Chapter 1 Introduction

1.1 Introduction

Mine waste is a source of pollution and contamination and research has shown that mining and smelting have affected vast areas in the world (Thorntorn, 1980). One thousand and ninety two square kilometres of the South West England has been contaminated by at least one of the following elements of Arsenic (As), Copper (Cu), Lead (Pb) and Zinc (Zn) (Abrahams, 1983). In Zimbabwe there are over eight thousand mine dumps and some of the research carried out on some of these dumps is detailed in chapter three.

Farmland and livestock ranches make up a large proportion of Zimbabwe and the majority of the derelict land containing mine waste is directly adjacent to them. The dumping of the mine waste results in the useful land being contaminated by the waste and agricultural and ranching land in Zimbabwe have been lost through dumping of mine waste. Poor animal health and poor crop performance are the consequences of secondary contamination from mine waste in these areas (Waller, 1995). Contamination of water supply by acid mine drainage, inhalation and ingestion of dust derived from mine waste are a potential problem in the community (Thornton, 1975, Culbard and Johnson, 1984). Thornton (1975), IARC (1987) have linked cancer to heavy metal contamination in soil.

The extent of contamination out of the mining area itself is greatly affected by dispersion processes. Physical and chemical properties of the mine waste determine the nature and extent of the secondary contamination. Fine particles, which are easily entrained, are dispersed by wind; during the dry season, clay particles lose their adhesive properties and increase the availability of fine particles for wind dispersion (Waller, 1995). Slimes dams are liable to gravity slumping and during heavy rainfall periods, clastic material is transported down stream, while the heavy metal solubility is increased due to pH lowering and these metals are then leached out and transported. The physical characteristics of the slimes affect the leaching process and affect the dispersion of the heavy metals.

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Considering the past intensive activity within the mining area and lack of an environmental monitoring programme, some questions can be posed which this research will attempt to answer;

i)   To what extent are the slimes a major source of pollution?

ii)   What are the main pollutants resulting from the mine waste?

iii)   What is the extent of the effects of the slimes waste on groundwater and surface water and how far does the contamination extend from the dump?

iv)   How much acid is being generated and what are the effects on the soil, surface and groundwater?

The extent of contamination will be assessed in the context of the above questions.

1.2 Outline of the problem

Since 1902, when large-scale mining and smelting of copper began, the flat areas have been used as dumping sites for wastes, at Athens mine in Mvuma. The waste include slimes from the flotation process that separated copper and later gold from the ore and waste rock that was removed as overburden or discarded as too low grade to be separated. These waste dumps contain considerable amounts sulphide minerals. Drainage from tailings and waste produced by mining operations contain high metal concentrations and has an acid pH because of the various chemical, microbiological and hydrological weathering processes that act on the waste. High metal concentrations are toxic to biota, and acid environment, which mobilise many metals, is less favourable for many organisms than are near-neutral pH environments. The waste thus constitutes a potential source of contamination to the environment, surface and groundwater at the mine.

The hydrology, hydrogeology and geochemistry within the mining area, are very complex due to a variety and multitude of pathways to the surface drainage and groundwater aquifers, and the complexity of the waste materials. Acid production and heavy metal release from the mine waste are the major problem at Athens. Process chemicals used, flotation reagents, surfactants, leaching agents, oxidants, solvent extractants are a potential threat to the organisms on the site (Ritcey, 1989). For example, among the chemicals used for the gold extraction, is the highly toxic sodium cyanide.

The vegetation around the slime dumps has been destroyed and revegetation efforts have completely failed. Acid pH environment within the mining area caused the failure of revegetation. The presence of slimes in the three streams that flow through the mining area into Mackenzie dam indicate how far the pollutants extend from the mining area.

1.3 Mining history of Mvuma

The survival of the mine the town of Mvuma depended mostly on the operation of the mine and ranching by the surrounding farmers. The closure of the mine in 1926 reduced what was once the third largest town in Zimbabwe to a village with a population of only 1500 people, which serves as a business centre for the neighbouring communal and resettlement areas. With the reopening of the mine in 1974, the population of Mvuma grew to about four thousand people and the Zimbabwean Government upgraded the village to a growth point in 1981.

Mining at Athens mine started at least in the 15th century with the indigenous miners who were active in Southern Africa during the 15th and 16th centuries and the mining was at very small scale. At Athens they excavated small shafts barely large enough to allow a human body to pass. They also used the open stopes method and this marked the surface outcrop of the ore bodies. The 15th century workers mined the cupriferous gossans for gold, washing away the oxidised copper sulphides and carbonates (Summers, 1969).

Athens was primarily pegged for copper in 1902 and became the largest copper mine in the country (Summers, 1969). Between 1914 and 1955, the mine produced 34 420 tonnes of copper with an average ore grade of 1.6% (Bliss, 1962). The mine during this time employed one thousand people at any one time and Mvuma was the third largest town in Zimbabwe (Fabiani, 1989).

The French South Africa Development Company in 1902, were the first to peg the claims (Taylor, 1976) but did not develop the mine. In 1908, J A Chalmers re-pegged the claims for Falcon Limited, a company that was registered on February 26th 1910 (Bowen, 1979). By the end of 1914, their first year of production, 53 429 tonnes had been milled yielding 1013 tonnes of copper and 403,97kg of gold at a recovery of 7,56 g/t (Fabiani, 1989). Production increased in the following years and the mine deepened.

In October 1925, the mine was closed because of the sharp drop in the base metal prices and a decrease in gold and copper content with depth (Fabiani, 1989). It was by then the fourth largest gold producer in the country (Lightfoot, 1934). The Tilbury brothers, Tom and Wally, owners of Lioness and Cub mines, bought the claims and worked them until 1950 (Fabiani, 1989). In 1964, Anglo American Corporation bought the claims from the Tilburys and carried out extensive geochemical investigations (Fabiani, 1989). They did not operate due to low copper and gold prices and the high operating costs (Fabiani, 1989). Lonhro Zimbabwe purchased the claims in 1974 and used the selective mining method (Fabiani, 1989). They also started reworking the old dumps from the Falcon shaft for gold (Fabiani, 1989). Lonhro closed the mine in 1999 due to low gold prices and it transferred some employees to its other mines and retrenched the remainder.

The mine has changed hands twice since Lonhro disposed of the claims. A group of farmers from Matebeleland, who are the new owners, are concentrating on reworking the old dumps (see fig 1.1 and 1.2 for the mining method) and underground mining has ceased. By 2001, the mine employed only thirty-six people.

Figure 1.1. Re-working on the Falcon old dump. Mining is done using water under pressure to break the compacted slimes. The mining process is affecting the surrounding vegetation and the nearby stream.

Fig 1.2 Slimes being mined hydraulically and flowing to the processing tanks

1.4   Objectives of study

The objectives of this research are: -

a.   To determine the seasonal variation in the arsenic and heavy metal concentrations in the leachate and the active slimes dam,

b.   To determine the dispersion of the heavy metals and arsenic into the soils, streams and groundwater,

c.   To determine role of acid mine drainage (AMD),

d.   To identify the secondary minerals occurring on the surface of the active slimes and

f.   To propose possible remediation measures based on the study.

Chapter 2 Introduction to Study Area

2.1 The physical setting and relief of Zimbabwe.

Zimbabwe is a landlocked southern African country lying between latitudes fifteen degrees (15º00'S) to twenty- three-degree south (23º00'S) and longitudes twenty-five degrees (25º00'E) to thirty-three degrees east (33º00'E). It has a total area of thirty-nine million hectares and is part of the great plateau of southern and central Africa.

Three major regions are generally recognized on the basis of their elevation. The highveld has elevations from one thousand two hundred to one thousand five hundred metres above sea level (ASL) with the eastern highlands reaching up to two thousand six hundred metres ASL. The middleveld is nine hundred metres to one thousand two hundred metres ASL whereas the lowveld is below nine hundred metres (Figure 2.1). The lowveld is located in the extreme south and north of the country with the water-shad forming the highveld running East-west through the centre of the country.

2.1.2 Geology

Zimbabwe has a diverse geology, consisting of the Archean Craton, which occupies about sixty five percent of the country's surface area (Mugumbate *et al*., 1999), the Paleoproterozoic Magondi, that occupies the north-western part of the country, the Mesoproterozoic restricted to the Kamativi area, the Neoproterozoic Zambezi belt in the north and northeast and the Palaeozoic Karoo together with the Kalahari sands. The Craton is comprised of granitoids and gneisses containing the greenstone belts, which are well known for hosting gold and base metals (Figure 2.2). Athens mine, the focus of this thesis, is located in the Midlands Greenstone belt.

The Great Dyke, a layered mafic-ultramafic complex that cuts across the Craton in a north-northeast to south-southwest direction, marks the upper boundary of the Achaean. The great dyke is renowned for world- class deposits of chromite ore and Platinum Group Metals.

The metamorphic belts surround the Craton, the Limpopo belt to the south, Magondi to the northwest and the Zambezi belt to the north and east. Sedimentary basins cover the periphery of the Craton.
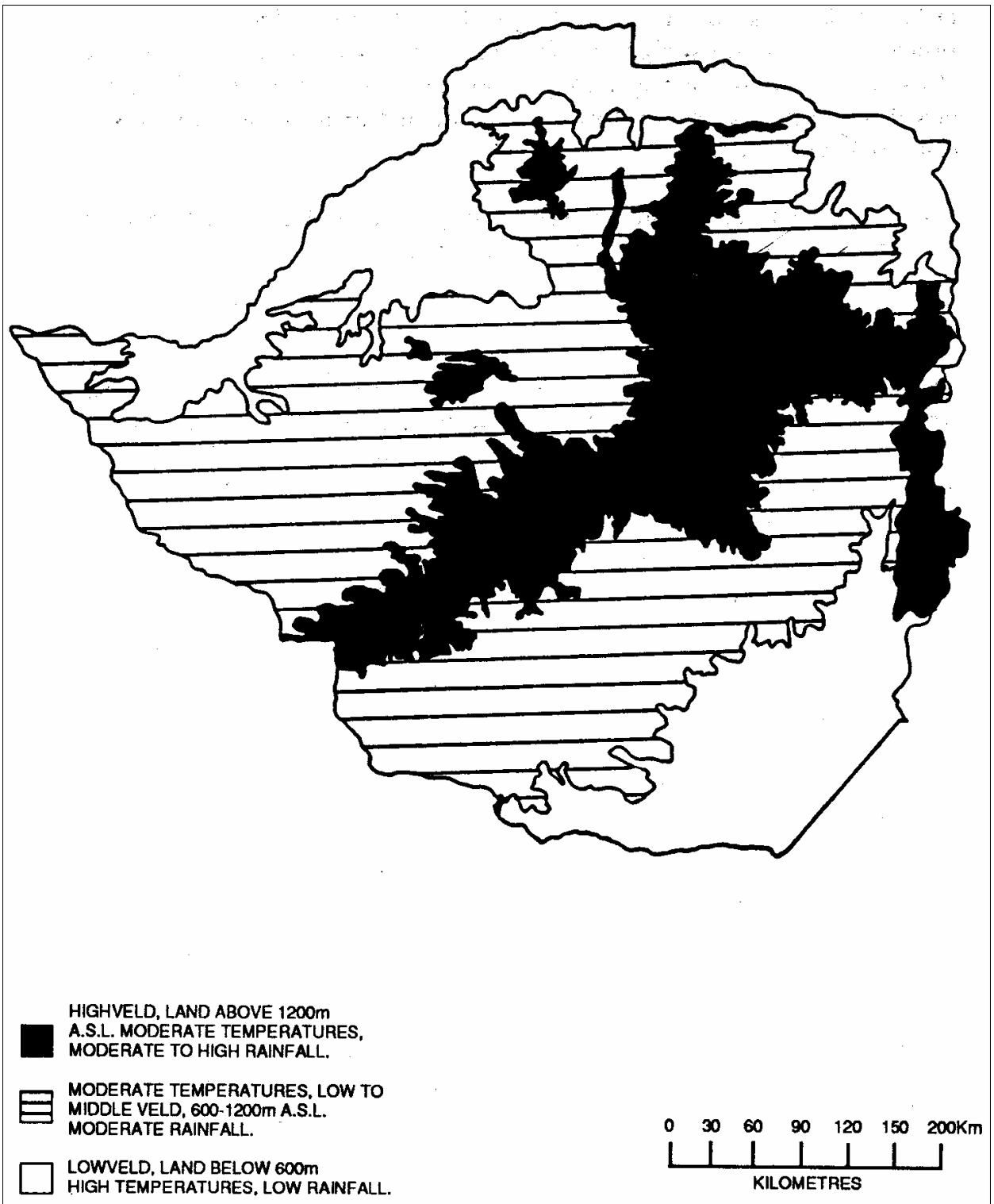
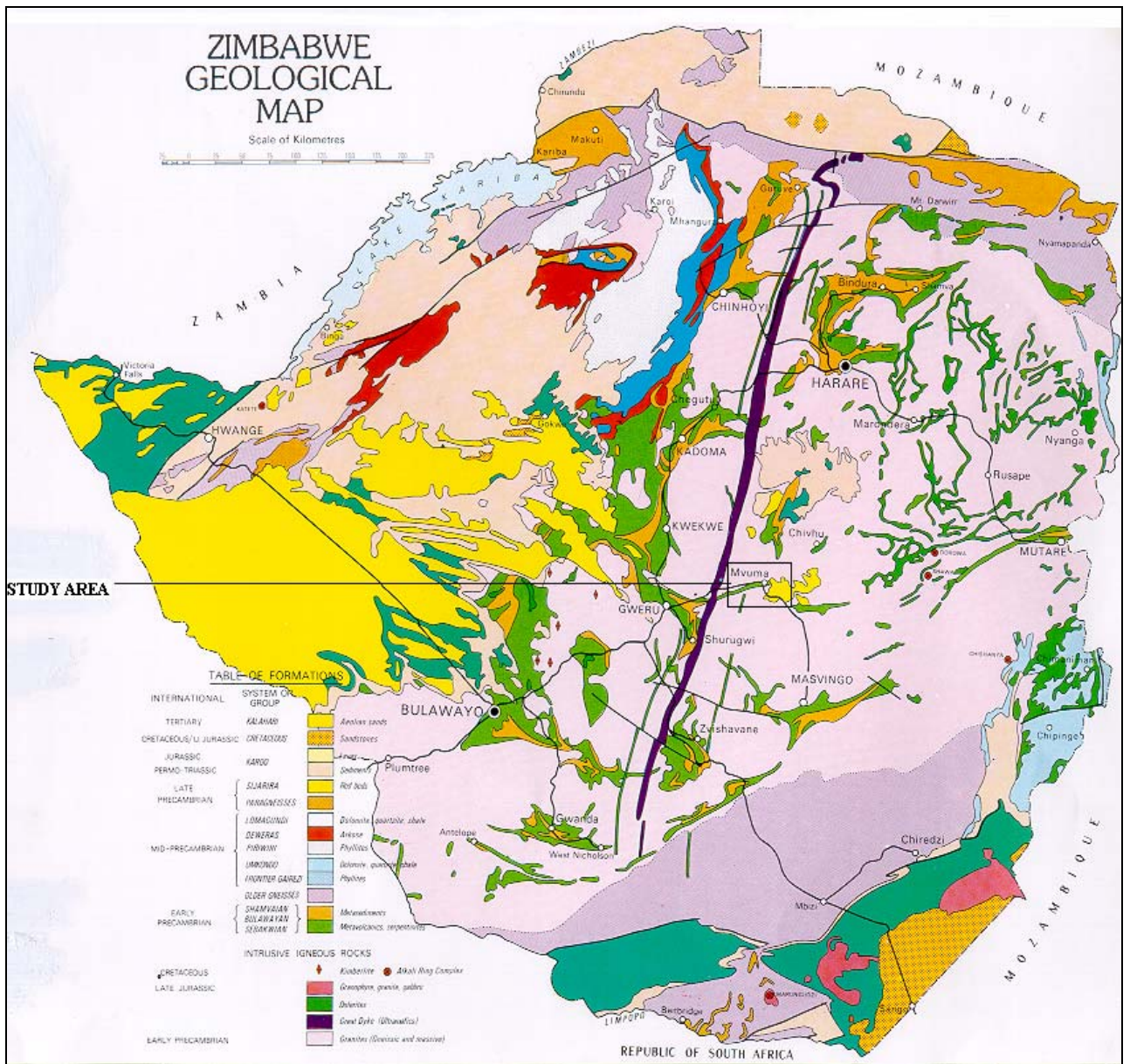**Figure 2.1** Map showing the three physiographic regions of Zimbabwe (Nyamapfene 1991).

The legend reads:

HIGHVELD, LAND ABOVE 1200m A.S.L. MODERATE TEMPERATURES, MODERATE TO HIGH RAINFALL.

MODERATE TEMPERATURES, LOW TO MIDDLE VELD, 600-1200m A.S.L. MODERATE RAINFALL.

LOWVELD, LAND BELOW 600m HIGH TEMPERATURES, LOW RAINFALL.

Figure 2.2 Showing the geology of Zimbabwe and the location of the study site (Geological Society of Zimbabwe 1997).

More than ninety percent of gold deposits are located in the greenstone belts and their immediate granitic environments (Figure 2.3). Some deposits are located in the Magondi and Limpopo mobile belts. Since 1980 over three hundred and eight tonnes of gold have been produced from over six thousand small mines (Mugumbate, *et al*, 1999).
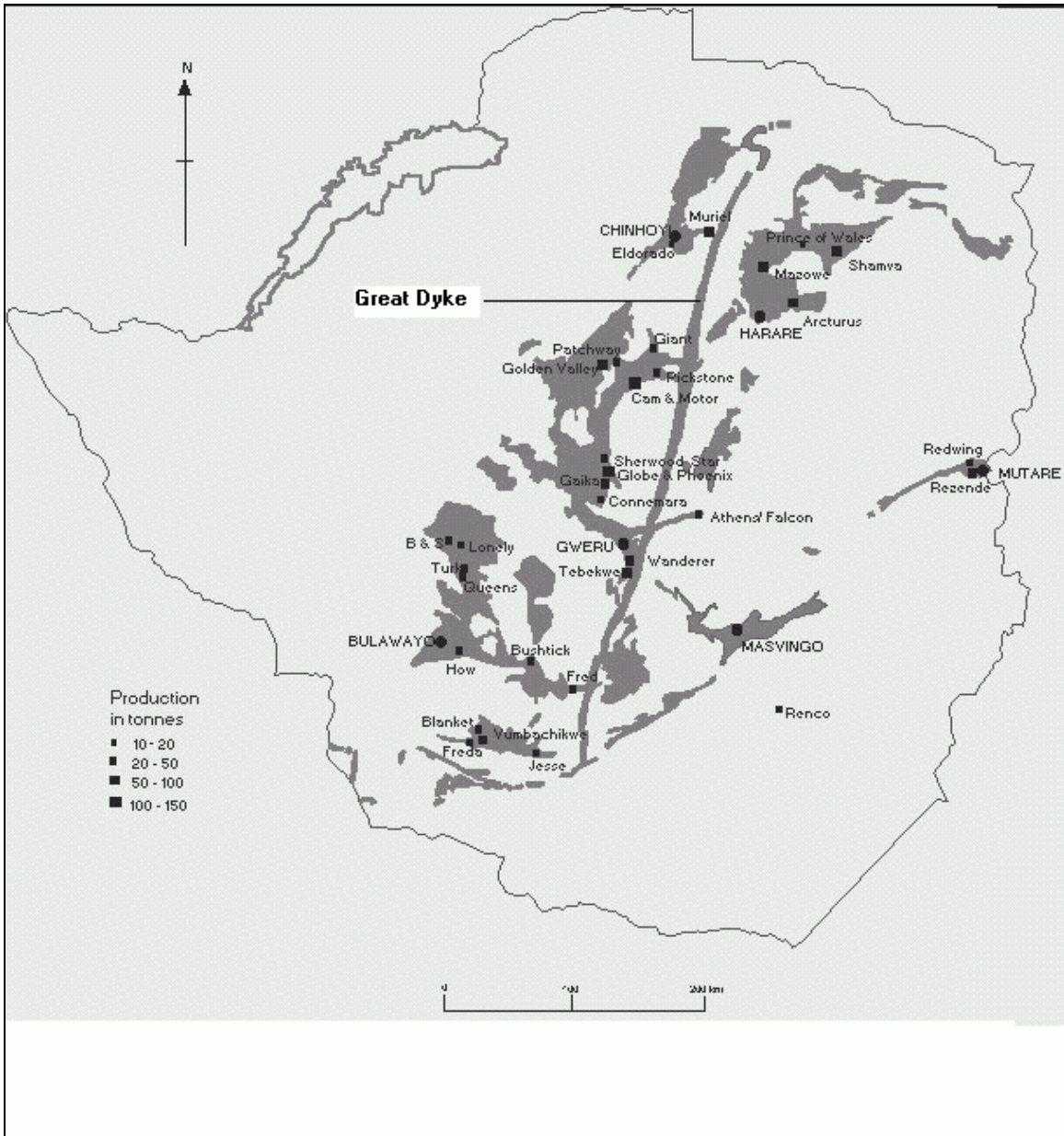
Figure 2.3 Gold deposits with more than ten tonnes production (after Mugumbate, Mupaya and Kwenda 1999).
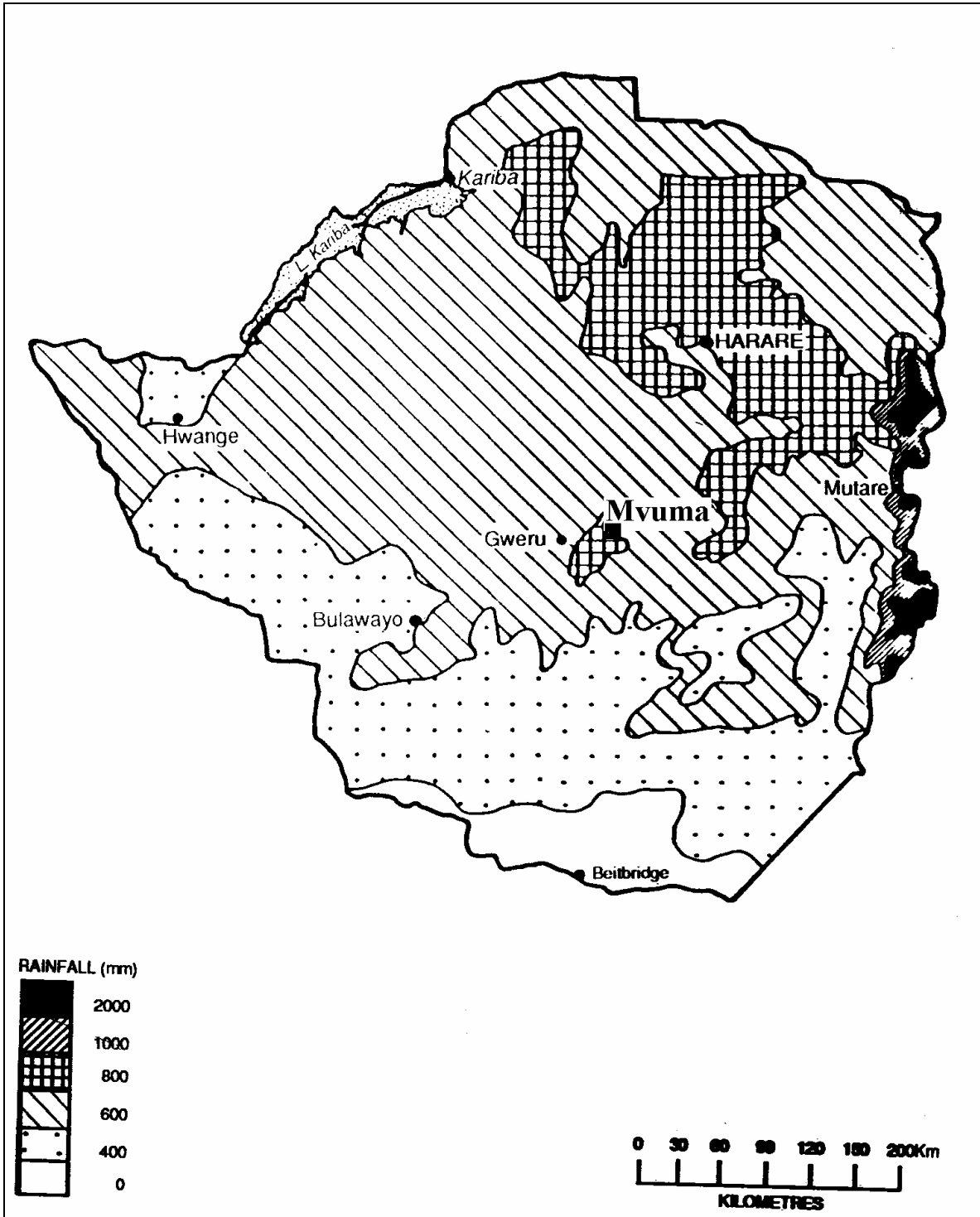
Figure 2.4 Mean annual rainfall in Zimbabwe (Nyamapfene 1991).

2.1.3 Climate and vegetation

The country has a single rainfall season, from November to March with an average rainfall of six hundred and seventy five millimetres (Owen, 1989) and most of the year is dry. A significant feature of the rainfall pattern is its unreliability both in terms of amount and duration. The eastern highlands receive the highest rainfall and the southern part of the country receives the lowest and least reliable rainfall (Figure 2.4). Most of the rain in Zimbabwe is convectional derived from the International Convergence Zone (ITCZ). However, orographic rainfall is important in the eastern highlands at various times of the year (Nyamapfene, 1991), resulting in the eastern highlands experiencing the highest rainfall.

The country is divided into largely agro-climatic natural regions. Soils and vegetation in these regions are formed on the basis of the geology and rainfall pattern of the areas. The impacts of human activities have been felt some parts of Zimbabwe leaving little natural vegetation.

2.2 Study Site:
2.2.1 Location

Mvuma lies on latitude 19º 17′ and longitude 30º 31′ and is one hundred and ninety two kilometres south of Harare, in the Midlands Province of Zimbabwe. Access to the area is via the main tarred highway from Harare to Masvingo and a railway line that passes through Mvuma and connecting to Gweru eighty four kilometres west and to Masvingo one hundred kilometres south east.

The mine is situated five hundred metres south of Mvuma at the eastern end of the Mvuma greenstone belt in the central part of the Zimbabwe Archean craton (Figure 2.2).

2.2.2 Infrastructure

Mvuma is well served by communication lines; road and railway line, and is connected to the country wide electrical and telephone networks. It has piped water supply pumped from Nyamafufu dam twenty kilometres west of Mvuma along the road to Gweru.

There are three government primary schools and one secondary school, a general hospital, a police station, a post office and the Districts Administrator's office for Chirumanzu Rural District Council at the centre.

2.2.3 Climate and Vegetation of Mvuma

The vegetation is typical of the highveld, with fairly thick stands of Miombo woodland, dominated by indigenous species such as mupfuti, msasa and munhondo *(B. boehmii, Brachystegia speciformis and Julbernadia globiflora)*. These are mainly on the greenstone ridges and over areas with serpentinite. In comparison, the vegetation is sparser over the granitic terrain. Msasa (*Brachystegia speciformis*), *Termnalia*, various types of acacia and the mobola plum *(Parinari curatellifolia)* are the common species found on the granites terrain and areas of poor drainage with Miombo woodlands occurring on favourable areas. To the south, exotic blue gum (*Eucalyptus spp.*) plantations are thriving on the Kalahari sand. The natural vegetation on the Kalahari sands is Miombo woodland.

The rainfall figures for Mvuma are shown in Appendix 1 for the period 1911 to 1997 and Figure 2.5 shows the data from 1980 to 1997. The recording stopped with the closure of the mine and there are no reliable readings from 1998 to date.

The area forms part of the central watershed and is in the Sanyati catchment. The small streams in the area flow northwards into the Sebakwe river, which is part of the Zambezi drainage system. The water is mainly used for processing in the plant and ranching in the Central Estate that is situated on the western and northern part of the mine. Some small scale crop farming is irrigated during dry spells around the mine compound.
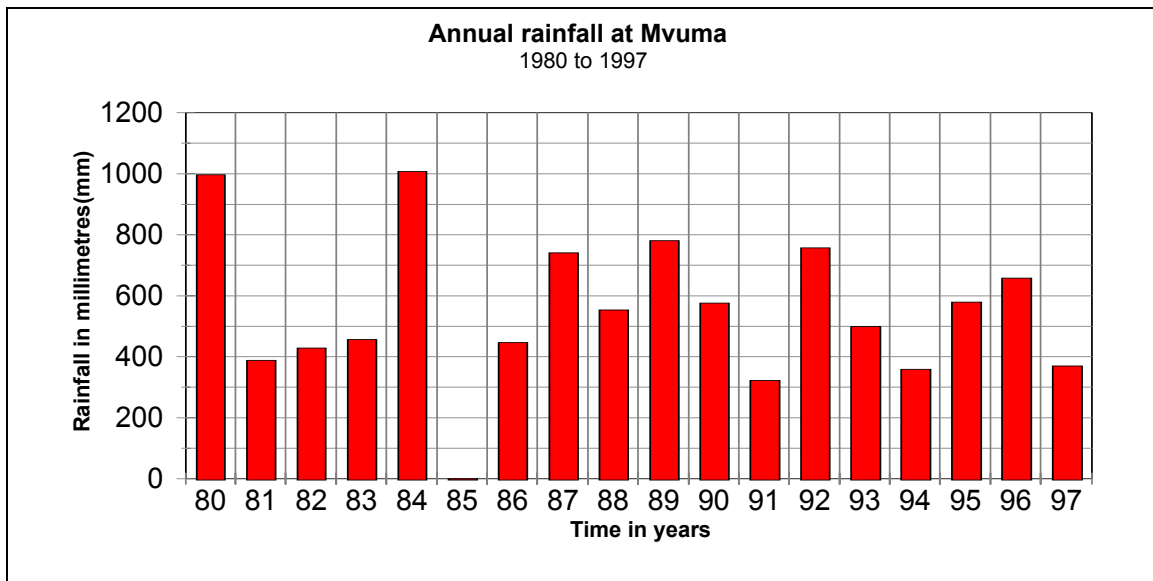
Figure 2.5 Annual rainfalls at Mvuma for eighteen years (1980 to 1997) in mm with an average of 550.82mm. No readings were recorded in 1985 (Metrological Station 1997).

2.2.4 Geology of Mvuma

The area comprises of the Mvuma greenstone belt, mainly of talc and chlorite schist with intercalated iron-formations, and surrounding granites (Fabiani, 1989). The granites around Mvuma are part of the Chilimanzi suite and form part of the Chilimanzi batholith, from which they are named (Bliss, 1962). The greenstones are probably of Upper Greenstone age (Fabiani, 1989), forming part of the Bulawayo Group (approximately 2.7Ga old). The geology of the Mvuma area is shown in Figure 2.6.

The intrusive granitic rocks occur to the north of Athens mine forming the northern margin of the Mvuma greenstone belt. These granites underlie large areas of the Chirumanzu communal land and extend westwards across the Great Dyke into the Gweru area (Fabiani, 1989).

