu wais between 1.3 ppm and 9.79 ppm, Fe was between 1 ppm and 13.5 ppm, Ni was between 1.2 ppm and 4.20 ppm, Se was between 0.01 ppm and 0.03 ppm, and Zn was between 0.6 ppm and 5.79 ppm.

Strong correlation of heavy ions especially those of Fe, Ni, Cu and Co in tailings dump, soils, PAM, plants and caterpillar is indicative of interaction of contaminants from the mining and smelting activities to the physical environment. High acidity of soils is reflected by on-going AMD activity which is depicted by the formation of dead zones. Low soil pH promotes the leaching and precipitation of ions including those of heavy metals namely Cd, Co, Cr, Cu, Fe, Ni, Se and Zn. Pyrrhotite (Fe_7S_8-FeS) and pyrite (FeS_2) in tailings dump are oxidized on exposure to water to form sulphate and sulphuric acid. Other observable phenomena were stunted growth of *Colophospermum mopane* (mopane tree) and *Imbrasia belina* (phane caterpillar) as a result of high concentrations of heavy metals in their organic systems.

6.4 Responses to queries

The findings obtained from field observations and analyses depict the following responses to queries introduced in Chapter one:

- The mining of Ni-Cu ore bodies, and the concentration and smelting of Ni-Cu-Co affected the physical environmental quality of the Selebi Phikwe mine area.
- New mineral phases were formed in the tailings, PAM and soil. The new minerals augmented heavy metals concentrations in the in the physical environment. The soils, biomass and air were enriched with both new minerals and heavy metals from mining and smelting activities.
- The concentrations of some heavy metals in soils, PAM and biomass were quite high and need to be addressed by interested parties.
- Noticeable alterations of the physico-chemical properties of the soil, and clay fraction of soil due to mining and extraction metallurgical activities in terms of PS, PSD, pH, EC, and CEC, as well as soil colour were reported and discussed.

- There was a direct relationship of the mineralogy of the soil to that of the ore bodies. This implies that soil constituents were partly from ore bodies either by weathering or contamination.
- The values obtained for heavy metals concentrations in PAM were indicative of atmospheric contamination.
- Laboratory results were indicative of contamination of the environmental quality due to mining activities.
- Contamination of the physical environment has occurred, and it should be contained by the application of some suggested measures such as phytomining, phytosabilisation, and biotechnology.
- Mining activities could continue provided the interested parties address the present contamination levels in the environment, and make provision for future pollution control through monitoring.

6.5 Recommendations

The recommendations are to the population, Selebi Phikwe Mine and Smelter Plant workers, Government, Local Government and Mining Authorities, and Researchers. The four categories of recommendations are listed below.

6.5.1 Recommendations to the population

- The population should gradually desist from harvesting phane located close to the mines and smelter environments.
- Phane harvesting should drift to the leeward side of Selebi Phikwe where there is less wind current and very likely low concentration levels of heavy metals.
- As much as possible, the population should avoid staying outdoors where risk exposure to contaminated air is quite high.
- The people of Selebi Phikwe should report to Health Authorities for regular check-ups of their health state. The medical visits will include checking the cardio-pulmonary system, the circulatory system, and urine.
- People considered to be frail in health should consider relocation to other township areas away from the sulphur-rich gases and fumes.

6.5.2 Recommendations to the mine and smelter plant workers

- Workers should apply all the necessary measures in reducing occupational hazards. Safety/Protective clothing and gear should be used at all times when carrying out their daily tasks.
- In areas, which may be considered to be more hazardous, workers should not be exposed for very long periods.

- The workers should report to Health Authorities for regular check-ups of their health state. The medical visits will include checking the cardio-pulmonary system, the circulatory system, and urine.
- Workers considered to be frail in health should seek employment and relocation to other township areas away from the sulphur-rich gases and fumes.
- Risk based medical examinations should be conducted annually.
- Induction training coversing education on these contaminants should be conducted annually.
- Environmental control measures should be implemented
- An occupational exposure (Occupational Hygiene) programme should be compiled and implemented.
- Policy and procedures with regard to managing the contamination should be compiled and implemented.

6.5.3 Recommendations to Government, Local Council and Mine Authorities

- Government and related agencies as well as Mine Authorities should work as a team in monitoring pollution activities at Selebi Phikwe.
- The interested parties should apply environmental management techniques such as environmental desulphurisation, phytomining,

phytostabilisation, phytoremediation and biotechnology to regain areas where dead zones have developed.

- The agencies should derive health monitoring programmes geared at ensuring quality lifestyle for sustainable development.
- Applied research efforts should be encouraged by authorising bodies.
- Expansion of Selebi Phikwe township should be regulated in such a way that the growing population is least exposed to atmospheric gases.