The Kalahari sands of Miocene age occur as a large outlier on the central watershed mainly in the east and south of Mvuma. They lie directly on the granite greenstone, are unconsolidated, have a very low drainage density and form flat landscapes.
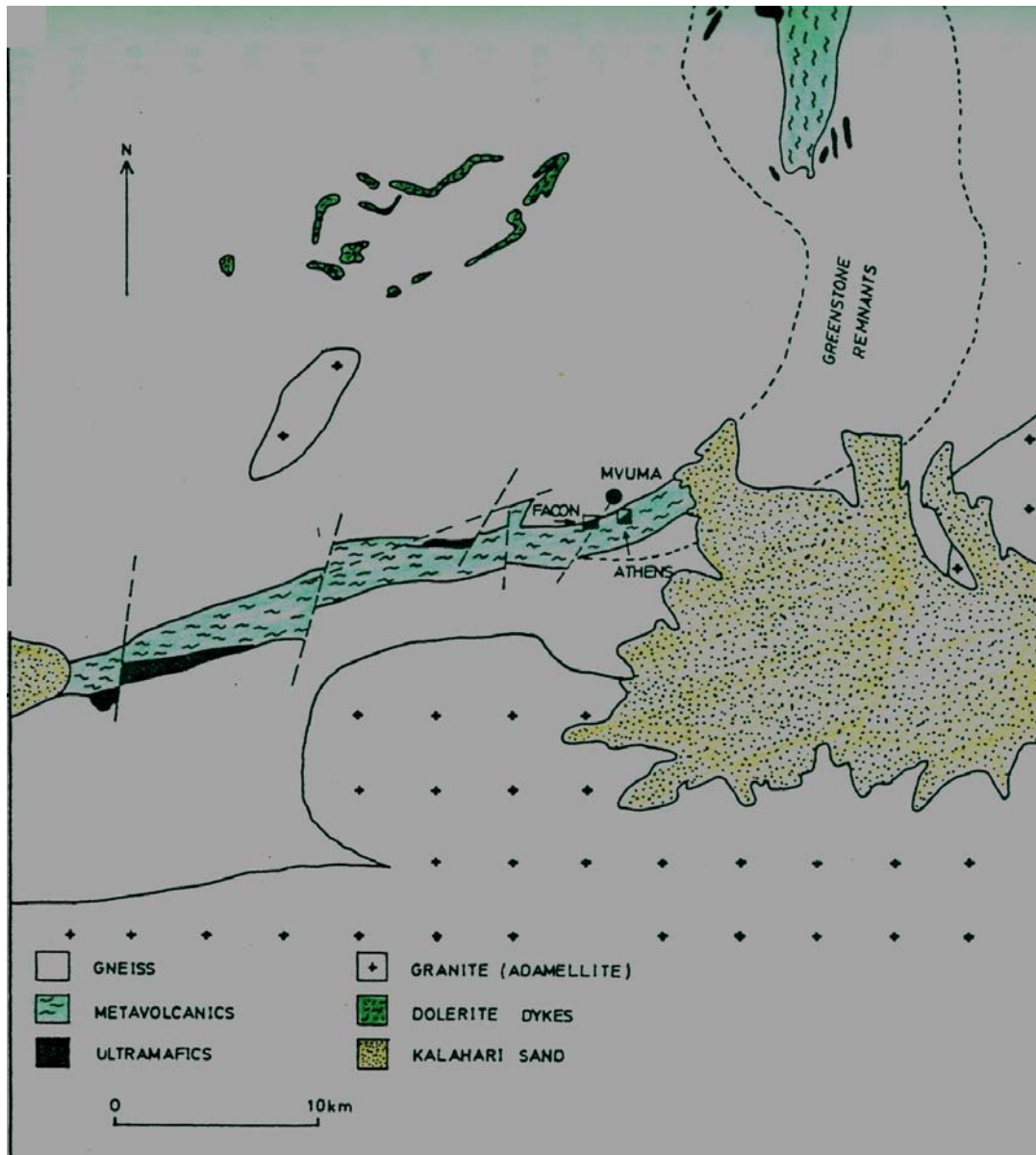
Figure 2.6 Geology of Mvuma (after Fabiani 1989)

2.2.5 Mineralisation

The mineralisation occurs as massive lenses of disseminated copper-iron sulphides and magnetite in chert horizons in the adjacent mafic schist. The lenses of massive pyrite-pyrrhotite ($Fe_{1-x}S$)-chalcopyrite host economic levels of gold. Pyrite (FeS_2)-chalcopyrite ($CuFeS_2$) mineralisation was economically important because it contained up to twenty-seven grams of gold per ton and had high copper content. Pyrite makes up about fifteen percent of the total mined ore and occurs as a matrix to rounded quartz fragments in the pyrite-chalcopyrite mineralisation. Chalcopyrite makes less than five percent. The other sulphides associated with the mineralisation at the mine are arsenopyrite ($FeAsS$),

marcasite (FeS_2), Ti-rich sphalerite (ZnS), pentlandite (($Fe, Ni)_9S_8$), bismuthinite (Bi_2S_3), and galena (PbS) (Fabiani, 1989). Covellite (CuS) was found in chalcopyrite samples. The covellite develops from the decomposition of chalcopyrite and forms irregular rims around the grains. Gold (Au), hedleyite (Bi_7Te_3) and bismuth (Bi) are also associated with the mineralisation.

2.2.6 Type of waste; waste rock and slimes

2.2.6.1 Waste rock

The waste rock at Athens contains mineralisation of little or no value to be economically recovered and is randomly deposited around the mining area. It is used as fill, for road construction and the storage ponds construction at the active slimes dam. In general the waste rock is more than ten centimetres in diameter with a few that are less and does not retain any water. It constitutes a problem to the immediate environment and receiving water due to the release of the dissolved metals by the sulphuric acid produced by the oxidation of the sulphides. Table 1 shows the common sulphides and heavy metals and metalloids that can be released into the environment.

2.2.6.2 Slimes

Slimes are fine material, uniform in size and less than 1mm. The fine size results in low water percolation rate and the dumps are liable to gulley erosion by water run-off during the wet season (Figure 2.10) and are susceptible to wind entrainment during the dry season. The surface crust is compacted and this contributes to their low percolation (Figure 2.8).

2.2.6.3 Disposal

The slimes system at Athens has the following components: slimes impoundment, water recycling, slimes treatment and disposal site, effluent treatment, and evaporation ponds.

Waste rock is disposed randomly in unconfined areas close to the shaft and the plant. This material contains sulphides, which are oxidized on weathering and result in acid rock drainage (ARD).

The active slimes dam is located two kilometres from the mine in the granitic terrain and is thirty-three metres high. Several other old dams are scattered around the mining area in

the area underlain by greenstone belt rocks. Slimes were disposed of as slurry with high water content transported from the mine to the slimes dam site through PVC pipes. The residues contained in the slimes dam consist of sediments with a grain size of between 65 microns and 75 microns. The design and structure of the slimes dam is shown in Figures 2.9 and 2.10. The dam is designed in such a way that the slurry is discharged at the edge of the dam and then flows down a gentle slope to the centre leaving the heavier and coarser material deposited around the edges. Surrounding the dam is a receiving trench, into which flows leachate that has percolated through the slimes and then drains laterally into the trench. The receiving trenches drain into storage ponds (See Figure 2.7) from where the water is pumped back to the mine for re-use in the processing plant. Adjacent to the ponds is a stream that drains into Mackenzie dam.

Table 1. Common ore minerals of non-iron (II) metals (Peters, 1978; Rose *et al.*, 1979)

Metal	Ore minerals	Associated heavy metals and metalloids
Ag	Ag_2S, PbS	Au, Cu, Sb, Zn, Pb, Se, Te
As	FeAsS, AsS	As, Au, Ag, Hg, U, Bi
	Cu ores	Mo, Sn, Cu
Au	Native Au, $AuTe_2$	Te, Ag , As, Sb, Hg, Se
	(Au, Ag) Te_2	
Ba	$BaSO_4$	Pb, Zn
Bi	Pb ore	Sb, As
Cd	ZnS	Zn, Pb, Cu
Cr	$FeCr_2O_4$	Ni, Co
Cu	$CuFeS_2$, $CuFeS_4$	Zn, Cd, Pb, As, Se, Sb, Ni, Pt, Mo, Au, Te
	Cu_2S, Cu_3,AsS_4	
	CuS, Native Cu	
Hg	HgS, Native Hg	Sb, Se, Te, Ag, Zn, Pb
	Zn ores	
Mn	MnO_2	Various (e.g. Fe, Co, Ni, Zn, Pb)
Mo	MoS_2	Cu, Re, W, Sn
Ni	$(Ni, Fe)_9S_8$, NiAs	Co, Cr, As, Pt, Se, Te
	$(Co,Ni)_3S_4$	
Pb	PbS	Ag, Zn, Cu, Cd, Sb, TI, Se, Te
Pt	Native Pt, $PtAs_2$	Ni, Cu, Cr
Sb	Sb_2S_3, Ag, SbS_2	Ag, Au, Hg, As
Se	Cu ores	As, Sb, Cu, Ag, Au
Sn	SnO_2,	
	$Cu_2 (Fe,Zn)SnS_4$	Nb, Ta, W, Rb
U	U_3O_8	V, As, Mo, Se, Pb, Cu, Co, Ag
V	V_2O5, VS_4	U
W	WO_3, $CaWO_4$	Mo, Sn, Nb
Zn	ZnS	Cd, Cu, Pb, As, Se, Sb, Ag, Au, In

The evaporation ponds are situated adjacent to the active dam on the northern side and cover a large area. There are three distinct ponds. The leachate flows into pond 1 and when it is full, it flows into pond 2 where some of the water is pumped back to the processing plant for reuse. Pond 3 is called the storage pond, water is only pumped into it

when the first two are full and it is not linked to the other two. All the ponds are not lined at the bottom nor are they covered on top. There is seepage from the ponds into the environment.

Figure 2.7 Shows what was once two separate storage ponds 1 and 2, the deep red water is an indication of iron (Fe^{3+}). The vegetation on the top left side of photograph across the main road shows no sign of effects from the acidic waters from the dam while the vegetation close to the dump has been affected. Buses for scale.

Figure 2.8. Compacted surface crust on the slimes dump at Athens lowers percolation of water and forms a hard pan on the sides of the dump. The reduction of percolation results in water logging on top of the slimes.
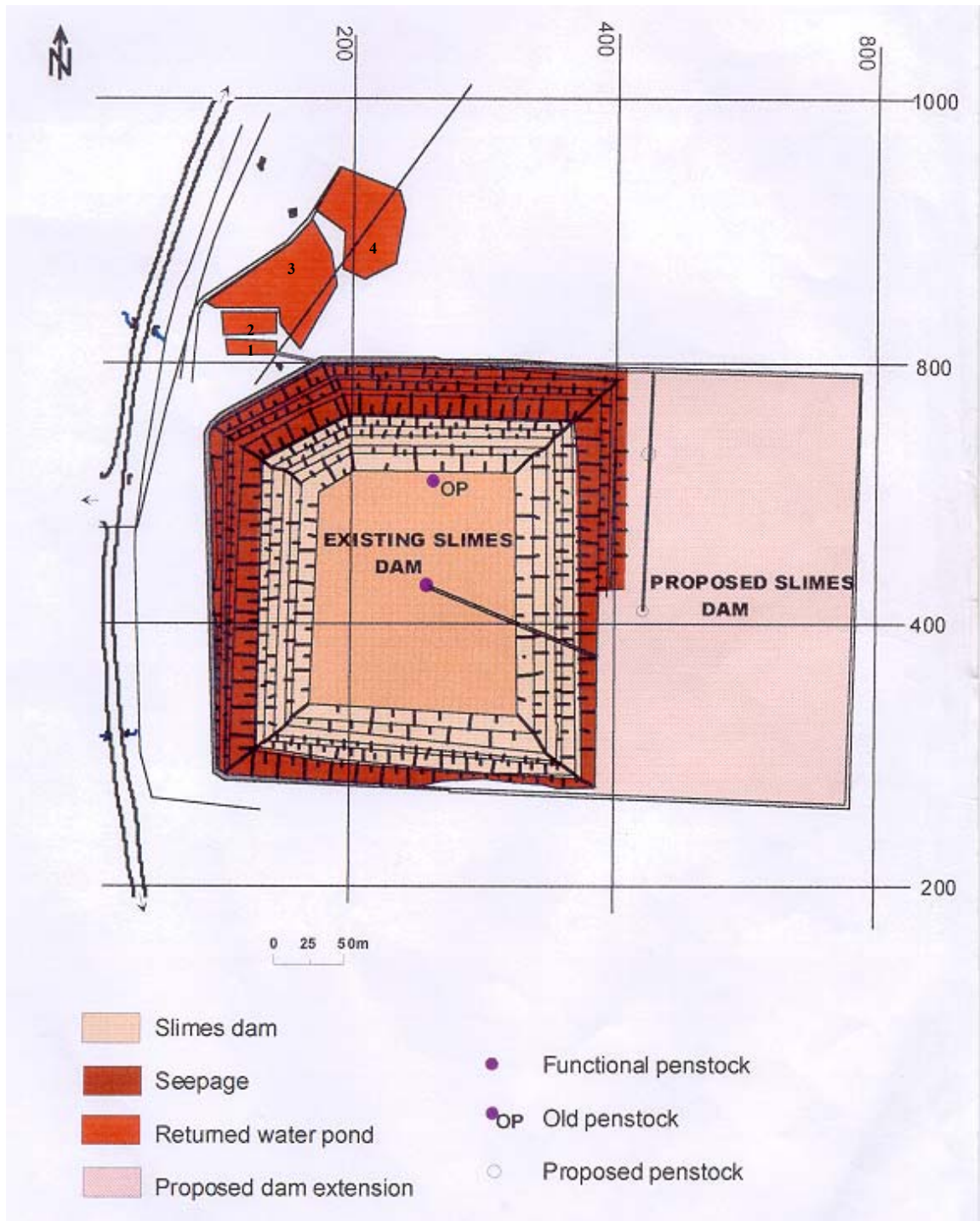
Figure 2.9 Slimes dam design at Athens mine, Mvuma (After Goliath, 1997).

Figure 2.10 The slimes dam with compacted layers and the crystals at the base with the gullies from run off water on the surface of the dump and slimes water sapping at the base of the dump.

Chapter 3.

Review of previous work on Environmental studies in Zimbabwe and Geological studies at Athens Mine.

3.1 Acid mine drainage (AMD) – an overview

Acid mine drainage (AMD) is an acidic solution, containing metal and sulphate ions that form under natural conditions when rocks containing sulphides are exposed to oxidising conditions (Skousen, 1995). AMD is characterised by low pH, high sulphate and high metal content (Caruccio et al., 1988). In the absence of neutralisation, 1.63kg of concentrated H_2SO_4 is produced for every kilogram of pyrite that is fully oxidised (Watkins, 1999). Once oxidation commences, there is a linear correlation between oxidation rate and its surface area (Caruccio et al., 1988).

Pyrite and marcasite (FeS_2) are the most prominent acid producers, but other minerals comprising metals complexed with sulphides may also be responsible (Table 2).

Table 2: Some of the important metal sulphides, which form sulphuric acid when exposed to oxidising conditions (after Skousen, 1995).

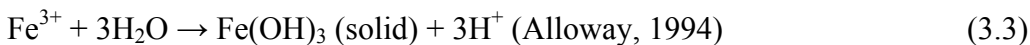| FeS_2	pyrite	$CuFeS_2$	chalcopyrite
FeS_2	marcasite	MoS_2	molybdenite
FeS_{1-x}	pyrrhotite	NiS	millerite
Cu_2S	chalcocsite	PbS	galena
CuS	covellite	ZnS	sphalerite
$FeAsS$	arsenopyrite		

These sulphide minerals oxidise in the presence of water and oxygen to give highly acidic sulphate rich drainage. The oxidation of iron disulphides and the conversion to acid occur through the following reactions:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \text{ (McKibben and Barnes, 1986)} \quad (3.1)$$
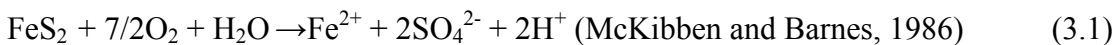
Iron sulphide is oxidised releasing iron(II) (reduced form of iron) and acid

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \text{ (Alloway, 1994)} \quad (3.2)$$

Iron(II) is oxidised forming iron(III) and water

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 \text{ (solid)} + 3H^+ \text{ (Alloway, 1994)} \quad (3.3)$$

Iron(III) can be hydrolysed forming iron(III) hydroxide (forming the 'yellow boy', deposit seen in figure 3.1) and acid

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15 Fe^{2+} + 2SO_4^{2-} + 16H^+ \text{ (McKibben and Barnes, 1986)} \quad (3.4)$$
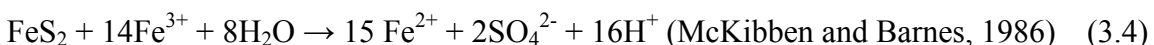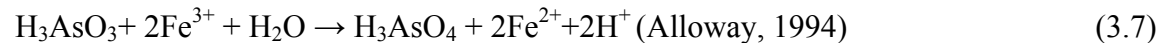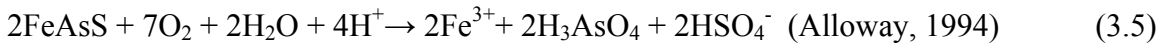
Iron(III) ion can also attack pyrite directly acting as a catalyst generating greater amounts of Iron(II) sulphate and acid.
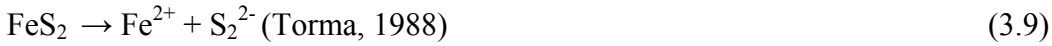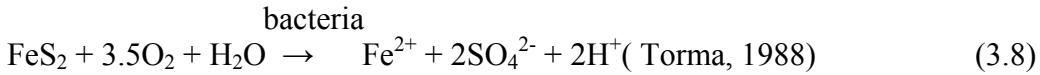

Figure 3.1 Yellow boy, typical indicator of AMD in a stream adjacent to the Falcon shaft at Athens Mine.

The oxidation not only results in acidification but also in the release of toxic materials into the environment, such as, iron, copper, cadmium, zinc and arsenic (Figure 3.2). Sulphides present environmental problems when the mining operations have ceased as long as they are in contact with air and oxygenated water. The dissolution of FeAsS for example, liberates arsenic into natural waters following the equations:

$2FeAsS + 7O_2 + 2H_2O + 4H^+ \rightarrow 2Fe^{3+} + 2H_3AsO_4 + 2HSO_4^-$ (Alloway, 1994)   (3.5)

$4FeAsS + 11O_2 + 6H_2O \rightarrow 4FeSO_4 + 4H_3AsO_3$ (Alloway, 1994)   (3.6)

$H_3AsO_3 + 2Fe^{3+} + H_2O \rightarrow H_3AsO_4 + 2Fe^{2+} + 2H^+$ (Alloway, 1994)   (3.7)

Bacteria such as *Thiobacillus ferrooxidants* can catalyse the oxidation reactions in slimes and weathering orebodies (Alloway and Ayares., 1994). They act as a catalyst in the oxidising reaction, which oxidise iron (II) to iron (III) in the presence of oxygen and sulphuric acid (Equation 3.2). The mechanisms by which the bacteria contribute to oxidation of pyrite are classified into two: direct metabolic reactions and indirect metabolic reactions.

The direct metabolic oxidation (DMO) reaction requires physical contact between bacteria and pyrite releasing a disulphide.

$$FeS_2 + 3.5O_2 + H_2O \xrightarrow{bacteria} Fe^{2+} + 2SO_4^{2-} + 2H^+ \; (\text{Torma, 1988}) \qquad (3.8)$$

$$FeS_2 \rightarrow Fe^{2+} + S_2^{2-} \; (\text{Torma, 1988}) \qquad (3.9)$$

The disulphide is immediately bound by bacterial enzymes and is oxidised to sulphate as shown below:

$$S_2^{2-} + 4O_2 \xrightarrow{bacteria} 2SO_4^{2-} \quad (\text{Torma, 1988}) \qquad (3.10)$$

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4 \; (\text{Konishi et al., 1990}) \qquad (3.11)$$
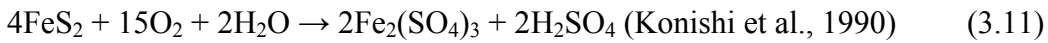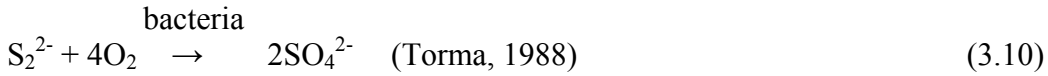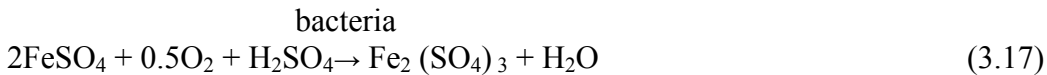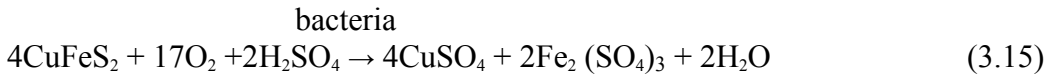

Figure 3.2 A storage pond at Athens mine. Note the green colour of the water due to copper, and the white salt deposits on the sides.

Indirect metabolic oxidation (IMO), involves the oxidation of pyrite by iron (III) and regeneration of the iron (III) from the oxidation of iron (II) and elemental sulphur, as shown in the following reactions (Torma 1988):

$$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S^0 \qquad (3.12)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2H_2O \qquad (3.13)$$

$$2S^0 + 3O_2 + 2H_2O \rightarrow H_2SO_4 \qquad (3.14)$$

The role of bacteria in the oxidising of pyrite can therefore be seen as indirect in which their function is to regenerate Fe^{3+}, the major oxidant.

Bacterial oxidation of mineral sulphides (at pH 2) results in the disruption of the mineral crystal lattice and the increase of the ionic species in solution (Konishi et al., 1990). Chalcopyrite, for example, disintegrates with the appearance of Cu^{2+}, Fe^{3+} and SO_4^{2-} as shown in the following equations (Konishi et al., 1990): -

$$\overset{bacteria}{4CuFeS_2 + 17O_2 + 2H_2SO_4 \rightarrow 4CuSO_4 + 2Fe_2(SO_4)_3 + 2H_2O} \tag{3.15}$$

$$CuFeS_2 + 2Fe_2(SO_4)_3 \rightarrow CuSO_4 + 5FeSO_4 + 2S^o \tag{3.16}$$

$$\overset{bacteria}{2FeSO_4 + 0.5O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O} \tag{3.17}$$

The Fe^{3+} produced in the reaction (Eq 3.15) acts as an oxidant on un-reacted sulphide (Eq 3.16). The secondary reaction of bacteria is accelerated by the oxidation of the reduced Fe^{2+} back to Fe^{3+} (Eq 3.17) while maintaining an Eh potential of >659V (Jordan et al., 1993). The chemical oxidation reaction gives the metal depletion of the mineral allowing the release of metallic cations at the expense of the sulphur-enriched residue.

3.2 Toxicity of heavy metals.

Toxicity is defined as a poisonous effect on a living organism and it can be either acute or chronic toxicity (Sheila and Katherine, 1994).. Acute is a large dose of poison for a short duration, which is lethal, while chronic is low dose over a long period of time and can be lethal or sub-lethal (Sheila and Katherine, 1994). Effluent arising from the mining process and metal extraction can be toxic in varying degrees to human, animals and plants (Ritcey, 1989). It can be highly acidic or alkaline and may contain dissolved metals, and soluble and insoluble complex organic constituents from the mill process. pH, dissolved oxygen and temperature are important aspects in the toxicity of the receiving environment. The sensitivity of organisms to metal toxicity varies with species of plants, animals and genotypes within species and the response to the toxic dose of metals can be modified by many factors. In the cationic form, heavy metals are lethal at relatively low concentration to fish and other aquatic organisms and may enter the food pathway to man (Ritcey, 1989). Hg, Cu, Ni, Pb, Co, Cd, Ag, Be and Sn are the most toxic metals to higher plants and several microorganisms (Kabata-Pendias and Pendias, 1984).

As, Cu and Hg are the most toxic to humans but the extent of toxicity is affected by human homeostatic mechanisms (Kabata-Pendias and Pendias, 1984).

3.2.1 Arsenic (As)

Arsenic occurs naturally as arsenates, arsenites, arsenides and sulphides in specific rock types. It also occurs in hydrated clay species (Welch et al., 1988). Arsenic oxide minerals, such as Scorodite, are important in the oxidised zones of sulphide ore deposits and in oxidised dumps where they form by breaking down of arsenopyrite. The oxidation of sulphide minerals has the potential for the release of large quantities of As into solution. As a result, high arsenical waters and soils are found in mineralised areas mostly where mining activities have catalysed the sulphide oxidation process. Elevated arsenic concentrations are commonly associated with sediments partially derived from volcanic rocks of intermediate to acidic composition (Welch et al., 1988).

Arsenic is present in water principally as an arsenate (As (V)) and arsenite (As (III)) oxy anions, with H_2AsO_4, $HAsO_4^{2-}$ and H_3AsO_3 being the most common (Fergusson, 1985). These are soluble species but the concentrations of dissolved As may be limited due to precipitation of sulphide minerals or iron hydroxides (Fergusson, 1985).

Toxicity of arsenic is dependent on valence with compounds of valence 5+ less toxic than those of 3+ (Reimann de Caritat, 1998). Skin diseases are the most typical symptoms of chronic exposure to arsenic in drinking water. These symptoms include pigmentation disorders, hyperkeratosis and skin cancer (Baird, 1995). The other symptoms are renal, gastrointestinal, neurological, haematological, cardiovascular and respiratory problems (Baird, 1995). Lung cancer results from inhalation of arsenic, cancer of the bladder and kidneys from the ingestion of arsenic (Baird, 1995). Sever vomiting and diarrhoea is a result of gastrointestinal damage due to consumption of acute dosages. The symptoms become visible within eight minutes after taking a contaminated liquid and up to ten hours after taking a contaminated solid (Baird, 1995).

In animals, As poisoning causes staggering gait, extreme weakness, trembling, collapse, vomiting, diarrhoea and serious abdominal pains (Waldron, 1980). The toxicity of the

arsenic compounds depends on the route of entry, solubility, animal species, their nutritional, medical condition, chemical and physical properties (Chihota, 1995).

In soils, arsenic availability is affected by changes with toxicity increasing as the soils become more acid, mostly at pHs below 5 (Alloway, 1995). At pHs below 5, the arsenic binding species such as iron and aluminium, become more soluble releasing the As (Alloway, 1995).

3.2.2 Cadmium (Cd)

Cadmium (Cd^{2+}) is a serious metal toxin, which has effects on the bone structure and kidneys, for example the itai-itai disease which caused large-scale demineralisation of bones that leads to shrinkage, distortion and embrittlement (Fergusson, 1985). A major occurrence of this was in the 1960's in Japan (Fergusson, 1985). Cadmium forms inactive Cd-enzymes by replacing Zn in biological systems mostly when it is bonded to sulphur. Cd^{2+} ion forms a stronger bond with the sulphur atoms than Zn^{2+} (Fergusson, 1985). Inhaled cadmium in high concentrations causes emphysema and related acute lung conditions. The metal is less adsorbed hence is more bio-available than other divalent metals (Fergusson, 1985). Table 3 shows the toxic levels and effects in plants.

3.2.3 Chromium (Cr)

Cr exists in trivalent (chromite, Cr(III)) and hexavalent (chromate, Cr(VI)) forms, with Cr(VI) being more phytotoxic (Alloway and Ayares, 1994). Cr(III) is more toxic to fish with toxic concentration ranges of 0.2 to 5μg/ml and Cr(VI) is toxic to many species of algae and microorganisms (Langard, 1980). Cr(VI) is reduced to Cr(III) in the presence of organic matter and its toxicity is reduced. In humans, Cr in high concentrations, is carcinogenic and causes cancer of the respiratory organs.

3.2.4 Lead (Pb)

Lead is the most abundant of the heavy metals and the main sources of environmental pollution are petrol, mining (smelting of the ore, slimes from ore dressing smelter fumes) and paints. It is a cumulative toxin in mammals but is not as bioavailable as the other heavy metals (Alloway and Ayares, 1994). The toxic concentrations accumulate in bone marrow affecting the formation of haemoglobin resulting in anaemia (Waldon, 1980).

Exposure to Pb can also result in kidney damage (Alloway and Ayares, 1994). The toxic levels in plants and the biochemical process affected are shown in Table 2.

3.2.5 Copper (Cu)

Copper is required for collagen formation. Copper deficiency is association with atherosclerosis and other cardiovascular conditions. Excess copper or biounavailable copper often cause connective tissue problems, interfering with the disulfide bonds in connective tissue. Symptoms may include stretch marks, tendon and ligament weakness, mitral valve prolapse, skin and hair problems and other conditions affecting connective tissue (Eck and Wilson, 1989). Exposure to copper salts and dust cause an allergic reaction with greenish black discolouration symptoms (Nriagu, 1979). Copper salts cause conjunctivitis and edema of the eyelids (Nriagu, 1979). Copper deficiency is rare as copper is present in most diets.

In animals, primary chronic poisoning is seen most commonly in sheep when excessive amounts of copper are ingested over a prolonged period (Martin J. S. 1998). The toxicosis remains subclinical until the copper that is stored in the liver is released in massive amounts. Blood copper concentrations increase suddenly, causing lipid peroxidation and intravascular hemolysis (Martin J. S. 1998). The haemolytic crisis may be precipitated by many factors, including transportation, lactation, strenuous exercise, or a deteriorating plane of nutrition (Martin J. S. 1998).

Acute poisoning may follow intakes of 20-100 mg of copper/kg body wt in sheep and young calves and of 200-800 mg/kg in mature cattle (Martin J. S. 1998). Chronic poisoning of sheep may occur with daily intakes of 3.5 mg of copper/kg body wt when grazing pastures that contain 15-20 ppm (dry matter) of copper and low levels of molybdenum (Martin J. S. 1998). Clinical disease may occur in sheep that ingest cattle rations, which normally contain higher levels of copper, or when their water is supplied via copper plumbing; cattle are more resistant to copper poisoning than sheep, and thus are not affected in these instances (Martin J. S. 1998). Young calves or sheep injected with soluble forms of copper may develop acute clinical signs of toxicity (Martin J. S. 1998). Copper is used as a feed additive for pigs at 125-250 ppm; levels >250 ppm are

dangerous although as for sheep, other factors may be protective, such as, high levels of protein, zinc, or iron (Martin J. S. 1998).

3.2.6 Antimony (Sb), and Zinc (Zn)

This group of elements mostly affect plants and as shown in Table 1. Antimony may be lethal at levels of 40 – 1000 mg/l and for potassium antimony (V) tartrate, a dose of 4-30 mg is lethal (Bowen, 1982). Sb is immobile and its adsorption by soil is over a long period of time (Alloway, 1990).

Zinc is mainly a cause of phytotoxicity and has a relative low toxicity to animals and humans. In extreme deficiency cases, it causes short stature and delayed sexual maturity (Alloway 1994).

3.2.7 Iron (Fe)

Iron toxicity in plants is primarily caused by the toxic effect of excessive Fe uptake due to high solution Fe concentrations. Large amounts of Fe in plants can give rise to the formation of oxygen radicals, which are highly phytotoxic and responsible for protein degradation and peroxidation of membrane lipids (Dobermann A. et al., 2000). The optimal ranges and critical levels for occurrence of Fe toxicity in plants are 100-150 mg/kg and >300 – 500 mg/kg.

Iron overdose has been one of the leading causes of death caused by toxicological agents in children younger than 6 years and there are no reports of survival with iron levels > 2687 mumol/L (> 15,000 micrograms/dL) (Cheney K. et al., 1995). The toxicity of iron is governed by absorption. The more you take in the more you are at risk. The iron is absorbed in the ferrous state by cells of the intestinal mucous. Excess body iron can be highly toxic. This toxicity involves many organs leading to a variety of serious diseases such as liver disease, heart disease, diabetes mellitus, hormonal abnormalities and dysfunctional immune system (Kang J. O. 2001). The tissue damage associated with iron overload is believed to result primarily from free radical reactions mediated by iron. Iron is an effective catalyst in free radical reactions (Kang J. O. 2001).

3.2.8 Nickel (Ni)

Pulmonary absorption is the major route of concern for nickel-induced toxicity. Nickel may be absorbed as the soluble nickel ion (Ni^{+2}) while sparingly soluble nickel compounds may be phagocytized (ATSDR 1988). The chemical form and its deposition site in the lungs will affect the extent of absorption (ATSDR 1988). Nickel may be removed from portions of the respiratory tract via mucociliary transport resulting in the material entering the gastrointestinal tract. Although nickel is poorly absorbed from the gastrointestinal tract, dietary exposure and exposure via drinking water provide most of the intake of nickel and nickel compounds (Coogan et al. 1989, Goyer 1991).

Nickel is not destroyed in the body, but its chemical form may be altered. The metabolism of nickel is most appropriately viewed in light of its binding to form ligands and its transport throughout the body. Much of the toxicity of nickel may be associated with its interference with the physiological processes of manganese, zinc, calcium, and magnesium (Coogan et al. 1989). Various disease states (myocardial infarction and acute stroke) and injuries (burn injury) are associated with altered transport and serum concentrations of nickel (ATSDR 1988).

In animals, generally, soluble nickel compounds are more toxic than insoluble compounds. In acute cases, values for rats range from, 67 mg nickel/kg for nickel sulfate hexahydrate to >9000 mg nickel/kg for nickel powder (ATSDR, 1988).

3.2.9 Cobalt (Co)

Cobalt Toxicity is generally also not a concern since it doesn't develop from the normal consumption of foods and beverages, unless - as with nickel - there is a natural tendency to retain too much cobalt, in which case asthma, anxiety or cardiac symptoms may be experienced. Other effects of overdosing on cobalt (> 5mg / day) include abnormal thyroid functions, polycythemia and overproduction of red blood cells (erythropoiesis), with increased production of the hormone erythropoietin (EPO) from the kidneys (Bowen, H.J.M., 1979).

The toxicity of cobalt is quite low compared to many other metals in soil. Exposure to very high levels of cobalt can cause health effects. Effects on the lungs, including asthma, pneumonia, and wheezing, have been found in workers who breathed high levels of

cobalt in the air (Bowen, H.J.M., 1979). Where cobalt concentrations in soil are greater than 40 ppm, and cobalt toxicity to vegetation is suspected, cobalt uptake into plants can be reduced by liming the soil and by incorporating uncontaminated soil, peat moss, compost or manure into the soil (Frank, R. et al., 1976).

3.3 Disposal of Mining Waste: Introduction

Metals utilized in manufacturing are obtained from either mining of ore bodies in the Earth's crust or recycling of scrap metal originally derived from geological sources. With increasing demand and improvements in technology of mineral extraction there is a trend for low-grade orebodies to be mined and these result in large volumes of waste materials (Alloway and Ayares 1994). This suggests that the environmental impacts of mining low-grade orebodies may be greater than mining areas of high-grade orebodies.

Large quantities of waste rock, chemical precipitates, fine clays, flotation slimes, slimes and mine waters have to be disposed of during the mining and extraction of the metal ore concentrates using various techniques depending on the density, magnetism and surface tension of the ore. The bulk of the waste will be disposed of on the surface, posing an immediate pollution threat to the surrounding area. Waste is disposed of in surface structures such as slimes dams, return water dams, evaporation ponds and rock dumps. These waste disposal sites are the major source of metals and element pollution of the environment. Sulphide minerals in the waste dumps oxidise, forming acid that decrease adsorption and increase the solubility and mobility of the metals in soils, sediments and water (Alloway and Ayares 1994). Bacteria such as *Thiobacillus thiooxidans* help to catalyse the oxidation reactions in slimes dams and in weathering orebodies. Acid mine drainage (AMD) and acid rock drainage (ARD) are serious problems at both operating and abandoned mines.

Most major ore minerals have several other metals associated with them (Table 1) and many of these will contaminate the environment in the vicinity of mining areas. At Athens mine the target metals were Cu and Au. Many other heavy metals especially Cd, Pb, Zn, Sn, Cr, As and Mo are dispersed into the environment in leachate and affect air, water and soils quality.

Table 3. Showing the concentration of normal and toxic ranges and biochemical processes affected by excess heavy metal concentrations in plants (Alloway, 1990, Bowen, 1979, Fergusson, 1990).

Element	Normal Range ($\mu g/g$)	Toxicity ($\mu g/g$)	Affected Biochemical Process
As	0.02 – 7	5 – 20	Competition for sites with essential metabolites, Occupation of sites for essential groups phosphate-tungstate, bromate, fluorate
Cd	0.1-2.4	5-30	Change in permeability of cell membranes, Bonding to sulphydryl groups, Inhibition of enzymes, Respiration, Photosynthesis, Transpiration & Chlorosis
Cu	5-20	20-100	Change in permeability of cell membranes and Dark green leaves
Cr	0.03- 14	5-30	Chlorosis
Ni	0.02-5	10-100	Chlorosis
Pb	5-10	30-300	Change in permeability of cell membranes, Bonding to sulphydryl groups, Inhibition of enzymes, Respiration, Photosynthesis, Transpiration & dark green leaves
Sb	0.0001-2	1-2	Competition for sites with essential metabolites
Zn	1-400	100-400	Chlorosis & photosynthesis
Co			Chlorosis
Fe			Dark green leaves

3.3.1 Mineral processing

In gold processing at Athens mine the cyanide carbon leach method was employed while the flotation method was used for copper processing (see Appendix 2 for a detailed flow chart for the processing at Athens mine). Gold is adsorbed or reduced onto the activated carbon and is then sent through several processes to recover it from the carbon (figure 3.4).

The basic process of producing a required commodity from ores is summarized in Figure 3.3 below.
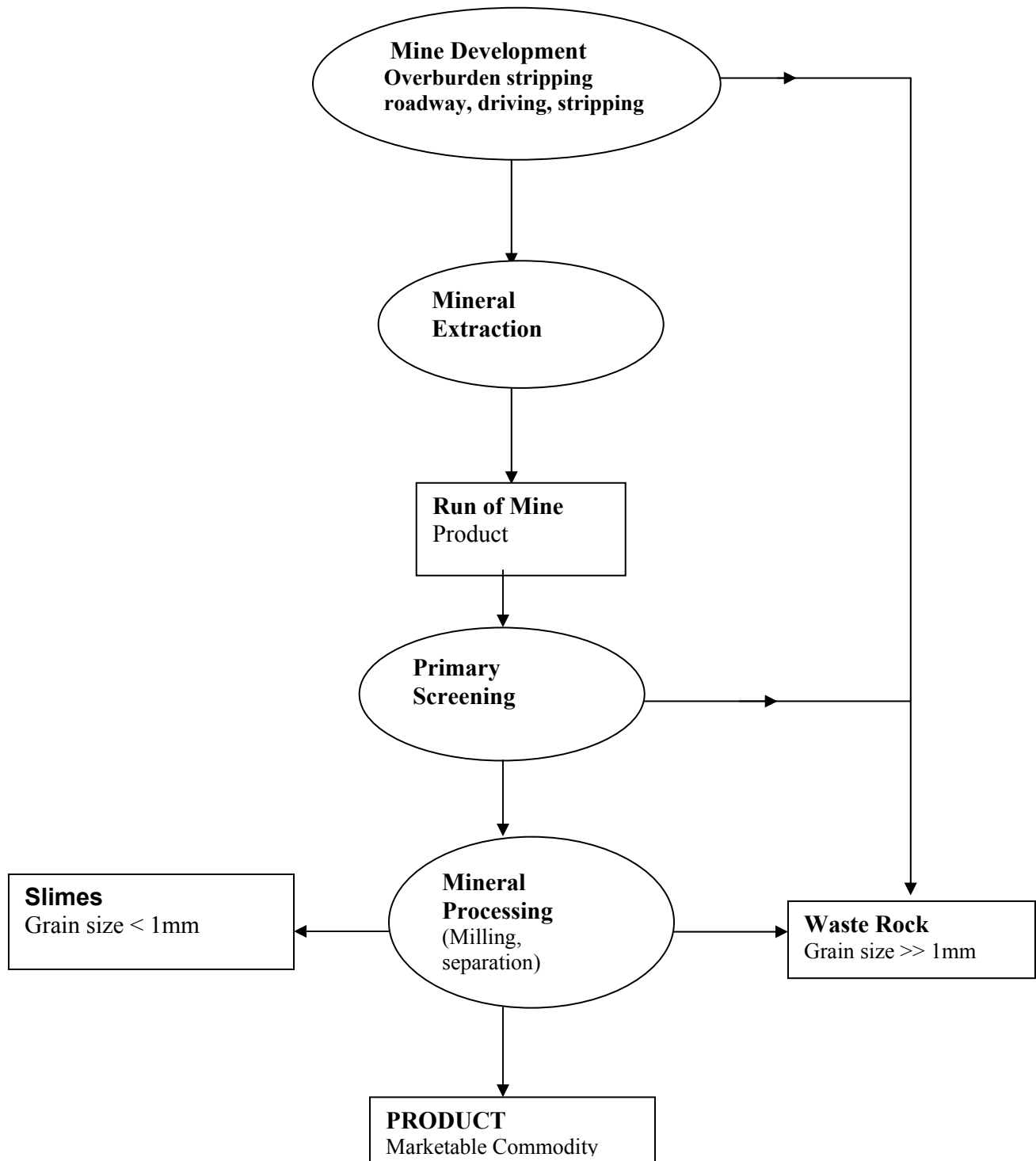
Figure 3.3 Classification of mine wastes, according to their origins within the mining and mineral processing cycle (Younger et al., 2002)
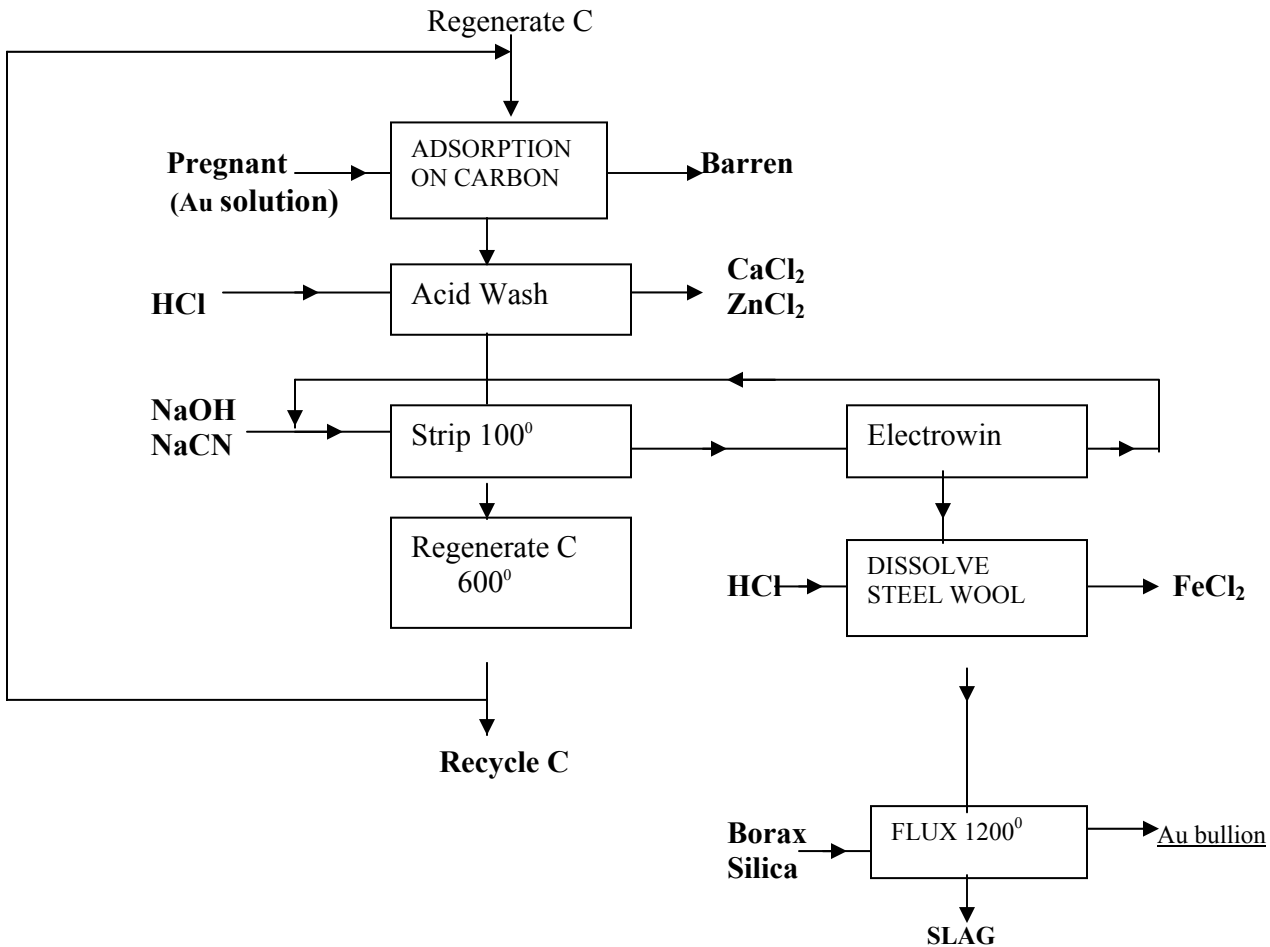
Figure 3.4 Stripping and gold recovery from carbon (Muir, 1982)

3.4 Environmental studies of sulphide mines in Zimbabwe

Numerous projects have been carried in the country looking at the different aspects of environment as related to mining activities. Most of the projects investigated the effects of mining and mineral processing on the soils, ground and surface waters.

Chihota (1995) investigated the distribution of arsenic, lead, copper and zinc in soils, surface and ground water at a gold mine in Zimbabwe. The sampling was done at a grid of 100m by 100m close to the crushing plant, mill, slimes dam and waste rock piles. It

was established that groundwater contamination by heavy metals was minimal due to the pH, which averaged 7.6. A few areas with acidic pH of 4.6 had slightly higher values of the metals. Strong scavenging effects of the iron and manganese, clays and organic matter rendered the As immobile. Surface runoff and wind blown dust from the slimes, polluted the adjacent stream. Cyanide pollution, originating from the mill and the natural mineralisation areas, polluted the soils in the mineralised areas.

Smythe (1989) investigated AMD at the same mine. Waste rock, leachate, runoff from the waste dump, surface and ground water were sampled and analysed for copper, iron, manganese, zinc, lead, nickel, chromium, sulphate, total dissolved solids and pH determination. He concluded that the AMD was going to cease once the mining ceases.

At Iron Duke mine in Mazowe district, Gratwicke (1999) concluded that mining activities were polluting the Yellow Jacket and Mazowe rivers. Organic matter and acid mine drainage (AMD) were the main problems and had seriously affected aquatic life in the two rivers in the vicinity of the mine. A monitoring programme was recommended. At the same mine, Mandingaisa (2000) and Ravengai (2001) studied the effects of disposal of mine wastewater on the groundwater and surface water. Seepage from the evaporation ponds was the major cause of pollution for both surface and ground water. High acid generation in the evaporation ponds resulted in seepage of leachate of very low pH (pH 2.8) into the groundwater, which subsequently discharges downstream into the Yellow Jacket River. Aquatic life in the Yellow Jacket river has been seriously affected by the AMD both at the seepage point and downstream.

Williams and Smith, (2000) studied the supergene geochemistry of arsenic, antimony and associated elements at Globe and Phoenix mine in Kwekwe. Mineralised rock samples, slimes and surface water were sampled and analysed for heavy metals. Heavy metal release and acid generation is expected to continue at the mine with increased levels and become more widespread during the wet season. Low pH, which promotes the dissolution and release of metals into the environment, was noted around the mine.

Shoko (1996) studied the speciation of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the slimes dam at Trojan nickel mine, Bindura. Eight samples were collected from different

depths in at the slimes. It was observed that the finer fraction (less than 180 microns) contained the highest metal concentrations. Scavenging by iron and manganese oxides for Zn, Co, Pb, Cu and Ni was noticed in some of the fractions and Ni and Cu concentrations were significant in the organic bound fraction. The firm bond in the residual fraction of the samples restricted the downward mobility of metals. Investigation of other dumps in the area was recommended.

Manyumwa (2000) determined chromium (III) in environmental samples from Mutorashanga using spectrophotometry methods. Water and sediments from the stream and soil from urban settlement and mining areas were collected. Control samples were collected from a river twenty kilometres from the mining site. No chromium pollution was noticed in the river water but chromium pollution was noted in the stream sediments.

Ruzive (2000) investigated the impact of chromite mining on the environment in Mutorashanga. Streambed sediments and surface water were sampled and analysed for nickel, chromium, cobalt, iron and manganese. Electrical conductivity and pH of the sampled medium were measured. The surface water and streambed sediments contained metal levels higher than the World Health Organisation acceptable limits for drinking water. Erosion of the dumps at Mutorashanga is causing siltation of rivers and dams in the neighbouring farms.

Mukono (1995) studied the water quality in Jumbo stream and Doxford dam in Mazowe. There is evidence that mining activities at Jumbo mine has affected the Jumbo stream and Doxford dam. The effects were considered to be as a result of seepage from sewage tanks, agricultural runoff and pollution from mine dumps.

Ngwenya (1997) investigated the environmental effects of mining and mine waste disposal at a gold mining complex in the Midlands greenstone belt. Soil, sediment, groundwater and surface water samples were collected and analysed for Cu, As, Pb, Hg and Sb. Wind transport was found to be the main cause of the spread of pollution of the main heavy metals around the slimes dams and the crusher and processing plants. The water around the mine was severely polluted by most of the heavy metals with the exception of the copper, which was low due to its lack of mobility.

3.5 Environmental work at Athens mine, Mvuma.

There are only two other environmental studies that have been done at the Athens gold mine, by Ndhlovu (1997) and Bosecker (1999). The study by Ndhlovu was on "Cyanide detoxification at a gold mine, its spread and distribution from the operational slimes dam in Zimbabwe". In this study, trace levels of cyanide were found and this was attributed to natural degradation of cyanide. Determinations were done in soils, dams, rivers and groundwater. Iron, copper, zinc, lead and pH were also determined and most of them were found to be at trace levels with the exception of copper which had a maximum concentration of eighty parts per million (ppm).

Bosecker (1999) collected rock samples and slimes from Arcturus, Shamva and Athens mines for detection and quantitative determination of bacteria. Four samples were collected from Athens mine slimes and analysed for various elements, oxides and bacteria. Copper, nickel, vanadium, zinc, arsenic and chromium were found to be high in all the samples. *Thiobacibacillus ferroxidans* and *Thiobacibacillus thiooxidans* were found in all the samples from Athens mine. The pH of the samples was found to be less than pH 4. The results are attached as Appendix 3.

The presence of bacteria in the slimes at Athens means that the bacteria are to develop dissolution processes of the elements, which are oxidation-reduction reactions where iron and sulphur are used as energy sources (electron donors) or electron acceptors (Cotter-Howells, J. D. et al., 2000). These bacteria are directly involved in the dissolution of sulphide minerals such as, pyrite, chalcopyrite and arsenopyrite forming sulphates and acid (equation 3.11). *Thiobacibacillus ferroxidans* can oxidise Fe (II) to Fe (III) an indication that the bacteria form a strong oxidiser. Indirect chemical oxidation of sulphides by the bacteria is aiding the acid generation at Athens mine.

3.6 Geological Studies at Athens mine

Maclaren (1924) wrote a geological report on behalf of the Gold Fields Rhodesian Development Co. Ltd. He concluded that the Athens lode was not a continuation of the Falcon; it was poorer in copper and occurred in different rock formation. He was of the opinion that mineralisation was bounded both to the east and to the west by shear zones,

36

leaving the only potential for further ore reserves at depth. Development below the sixteenth level was recommended.

Gewald (1960) produced a surface geological map at a scale of one to one thousand for Anglo American Corporation. This was after an intensive surface geochemical study but there was no final geological report accompanying the map. Taylor (1974) produced a detailed underground plan and sections accompanied with an unpublished Lonhro report.

Bliss (1962) produced the first comprehensive review of the geology of Mvuma greenstone belt. The Archaean rocks around Mvuma comprise a pre-Bulawayan basement overlain by younger Bulawayan group volcanics and sediments of the Mvuma greenstone belt. The pre-Bulawayan was described as a sedimentary sequence represented by epidosites, quartz - fuchsite rocks, grunerite and quartz-diopside-bearing rocks that have been extensively intruded by granodiorite, now evident as a gneiss. Bliss (1962) also described in detail the younger sedimentary rocks of the Karoo system, which occur as small outliers in the area and the Kalahari sands to the east of Mvuma.

Bliss (1962) indicated that the mine was situated in a synclinal structure and the mineralisation was transgressive towards the westward pitch of the syncline. Taylor (1974) recognised two main periods of sulphide and quartz mineralisation; an early phase of pyrite and pyrrhotite associated with minor quartz with little gold. This was followed by a later cross cutting phase of pyrite, pyrrhotite and chalcopyrite associated with quartz and gold. Copper and gold were shown to occur together but only in the second phase of mineralisation. Taylor (1975) collected thirty-one sulphide-mineralised samples and analysed for twenty-one (Ca, Fe, K, Mg, Na, S, Ba, As, Bi, Co, Cr, Cu, F, Mo, Ni, Pb, Sb, Sn, Zn, Au and Ag) major and trace elements and two oxides (SiO_2 and TiO_2).

Fabiani (1989) stated that the banded gneisses that crop out on both sides of the Mvuma greenstone belt form the original basement to the greenstone sequence. He also noted that there are three major styles of mineralisation namely pyrite- chalcopyrite in the southern orebody, pyrrhotite-chalcopyrite in the northern orebody and pyrite - magnetite that occurs in both oredies forming a thin zone extending into Falcon mine. In the southern

orebody, massive pyrite - arsenopyrite and bleached anthophyllite styles of mineralisation were distinguished. Gold in both cases is associated with bismuth sulphides and galena.

The presence of pyrite (FeS_2), chalcopyrite ($CuFeS_2$), galena (PbS), sphalerite (ZnS) and arsenopyrite ($FeAsS$) in the mineralogy, indicate the potential of acid generation and the release of copper, iron, lead, zinc and arsenic into the environment.

Chapter 4: Outline of sampling methods and the analytical techniques.

4.1 Introduction

The aim of this project is to compare and contrast dispersion of heavy metals during the dry and wet seasons. To enable that to be done the site had to be studied in terms of physical and geochemical characteristics. This is required to obtain background information, which would assist in determining the extent of dispersion of the elements in water and soils. In order to characterise the site, a sampling programme was embarked on slimes, soil, stream sediments, leachate, crystals, surface water and groundwater for which samples were collected.

The samples were analysed for heavy metal content, the suite of the relevant heavy metals having been determined from an analysis of the slimes. The geochemistry and the mineralogy of the parent waste are the main control of the accumulation of the elements. A preliminary analysis of the slimes was done using X-ray fluorescence spectrometry (XRF) at the Institute of Mining and Research, University of Zimbabwe. This technique was chosen over AAS because of its rapid analysis and quantitative results (this was a total determination to give an indication of which elements were present).

A partial determination was done on all the samples to investigate bioavailable elements. The bioavailability of trace elements at mining sites is a key issue in both human and ecological risk assessments (Davis et al., 1992, Pascoe et al., 1994). The mining activities pollute the soils, stream sediments and surface water with elements such as arsenic, copper, lead and zinc. The constraints on bioavailability would limit the toxicity of the metals on environmental media affected by the waste.

Table 4 gives a summary of sampled media, element analysed and method of analysis.

4.2 Reconnaissance Survey

A reconnaissance sampling programme was carried out during the 1999 dry and wet seasons on a 200m by 200m grid covering the whole mining area at Athens mine. The aim of the survey was to establish which elements were present and in what concentrations. The qualitative determination of elements present in mine waste (slimes) had been done when looking for the project area using the XRF.

Three kilograms of soil samples were collected from each of three different zones in the pits dug at each sampling point of the grid. The sampled zones were determined by the change in soil type (Figure 4.1). The surface layer was removed, including any organic litter or vegetation and placed in a plastic bag and sealed. The sample weight was kept constant to eliminate any sampling bias in the field as a result of judgement by the sampler and to ensure adequate material for chemical analyses. No field treatment was done to the soil samples.
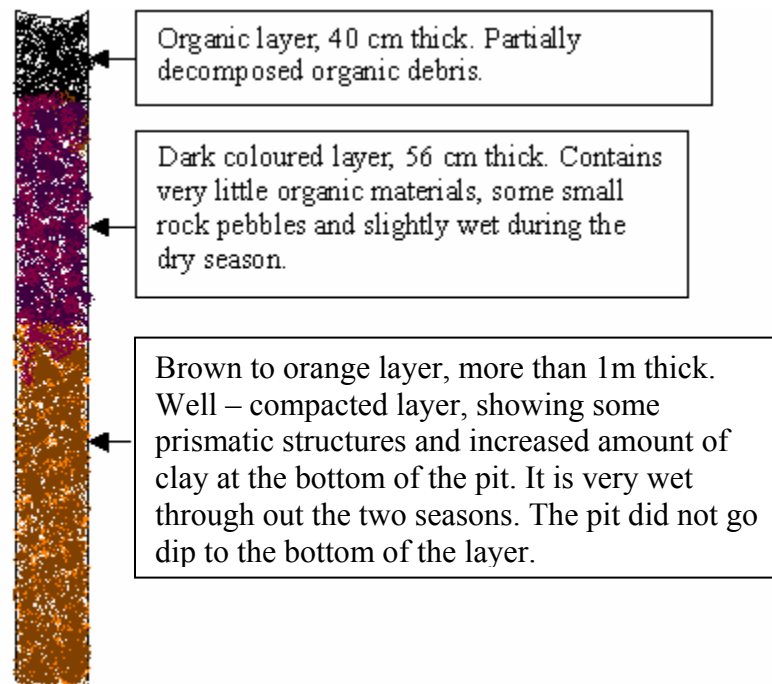
Figure 4.1 Showing the soil profiles and the descriptions of the of the pits dug around the mining area during the reconnaissance. The pits were 2m metres dip and only three layers were seen in all the pits.

Four kilograms of sediments and two hundred millilitres surface water were sampled from selected points in streams within the grid where they were available. The sediments were put in a bag and sealed. Surface water samples were filtered through a 0.1μm membrane filter into 250ml bottles.

Table 4: Sampled medium, determinations and method of determinations

Sampled Medium	Elements analysed	Method of analysis
Crystals	Identification, Fe, Cu, Zn, Pb, Cd, Cr, Ni, Co, Sb, As and pH	XRD, ICP-MS and pH electrode measurement.
Groundwater	Fe, Cu, Zn, Pb, Cd, Cr, Ni, Co, Sb, As, pH and TDS	AAS and pH electrode measurement.
Leachate	Fe, Cu, Zn, Pb, Cd, Cr, Ni, Co, Sb, As and pH	AAS and pH electrode measurement
Stream sediments	Fe, Cu, Zn, Pb, Cd, Cr, Ni, Co, Sb, As and pH	ICP-MS and pH electrode measurement.
Slimes	Oxygen determination, Sulphides, Water content, Fe, Cu, Zn, Pb, Cd, Cr, Ni, Co, Sb, As and pH	Oxygen metre, ICP-MS and pH electrode measurement.
Soil	Fe, Cu, Zn, Pb, Cd, Cr, Ni, Co, Sb, As and pH	ICP-MS and pH electrode measurement.
Surface water	Fe, Cu, Zn, Pb, Cd, Cr, Ni, Co, Sb, As and pH	AAS and pH electrode measurement

The pH of the samples was measured using the Orion metre model 250A and acidified with 65% Nitric acid to a pH less than two (pH<2). The acidification was done to prevent most bacterial growth and adsorption or precipitation.

Two hundred and fifty millilitres of groundwater samples were collected from the existing boreholes using a sampling belly. The same treatment as for surface water samples was applied.

4.2.1 Sample preparation in the laboratory

All the soil and sediment samples were dried within 4 hours of sampling in an oven at $80^{o}C$ for 24 hours. This was meant to prevent degradation of sulphide minerals (important for partial extractions) and to ensure that they were dry for the digestion process. Any lumps were disaggregated using a pestle and mortar. The samples were homogenised and then split using the cone and quartering method to get a representative sub-sample of each. Two quarters from each sample were sieved through an 80-mesh sieve (0.185mm) stainless steel sieve and placed into two separate bags.

Two partial extraction methods were used to digest the samples: cold extraction and hot extraction. This was done to see if there was any variation in the two methods and to test which one produced the more reliable results. The cold extraction method uses cold hydrochloric acid (HCl) overnight while the hot extraction method uses hot HCl. The hot extraction method was found to be more suitable for available elements and gives a good contrast compared to cold extraction for a number of elements including lead, zinc, arsenic, antimony, chromium, cobalt, copper and iron.

The procedure for the dissolution is:

1. Each sample was re-homogenised by stirring through the bag with a spatula and 500mg of sample were weighed in a weighing boat on a top loading balance.

2. The weighed samples were transferred into a 30ml extraction tubes labelled with the sample numbers.

3. 2 ml of 1:1 HCl were added to each test and were mixed thoroughly on a vortex shaker.

4. The tubes were placed in a rack and then into a shaking water bath set at $90^{o}C$ for two hours, with added agitation after every 30 minutes on the vortex shaker.

5. 8 ml of deionised water were added to each test tube using a dispenser followed by thorough mixing on the vortex shaker.

6. The tubes were covered and left to settle overnight.

The cold extraction method follows the same procedure but uses cold HCl and mixing on the vortex shaker is only done at the start of the method.

No further water treatment was done on the water samples in the laboratory.

The heavy metal determination was carried out using a Varian Spectra 200HT atomic absorption spectrophotometer (AAS) at the University of Zimbabwe, Geology Department. Standards used for the instrument calibration are shown in Table 5 and the basic theory of AAS is given in appendix 5.

Based on these results, it was decided that a more detailed survey around the active slimes dump, storage ponds, selected points on the streams and nine boreholes (Figure 4.2) was required. The following elements were selected to be determined: arsenic, copper, iron, zinc, lead, cadmium, chromium, cobalt, antimony and nickel. Cyanide was determined in the field using a field kit.

Table 5. The working standards prepared from one thousand parts per million (1000ppm) stock solutions of each element in ppm (or mg/l) (AAS Varian manual 1989).

Element	Fe	Cu	As	Pb	Cr	Zn	Co	Ni	Sb	Cd
Standard 1	5.0	2.0	50.0	10.0	5.0	0.5	5.0	5.0	20.0	1.0
Standard 2	10.0	4.0	100.0	20.0	10.0	1.0	10.0	10.0	40.0	2.0
Standard 3	15.0	6.0	150.0	30.0	15.0	1.5	15.0	15.0	60.0	3.0
Standard 4	20.0	8.0		40.0	20.0	2.0	20.0	20.0	80.0	4.0

4.3 Detailed sample survey

The sampling was concentrated around the active dump to determine how far the selected heavy metals spread into the soils away from the dump and what the variations were between the two seasons. The active dump was being used during the sampling period and the non-active dumps were those were dumping had been stopped. Soil, stream sediment, slimes, leachate, crystals, groundwater and surface water were sampled. In addition, gas sampling and analysis and multi-channel resistivity profiling were carried out at the dump.