6.5.4 Further research

- Studies on contaminant hydrology may be carried out to determine the spatial extent and degree of contamination of water bodies within the study area.
- A study to characterise the different species of heavy metals in the area may aid in evaluating the physical quality of the environment.
- Studies on health hazards and related sicknesses due to exploitation of Ni-Cu minerals at Selebi Phikwe may aid in setting guidelines on types of exposure and contact period workers may be allowed to bear.
- Further research on gases and fumes from smelting processes released and their effects to the population and environment needs to be conducted.

6.6 Concluding remarks

The study has considered problems currently encountered in the understanding of the physical environmental quality due to migration of heavy metals from mining and smelting activities. It has advanced certain recommendations that may bring solution to some of the existing environmental pollution problems at Selebi Phikwe. The findings of the study may serve as useful guidelines in interpreting the physical environmental quality of Selebi Phikwe and possibly similar settings around the world.

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Appendix 1

Coding of samples

Each type of sample was coded as shown in Table 3.4. The tables A1, A2, A3, A4 and A5 below indicated the type of sample, when it was sampled and the code given for samples of tailings dump, soil, PAM, phane and mopane leaves. It should be noted that tailings dump 1, 2 and 3 were not from sampling sites 1, 2 and 3. They signified the three areas within the tailings dump from which samples were obtained for analyses.

Table A1: Type of sample and sample code

Type of sample	**Sample code**
Tailings dump	T
Soil	S
Mopane leaves	L
Phane caterpillar	C
PAM	P

Table A2: Codes for samples of tailings dump

Date of sampling	**Tailings dump 1**	**Tailings dump 2**	**Tailings dump 3**
January 15	T1A	T2A	T3A
January 29	T1B	T2B	T3B
February 12	T1C	T2C	T3C
February 26	T1D	T2D	T3D
March 11	T1E	T2E	T3E
March 25	T1F	T2F	T3F
April 15	T1G	T2G	T3G
April 29	T1H	T2H	T3H
May 13	T1I	T2I	T3I
May 27	TIJ	T2J	T3J
June 10	T1K	T2K	T3K
June 24	T1L	T2L	T3L
July 15	T1M	T2M	T3M
July 29	T1N	T2N	T3N

Table A3: Codes for soil samples

Date of sampling	**Site 1**	**Site 2**	**Site 3**	**Site 4**	**Site 5**	**Site 6**	**Site 7**	**Site 8**	**Site 9**	**Site 10**
Jan 15	S1A	S2A	S3A	S4A	S5A	S6A	S7A	S8A	S9A	S10A
Jan 29	S1B	S2B	S3B	S4B	S5B	S6B	S7B	S8B	S9B	S10B
Feb 12	S1C	S2C	S3C	S4C	S5C	S6C	S7C	S8C	S9C	S10C
Feb 26	S1D	S2D	S3D	S4D	S5D	S6D	S7D	S8D	S9D	S10D
Mar 11	S1E	S2E	S3E	S4E	S5E	S6E	S7E	S8E	S9E	S10E
Mar 25	S1F	S2F	S3F	S4F	S5F	S6F	S7F	S8F	S9F	S10F
April 15	S1G	S2G	S3G	S4G	S5G	S6G	S7G	S8G	S9G	S10G
April 29	S1H	S2H	S3H	S4H	S5H	S6H	S7H	S8H	S9H	S10G
May 13	S1I	S2I	S3I	S4I	S5I	S6I	S7I	S8I	S9I	S10I
May 27	SIJ	S2J	S3J	S4J	S5J	S6J	S7J	S8J	S9J	S10J
June 10	S1K	S2K	S3K	S4K	S5K	S6K	S7K	S8K	S9K	S10K
June 24	S1L	S2L	S3L	S4L	S5L	S6L	S7L	S8L	S9L	S10K
July 15	S1M	S2M	S3M	S4M	S5M	S6M	S7M	S8M	S9M	S10M
July 29	S1N	S2N	S3N	S4N	S5N	S6N	S7N	S8N	S9N	S10N

Table A4: Codes for particulate air matter samples

Date of sampling	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Jan 15	P1A	P2A	P3A	P4A	P5A	P6A	P7A	P8A	P9A	P10A
Jan 29	P1B	P2B	P3B	P4B	P5B	P6B	P7B	P8B	P9B	P10B
Feb 12	P1C	P2C	P3C	P4C	P5C	P6C	7PC	P8C	P9C	P10C
May 27	PIJ	P2J	P3J	P4J	P5J	P6J	P7J	P8J	P9J	P10J
June 10	P1K	P2K	P3K	P4K	P5K	P6K	P7K	P8K	P9K	P10K
June 24	P1L	P2L	P3L	P4L	P5L	P6L	P7L	P8L	P9L	P10K
July 15	P1M	P2M	P3M	P4M	P5M	P6M	P7M	P8M	P9M	P10M
July 29	P1N	P2N	P3N	P4N	P5N	P6N	7PN	P8N	P9N	P10N