4.3.1 Crystal sampling

Different types of crystals were collected from the surface of the slimes dump, along the stream banks and along edges of the storage ponds based on their colour and crystal habit. The different coloured crystals are shown in figure 4.3 and described in Table 5. The crystals were sampled carefully using flat wooden spatulas to avoid including the slimes. They were put in plastic bags and sealed and then placed into khaki envelopes and taken to the laboratory for identification using X-ray diffraction (XRD) and chemical analysis for the heavy metals.

At Camborne School of Mines, Redruth, UK, the undried samples were ground to fine powders using a pestle and mortar. They were then pressed into labelled sample holders and were all loaded into a Seimens D5000 defractometer. The instrument uses a search/match program which has a graphic evaluation program and a diffraction data base maintenance program which allows the display of the unprocessed scan and all the normal operations on diffraction scans (smoothing, integration, fit, superimposition of scans, peak search and background subtraction). The X-ray peaks for each element were

obtained and the various minerals contained in the crystals were identified from the peaks using the search / match method. The programme has a detection limit of 3%, which means it can only include metals that have a concentration of more than 3% of the total metal content. The results are given in chapter 5.

For the detailed background to the program, see Appendix 4.

Heavy metal determinations were carried out at Southwest Water's laboratory in Exeter, UK using an inductively coupled plasma mass spectrometer (ICP-MS). 20g of sample were digested using the hot extraction method and 250 ml were sent to the laboratory for analysis.
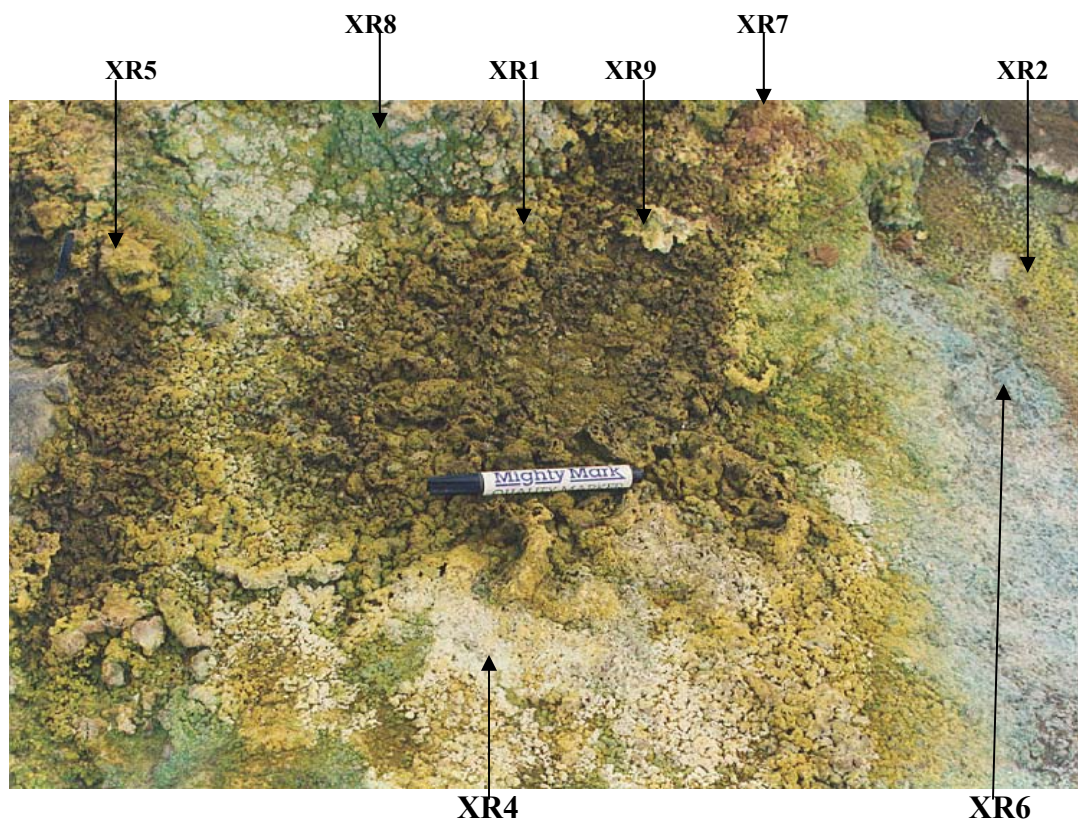
Figure 4.3. Some of the crystals sampled for identification and chemical analysis from the surface of the slimes damp at Athens.

4.3.2 Oxygen sampling and analysis

Oxygen (O_2) level, together with the slimes mineralogy, indicates the degree and depth of any oxidation. It can enter and move through the slimes by barometric pumping, wind action; volume displacement during infiltration, diffusion in the gas phase and with infiltrating water containing dissolved oxygen (Massmann and Farrier, 1992). Oxygen plays a major role in the processes that take place within the slimes, which include

oxidation, processes, mineral dissolution and precipitation, hence the need to quantify the amount of oxygen within the dump.

Oxygen was sampled from the dump using a gas sampler for every metre down to seven metres in the boreholes that were dug. Twenty-five millimetre (17mm) diameter PVC tubes of 7m, 6m, 5m, 4m, 3m, 2m and 1m lengths were driven into the holes drilled from the top of the slimes dam. The sampling was done to only seven metres due to lack of equipment and the collapse in the holes when drilling in water. The end of each tube was sealed and holes were drilled on the sides of the tube to cover half a metre (Figure 4.4). The perforated half a metre was covered with coarse sand and rest of the tube was firmly covered with clay and slimes. A rubber tubing was tightly fitted to the top end of each tube. A gas sampler, Infrared gas analyser (GAS 94A), was connected through the tube. Before any reading was taken, the air was pumped out from the tube and then three gas readings were taken from each point. The pressure was also recorded with each oxygen reading.
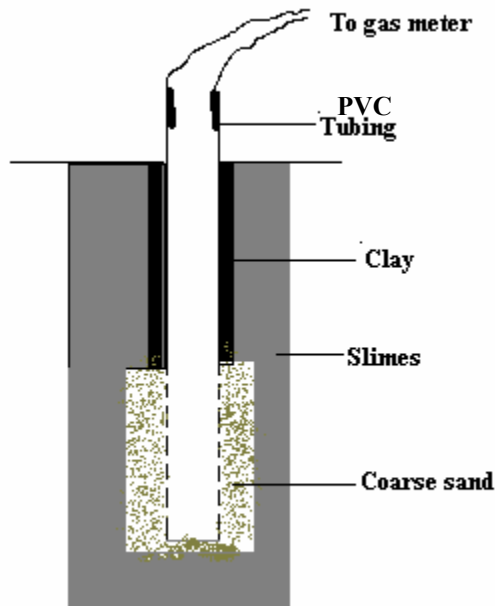
Figure 4.4 Design of the gas sampling tube used at Athens slimes dam

4.3.3 Slimes sampling

Core samples were collected from the slimes dam into plastic bags after every metre to a depth of thirty-three metres drilled with an auger drill, the Vonder rig. The same method as in the soils and sediments was used for the sample dissolution and analysis.

These were analysed in the Geology Department, UZ and Southwest Water Laboratory in Exeter, United Kingdom (UK) for the heavy metals.

A second set of core samples of the slimes was collected during the setting up of the oxygen-sampling casing (section 4.3.2). A total of seven core samples were collected in duplicates. One set was sent to Denmark Technical University for sulphide separation and the second set was used for water content determination in the Geology department laboratory, UZ.

The water content in the samples was determined in the laboratory as follows:

1. 150g of each sample were weighed on a top loading balance.

2. The weighed samples were placed in an oven set at 105°C for 24 hours.

3. The samples were weighed on the same balance and the amount of water lost in each sample was calculated.

4.3.4 Geophysical Investigations.

The geophysical investigations were carried out to determine the nature of the subsurface materials in the slimes dam, in the terrain below and the surrounding the slimes. Any horizontal or vertical discontinuities in the ground would indicate the possibility of seepage the into ground water systems. At Athens, the multichannel resistivity method was used to determine if there is a link between the ground water and effluent from the dump. The method was chosen because porosity is a major control of both the resistivity of rocks (Kearey et. al., 1989) and the passage of effluent through rocks and soil. The basic theory is given in Appendix 6.

4.3.5 Multi-channel resistivity at Athens Mine damp

  Mr A Maziti, Physics Department, UZ did a multi-channel resistivity survey on and around the active dump to assess the conductivities of the ground and the waste. The profile lines are shown in figure 4.5. The ABEM LUND IMAGING SYSTEM employs a multi – electrode array with automated selection of current and potential electrodes

controlled by a computerised electrode selector. The technique allows continuous vertical electrical sounding (CVES), which is displayed as a 2D resistivity profile. The variation of the spacing at which the readings are taken enables depth of measurement to be varied. The use of the multi-electrode array speeds up the measurement procedure. The measured apparent resistivities are stored in a computer that also controls the measurement procedure. A choice of reading protocols is available, enabling the Wenner (constant spacing), Schlumberger (constant mid-point and varying separation), and other layouts to be measured. The Wenner array with a four-cable layout was used for the longer profiles and two-cable layout was used for measurement on top of the dump.

The minimum electrode separation was 5m and this allowed a resolution of 10m anomalies.

4.3.6 PROFILE DESCRIPTIONS

T1, T2 and T3 profiles are running E-W and traverse the top of the dam (Figure 4.5). T2 is in the centre and   crosses a pond at the top of the dam, at stations 100m-130m. The profiles were meant to delineate cracks and flow pathways within the dam.

Profiles L1 and L2 are 700m long, 80m apart and run North-South (Figure 4.5). The resistivity readings were taken at 5m spacing using a Wenner layout. The stations 0 (zero) are at the northern end of the waste dam. L2 starts just across a dry stream to the northern end and crossed two drain channels running round the dam. L1 cut across an abandoned and dry disposal pond before the main dam.

L4, L5 and L6 (Figure 4.5 were measured starting from the northern end of the dam. L5 and L6 were set to provide background information away from the dam. L4 cuts across relatively wet ground from the flow of the contaminated leachate out of the dam, two receiving trenches and the stream at 50m station. L5 also crosses the same stream at 30m station.

L3, L7 and L8 profiles run east west (Figure 4.5). L3 runs across the dam and crosses Masvingo-Chivhu main road by the junction-bridge. L7 is on the northern end of the dam, cuts across the two receiving trenches and the storage pond. L8 is on the southern

end of the dam and runs between garbage dam site and the dam. The garbage dam is at stations 600-700m.
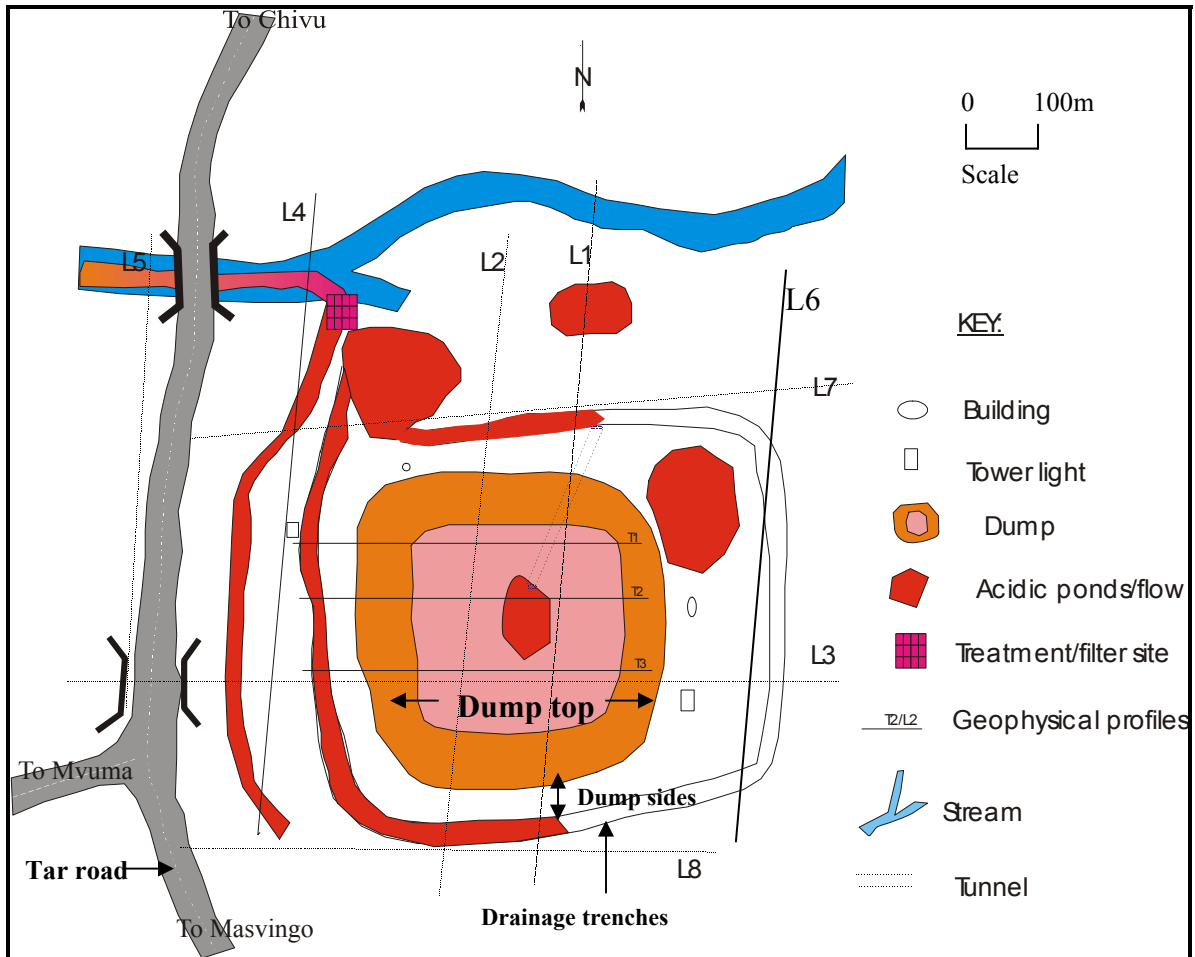
Figure 4.5 Showing the geophysical profiles carried out at the active dump at Athens mine, Mvuma.

4.3.7 Soil sampling

Soil samples were collected from areas around the dump at a depth of 1m using a soil auger and stored in Kraft bags. Sampling on the eastern side of the dump was done only during the dry season due to the extension of the slimes dam over this area before the wet season. Only two points could be established on the northern side because of the stream, which would act as a barrier to any dispersion. On the southern and the western side at total of twenty one samples were sampled during each of the two season at five metre intervals. A control sample was collected a kilometre from the dump, marked CS in Figure 4.2. No field treatment was done to the samples. The sampling programme lasted from May to August 1999 (dry season) and November 1999 to March 2000 (wet season).

In the laboratory, samples were placed overnight in a drying oven at eighty degrees Celsius (80ºC). When dry, the samples were disaggregated using a pestle and mortar and sieved through minus 80-mesh (0.185mm) sieve. The minus 80-mesh fraction was used for the analysis. The sieves and mortars were cleaned thoroughly before proceeding with the next sample.

A partial extraction method was used for the dissolution of the samples, as described in section 4.2.1. The weights and volumes used in the method described in section 4.2.1 were doubled so as produce duplicate samples. A duplicate set of samples was analysed in the Chemistry Department, UZ using a Varian AAS.

4.3.8 Soil pH determination

The samples for pH determinations were not dried and particles greater than fifty millimetres (>50mm) diameter were removed. The pH of this medium is very sensitive to oxidation-reduction reactions.

The following method was used for the pH determination for soil, sediment and slime samples:

1. A mixture of 1:2.5 w/v of each sample and deionised water was prepared. It was agitated and left to settle for ten minutes.

2. The Orion pH metre model 250A, was calibrated with pH 4 and pH 7 buffer solutions before measuring the solutions.

3. The pH of the solutions were measured and recorded. The electrode was rinsed with distilled water after every reading and was checked after every fifteen samples with the buffer solutions. If there was a significant drift (± 0.05 of a pH unit), the instrument was recalibrated and the previous samples were reanalysed.

4.3.9 Surface water sampling.

Surface water samples were collected from fourteen sites within the mining and surrounding areas, including tailing ponds and Blinkwater and Mackenzie dams (Figure 4.2). During the wet season, water was sampled from the same places as the stream sediments but this was not possible in the dry season when surface water was collected where available. A control sample was collected up stream (marked with a prefix CSw on figure 4.2) of the stream that flows into Blinkwater dam. At each site, 250ml of sample was collected and filtered through a 0.1μm membrane filter into 250ml bottles. Field

duplicate samples were collected from a point marked with a prefix DSw (Figure 4.2) and were treated in the same manner as the other samples.

The pH of the samples was measured using the Orion metre model 250A and recorded. Those samples that had a pH higher than 2 were acidified with 65% Nitric acid (HNO_3). The acidification was to prevent most bacterial growth and adsorption or precipitation. Calibration of the electrodes was undertaken prior to each measurement using a series of commercial buffer solutions (pH4.01, pH7.00 and pH10.01) to cover the acidic range and alkaline range.

A field cyanide rapid test, using test strips was done on all the samples. The method is given below:

4.3.10 Stream sediments

The stream sediment samples were collected from selected places on the stream and receiving trenches as shown in Figure 4.2 marked with prefix Sed. No treatment was carried out on the samples in the field. Samples were collected during the two seasons from the same position and control samples (marked Csed) were taken.

In the laboratory the samples were treated the same way as the soils, (section 4.3.7).

4.3.11 Groundwater sampling

250ml glass and plastic bottles were soaked for forty-eight hours in 10% nitric acid (HNO_3) to remove metals that could have been adsorbed on surface of the containers and then thoroughly washed with deionised water. At each site, the bottle was rinsed three times with the sample to be taken. Groundwater was sampled from the nine boreholes (Figure 4.2) using the sampling belly and was filtered through a 0.1μm membrane filter into 250 ml glass bottles. 65% HNO_3 was added until the pH was less than two. A second groundwater sample was taken and the pH, CN^- and iron II (Fe^{2+}) concentrations were measured in the field. A control sample was collected from the point marked with the prefix CGw in figure 4.2. The pH was measured using an Orion metre model 250A. Calibration of the electrode was undertaken prior to each measurement using a series of commercial buffer solutions while cyanide was measured using specific field test kit. The samples were taken to the laboratory for analysis.

The samples were transported to laboratory and analysed for arsenic, copper, iron, zinc, lead, cadmium, chromium, cobalt and antimony on a Varian Spectra 200HT AAS in the Geology Department, UZ. The calibration standards used are shown in Table 4. The second set of samples was analysed in the Chemistry department, UZ and ZNWAL.

The samples included blanks, laboratory quality control standards (5ppm Cu), duplicate samples and laboratory duplicates for precision control.

4.3.12 Cyanide Test (reference, CN⁻ Merck manual)

The cyanide test is a semi-quantitative determination with the CN^- reacting with chlorine to form cyanogen chloride, which opens the pyridine ring giving glutaconic dialdehyde. The barbituric acid derivative on the test zone of the strip reacts with the dialdehyde and produces a red polymethine dye. Complex bound cyanides, and cyanides of copper, palladium, mercury and silver are either not detected or only partially detected. The measurements were done following the steps below:

1. Measuring vessel was rinsed three times before each measurement with the sample to be tested and was filled to the 5-ml mark.

2. The pH was determined and it was adjusted to between 6 and 7.

3. 1 level-dosing spoon of reagent 1 was added and dissolved.

4. 5 drops of reagent 2 were added and then mixed well.

5. The reaction zone of the strip was immersed into the solution for 30 seconds

6. Comparison with the test strip and the colour scale was done within 10 seconds. The white colour band indicates the absence of cyanide and the different shades of purple indicate varying amounts of cyanide ranging from 1mg/l CN^- (lighter purple colour) to 30mg/l CN^- (darkest purple colour).

 The samples were transported to the Geology Department, UZ laboratory and analysed for arsenic, copper, iron, zinc, lead, cadmium, chromium, cobalt and antimony on the Varian Spectra 200HT AAS. The calibration standards used are shown in Table 4. The second set of samples were analysed in the Chemistry Department, UZ and the Zimbabwe National Water Authority laboratory (ZNWAL).

The samples included blanks, laboratory quality control standards (5ppm Cu), duplicate samples and laboratory duplicates for precision control.

4.4 Quality control

A quality assurance program was utilised to evaluate the data quality for the soils, sediments extractions and water. In house standards (GEOKM1, GEOKM2 and GEOKM3), field duplicates and laboratory duplicates (after every ten samples) were also analysed with the samples. These were meant to evaluate the precision obtainable and errors in precision measurements and are a reflection of sub-sampling, extraction and analytical sources of error (Schafer and Smith, 1989). Reagent blanks were included in the analysis to identify potential sources of contamination or bias.

CHAPTER 5: RESULTS

5.0 Introduction

This chapter gives results of the identification and chemical analysis of the crystals, oxides, oxygen, sulphides, water content and element concentrations in the slimes, in the leachate, multi-channel resistivity, element concentrations in soils around the slimes dump, stream sediments, surface water, ground water and pH of the sampled media. The section also includes the quality control of various results from different laboratories, field and laboratory duplicates.

The crystals were found throughout the whole mining area during the dry season. Some of the waste rocks and slimes were used for roads repair within the mining area, resulting with the crystals found in all these areas. The secondary minerals covered a vast area of the dump and all other areas within the mining area. Analysed elements in the crystals precipitated from the solution during the dry season, then dissolved and released during the wet season into surface water, ground water and the environment. Transition group of metals do not form separate mineral phases, but occur as contaminates of the other minerals recognised by XRD.

5.1 Crystals.

Mineral phase identification was done at Camborne School of Mines, Redruth in the United Kingdom, using a Seimens D500 defractometer and the defractograms from the minerals identified are shown in Appendix 7. Chemical analysis was done at Southwest Water laboratory in Exeter, in the United Kingdom.

5.1.1 Mineral phases and element concentration

The crystals (Figure 5.1a.XL1) are yellow in colour, feel slightly wet and in the field they always appear next to brown crystals. Crystals have a sugary texture and partially dissolve in water. XRD results showed that the main phase of these crystals is thenardite (Na_2SO_4) with gypsum ($CaSO_4.2H_2O$) as a minor phase and quartz (SiO_2) grains are also present in the crystals. Some XRD peaks could not be identified Table 6.
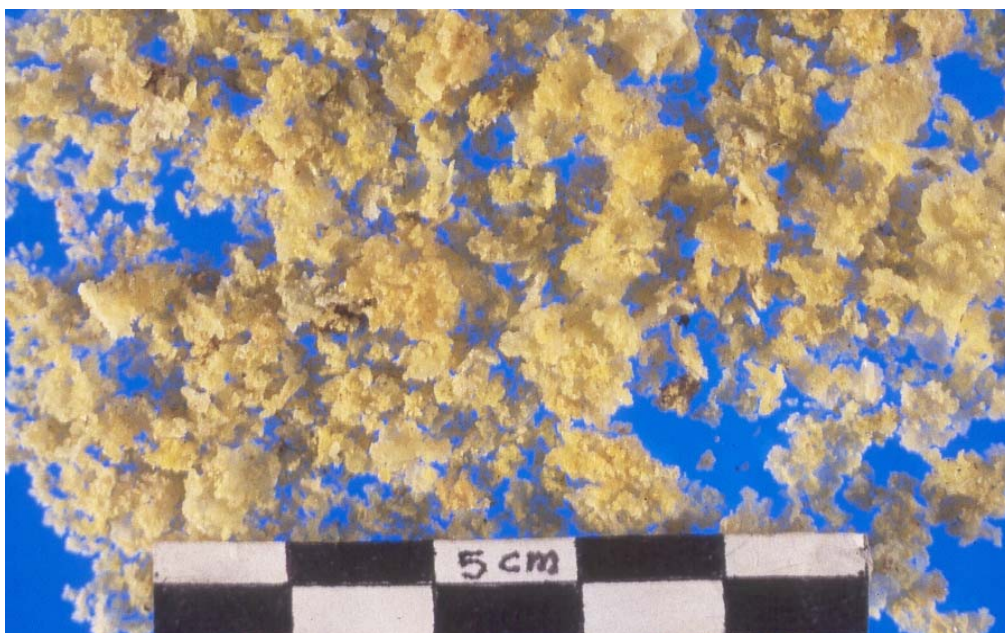
Figure 5.1a. XL1
XRD results: Thenardite (Na_2SO_4), gypsum ($CaSO_4.2H_2O$) and quartz (SiO_2).
Chemical analysis: 26.5ppm Fe, 8.60 ppm Cu, <0.300ppm Zn, <0.300ppm Pb, <0.100 ppm Cd, <0.300ppm Cr, 2.50 ppm Ni, 139ppm Co, 0.330ppm Sb and 0.510 ppm As. **pH** 5

The chemical analysis show that cobalt has a concentration of 139ppm then iron with 26.5ppm, copper with 8.60ppm, nickel with 2.50ppm and all the other elements are below 1ppm (Figure5.1a.XL1). These elements could be responsible for the colour of the crystals since both the thernadite and gypsum are white in colour.
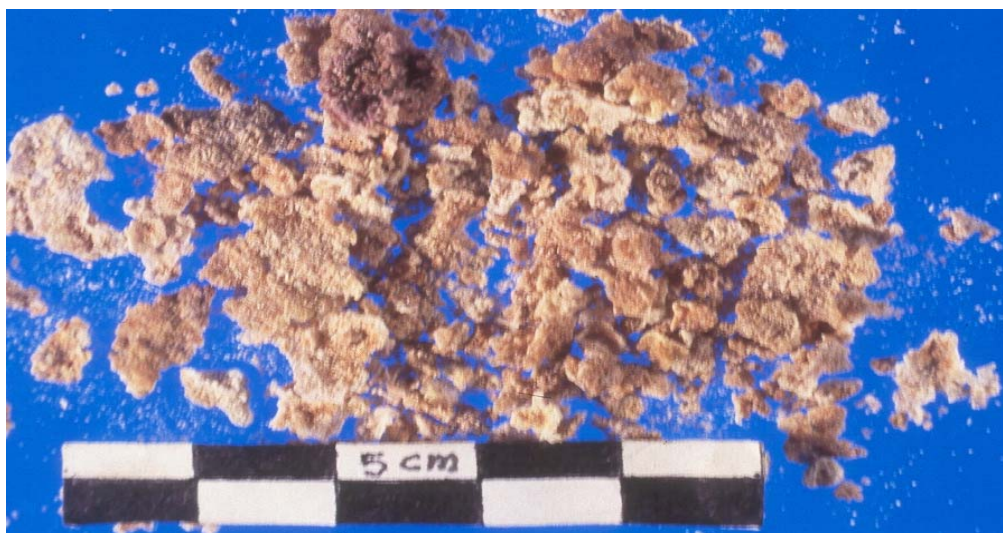
Figure 5.1b. XR 2
XRD results: Thenardite (Na_2SO_4), boussingaultite (($NH_4)_2Mg(SO_4)_2.6H_2O$),
gypsum ($CaSO_4.2H_2O$) and quartz (SiO_2).
Chemical analysis: 417 ppm Fe, 3.00ppm Cu, 0.600ppm Zn, 0.400ppm Pb, <0.100ppm Cd, <0.300ppm Cr, 42.8 ppm Ni, 48.1 ppm Co, 0.0200ppmSb and 0.180ppm As. **pH** 4.1

The crystals (Figure 5.1b.XR 2) are yellowish and brownish in colour and always appear next to purple (XR7) and white crystals (XR4 and XR9). They are fine grained, partially dissolve in distilled water and contain six molecules of water. Three phases are present in these crystals: thenardite (Na_2SO_4) is the major phase, boussingaultite (($NH_4)_2Mg(SO_4)_2.6H_2O$) is the minor phase and gypsum ($CaSO_4.2H_2O$) is the trace phase. Quartz (SiO_2) is also present in the crystals.

Iron has the highest concentration, of 417ppm, cobalt has 48.1ppm, nickel has 42.8ppm, copper has 3ppm and all the other elements are less than 1ppm (Figure 5.1b.XR 2). The iron could not be detected by XRD because it is less than three percent but it has coated the white crystals. As the pH gets more acidic, more iron in being released into solution.

Figure 5.1c.XR 3
XRD results: Copiapite ($Fe_{14}O_3(SO_4)_{18}.63H_2O$), gypsum ($CaSO_4.2H_2O$) and quartz ($SiO_2$).
Chemical analysis: 53800 ppm Fe, 8700 ppm Cu, 41.1 ppm Zn, 7.40 ppm Pb, 0.800 ppm Cd, 192 ppm Cr, 491 ppm Ni, 914 ppm Co, 0.110 ppm Sb and 59.0 ppm As. **pH** 2.1

The crystals (Figure 5.1c.XR 3) are yellow in colour with a distinct sulphur smell. They appear as lumps and dry on the surface of the dump yet they contain the highest amount of water (65 molecules of water) with the lowest pH of 2.1. Only two phases were identified, Copiapite ($Fe_{14}O_3(SO_4)_{18}.63H_2O$) as the main phase and gypsum ($CaSO_4.2H_2O$) as the minor phase. All the peaks were identified.

All the analysed elements are high in these crystals with iron being the highest with 53800 ppm and only cadmium and antimony have concentrations less than 1 ppm (Figure 5.1c.XR 3). The high iron, copper and cobalt are responsible for the yellow colour of the crystals.

The crystals (Figure 5.1d. XR 4) are white and form hard crusts on the surface of the dump. They contain other fine-grained brown material, quartz grains and partially dissolve in distilled water. Three phases were identified, thernadite as the major phase, boussingaultite ($(NH_4)_2Mg(SO_4)_2.6H_2O$) as the minor phase and, halite (NaCl) and gypsum ($CaSO_4.2H_2O$) as trace phase. A number of peaks could not be matched (Table 6).

Element concentrations are high in these crystals with only antimony being less than 1 ppm (Figure 5.1d. XR 4). The sodium contributes significantly to the white colour of the crystals.

Figure 5.1d. XR 4
XRD results: Thenardite (Na_2SO_4), boussingaultite ($(NH_4)_2Mg(SO_4)_2.6H_2O$), halite (NaCl),
            gypsum ($CaSO_4.2H_2O$) and quartz (SiO_2).
Chemical analysis: 440 ppm Fe, 1810 ppm Cu, 23.1 ppm Zn, 17.1 ppm Pb, 1.50 ppm Cd,
            2.00 ppm Cr, 353 ppm Ni, 426 ppm Co, 0.00500 ppm Sb and 2.10 ppm As . **pH** 4
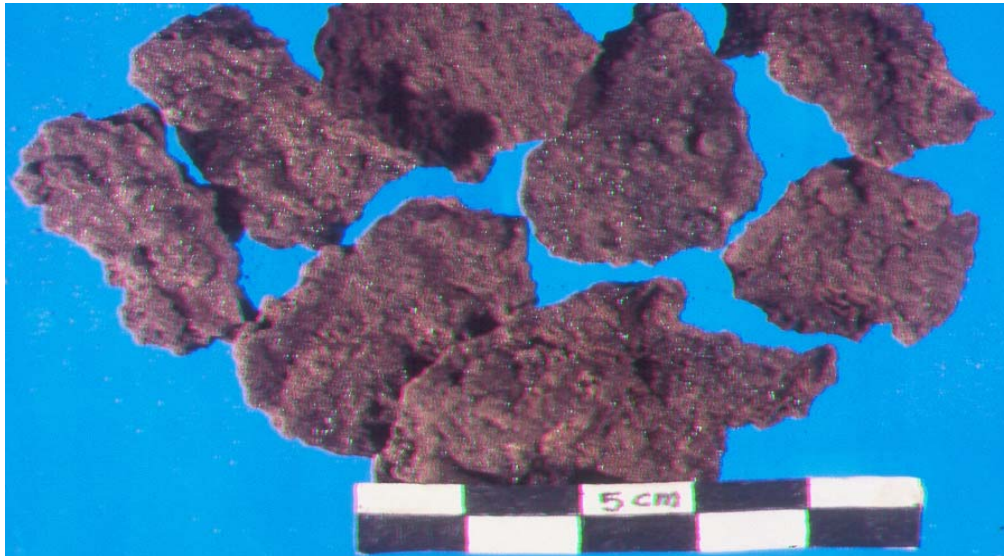
Figure 5.1e. XR 5
XRD results: Thenardite (Na_2SO_4), boussingaultite ((NH_4)$_2Mg(SO_4)_2.6H_2O$), halite (NaCl),
gypsum ($CaSO_4.2H_2O$) and quartz (SiO_2).
Chemical analysis: 13900 ppm Fe, 510 ppm Cu, 51.7 ppm Zn, 1.6 ppm Pb, 1.8 ppm Cd,
3.70 ppm Cr, 891 ppm Ni, 440 ppm Co, 0.370 ppm Sb and 18.0 ppm As. **pH** 2.9

The crystals (Figure 5.1e. XR 5) are brown in colour and form a hard crusts which partially dissolve in distilled water. Three phases were identified with thenardite (Na_2SO_4) as the main phase, boussingaultite ((NH_4)$_2Mg(SO_4)_2.6H_2O$) and gypsum ($CaSO_4.2H_2O$) as the minor phase and halite (NaCl) as the trace phase. A number of peaks were not identified (Table 6). The crystals are iron coated and spots of either thenardite or gypsum is still visible in the crystals (Figure 5.1e. XR 5).

All the analysed elements are high with the exception of antimony, which remains less than 1 ppm. The high iron concentration is responsible of dark brown colour of the crystals.

The crystals (Figure 5.1f. XR 6) are blue in colour, feel slightly wet and partially dissolve in distilled water. Three phases were identified with thenardite (Na_2SO_4) as the main phase, boussingaultite ((NH_4)$_2Mg(SO_4)_2.6H_2O$) as the minor phase and halite (NaCl) and gypsum ($CaSO_4.2H_2O$) as the trace phase. All the peaks were identified (Table 6).
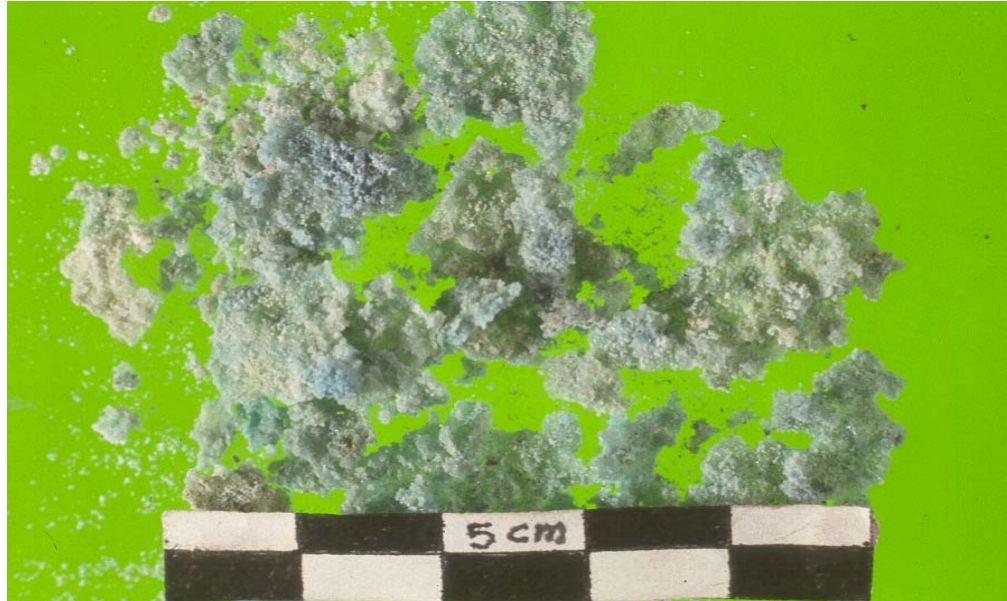
Figure 5.1f. XR 6
XRD results: Thenardite (Na_2SO_4), boussingaultite (($NH_4)_2Mg(SO_4)_2.6H_2O$), halite (NaCl), gypsum ($CaSO_4.2H_2O$) and quartz (SiO_2).
Chemical analysis: 45.1 ppm Fe, 6.80 ppm Cu, 1.90 ppm Zn, 0.500 ppm Pb, <0.1 ppm Cd, <0.3 ppm Cr, 374 ppm Ni, 433 ppm Co, 0.007 ppm Sb and 0.660 ppm As. **pH** 4.8

Element concentration shows an increase in cobalt with the highest concentrations of 433 ppm as compared to all the other crystals. Nickel is also high with a concentration of 374 ppm. The colour of the crystals could be due to the cobalt and copper (Figure 5.1f. XR 6).
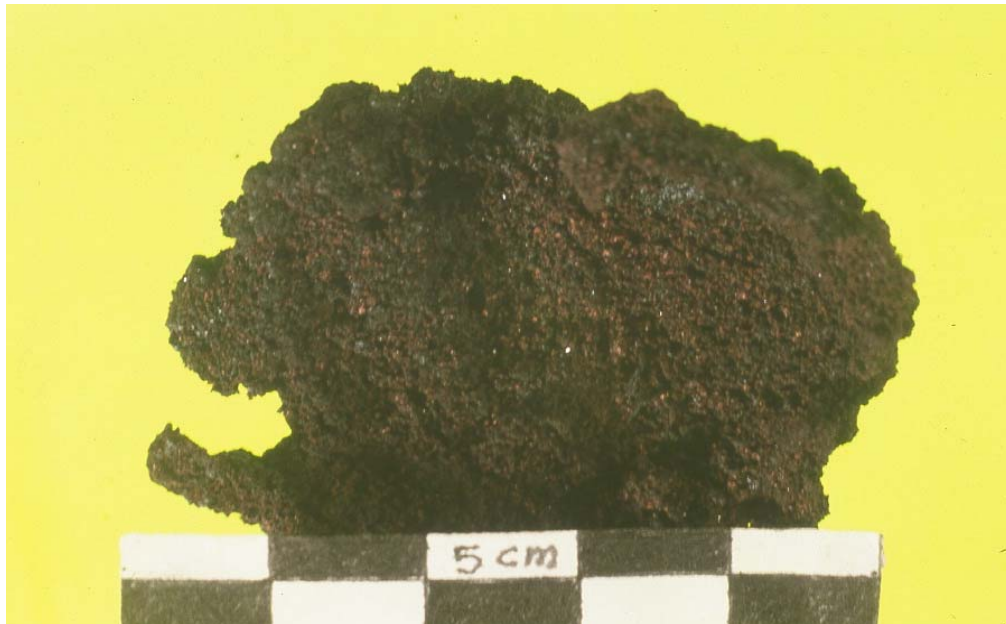
Figure 5.1g. XR 7
XRD results: Thenardite (Na_2SO_4), analcime ($NaSi_2AlO_6.H_2O$), gypsum ($CaSO_4.2H_2O$) and quartz (SiO_2).
Chemical analysis: 958 ppm Fe, 42.1 ppm Cu, 2.00 ppm Zn, <0.3 ppm Pb, <0.1 ppm Cd, 1.100 ppm Cr, 7.20 ppm Ni, 20.1 ppm Co, 0.0260 ppm Sb and 4.30 ppm As. **pH** 3.7

The crystals (Figure 5.1g. XR 7) are purple in colour and have a red black staining when they are in contact with organic matter due to adsorption. They partially dissolve in distilled water. All the peaks were identified and thernadite (Na_2SO_4) is the major phase while analcime ($NaSi_2AlO_6.H_2O$) and gypsum ($CaSO_4.2H_2O$) are the trace phases.

Iron is high with a concentration of 958 ppm and is contributing significantly to the colour of the crystals (Figure 5.1g. XR 7).

The crystals (Figure 5.1h. XR 8)are pale green, hard and have a distinct sulphur smell. Three phases are present in these crystals with thernadite as the major phase, boussingaultite ($(NH_4)_2Mg(SO_4)_2.6H_2O$), halite ($NaCl$) and gypsum ($CaSO_4.2H_2O$) are the trace phases (Table 6).

Nickel, cobalt, iron and copper are the highest elements present with concentrations of 323 ppm, 194 ppm, 179 ppm and 45.4 ppm respectively (Figure 5.1h. XR 8).

Figure 5.1h. XR 8
XRD results: Thenardite (Na_2SO_4), boussingaultite ($(NH_4)_2Mg(SO_4)_2.6H_2O$), halite ($NaCl$),
            gypsum ($CaSO_4.2H_2O$) and quartz (SiO_2).
Chemical analysis: 179 ppm Fe, 45.4 ppm Cu, 6.70 ppm Zn, 2.25 ppm Pb, 0.400 ppm Cd,
            0.900 ppm Cr, 323 ppm Ni, 194 ppm Co, 0.004 ppm Sb and 0.630 ppm As. **pH** 4.7

Figure 5.1i. XR 9
XRD results: Thenardite (Na_2SO_4), boussingaultite (($NH_4)_2Mg(SO_4)_2.6H_2O$), halite (NaCl),
and quartz (SiO_2).
Chemical analysis: 4880 ppm Fe, 1590 ppm Cu, 28.3 ppm Zn, 13.1 ppm Pb, 0.800 ppm Cd,
6.600 ppm Cr, 348 ppm Ni, 329 ppm Co, 0.013 ppm Sb and 10.00 ppm As. **pH** 3

The white crystals (Figure 5.1i. XR 9) that form hard crusts on the surface of the dump but dissolve easily when added to distilled water. Thernadite (Na_2SO_4) is the major phase while boussingaultite (($NH_4)_2Mg(SO_4)_2.6H_2O$) is the minor phase and halite (NaCl) is the trace phase.

All the analysed metals show a marked increase in concentration with iron, copper, nickel and cobalt still having the highest concentrations (Figure 5.1j.XR 9).

Table 6. Showing the three phases that could be identified from the XRD using the search/match programme. There are some peaks that could not be identified in some of the diffractograms.

Sample No.	Major phase	Minor phase	Trace phase	Unidentified peaks
XL1	Thenardite	Gypsum		9.27,3.97,5.54
XR2	Thenardite	boussingaultite	Gypsum	
XR3	Copiapite	Gypsum		
XR4	Thenardite	boussingaultite	halite, gypsum	17.4,17.8,25.1,22.6,29.4
XR5	Thenardite	boussingaultite, gypsum	Halite	30.4,9.59,29.6,22.5
XR6	Thenardite	boussingaultite	halite, gypsum	
XR7	Thenardite		Analcime, gypsum	
XR8	Thenardite	boussingaultite	halite, gypsum	
XR9	Thenardite	boussingaultite	Halite	

The XRD results (Figures 5.1a – i and Appendix 7) show that the eight samples are hydrated sulphates and vary mainly in the amount of water they contain and elemental concentrations. All the crystals dissolved partially in distilled water. They are heterogeneous mineral aggregates with different phases as shown in Table 6. The major phase in all but one of the samples is thernadite (Na_2SO_4). XR3, containing copiapite ($Fe_{14}O_3(SO_4)_{18}.63H_2O$) and the sample is the only one with the main phase different from all the others and it also has the highest water content.

Although the composition of the crystals is the same, they however have different colours. The colour variations could be dependent on the cations whose concentrations are less than three percent. Most of the compounds forming the crystals are white in colour (Na_2SO_4 and $CaSO_4.2H_2O$) but due to a mixture of the cations such as iron, copper and cobalt, they vary in colour (Figures 5.1a. XL1 and). However, in some of the crystals, some cations such as antimony and arsenic appear in such insignificant amounts that their contribution to colour is insignificant (Figures 5.1e.XR 5 and 5.1g.XR 7). In such instances, one major cation (Fe) is contributing to the colour of the crystals.

All the samples contain quartz, a primary mineral that is a result of contamination from the sampling process of the secondary minerals. The thenardite is a product of the reaction between the sodium cyanide used in the plant and the acidic conditions at the slimes. The slimes contain sodium oxide (Na_2O) and sulphite (SO_3), see Appendix 8. Hydrogen cyanide may be present in the pore water of the slimes due to the breakdown of metal cyanide species by sulphuric acid formed by oxidation of sulphates present. The presence of pyrite, which reacts to form sulphuric acid (H_2SO_4), plays a major role in the reaction (equation 3.11).

Gypsum, which is present in most of the samples, is a result of the reaction of sulphuric acid (from the oxidation of pyrite) and the lime ($CaCO_3$) used for the pH control in the plant and on the slimes dump (Equation 5.1).

$$CaCO_3 + H_2SO_4 + 2H_2O \rightarrow CaSO_4.2H_2O + H_2CO_3 \qquad (5.1)$$
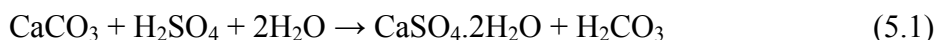
3.5g/l of lime was being added to try and control the pH that was dropping rapidly from 9 to 3 and this rate was exceeded when the pumps were not working with the ponds full

and over flowing into the nearby stream and during the wet season. The excess calcium sulphate results in the precipitation of more gypsum (Equation 5.2).

$$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4 \hspace{3cm} (5.2)$$

The growth of the crystals involved the transportation of the solute to the surface, adsorption onto the surface and incorporation of the species into the crystal lattice. The secondary minerals are scavengers of many of the elements dissolved in the water and remove elements from solution during the dry season. From the chemical analysis, iron is the most abundant element in the mineral aggregates, followed by copper and then nickel. There is a relationship between pH and metal concentration in the aggregates (Figures 5.1j and 5.1k).

In dumps at Athens mine, the rock forming minerals, plagioclase, pyroxenes and amphiboles are broken down resulting in the release of cations such as calcium (Ca), magnesium (Mg), aluminium (Al), sodium (Na) and potassium (K). The cations contribute significantly to the secondary minerals on the slimes dumps at the mine as shown in Figures 5.1j to 5.2i. The sulphates (SO_4) are from the break down of sulphides such as bonite (Cu_5FeS_4), pyrite (FeS_2) and Chacopyrite ($CuFeS_2$). During the break down of the sulphides, the iron, copper and sulphur are released into solution. Normally in slimes the additives constitute 10 to 15 % while the rock forming minerals constitute 85 to 90% of the sulphates and cations. At Athens, some of the additives of concern are, ferrous sulphate, sodium cyanide, sodium hydroxide, and sodium carbonate and lead nitrate. Analcime (Figure 5.2f.XR) indicates the presence of free aluminium because the mineral only forms when there is free aluminium.
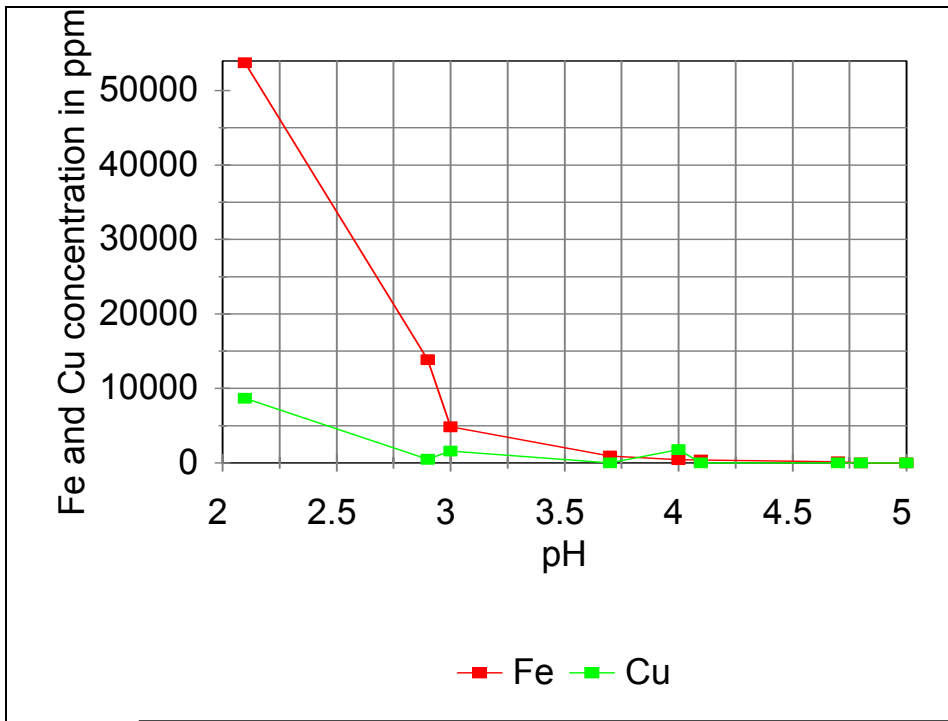
Figure 5.1j Iron and copper concentration in the crystals as a function of pH of the crystals.

Iron decreases sharply from 53800ppm at a pH of 2.1 to 26.5ppm at a pH of 5 and copper drops from 8700 ppm at pH of 2.1 down to 8.6 ppm at a pH of 5 (Figure 5.1j).

Cobalt, nickel and zinc decrease sharply from a pH of 2.1 to 3.4 but show no consistent trend above this (Figure 5.1k). Antimony, cadmium and chromium, are generally low (<0.1 ppm) in the minerals (see Appendix 9).
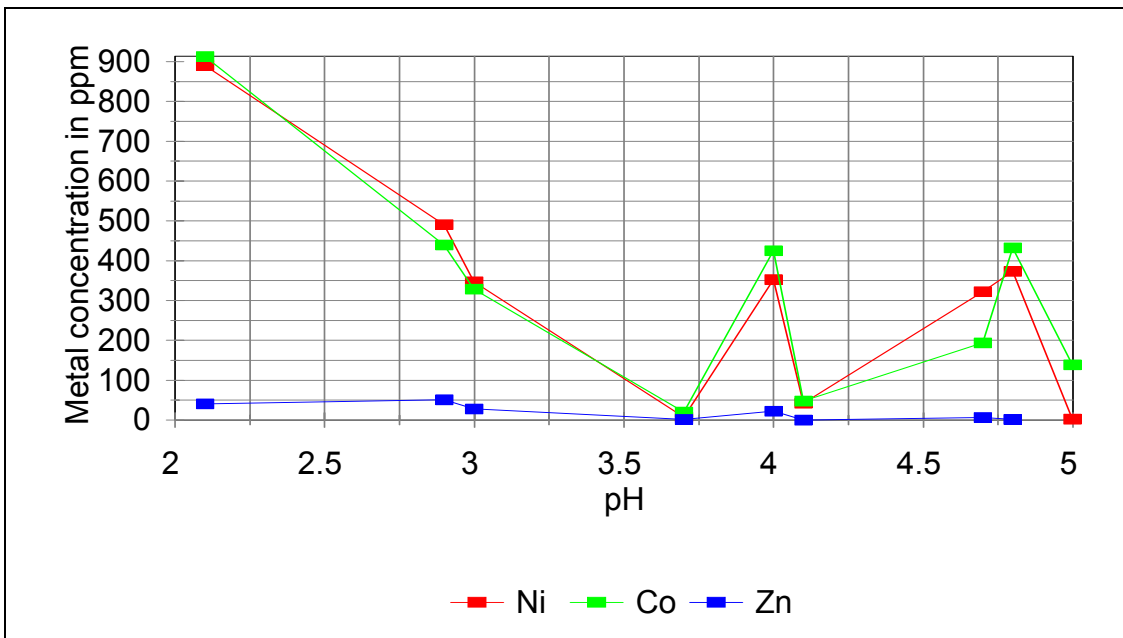

Figure 5.1k Cobalt, nickel and zinc concentrations in the mineral aggregates as a function of pH.

Iron, copper, nickel, cobalt and zinc concentrations decrease with an increase in pH for most of the analysed elements. The solubility of iron, copper and nickel in the secondary minerals increases noticeably at pH < 3.5 while above this pH the metal concentrations are < 500ppm. The low pH conditions increases the solubility of the metals hence is found in high concentration.

The presence of the secondary minerals during the dry season meant that there is reduced metal concentration in solution and the environment. During the wet season the crystals dissolve at low pH contributing significantly to the metals concentration in environmental. The identification of the crystals gave the indication of some of the metals that pollute the environment from the mining activities.

The high iron concentrations were from both the mineralogy and the addition of ferrous sulphate in the processing plant (APPENDIX 2). Other elements that were a result of chemical additions from processing apart from the mineralogy were, sodium from the addition of sodium hydroxide (NaOH) and sodium cyanide (NaCN) while lead was from the addition of lead nitrate (Pb(NO$_3$)$_2$) (APPENDIX 2).

The soluble salts can inflict chemical weathering effects on building materials (Cotter-Howells et al., 2000) and increase the solubility of minerals by the increase of ionic force. More damage is inflicted when the salts formed inside the affected materials than when they are on the surface. The crystallisation position is determined by the balance between water gained by capillary rise or from rain and water lost through drying by surface characteristics or salt solubility or the influence of salt mixtures (Cotter-Howells et al., 2000). Thenardite (Na$_2$SO$_4$) is among the most damaging salts.

5.2 Free oxygen and sulphides in slimes

At the active dump at Athens mine, the oxygen (O$_2$) concentration drops from atmospheric concentration (20.9%) to 3.8% within the upper five metres of the dump (Figure 5.2a). The drop is probably a result of pyrite oxidation, which is consuming oxygen within this upper part of the dump.
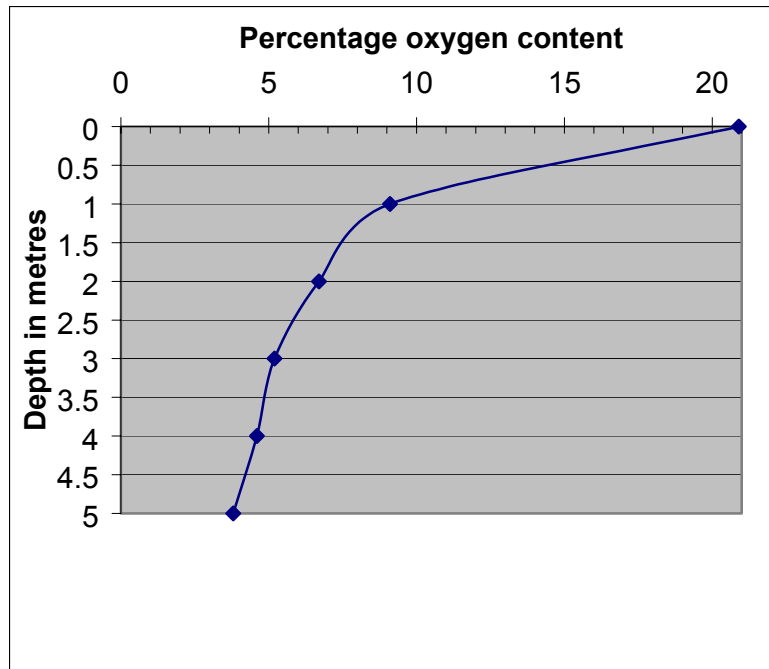
Figure 5.2a. Oxygen concentration plotted against depth at the dump at Athens mine.

Volume of oxygen calculation from graph, Figure 5.2a

Internal diameter of tubing used = 1.7cm

V_h = volume to a depth of h cm

$\pi = 3.14$

h = depth in centimetres

$V = \pi r^2 h$

$V = 3.14 (0.85)^2 \ cm^3$
$V = 2.26865 cm^3/m$
$V_{500} = 5 \times 2.26865 cm^3$
$V_{500} = 11.34325 cm^3$

The oxygen diffusion in the slimes is also dependent on the moisture content of the slimes, which increases with depth (Figure 5.2b). An increase in moisture results in the pores being filled with water resulting in a reduction in free oxygen movement. Observations of the oxygen concentrations and the sulphide concentrations in the slimes show that most of the oxidation is taking place within about four metres to five metres depth. Most of the slimes within the top 5m (oxygenated zone) are completely oxidised (Figure 5.2b and Appendix 10). Oxygenated zone is the area of the slimes that is at surface and near the surface that is in contact with atmospheric oxygen while reduction

zone is below and the chemical reactions take place in the absence of oxygen using water and dissolved oxygen as oxygen sources (Garga et al., 1983).
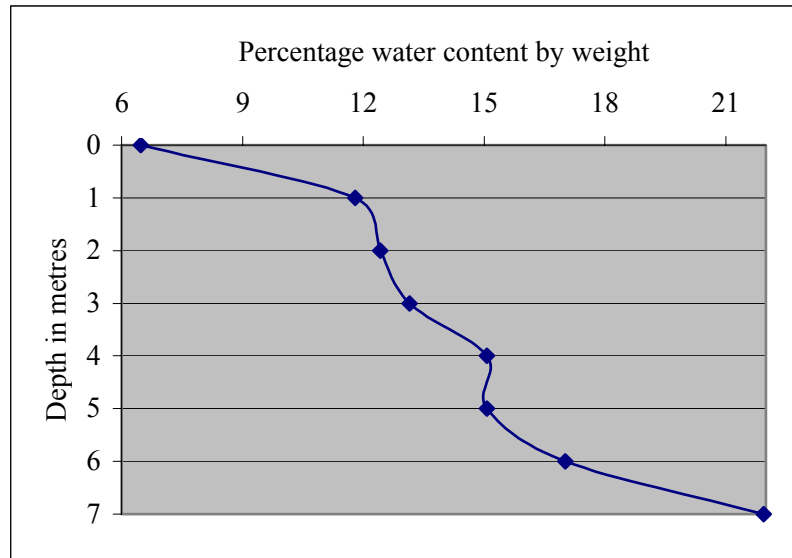
Figure 5.2b. Water content by weight with depth at the slimes dam. There is a general increase in the water content with depth.

The high oxygen values within the upper three metres are a result of the absence of pyrite and pyrrhotite and reduced moisture content within this zone. 0.1% of pyrite was found at 2m and no pyrrhotite was found. This layer is made up of reworked material, which had been exposed to the atmosphere for a long time, and oxidation had taken place resulting in low sulphide content. There is a slight increase in the sulphide concentration from 3m to 4m, marking the upper boundary between the oxidised and the unoxidised zones (Figure 5.2c). Pyrite oxidation is the driving force behind the acidity in the slimes and therefore the amount of pyrite has a bearing on the pH of the slimes. The acidic conditions of the dam indicate the potential for heavy metals to be leached from the slimes into the environment. Copper starts to be desorbed from adsorption sites at pH 6 and the process increases rapidly at pH 5.2 (Guy et al., 1975) and zinc becomes soluble at pH 6.5.
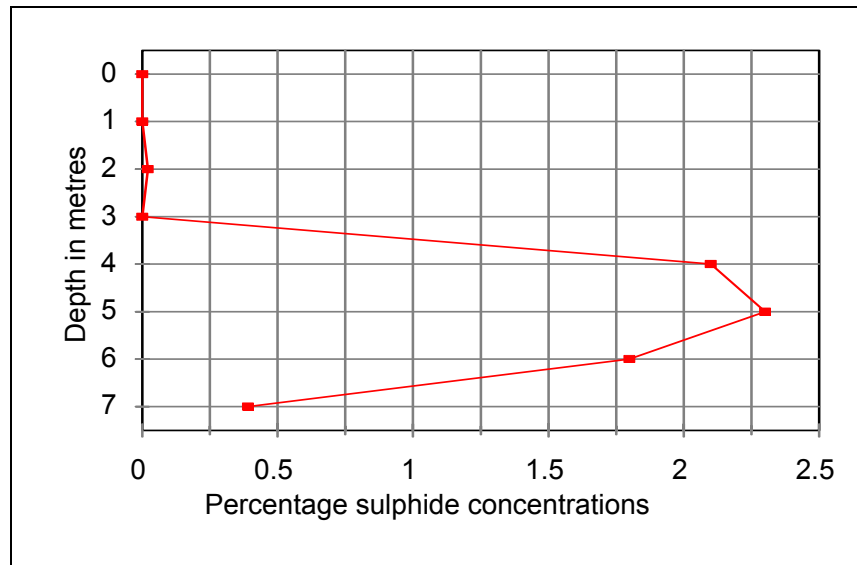
Figure 5.2c. Sulphide concentration plotted against depth at the dump at Athens mine. The slimes from 0m to about 4m are from the processing of the old dumps for gold after the closure of the underground operations. Below the 4m depths the slimes are from the underground mining for gold and the water level was at about 5.2m.

The amount of sulphides and free oxygen present in the slimes indicated that most of the acid generation was taking place from 1m to 3m. Below this depth the water content increased while the free oxygen content decreased indicating reduced acid generation.

5.3 Element concentration in the slimes.

The slimes contain high concentrations of iron, copper, zinc, lead, nickel, cobalt and chromium (Appendix 9). Cadmium, antimony and arsenic are low throughout the slimes with maximum concentrations of 0.8ppm, 0.021ppm and 19ppm respectively and not significantly elevated relative to normal rock concentrations around Athens. Arsenic in the bedded chert is 19ppm and 12ppm in the massive chert (Fabiani, 1989). The distribution of the elements within the slimes, show no particular trends. This is expected because the slimes are heterogeneous and there is a lot of mixing of materials. The full results are shown in Appendix 9.

5.4 Seasonal leachate variations

The pH of the leachate shows very little seasonal variations and remains acidic. The acidity was caused by chemical and bacteriological oxidation of pyrite in the slimes. Slight increases during the wet season maybe due to dilution of the acidic conditions as a result of the high rainfalls. The little variations were recorded in the second receiving

trench while the first trench showed no variations, indicating a strong influence of pH on the slimes.

Most of the elements analysed show an increase in the leachate during the wet season with iron having the highest metal concentration of 11054mg/l up from 3621mg/l in dry season. This represents an increase of about 205% (Table 8). At sample site LMA4, there is a 33.9% decrease of iron concentration, which could be due to dilution caused by run off from the top of the dam (Figure 5.4a and Appendix 11).