Table A5: Codes for phane caterpillar samples

Date of sampling	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Jan 15	C1A	C2A	C3A	C4A	C5A	C6A	C7A	C8A	C9A	C10A
Jan 29	C1B	C2B	C3B	C4B	C5B	C6B	C7B	C8B	C9B	C10B
Feb 12	C1C	C2C	C3C	C4C	C5C	C6C	C7C	C8C	C9C	C10C
Feb 26	C1D	C2D	C3D	C4D	C5D	C6D	C7D	C8D	C9D	C10D

Table A6: Codes for samples of mopane leaves

Date of sampling	**Site 1**	**Site 2**	**Site 3**	**Site 4**	**Site 5**	**Site 6**	**Site 7**	**Site 8**	**Site 9**	**Site 10**
Jan 15	L1A	L2A	L3A	L4A	L5A	L6A	L7A	L8A	L9A	L10A
Jan 29	L1B	L2B	L3B	L4B	L5B	L6B	L7B	L8B	L9B	L10B
Feb 12	L1C	L2C	L3C	L4C	L5C	L6C	L7C	L8C	L9C	L10C
Feb 26	L1D	L2D	L3D	L4D	L5D	L6D	L7D	L8D	L9D	L10D
Mar 11	L1E	L2E	L3E	L4E	L5E	L6E	L7E	L8E	L9E	L10E
Mar 25	L1F	L2F	L3F	TLF	L5F	L6F	L7F	L8F	L9F	L10F
April 15	L1G	L2G	L3G	L4G	L5G	L6G	L7G	L8G	L9G	L10G
April 29	L1H	L2H	L3H	L4H	L5H	L6H	L7H	L8H	L9H	L10G
May 13	L1I	L2I	L3I	L4I	L5I	L6I	L7I	L8I	L9I	L10I
May 27	LIJ	L2J	L3J	L4J	L5J	L6J	L7J	L8J	L9J	L10J
June 10	L1K	L2K	L3K	L4K	L5K	L6K	L7K	L8K	L9K	L10K
June 24	L1L	L2L	L3L	L4L	L5L	L6L	L7L	L8L	L9L	L10K
July 15	L1M	L2M	L3M	L4M	L5M	L6M	L7M	L8M	L9M	L10M
July 29	L1N	L2N	L3N	L4N	L5N	L6N	L7N	L8N	L9N	L10N

Appendix 2

Minimum, maximum and mean concentrations, and standard deviation of heavy metals in the tailings dump.

	Sites											
Metals	1				2				3			
	Min .conc	Max. conc	Mean	Std.dev	Min. conc	Max. conc	Mean	Std .dev	Min. conc	Max conc	Mean	Std dev
Cadmium	11	15	13.14	1.25	9	13	11.29	1.16	11	16	13.93	1.28
Cobalt	82	89	86.57	1.92	68	78	70.64	2.99	66	85	76.93	5.27
Chromium	312	381	347.93	24.20	328	341	334.36	4.17	333	431	407.64	26.45
Copper	860	896	879.86	9.61	820	839	831.79	5.33	799	881	851.14	21.89
Iron	3000	3555	3552.43	116.43	3100	3188	3148.14	31.05	3210	3401	3326.57	56.79
Nickel	350	389	369.14	10.0	328	348	338.07	6.09	389	352	368.21	11.52
Selenium	1.9	2.1	1..98	0.09	1.7	2.0	1.86	0.10	1.8	2.2	1.96	0.13
Zinc	53	60	57.86	2.00	46	50	48	1.13	56.0	81.0	66.43	8.01

Appendix 3

Minimum, maximum and mean concentrations, and standard deviation of heavy metals in soils.