Copper shows the highest variation during the two seasons with a maximum of 10345mg/l during the wet season compared to 920mg/l during the dry season, an increase of over 1024% (Table 8).
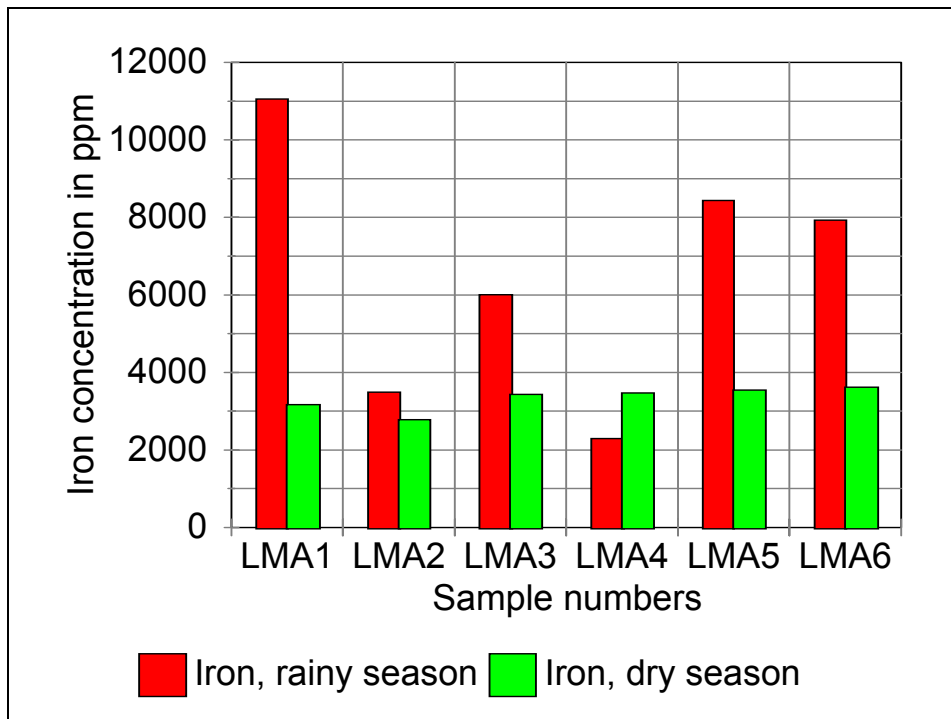
Figure 5.4a The seasonal variation of iron concentration in the leachate from the slimes dam.

This is due to the fact that the copper is very mobile in acidic conditions and accounts for the slightly lower concentrations in the slimes. Figure 5.4b shows the variations and the full results are in Appendix 11. Table 8 gives a summary of the results.

Arsenic, chromium, cobalt, lead, nickel and zinc concentrations showed an increase in the wet season (Appendix 11).

During the dry season the elements were removed from the leachate by precipitation with other elements due to addition of various chemicals during processing. At pH of 6.5 to 7.5, arsenic precipitate with ferrous sulphide resulting with it being removed from the leachate (Ritcey G. M., 1989). The pH of the slimes during dumping of the slurry was controlled at pH9 by adding lime. During the wet season the pH of the slimes dropped from 7.4 to 3 and this resulted with most precipitates dissolved and the metals going into the leachate hence the high concentrations.

Cadmium and antimony were left out in the further analysis because all their concentrations were found to be less than one parts per million (<1ppm) during both the dry and wet seasons.
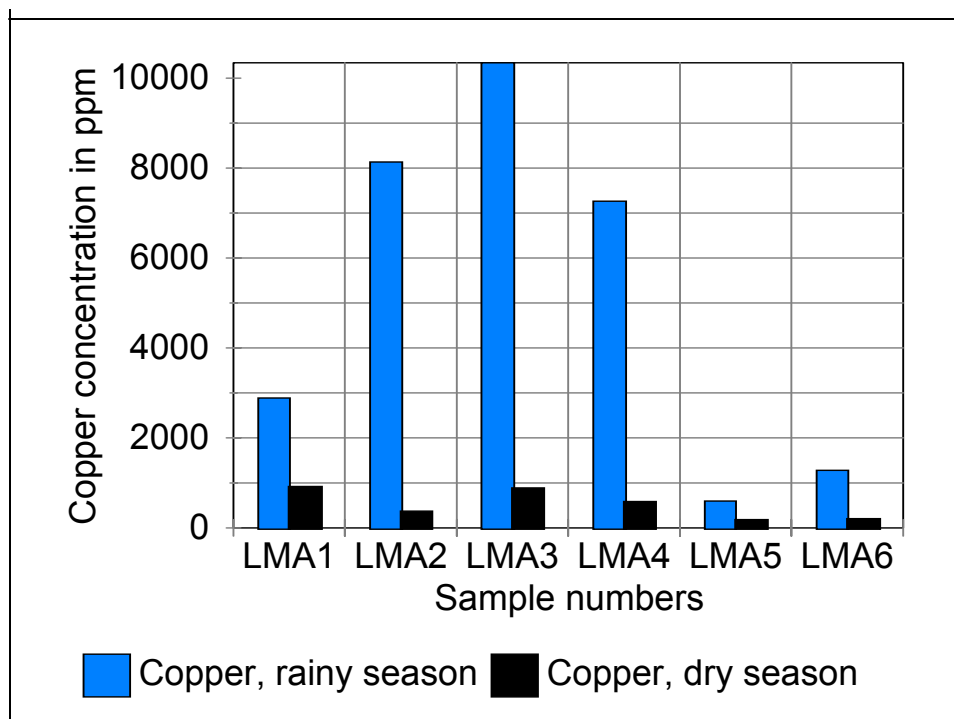
Figure 5.4b Seasonal variation of copper concentration in the leachate from the slimes dam at Athens.

Table 8: The maximum element concentration in the leachate from the slimes dam at Athens during the rainy and dry seasons in order of percentage increase.

Element	Maximum ppm		
	Wet season	Dry season	Percentage increase
Copper	10345.00	920.00	1024.46
Arsenic	7.61	1.71	343.99
Iron	11054.00	3621.00	205.17
Chromium	2.57.00	1.32	94.53
Cobalt	10.60	6.07	74.51
Zinc	0.97	0.89	8.99
Lead	0.37	0.37	-0.32
Nickel	5.43	10.69	-49.20

5.5 Geophysical results and observations:

T1 (Figure 5.5a) shows resistivities of 32-56 Ω-m for depths ranging from 1-5m. At depths of 5m down to 25m resistivities are below 18 Ω-m. After 25m from the top of the dam high resistivities (>100 Ω-m) were obtained. The low resistivities were obtained from 140m – 220m. From 80m to the end of the profile a highly conductive and slanting band can be seen at a depth greater than 4m.
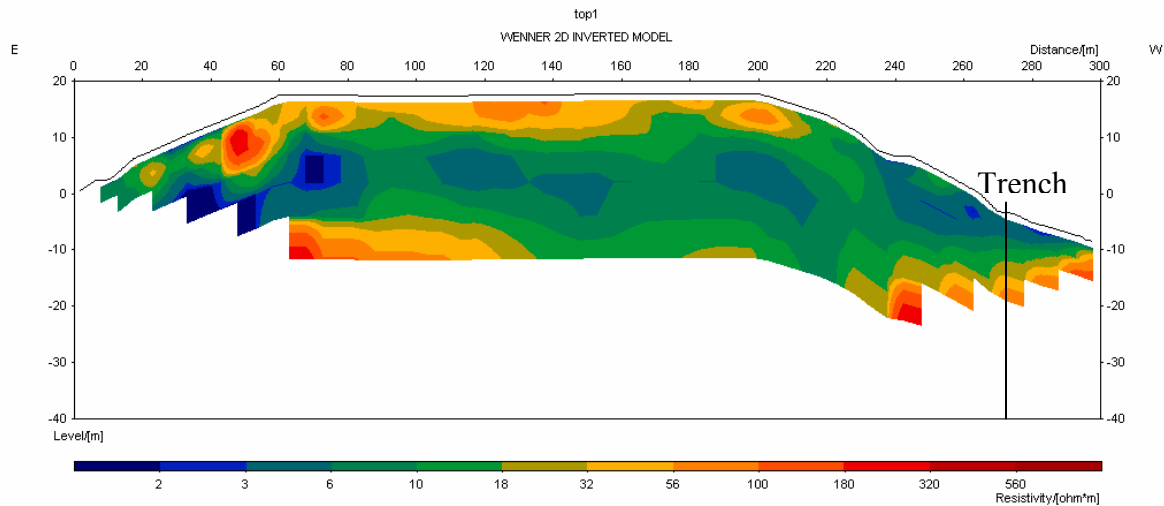
Figure 5.5a: T1 Profile running north south on top (Top1) of the slimes dam.

T2 (Figure 5.5b) has low resistivities of less than 6 Ω-m from 100m to 160m corresponding with the central position of the dam which is water saturated, spreading down at depths to a maximum of greater than 28m on the mid-western end of the dam.
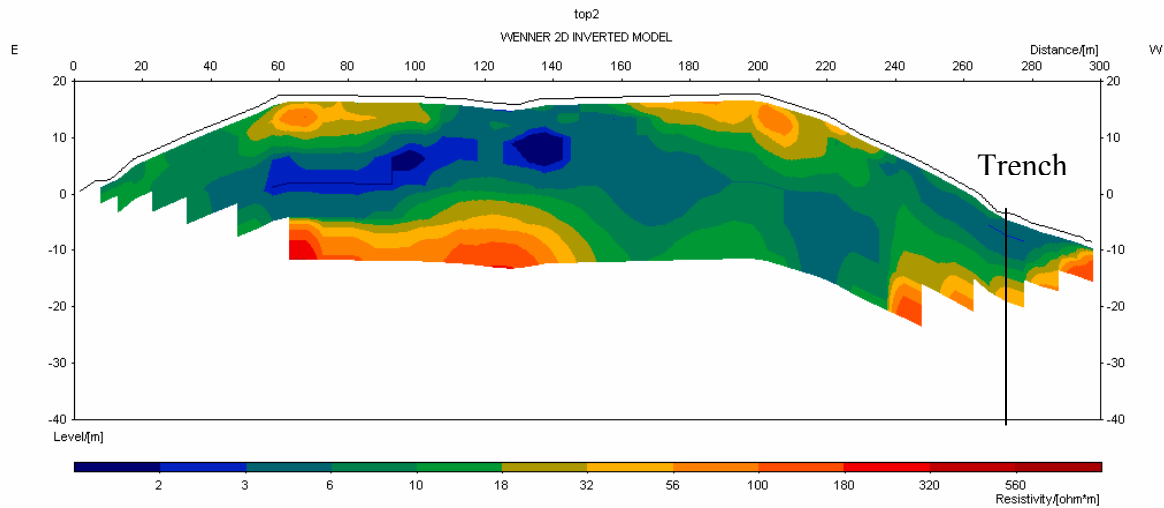
Figure 5.5b: T2 profile running east west on top and through the centre of the dam.
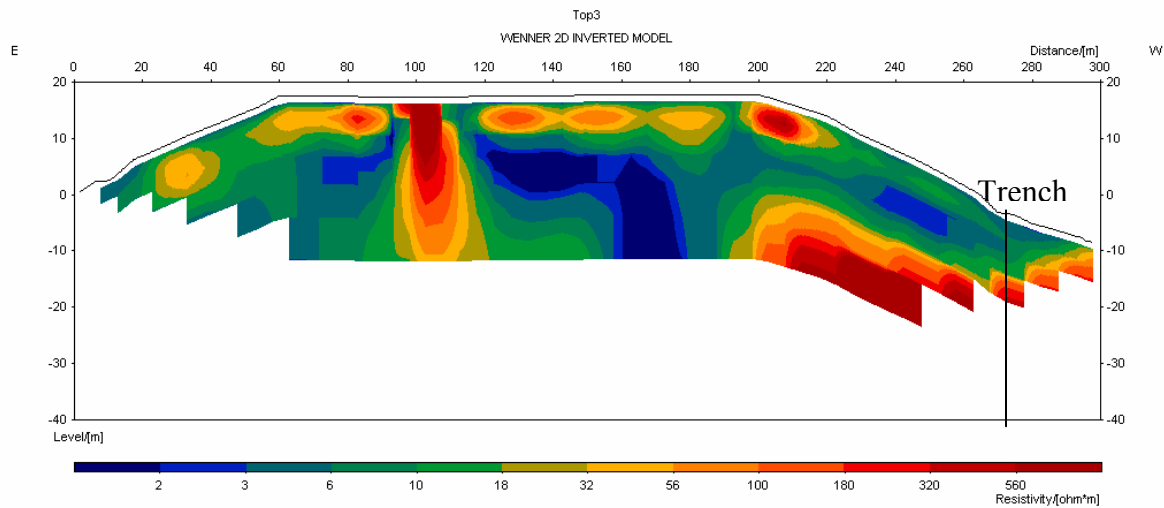

Figure 5.5c: T3 running east-west profile starting on top of the slimes dam.

T3 (Figure 5.5c) shows a different trend where the top is conductive, with resistivities between 10 and 18 Ω-M and is underlain by a 5m thickness of resistive layer (32-100 Ω-m). From station 105m there is a distinct break into a low resistivity column (2 – 3 Ω-m) that continues to greater than 30m around station 190m near the western end of the dam. The other conductive band is much smaller from station 90m to the eastern end of dam. A high resistance layer at about 25m depths is seen at station 200m on western end of the dam but is not evident from centre to the eastern end except at 100m where it shows as a vertical circular column.
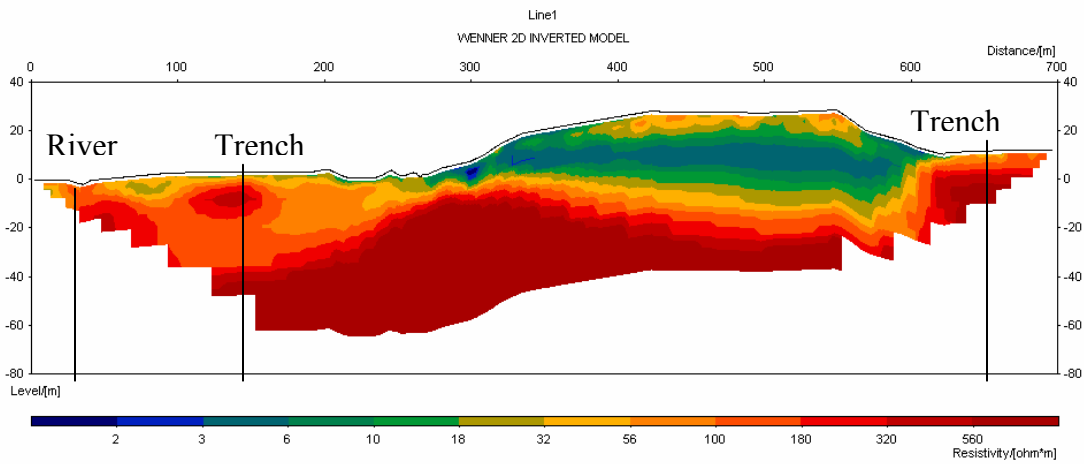
Figure 5.5d: L1 running north-south profile through the top of the slimes dam

L1 (Figure 5.5d) shows low resistivities on the top thin layer from station 200m to 280m station. Between stations 280m and 600m is the top of the dump and show layers of varying resistivities ranging from 3 to 32Ω-m. The top 5m, between stations 390m and 580m have resistivities between18 and 100 Ω-m and below this layer, is 3m thick layer of 6-18 Ω-m resistivities between stations 320m and 600m. Between stations 290m and 590m there is a 5m layer of 2-3 Ω-m resistivities, which is underlain by a 3m layer of 6-18 Ω-m resistivities. A narrow layer of between 18 Ω-m and 32 Ω-m stretches from station 180m to 610m and below it a layer of 32 Ω-m to 56 Ω-m resistivities that stretches from station 60m to 660m. From a depth of about 26m to 60m, there is little variation in resistivity with that band between 100 Ω-m and 320 Ω-m. The low resistivities do not extend beyond the receiving trenches but lie between the trenches.
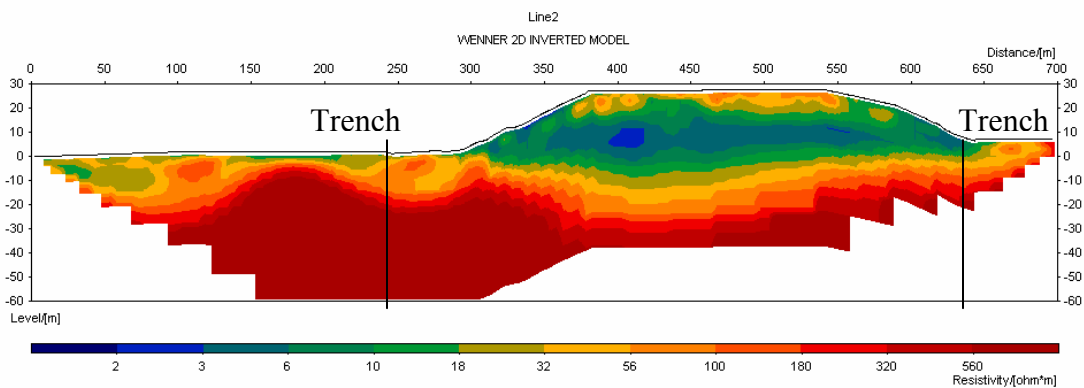

Figure 5.5e: L2 running north-south profile through the top of the dam

L2 (Figure 5.5e) shows a similar resistivity pattern as in Figure 5.5d, L1.The 5m between stations 360m and 560 m have resistivities between 18 Ω-m and 100 Ω-m. Between 320m and 360m and between 610m and 630m, there is narrow 2m layer of low resistivity (2-3 Ω-m). Below the 5m layer, there is a 6 Ω-m – 18 Ω-m resistivity layer surrounding a 2 Ω-m – 6 Ω-m resistivity layer, which lies between stations 300m and 650m. A thin 6 – 18 Ω-m layer stretches from station1m to 250m. From station 1m to 680m the section there is a layer of 32 - 100 Ω-m resistivity layer varying in thickness which is underlain by a thick 100 to 560 Ω-m resistivity layer from a depth of 8m to 60m (between stations 100m and 300m) and 18m to 60m (between stations 50m to 650m). The low resistivities extend beyond the receiving trenches.
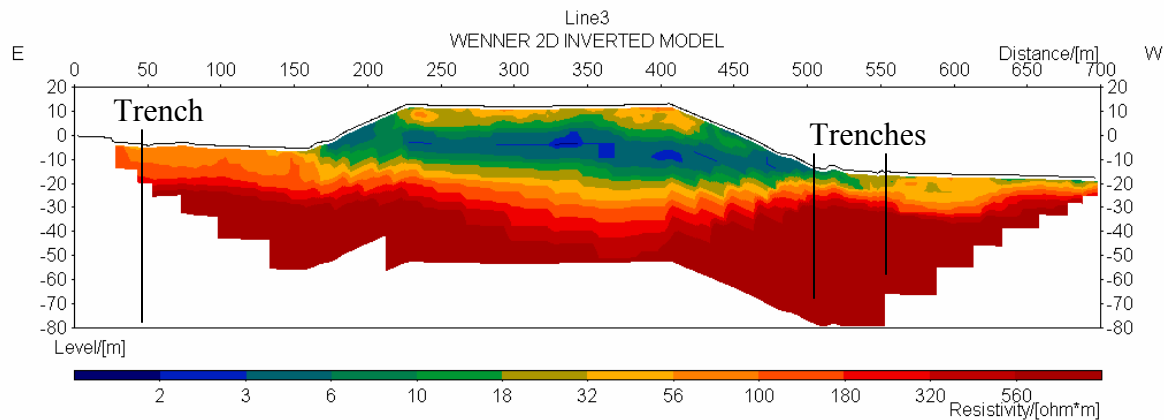
Figure 5.5f: L3 profile running east-west through the top of the slimes dam parallel to L7 and L8

The top 4m between stations 220m and 430m (Figure 5.5f) there is an 18 - 100 Ω-m resistivity layer that is followed by a 6 – 18 Ω-m resistivity layer between stations 160m and 540m which surrounds a low resistivity layer of 1 – 6 Ω-m. At a depth of about 7m between stations 160m and 560m there is an 18 – 32 Ω-m, resistivity layer 2m thick, and below it is 56 –320 Ω-m that stretches to a depth of 60m. On the western side of the section, the low resistivities extend beyond the two trenches while on the eastern side the low resistivities stops at station 150m.
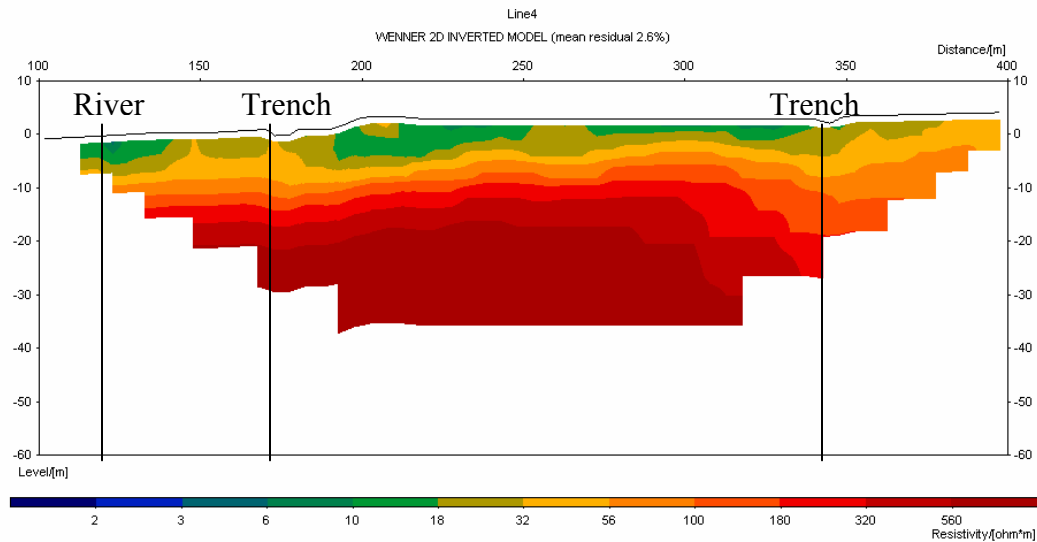
Figure 5.5g: L4 profile running north south on the western side of the slimes dam between the two receiving trenches and crossing the stream in the northern end.

This profile (Figure 5.5g) shows low resistivities of 6 – 18 Ω-m between stations 125m and 145m, 190m – 255m and 275m to 345m. These coincide with the river and flat area between the two receiving trenches, which are always flowing with leachate from the slimes dump (Figure 4.5). From 8m depths to 38m depths, between stations 120m and 399m, there are various resistivity layers of between 32 Ω-m and 560 Ω-m.
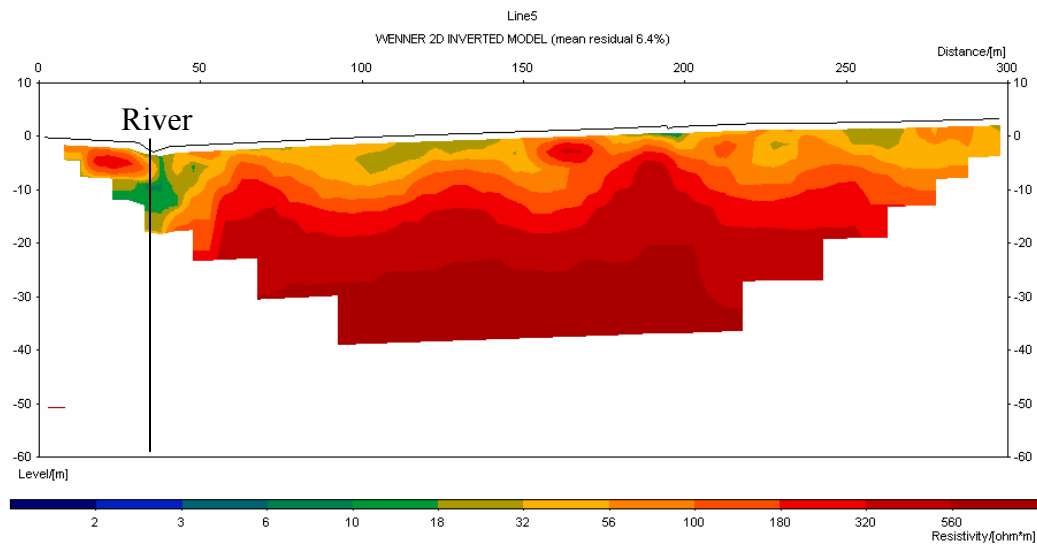

Figure 5.5h: L5 profile running north south on the west and parallel to L4.

The low resistivities of 6 - 18 Ω-m on this section (Figure 5.5h) are found at the river intersection and small bridge (Figure 4.5) stations 60m and 200m respectively. The profile runs parallel to the Chivu – Masvingo road on the western side. Resistivities of between 18 – 100 Ω-m are found between 60m and 150m and 200m to 299m. These

75

layers (between 18 – 100 Ω-m) are of varying thickness and are underlain by thick resistivity layer of 100 – 560 Ω-m resistivity up to a depth of 40m.
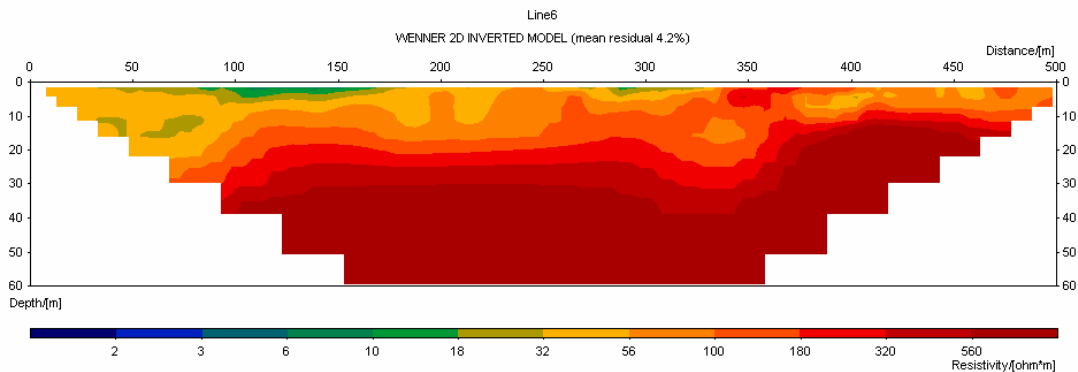

Figure 5.5i: L6 profile running north south on the far eastern side of the extension to the slimes dam

The low resistivities (6 -100Ω-m) are sound between stations 2m and 330m (Figure 5.5i) and they extend to a depth of 25m. This is a result of the extension of the slimes dam. Below his layer there is 35m thick (25m depth to 60m depth) resistivity layer of 320 – 560 Ω-m from stations 180m to 460m.
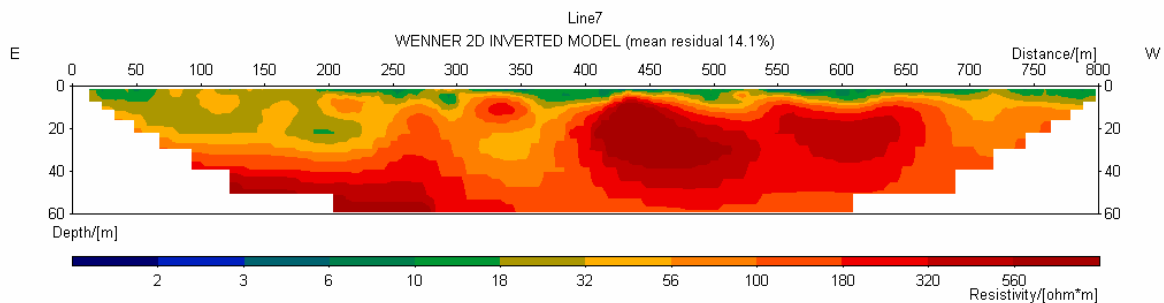

Figure 5.5j: L7 profile running east west on the northern side of the slimes dam cutting through the storage pond and receiving trenches on the western end.

The top 20m of the eastern side of the section (Figure 5.5j) between stations 10m and 250m have low resistivities of 6 – 32 Ω-m. This area is adjacent to slimes extension (Figure 4.5) and the law resistivities are the effects of the seepage from the slimes. This zone shows progressive seepage into the environment. From stations 250m to 800m the top 1m to 4m have the low resistivities of 6 – 18 Ω-m underlain by a thin layer of 32 - 56Ω-m. These are probably due to seepage from the storage ponds and the receiving

trenches (Figure 4.5). From 4m to 60m depths, between stations 400m and 720, there is an area of high resistivities of 180 – 560 Ω-m.
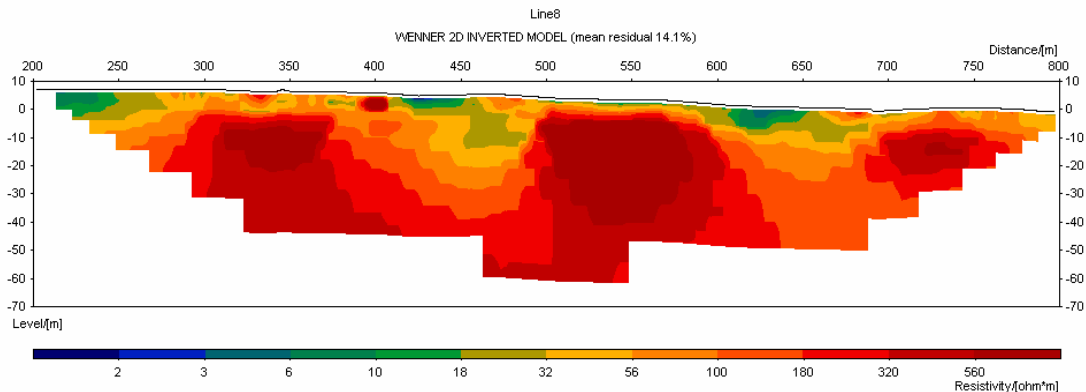

Figure 5.5k: L8 profile running east west on the southern side of the dam, lying between the garbage dump and the slimes dam

The section shows low resistivities of 6-100 Ω-m within the top 15m depth between stations 200m and 300m. This is seepage from the extension slimes dump on the eastern side. Low resistivities (6 – 100 Ω-m) are also found between stations 400m and 500m and 600m and 700m and this due to seepage from the active dump. Receiving trenches at these two stations were completely filled with slimes during the wet season. The leachate is now seeping into the surrounding environment.

Lines T1 to T3 and L1 to L3 (Figures 5.5a – f) all run through the top of the slime dump. It is clearly seen that the dry top of the dam has high resistivities and that the sides of the dam are conductive even at the surface. Figures 5.5a-c indicates that there is a significant seepage on the sides of the slimes dump. This is not surprising from the fact that salts have crystallised at the sides of the dam especially at points where effluent used to seep out of the dam. The low resistivity layers are a result of the water logging within the dump. Basement rocks have no major fractures resulting in high resistivities below the dump indicating no seepage directly below the dump. Lines L4 – L8 (Figures 5.5g – 5.5k are not in direct contact with the dump but all show progressive seepage within the top 20m. The basement rocks show no indication of seepage.

Seepage is a serious problem on the southern and eastern sides of the active dump and the area around the evaporation ponds. Receiving trenches were closed on the southern side

while on the eastern side was a result of the extension to the active dump. There was also direct seepage into the stream on the northern side of the dump (Figures 4.5, 5.5d, 5.5g and 5.5h).