	Cadmium				Cobalt				Chromium				Copper			
Site	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev
1	1.25	2.00	1.68	0.29	24	36	31.14	3.52	166	184	177.5	5.19	225	250	244.36	6.32
2	1.10	1.69	1.29	0.20	18	24	21.36	1.72	138	161	149.93	6.65	241	260	250.79	6.41
3	1.1	1.8	12.5	0.18	9	16	12.5	2.41	100	140	116.5	12.43	215	264	248.07	11.52
4	1.05	1.45	1.24	0.13	6	15	10.43	2.70	85	141	107.93	18.23	275	334	311.86	22.56
5	2.33	3.50	3.10	0.35	46	63	56.14	5.01	201	240	227.79	12.20	300	590	353.64	87.85
6	2.15	3.00	2.56	0.28	53	59	55.86	1.85	215	251	236.79	11.82	350	387	371.64	9.79
7	1.25	1.79	1.29	0.12	37	57	43.57	6.10	221	248	230.71	7.36	240	300	270.5	18.91
8	1.20	1.50	1.33	0.10	20	42	30.79	6.71	36	100	36.64	15.17	121	154	136.5	10.18
9	0.85	1.00	0.94	0.05	11	16	13.57	1.45	23	30	26.43	1.99	73	101	83.86	8.58
10	0.50	1.00	0.64	0.13	10.0	14.0	12.36	1.23	20.0	26.0	23.0	1.60	17.0	23.0	20	1.60

	Iron				Nickel				Selenium				Zinc			
Site	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev	Min con	Max conc	Mean	Std dev
1	128	182	161	16.25	131	171	155	13.97	0.05	0.08	0.06	0.01	38	50	44.29	3.37
2	168	224	198.07	19.71	143	178	163	7.32	0.05	0.25	0.14	0.05	40	48	43.64	2.06
3	200	216	207.07	4.15	160	183	170.29	7.82	0.30	0.45	0.37	0.05	27	39	33	4.36
4	214	227	221.21	4.02	259	273	266.57	5.16	0.80	1.05	0.86	0.22	22	30	26.29	2.74
5	210	251	235.21	12.00	140	284	230.5	40.42	0.8	1.0	0.9	0.05	30	49	38	4.47
6	240	260	251.36	5.79	156	196	173.14	9.22	0.70	1.00	0.84	0.09	49	28	22.21	2.40
7	131	180	153.29	14.91	93	120	105.86	7.04	0.70	1.00	0.83	0.09	28	25	20.57	2.66
8	71	93	78.43	7.10	61	73	66.57	3.77	0.20	0.35	0.26	0.04	25	27	22.21	2.34
9	34	63	43.71	8.28	41	50	45.79	2.45	0.07	0.15	0.09	0.02	27	27	22.93	2.46
10	18.0	26.0	21.71	2.55	19.0	26.0	22.29	2.02	0.05	0.8	0.14	0.19	30	30	25.21	2.88

Appendix 4

Minimum, maximum and mean concentrations, and standard deviation of heavy metals in mopane leaves

	Cadmium				Cobalt				Chromium				Copper			
Site	Min con	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev
1	.001	0.002	0.002	0.001	0.02	0.03	0.03	0.001	0.03	0.04	0.04	0.01	5.01	5.25	5.16	0.09
2		0.002	0.002	0.0004	0.02	0.03	0.04	0.005	Site	0.04	0.04	0.005	5.15	5.25	5.17	0.05
3		0.002	0.002	0.0004	0.03	0.04	0.03	0.004	0.03	0.04	0.04	0.005	5.31	5.35	5.34	0.02
4	.002	0.003	0.003	0.0004	0.02	0.04	0.03	0.007	0.03	0.04	0.04	0.004	5.37	5.41	5.39	0.01
5	.007	0.008	0.008	0.0005	0.05	0.06	0.05	0.004	0.06	0.07	0.06	0.004	6.10	6.19	6.16	0.03
6	.005	0.006	0.006	0.0005	0.05	0.07	0.06	0.007	0.06	0.07	0.07	0.005	5.16	6.09	5.83	0.39
7	.005	0.006	0.006	0.0005	0.05	0.07	0.06	0.007	0.06	0.07	0.07	0.005	5.06	5.15	5.10	0.03
8	.002	0.003	0.003	0.0005	0.05	0.06	0.06	0.005	0.06	0.07	0.07	0.005	4.89	5.00	4.94	0.04
9	.001	0.001	0.001	0	0.01	0.02	0.02	0.004	0.03	0.04	0.03	0.004	4.44	4.56	4.49	0.05
10	.001	0.001	0.002	0.0005	0.01	0.01	0.02	0.005	0.02	0.03	0.03	0.004	4.00	4.25	4.15	0.10