5.6 Soils

Soil pollution often goes unnoticed for long periods of time as compared to water and air pollution, which are usually visible and noticeable. The ground in not transparent and has a considerable buffer capacity, resulting with the pollution remaining concealed. All acid induced soils reduce plant growth.
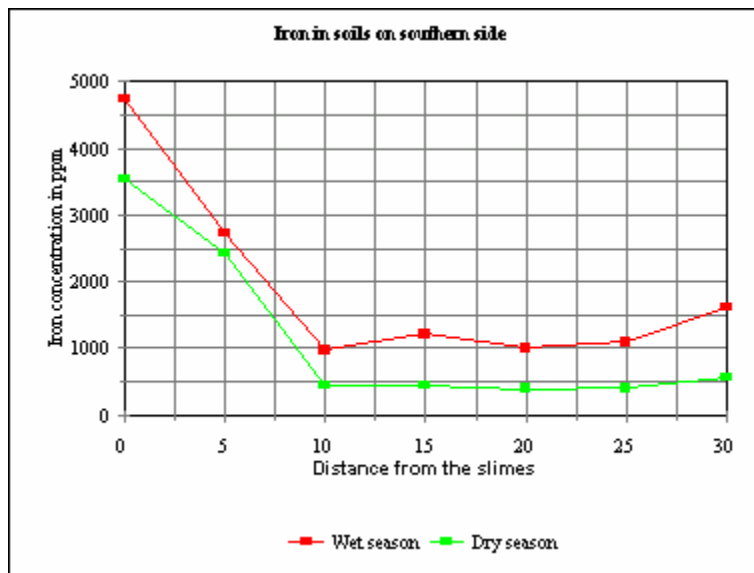

Figure 5.6a: Analysed available iron content of soils during the wet and dry seasons on the southern side of the slimes dam.

Iron in soils on the southern side of the slimes dump shows a similar trend with elevated concentrations during the wet season (Figure 5.6a). The iron concentration decrease with distance away from the dump to a distance of 10m and then remained constant to a distance of 25m. There is an increase in concentration from 25m to 30m with a significant increase noticed during the wet season.

The high concentration during the wet season is a result of the release of more iron as the secondary minerals dissolve from the dump surface and the increase element release from the dump due to the increase in acid generation. High iron reflects the addition of iron during the processing and the increase from 25m to 30 can be the influence of the solid waste dump situated on the southern part of the slimes dump (Figure 4.1).
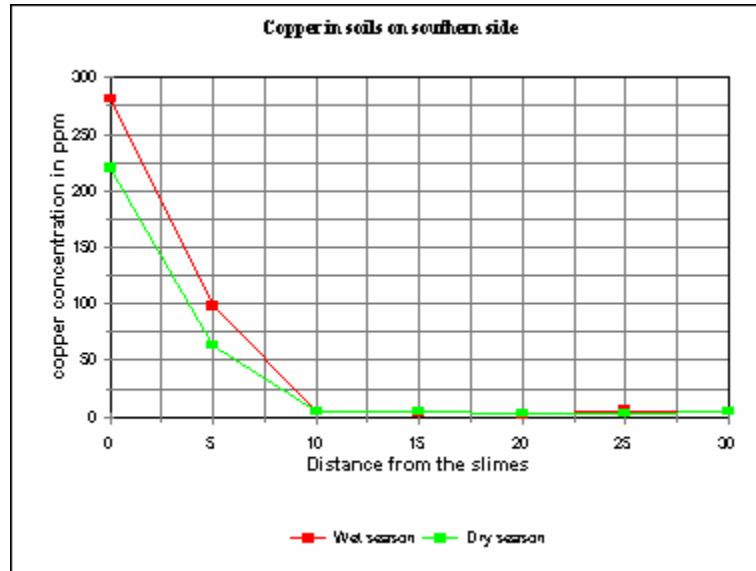
Figure 5.6b: Analysed available copper content of soils during the wet and dry seasons on the southern side of the slimes dam.

Copper concentration in soils shows a similar pattern to that of iron for the first 10m and then remains low for the remaining sampled distance (Figure 5.6b). The first 10m shows a slight increase in the copper concentration during the wet season and shows no variation in concentration during the two seasons for the sampled distance.

Copper is mobile and washes out of the soil more readily than metals such as lead and cadmium. Its solubility in the soils increase noticeably at pH < 5 and the mobility is less in the upper humus of forest soils compared to mineral layers beneath the upper humus (Fellenburg 2000). During the wet season as more acid was generated, more copper leach out of the slimes into the environment, the soil pH is 4.1 compared to pH 5.6 in the dry season. This resulted with higher copper concentrations during the wet season than the dry season though the trend is the same during the two seasons.

Zinc concentration decreases from 0m to 10m and then remained low throughout the sampled distance during both seasons (Figure 5.6c). Unlike copper the concentration of Zinc is slightly higher during the wet season than in dry season. The low zinc concentrations are a result of adsorption by clays and organic matter in the soils. The acidic conditions mean that the adsorption is due to cation exchange sites with iron and copper.

79

The solubility and mobility of zinc in soils increase significantly at pH < 6 (Fellenburg 2000). At pH > 6 and in the presence of phosphates, zinc is appropriated by plants and is reduced due to adsorption by clay minerals and oxides such as iron oxides. Zinc pollution in the soils is a serious ecological problem as it damages plant forms from the concentrations of 200mg/kg upward. Spharelite was the source of the zinc found in the soils.
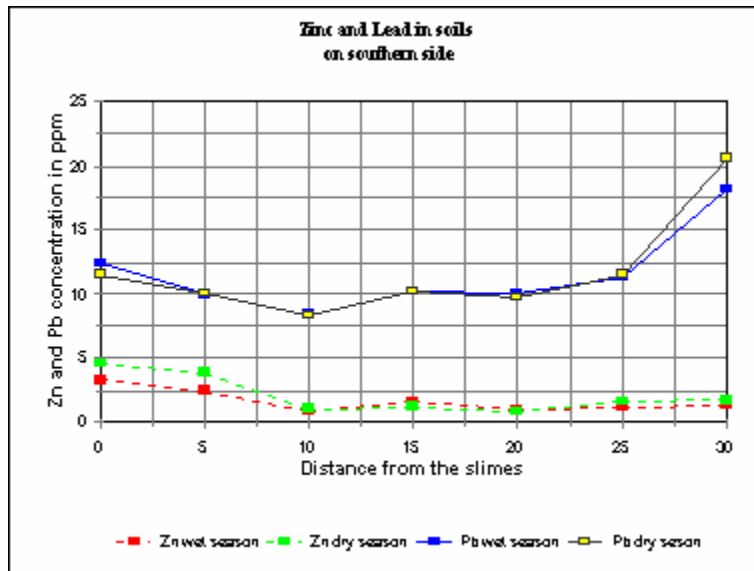

Figure 5.6c: Analysed available zinc and lead content of soils during the wet and dry seasons on the southern side of the slimes dam.

Lead concentration shows a gentle decrease from 0m to 10m and then a steady increase from the 10m to 25m during both seasons (Figure 5,8c). During the wet season lead concentrations between 0m and 10m are higher than during the dry season but the concentration during the dry season becomes higher during the dry season from 25m to 30m. Lead is mainly from the addition of lead nitrate (Pb (NO$_3$)$_2$) and the sharp increase from 25m could be a result of leaded fuel used by vehicles going to the dump and along the Masvingo − Chivu highway. Lead in the acidic soils is in cationic form with some organic complexation.

The main sources of lead were the addition of lead nitrate (Pb(NO$_3$)$_2$) during gold processing, the mineralogy (galena) and the leaded fuel to a lesser extent. Lead is not very mobile even at low pH (acidic) and accumulates in soils. Plants are more resistant to lead compared to humans and mammals so the accumulation has little effect to plants.
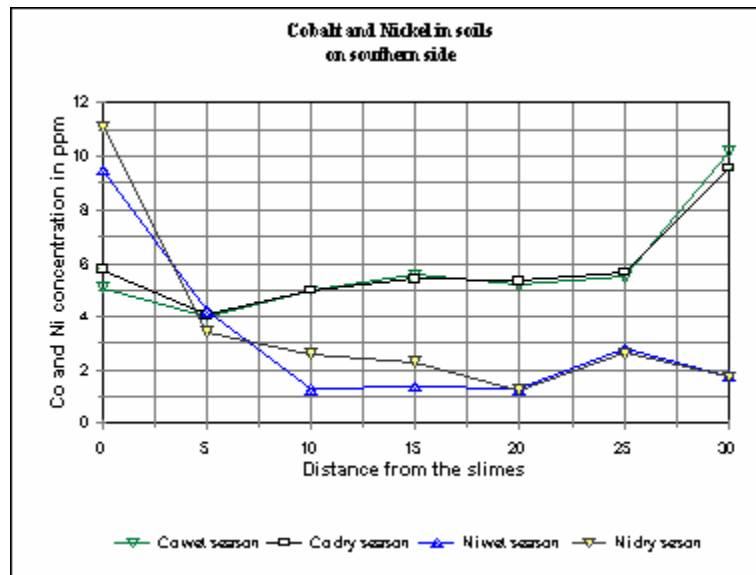
Figure 5.6d: Analysed available cobalt and nickel content of soils during the wet and dry seasons on the southern side of the slimes dam.

Cobalt concentration decrease gently from0m to 5m and then show a gently increase from 5m through to 30m (Figure 5.6d) during the two seasons. There are very little seasonal variations in the concentrations. A slight increase is recorded during the dry season within the first 5m and a slight increase during the wet season in last 5m (25m to 30m). The first 5m could be a result of dilution by the rainy water and the last 5m could be signifying the contribution from the garbage dump.

Nickel concentration decreases sharply from 0m to 5m during the dry season and to 10m during the wet season (Figure 5.6d). A higher concentration is recorded in the dry season, from 15m to 20m though both seasons show a gently decrease in nickel concentration. From 20m to 30m the concentration shows no variations during both seasons. The dry season shows slightly higher concentrations due to dilution from the acidic water seeping into the soils and releasing the nickel into solution.

Chromium concentration remains low in the soils as in the slimes but show the same trend of decreasing during the first 10m and show little variations from there to 30m (Figure 5.6e). During the wet season, the chromium from the dump as indicated by the high concentrations at 0m and is diluted as it seeps into the soil. From 5m, the

concentrations during the wet season are lower than the concentrations during the dry season because most of the chromium is in solution in the wet season.
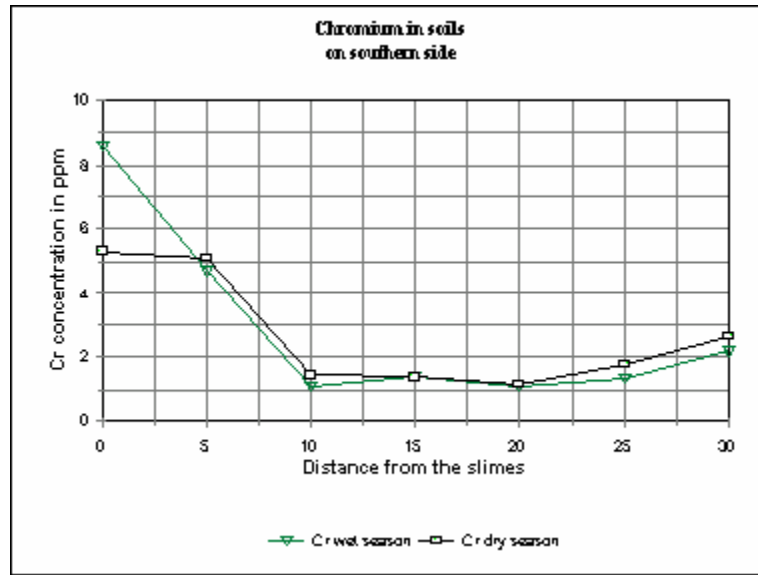

Figure 5.6e: Analysed available chromium content of soils during the wet and dry seasons on the southern side of the slimes dam.

The western side show a slightly different trend due to the presence of increased seepage throughout the year. Two receiving trenches had to be constructed on this side to try and collect excess leachate. The general trend is however maintained within the first 5m as shown in Figures 5.6f and 5.6g for iron and copper respectively. Cobalt nickel, lead, Zinc and chromium show a similar pattern as that of iron and copper. The element concentrations were generally low during both seasons (Appendix 9a and 9b).
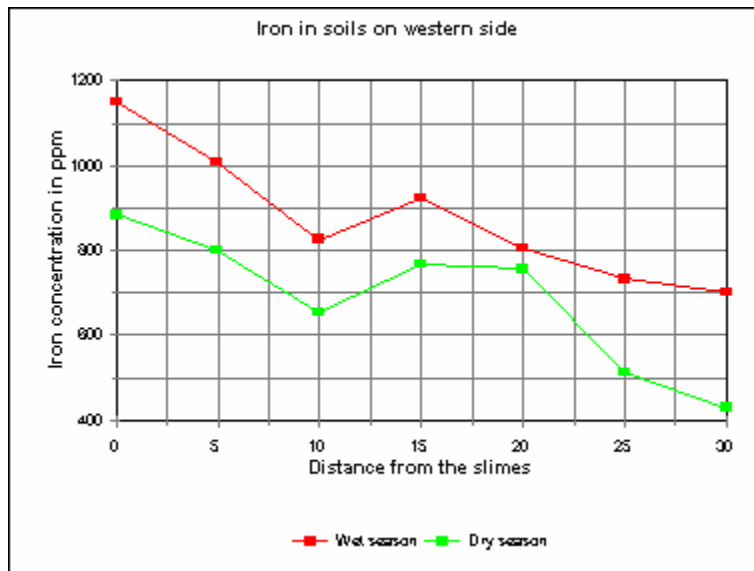
Figure 5.6f: Analysed available iron content of soils during the wet and dry seasons on the western side of the slimes dam.

Iron decreased from 0m to 10m during both the wet and dry season (Figure 5.6f) with the wet season having higher concentration than the dry season. There was an increase from 10m to 15m and then a decrease there to 30m during the two seasons. The decrease from 0m show the effects of the first receiving trench situated between the first sampling point (0m) and the second sampling point (5m), which acted as a barrier to the seepage. The same pattern is shown after the second receiving trench situated between 15m and 20m. The high iron concentrations during the wet season are due to the addition of ferrous sulphate and dissolving of the secondary minerals on the surface of the slimes.
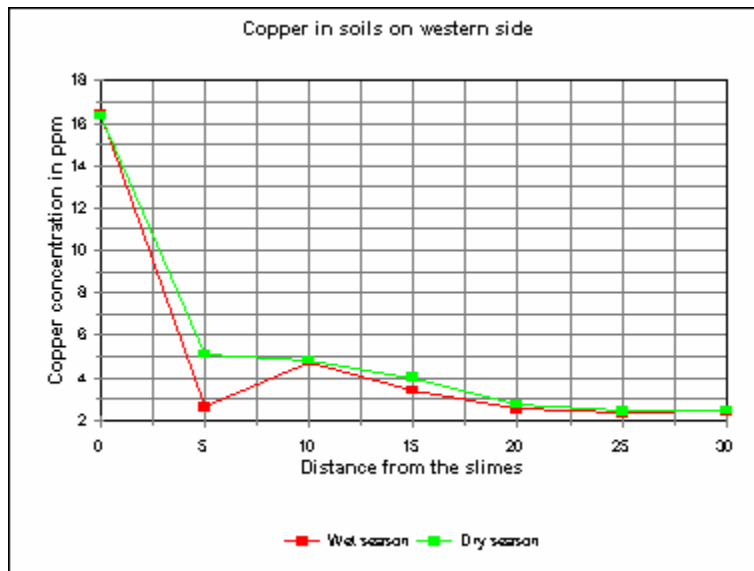
Figure 5.6g: Analysed available copper content of soils during the wet and dry seasons on the western side of the slimes dam.

Copper concentration decreases from 0m to 5m with the wet season having lower concentrations than the dry season (Figure 5.6g). This is because most of the copper is in solution due to acidic pH. The concentration remains low to 30m for both seasons.

The available metal concentrations are higher on the northern side of the slimes dam during the dry season, with river and the storage ponds acting as barriers to the dispersion of the metals northwards. The control sample concentrations are taken as the natural background concentration for the elements. The trend is the same during the wet season (Appendix 9a). On the northern side, the stream and storage ponds became barriers to the movement of elements. High concentrations are only obtained from two points, 0m and 5m.

On the eastern side, comparison could not be done because the sampling was only for dry season. During the season, the analysed elements do not show any particular pattern (Appendix 9b).

Generally the elements decrease with distance from the slimes during the two seasons. The trend is much clearer during the dry season where the high element concentrations are within 5m from the dam and level out. Iron has the highest available concentrations and all the other elements remain below their contamination thresholds. The adsorption

and coprecipitation of metals such as copper, nickel and zinc by iron and the acidic pH of the soils might have affected the concentration of the metal elements. Manganese oxides coprecipitates cobalt, nickel, zinc and lead in soils and sediments and this might also have affected the metal concentrations in the soils. Clay minerals also adsorb and coprecipitates nickel, cobalt, chromium, zinc, copper and lead in soils and sediments (Alloway, et al., 1994). The full results are shown in (Appendix 9a and 9b).

There is an increase in element concentration in the soils with slight changes in the trends of the concentration during the dry season and higher dispersion and dilution during the wet season. Higher concentrations are between 0m and 5m (Appendix 9a and 9b). The increase in element concentration is probably due to adsorption of the elements from the liquid phase on to the solid phase by clay minerals, iron, manganese oxides and organic matter. The elements are released from the oxides, organic matter and clay mineral surfaces with the migration of acidic or basic solutions through the soils. Acids can dissolve the lattice structure of clays, attacking aluminium, iron and silica. Once the lattice is destroyed the fine fragments may migrate (Grim, 1968).

5.7 Stream Sediments

A total of twenty-four stream sediments were sampled and analysed and from these, two are control samples. The control samples results for each element were used as the natural background values of each of the respective element and were subtracted. Results for these samples are presented in Appendix 12 and discussed in Figures 5.7a to Figure 5.7h. Sample points MA1, MA2, MA3, MA 12 and MA13 are always wet during the two seasons. There were very little pH variations during both seasons and all were acidic (Tables 9a and 9b).
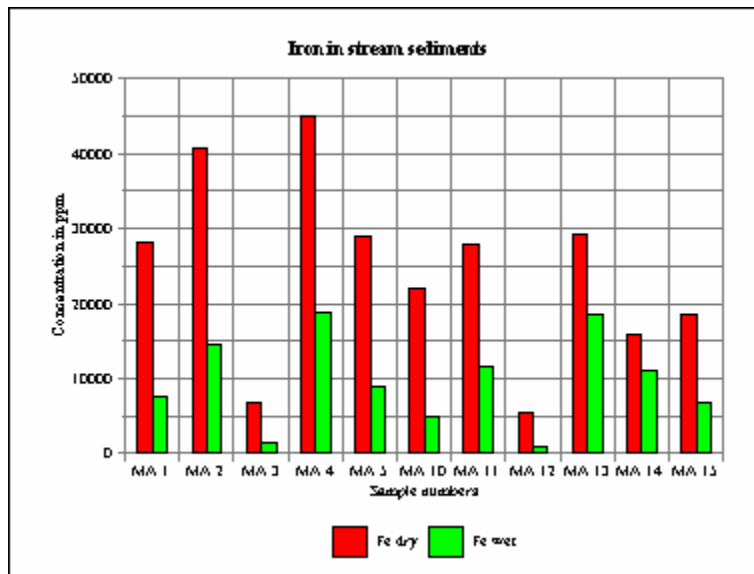
Figure 5.7a The variation of iron concentration in sediments during the wet and the dry season at Athens mine.

Iron concentration is higher during the dry season with the highest concentration at sampling points MA4 and MA2. The old dumps (Figure 4.1) and iron added during processing are contributing significantly to the concentrations at point MA4 since the small stream drained from the dumps. The storage ponds and the waste rocks that were used to cover the acidic water that is flowing into the stream contributed to the high iron concentration at MA2.

At sampling points MA1, MA5, MA10, MA11 and MA13 the concentrations are in the same range of 21987ppm to 29147ppm (Appendix 12). For MA1 there is significant contribution from the seepage into the stream from the extension to the active dump on the eastern side and the storage ponds. The other points receive contribution from old dumps. MA3 and MA12 have the lowest concentrations because of the Blinkwater and Mackenzie dams that act as barrier.

The trend is the same during the wet season but the element concentrations are lower due to dilution and dissolution. The natural background for iron during the wet season is 7469ppm and 9560ppm for the dry season.
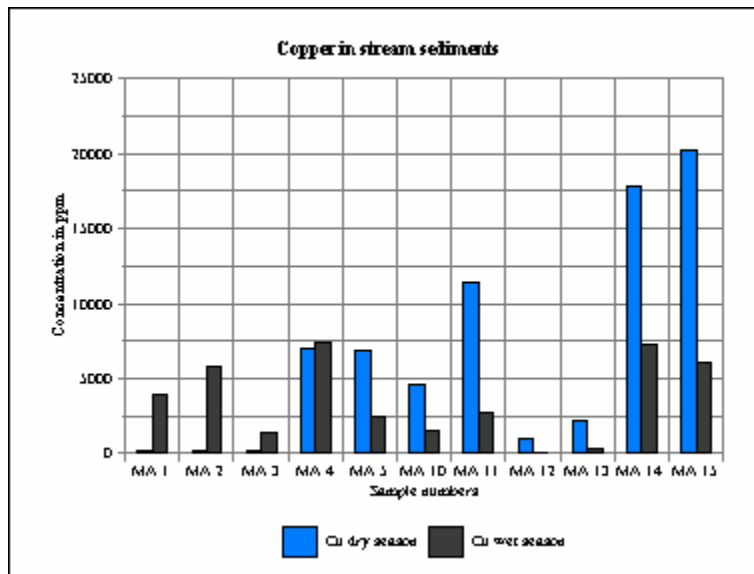
Figure 5.7b The variation of copper concentration in sediments during the wet and the dry season at Athens mine.

Copper shows a different trend with higher concentrations recorded during the dry season with the exception of all those sediments that are always wet (MA1, MA2, MA3, MA12 and MA13) that had lower concentrations (Figure 5.7b). The acidic water in the sediments release the copper into solution resulting in lower concentrations during the dry season at MA1, MA2, MA3, MA12 and MA13 sampling points. All the other samples show that there are higher copper concentrations during the dry season and lower during the wet season.

The natural background concentrations for copper are 978ppm during the wet season and 4414ppm during the dry season.
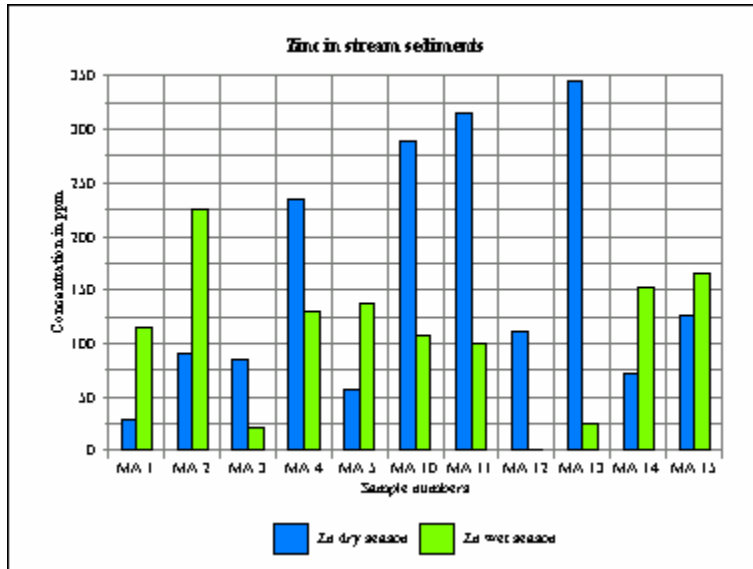
Figure 5.7c The variation of zinc concentration in sediments during the wet and the dry season at Athens mine.

Zinc shows no particular trend but on the average the dry season show higher concentrations than the wet season (Figure 5.7c). No zinc was found in stream sediments at MA12 during the wet season. The natural background concentrations for zinc were 46.60ppm during the wet season and 154.55ppm during the dry season.
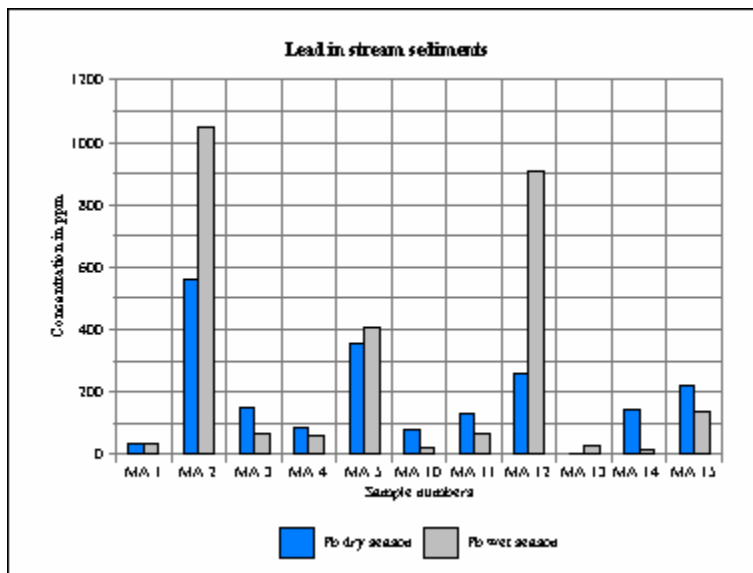

Figure 5.7d The variation of lead concentration in sediments during the wet and the dry season at Athens mine.

For lead generally low and high concentrations are recorded from four sampling points, MA2, MA5, MA12 and MA15 during the two seasons (Figure 5.7d). That is as a result of the added lead nitrate during processing leaching from the slimes and lead fuel used by

vehicle using the roads adjacent to the sampling points (Figure 4.1). There is a direct relationship between the lead concentration and the business of the road. The busier the road is, the higher the lead concentration present. There is no particular trend for lead concentration. The natural background concentrations for lead are 39.18ppm during the wet season and 80.68ppm during the dry season.

Figure 5.7e The variation of chromium concentration in sediments during the wet and the dry season at Athens mine.

Chromium is higher during the dry season than the wet season in all the samples with the exception of MA15, which is lower than in the wet season (Figure 5.7e). During the wet season, it has a trend similar to the dry season trend though with lower concentrations. MA12 and MA13 have the lowest concentrations during the wet season, which is due to the effects of Blinkwater dam (MA12) and the small pool (MA13).

The natural background concentrations for chromium are 276.16ppm during the wet season and 848.44ppm during the dry season.

Figure 5.7f The variation of nickel concentration in sediments during the wet and the dry season at Athens mine.

Levels of nickel are higher during the dry season with only the sample MA14 having lower concentration during the dry season than the wet season (Figure 5.7f). All points show significant amounts of nickel with no pattern. The natural background concentrations for nickel are 152.56ppm during the wet season and 231.53ppm during the dry season.

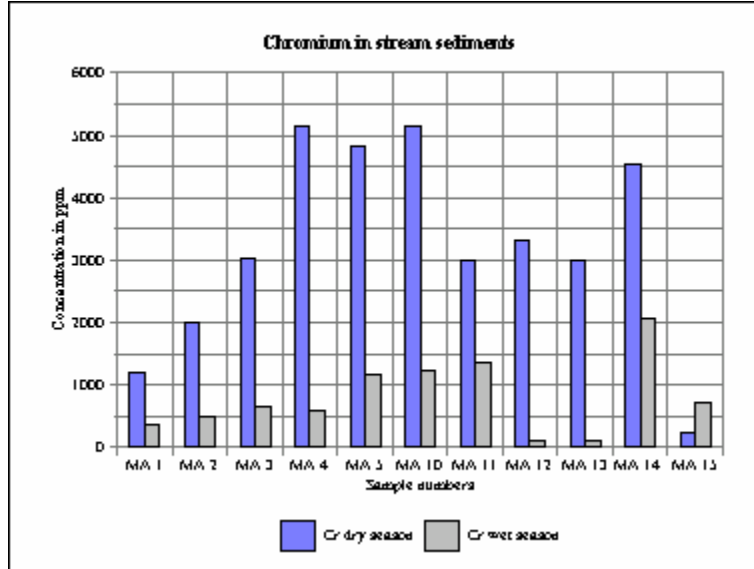**Figure 5.7g** The variation of cobalt concentration in sediments during the wet and the dry season at Athens mine.

Cobalt is high in all the samples with MA10 showing the highest concentration for both the wet and dry seasons (Figure 5.7g). The significant contribution to this high concentration could be coming from the old dump close to MA4 (Figure 4.1) or it could be just point source pollution.

The natural background concentrations for cobalt are 76.35ppm during the wet season and 188.15ppm during the dry season.

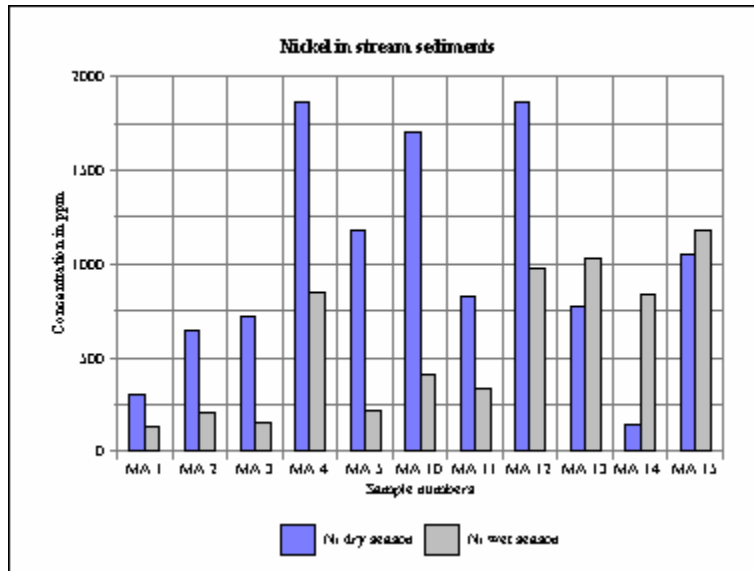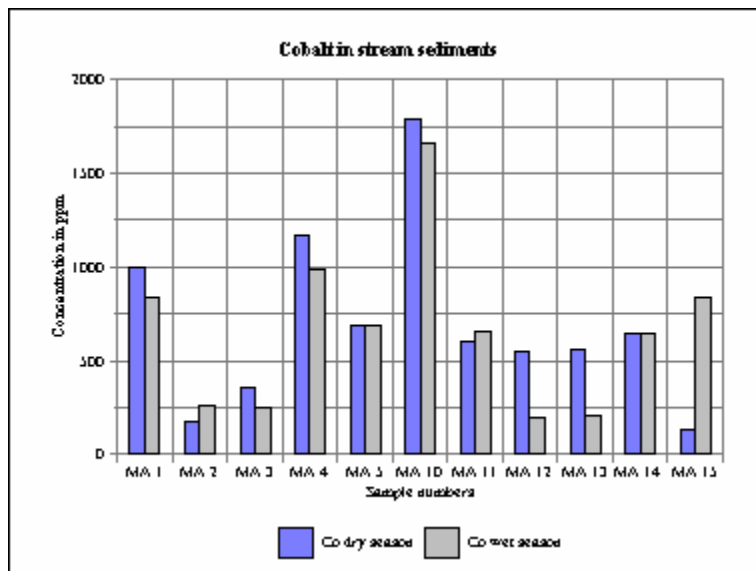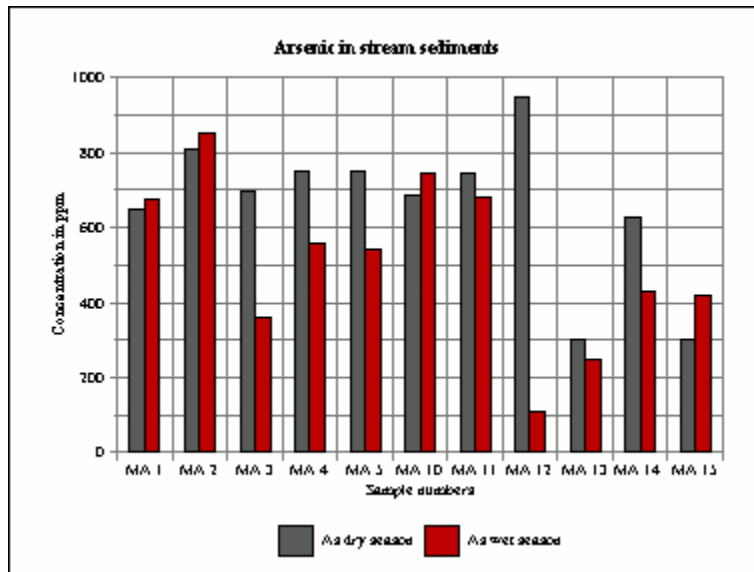**Figure 5.7h** The variation of arsenic concentration in sediments during the wet and the dry season at Athens mine.