	Iron				Nickel				Selenium				Zinc			
Site	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev
1	308	318	312	2.73	65	71	68.57	1.88	0.01	0.02	0.01	0.005	20	26	22.43	1.84
2	274	312	279.21	9.32	70	120	112.79	12.17	0.1	0.2	0.01	0.004	68	79	73.07	3.92
3	268	273	270.43	1.55	95	111	106.14	4.36	0.01	0.02	0.02	0.003	37	45	41.93	1.83
4	408	418	414.71	3.01	63	72	67.29	2.89	0.02	1.03	0.10	0.26	31	39	35.14	2.45
5	409	430	418.79	6.37	75	92	83.71	4.35	0.02	0.03	0.03	0.005	34	39	36.29	1.16
6	375	409	396.07	10.57	99	117	105.36	6.05	0.02	0.03	0.03	0.005	36	43	40.57	1.35
7	206	216	211	2.75	61	67	64.21	1.61	0.01	0.01	0.01	0.005	25	29	27.21	1.52
8	131	150	142.57	6.48	56	61	57.71	1.49	0.01	0.01	0.01	0	18	21	19.64	0.89
9	37	46	41.5	2.64	31	37	34.43	1.84	0.01	0.01	0.01	0	21	24	22.5	0.98
10	31	37	34.57	1.72	19	24	21.29	1.53	0.01	0.01	0.01	0	17	19	18	0.53

Appendix 5

Minimum, maximum and mean concentrations, and standard deviation of heavy metals in phane caterpillar.

	Cadmium				Cobalt				Chromium				Copper			
Site	Min con	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev
1	0.001	0.002	0.002	0.001	0.02	0.03	0.03	0.001	0.03	0.04	0.04	0.01	5.01	5.25	5.16	0.09
2	0.001	0.002	0.002	0.0004	0.02	0.03	0.04	0.005	0.03	0.04	0.04	0.005	5.15	5.25	5.17	0.05
3	0.001	0.002	0.002	0.0004	0.03	0.04	0.03	0.004	0.03	0.04	0.04	0.005	5.31	5.35	5.34	0.02
4	0.002	0.003	0.003	0.0004	0.02	0.04	0.03	0.007	0.03	0.04	0.04	0.004	5.37	5.41	5.39	0.01
5	0.007	0.008	0.008	0.0005	0.05	0.06	0.05	0.004	0.06	0.07	0.06	0.004	6.10	6.19	6.16	0.03
6	0.005	0.006	0.006	0.0005	0.05	0.07	0.06	0.007	0.06	0.07	0.07	0.005	5.16	6.09	5.83	0.39
7	0.005	0.006	0.006	0.0005	0.05	0.07	0.06	0.007	0.06	0.07	0.07	0.005	5.06	5.15	5.10	0.03
8	0.002	0.003	0.003	0.0005	0.05	0.06	0.06	0.005	0.06	0.07	0.07	0.005	4.89	5.00	4.94	0.04
9	0.001	0.001	0.001	0	0.01	0.02	0.02	0.004	0.03	0.04	0.03	0.004	4.44	4.56	4.49	0.05
10	0.001	0.001	0.002	0.0005	0.01	0.01	0.02	0.005	0.02	0.03	0.03	0.004	4.00	4.25	4.15	0.10
	Iron				Nickel				Selenium				Zinc			
Site	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev	Min conc	Max conc	Mean	Std dev
1	7.02	7.21	7.13	0.07	0.95	1.05	0.99	0.02	0.001	0.001	0.001	0	1.95	2.1	2.02	0.05
2	7.13	7.19	7.16	0.02	0.95	1.01	0.99	0.23	0.001	0.002	0.001	0.004	1.89	1.95	1.91	0.02
3	7.31	7.41	7.37	0.04	0.95	1.05	1.003	0.04	0.001	0.002	0.002	0.004	1.95	2.0	1.98	0.02
4	7.37	7.42	7.40	0.02	0.97	1.01	0.99	0.01	0.002	0.003	0.003	0.00l	1.98	2.01	2.00	0.01
5	7.89	7.95	7.94	0.03	2.02	2.10	2.06	0.03	0.005	0.006	0.006	0.001	3.00	3.08	3.03	0.03
6	6.51	6.85	6.64	0.13	1.90	1.96	1.94	0.020	0.004	0.005	0.005	0.001	2.81	2.95	2.88	0.05
7	5.50	5.69	5.57	0.08	1.80	1.89	1.85	0.04	0.003	0.004	0.004	0.004	2.55	2.56	2.60	0.04
8	5.06	5.11	5.09	0.02	1.76	1.79	1.78	0.01	0.003	0.004	0.004	0.001	2.39	2.45	2.41	0.02
9	4.79	4.88	4.83	0.04	1.21	1.27	1.24	0.02	0.001	0.002	0.002	0.001	1.80	1.91	1.86	0.04
10	3.96	4.0	3.98	0.01	0.95	0.99	0.97	0.01	0.001	0.001	0.002	0.001	1.45	1.49	1.46	0.03