Arsenic is high in all the samples during the two seasons with the exception of sample MA12 that has the highest arsenic concentration during the dry season and the lowest during the wet season (Figure 5.7h). This is expected because arsenic is associated with both the copper and gold mineralisation at Athens mine (Table 1).The low pH during the two seasons releases the arsenic from the arsenopyrite (FeAsS) which is deposited on to the sediments.

The natural background concentrations for arsenic are 121.67ppm during the wet season and 121.73ppm during the dry season.

In Tables 9a and 9b, the element concentrations are a result of the mining activities and other human activities within the mining area. The natural background concentrations

have been subtracted. The element concentrations are higher in the sediments during the dry season compared to the wet season (Figures 5.7a to 5.7h and Tables 9a and 9b).

Table 9a. Element concentrations in sediments during the dry season at Athens mine. Control sample (Csed) results were used as the thresholds for each of the analysed element during the dry season for the area and were subtracted from the results.

Sample no.	Fe(mg/l)	Cu(mg/l)	Zn(mg/l)	Pb(mg/l)	Cr(mg/l)	Ni(mg/l)	Co(mg/l)	As(mg/l)	pH
MA 1	28076	159	28.72	36.27	1201.17	304.48	995.88	646.65	3.66
MA 2	40627	240	90.63	559.88	2008.89	650.41	177.55	811.77	3.63
MA 3	6766	182	84.92	153.48	3031.40	724.23	354.66	696.87	5.01
MA 4	44886	7005	234.29	83.04	5141.67	1868.63	1166.29	752.70	4.85
MA 5	28908	6863	56.66	355.33	4824.15	1179.70	688.37	753.57	6.25
MA 10	21987	4640	289.71	78.74	5148.62	1709.05	1790.24	685.82	5.42
MA 11	27874	11379	314.90	127.76	2987.13	829.80	604.71	743.48	3.97
MA 12	5548	983	110.53	258.85	3333.37	1865.51	547.98	946.41	5.71
MA 13	29147	2142	344.01	5.61	2996.25	777.98	562.90	303.53	5.41
MA 14	15823	17835	72.32	146.13	4551.02	142.11	645.22	626.09	3.19
MA 15	18527	20246	126.64	220.78	241.74	1056.43	133.54	303.53	3.10
CSed	9560	4414	154.55	80.68	848.44	231.53	188.15	121.73	7.20

Table 9b. Element concentrations in sediments during the wet season at Athens mine. The control sample (Csed) results for each of the analysed element were used as the threshold for the area during the wet season and were subtracted.

Sample no.	Fe(mg/l)	Cu(mg/l)	Zn(mg/l)	Pb(mg/l)	Cr(mg/l)	Ni(mg/l)	Co(mg/l)	As(mg/l)	pH
MA 1	7639	3888	114.10	35.20	376.76	136.71	834.72	674.26	3.92
MA 2	14426	5864	225.71	1045.85	503.51	207.28	259.94	852.79	3.64
MA 3	1353	1341	21.09	69.61	666.16	150.98	248.33	360.14	5.11
MA 4	18900	7441	130.00	57.86	604.63	852.59	989.36	556.09	4.89
MA 5	8857	2487	138.05	408.86	1176.36	215.19	686.22	543.14	6.33
MA 10	4878	1572	107.79	19.04	1245.06	411.86	1660.13	746.96	5.60
MA 11	11682	2762	100.30	69.35	1369.98	335.97	657.83	682.84	4.30
MA 12	1018	105	0.00	905.18	111.17	979.56	191.44	108.77	5.76
MA 13	18612	307	25.87	29.55	97.70	1029.78	209.06	249.64	5.40
MA 14	10979	7222	153.39	18.02	2070.24	832.91	649.05	428.48	3.24
MA 15	6843	6024	165.51	137.41	729.40	1177.79	841.44	421.30	3.11
CSed	7470	978	46.60	39.18	276.16	152.56	76.35	121.67	7.23

During the wet season sedimentation is disturbed by the fast flowing rivers and most of the fine particles are carried down stream into Mackenzie dam. The acidic water in the streams from the slimes scattered around mining area released most of the elements into solution. While there is dilution and transportation of element in sediments during the wet season, there is concentration and undisturbed sedimentation during the dry season (Chapman, 1992).

5.8 Surface water

A complete comparison of the element concentrations during the two seasons is not possible because during the dry season most of the sampling points are dry with only four points (MA1, MA2, MA5 and MA12) with water (Table 10a). Comparing the four points during the seasons show an increase of element concentration during the wet season to the dry season. The concentrations are generally low because the water is not flowing and has settled. MA12 show the lowest concentrations during the dry season because Mackenzie dam is a barrier and sink for the pollutants (Figure 4.1).

Table 10a. Element concentrations during the dry season in available surface water around Athens mine. Most of the sampling points were dry during the season. NIL means there was no water to sample from the particular sampling point.

Sample no.	Fe (mg/l)	Cu (mg/l)	Zn (mg/l)	Pb (mg/l)	Cr (mg/l)	Ni (mg/l)	Co (mg/l)	As (mg/l)	pH
MA 1	2997	267	373	63.6	410	191	101	199	3.93
MA 2	2713	408	125	167	408	158	155	127	3.55
MA 3	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
MA 4	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
MA 5	2793	644	89.3	114	333	148	104	212	5.80
MA 10	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
MA 11	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
MA 12	2579	299	68.0	82.4	263	55.6	70.8	81.4	5.45
MA 13	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
MA 14	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
MA 15	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
CSed	1145	98.3	26.4	33.2	146	22.5	55.1	25.3	7.65

Table 10b. Element concentrations during the wet season in available surface water around Athens mine. All sample points were sampled and the control sample (results were used as the thresholds for each of the analysed elements.

Sample no.	Fe (mg/l)	Cu (mg/l)	Zn (mg/l)	Pb (mg/l)	Cr (mg/l)	Ni (mg/l)	Co (mg/l)	As (mg/l)	pH
MA 1	2720.60	2537.25	114.23	4.20	183.09	52.40	246.37	95.12	3.87
MA 2	7629.60	3182.75	37.88	51.66	109.37	47.67	39.14	110.44	3.73
MA 3	5267.60	404.74	8.58	9.70	171.31	93.08	61.22	24.11	5.03
MA 4	6873.60	6068.65	28.77	5.41	44.78	60.76	30.45	85.54	4.44
MA 5	1463.60	4226.75	29.91	17.50	73.79	21.72	162.77	25.62	5.97
MA 10	1219.60	1651.55	33.17	4.05	41.46	22.75	169.47	172.82	5.60
MA 11	1974.60	1414.45	26.98	23.10	13.01	54.39	65.77	77.82	4.58
MA 12	2688.60	683.72	20.53	2.08	8.00	23.86	32.08	60.92	5.88
MA 13	2364.60	595.05	28.10	21.28	3.58	25.26	17.76	47.22	5.52
MA 14	7123.60	7803.15	13.97	2.84	77.76	61.81	85.59	17.12	4.15
MA 15	7123.50	92.53	19.58	22.80	80.06	51.70	80.91	35.74	4.17
CSed	806.40	284.45	18.42	8.20	45.18	33.66	42.23	37.18	7.46

During the wet season the concentrations of iron, copper, zinc, lead, chromium, nickel, cobalt and arsenic increase significantly as they are released from the sediments, secondary minerals dissolving and from the old dumps scattered around the mining area as a lot of gullies drain into the streams (Table 10b). Iron and copper show the highest increase. The iron is from the addition of addition of ferrous sulphate during processing and from the dissolving secondary minerals due to low pH while copper is mainly from chalcopyrite ($CuFeS_2$) and chalcosite (Cu_2S).
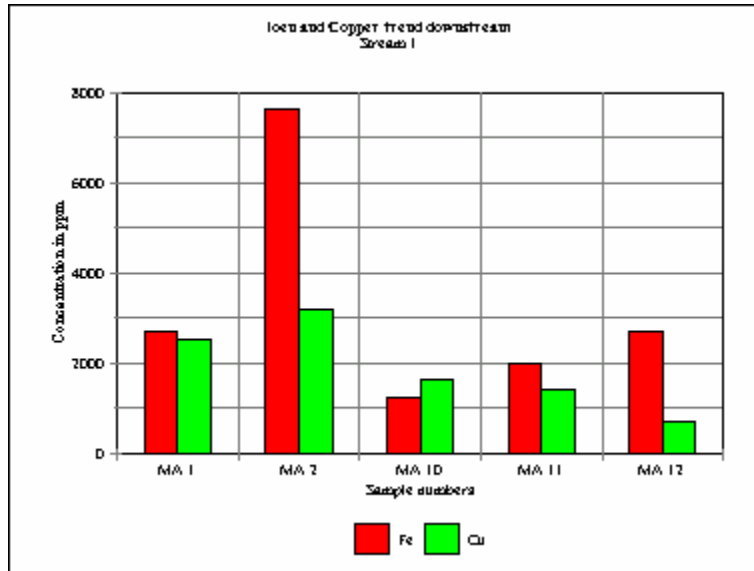

Figure 5.8a The variation of iron and copper in surface water downstream stream 1 during the wet season at Athens mine.

Along stream 1(Figure 4.1), iron shows the highest concentration at MA2, which is a significant contribution of the storage ponds and the leachate from the active dump. The concentration is diluted as stream 1 flow into stream 2 before sampling point MA 10 resulting in a lower concentration at this point. The increase at MA 11 (Figure 5.8a) could have been due to the contribution of the sewage ponds situated between points MA 10 and MA 11 (Figure 4.1). The sewage ponds are located in a quarry that has pyrite and chalcopyrite outcropping and these are the source of the iron. The sediments in Mackenzie dam are saturated and could not absorb any more iron resulting with more iron being released to the surface water that is sampled at MA12 as the dam over spilled. This results with a high iron concentration below the dam at MA12.   Copper follows a similar pattern as iron but has lower concentrations (Figure 5.8a).
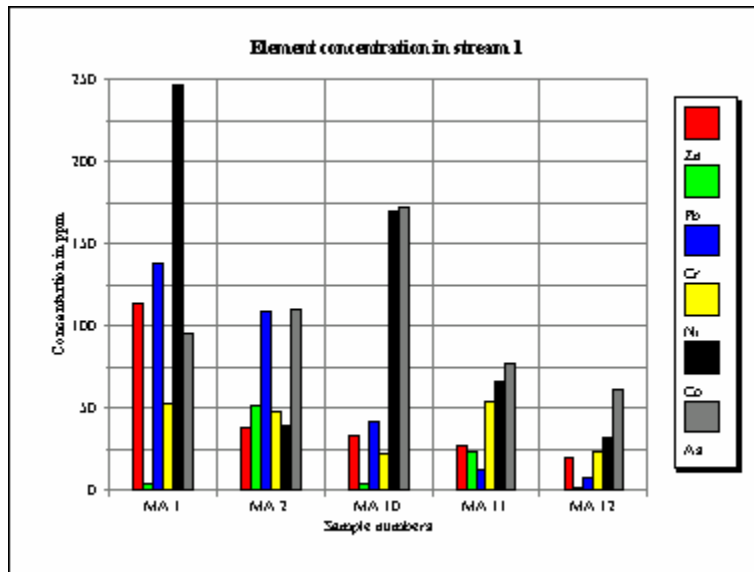
Figure 5.8b Zinc, lead, chromium, nickel, cobalt and arsenic in surface water downstream stream 1 during the wet season.

Zinc decreases down stream along stream 1 with the highest concentration at MA1 (Figure 5.8b) indicating the contribution from the leachate from the extension to the active dump. There is continuous dilution down the stream and there is no significant contribution in the zinc concentration down stream.

Lead shows high concentrations at MA 2 and MA 11 (Figure 5.8b), which is the contributions from the addition of lead nitrate ($Pb(NO_3)_2$) during the gold processing in the plant (Appendix 2) that is leaching from the active slimes dump and leaded fuel.

Chromium follows the same pattern as zinc with the highest concentration at MA1 and decrease down stream 1(Figure 5.8b). Nickel shows high concentration being released from the dump at MA1 and MA2, which is then diluted at MA10. The nickel concentration decreases from MA11 to MA12 and this could be due to most of the nickel remaining in Mackenzie dam or dilution before being sampled at MA12. Cobalt and arsenic have the highest concentrations among this group of elements in stream 1. This is expected for arsenic since it is associated with gold and copper mineralisation (Table 1) and cobalt is a by – product of copper or nickel extraction (Bartholomew, 1990).
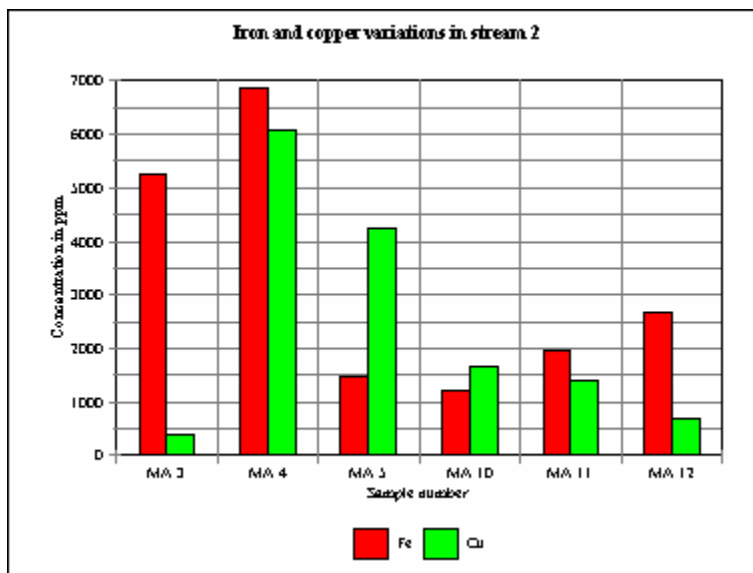
Figure 5.8c The variation of iron and copper in surface water downstream stream 2 during the wet season at Athens mine.

Samples MA 3 and MA 4 in stream 2, show the highest iron concentration in stream 2 (Figure 5.8c) and then decrease at MA 5 and MA10. An increase in the iron concentration is recorded from MA 11 to MA 12. The high iron concentration at MA 4 is a direct contribution from the addition of $FeSO_4$ added in the plant that is leaching out from the old dumps up stream of the sampling point (Figure 4.1) and the mineralogy. The decrease at MA5 is due to dilution and settling of sediments as the stream flows slowly at this point while the decrease at MA10 is due to dilution by the water from stream 1. The increase at MA 11 is the contribution of the pyrite exposed in the sewage ponds and at MA 12 is a result of more iron being released by saturated sediments in the dam to the surface water that is sampled at MA12 as the dam over spilled. Copper decrease from MA4 downstream stream 2 and is due to dilution.

Zinc and lead are generally low in stream 2 with noticeable increase for lead at MA 5 and MA 11(Figure 5.8d). The increases are due to contributions from the addition of $Pb(NO_3)_2$ during gold processing from the active slimes dump coming through stream 1, mineralogy and leaded fuel for samples MA5 and MA 11. Chromium and nickel in stream 2 also decrease downstream a similar pattern to that in stream 1 (Figures 5.8b and

96

5.8d). Cobalt and arsenic also show a similar pattern as in stream 1 with MA10 having the highest concentration indicating contribution from steam 1.
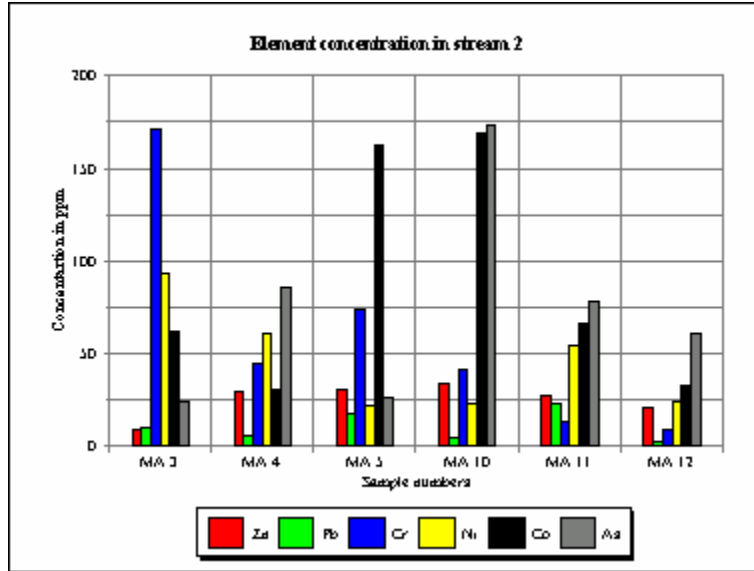

Figure 5.8d Zinc, lead, chromium, nickel, cobalt and arsenic in surface water downstream stream 2 during the wet season.

In stream 3 only three sampling points (Figure 4.1) were established due to inaccessibility of the stream.
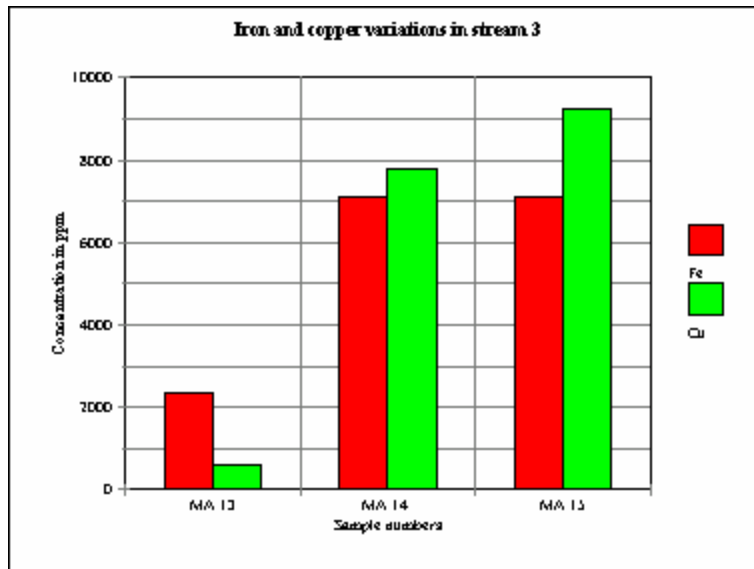

Figure 5.8e Iron and copper in surface water downstream stream 3 during the wet season.

Iron and copper were both low at MA 13 while MA14 and MA15 had high concentrations for the two elements (Figure 5.8e). The high concentrations at the two points are a direct contribution from the addition of $FeSO_4$ and old slimes dumps, that

were being reworked during the sampling time (Figures 1.1 and 1.2). Copper is mainly from the mineralisation at Athens mine.
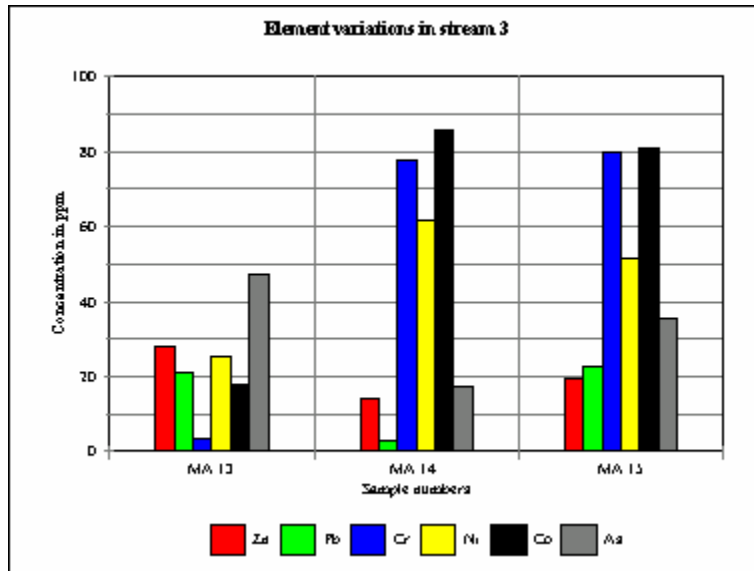

Figure5.8f Zinc, lead, chromium, nickel, cobalt and arsenic in surface water downstream stream 3 during the wet season.

Zinc concentration is highest at MA 13 an indication that it might be a result of other human activities and mineralogy upstream (Figures 5.8f and 4.2). Lead, as is the case in the other two streams, shows higher concentrations at points close to the roads. Chromium, nickel and cobalt have higher concentrations at MA 14 and MA 15 indicating that the dumps are contributing significantly to the element load in stream 3 (Figure 5.8f). Arsenic follows a similar pattern as zinc with the highest concentration at MA13.

The pH measurements show a direct link and effect of the dumps scattered around the mining area. Water flowing through sampling points MA1, MA2, MA4, MA14 and MA15 came into contact with dumps resulting in a drop in pH due to formation of sulphuric acid as shown in Equation 3.14. At MA2, waste rocks that were used to cover the acidic water that was flowing into the stream just below the pump back point also affected the pH. At MA14 and MA15 iron (III) hydroxide is precipitating out resulting in the drop in pH to 4.15 and 4.17 from 5.52 (Equation 3.3 and Figure 3.1). The drop at MA11 from 5.97 to 4.58 is the direct effect of sewage pond. There is some dilution at MA5 and MA10 as a result of mixing of the neutral water flowing from Blinkwater dam and the acidic water flowing through the dumps.

Iron and copper show severe contamination where the water has been in contact with the mine waste. Lead, nickel and zinc contamination is restricted to specific areas and this is a reflection of their low levels in the mine waste compared to iron, copper, arsenic and cobalt. High values for lead, as in sediments, are found close to roads. The free cyanide measured in the field was found to be less than 0.01mg/l, which is mainly a result of natural degradation of cyanide and complexing the cyanide forming thiocyanates.

The element concentrations indicate a general decrease downstream of streams 1 and 2 (Figures 5.8a– d and Table 10b) during the wet season. The effects of the active slimes are clearly shown at point MA2 (Figure 5.8aand 6 and Table 10b) with an increase in most elements. There is some dilution at MA10 when the two streams meet and Mackenzie dam acts as a barrier to the movement of the elements. Stream 3 has a few sample points that show a decrease in the element concentration down stream (Figures 5.8e and 5.8f and Table 10b). The effects of the chemicals used for the gold processing are very evident from the samples close to the active slimes and old dumps.

5.9 Comparison of the element concentrations in surface water and stream sediments.

The concentrations of elements in surface water are mostly depended on the concentrations in the stream sediments and the acidity of the surface water. Once the sediments are saturated with the elements, they release some of the elements into the surface water. During periods of calm, suspended solids settle, even in shallow water resulting in reduced element concentration in the surface water and increased concentration in steam sediments. The comparison of the elements concentrations in surface water and stream sediments at Athens mine were only done for the wet season because most of the sampling points were dry during the dry season.

Iron concentration is higher in the stream sediments than in the surface water as shown in Figure 5.9a. Samples MA 3 and MA 12 have increased iron concentration in the surface water than in sediments. This is a result of sediment exhaustion by the fast flowing water from the dams (Figure 4.1) during the wet season. MA 15 shows very little difference in iron concentration.

Copper shows higher concentration in the surface water in most of the samples. MA 5, MA 12, MA 13, MA 14 and MA 15 (Figure 5.9b) have copper concentration higher in surface water while MA 1, MA 2, MA 4 and MA 5 have lower concentration but significantly higher concentrations compared to the sediments. This copper trend is a result of most copper being in solution due to acidic conditions and the presence of copper in the slimes dumps, which is being leached out into the streams. MA 10 shows very little variation in surface water and stream sediments.

Figure 5.9a Comparison of iron concentration in the surface water and stream sediments during the wet season, at Athens mine.

Figure 5.9b Comparison of copper concentration in the surface water and stream sediments during the wet season, at Athens mine.

The stream sediments have higher zinc concentration than in the surface water in almost all the samples (Figure 5.9c). No zinc was found in the stream sediment MA 12 and only 20.53 ppm was found in the surface water. The zinc might have been attached to the finer particles that were released into the water as suspended solids hence its absence in the stream sediments. MA 3 remained with lower concentration while MA 1 shows very little variation in zinc concentration in both surface water and stream sediments and is the only one with a significant zinc concentration in the surface water.
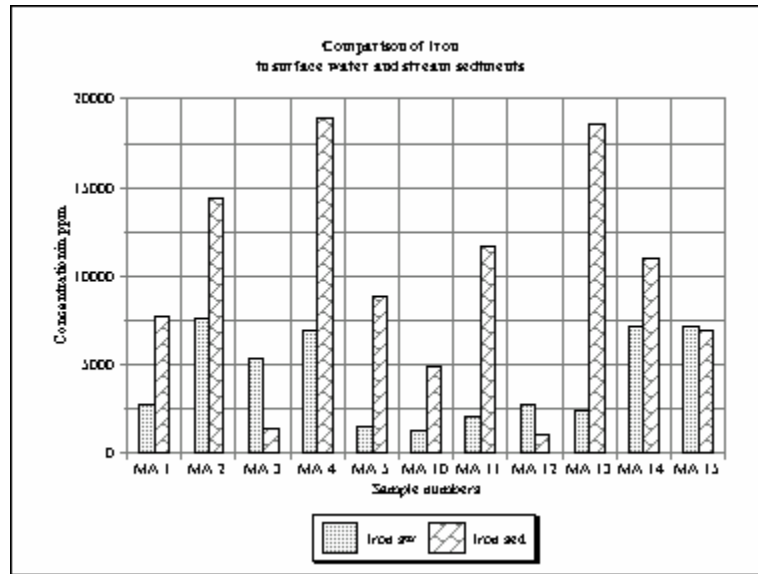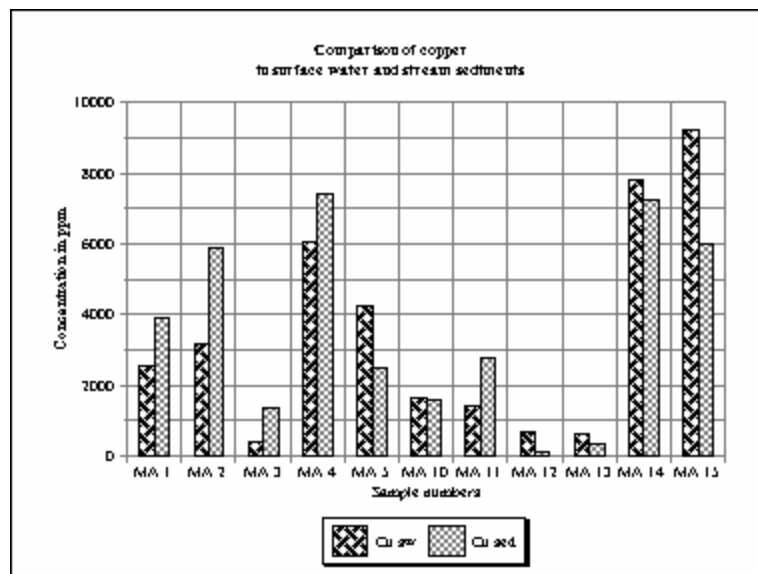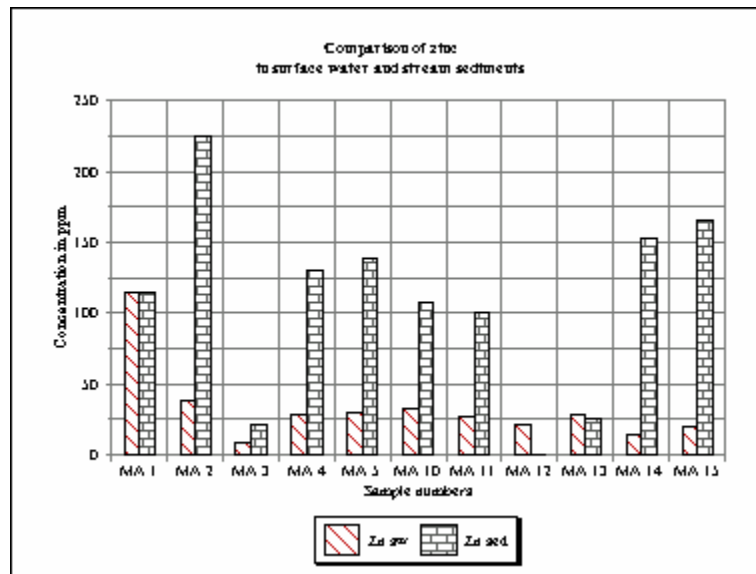

Figure 5.9c Comparison of zinc concentration in the surface water and stream sediments during the wet season, at Athens mine.
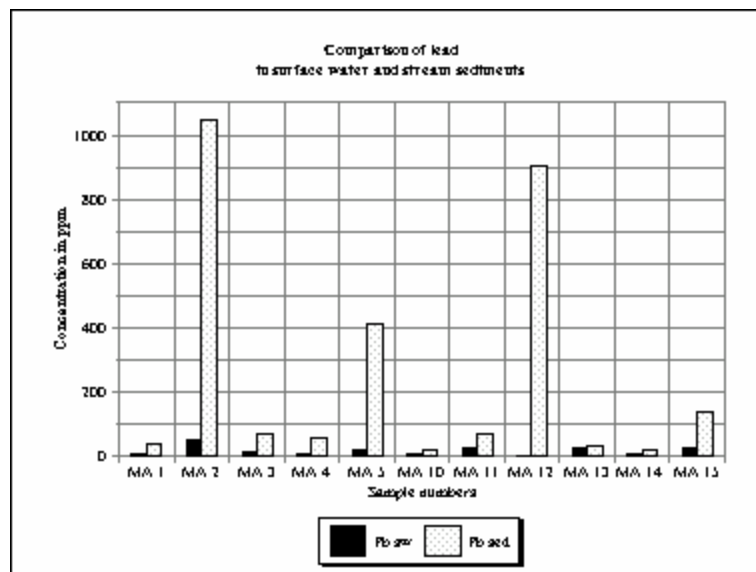

Figure 5.9d Comparison of lead concentration in the surface water and stream sediments during the wet season, at Athens mine.

101

Lead is low in both stream sediments and surface water but the sediments have higher concentrations (Figure 5.9d) than surface water. MA 2, MA 5 and MA12 have the highest concentrations in stream sediments (Table 9b and Figure 5.9d). The three samples were collected close to busy roads (Figure 4.1) and the concentration is attributed to the addition of lead nitrate and leaded fuel used by the vehicles. Low lead levels are a result of lead forming insoluble sulphides under the low pH

Figure 5.9e Comparison of chromium concentration in the surface water and stream sediments during the wet season, at Athens mine.

Figure 5.9f Comparison of nickel concentration in the surface water and stream sediments during the wet season, at Athens mine.

Sediments contain higher chromium concentration in the stream sediments in all the samples (Figure 5.9e) reaching a maximum of 2070.24 ppm. Most of the chromium is

attached to the stream sediments during the wet season and very little is released to the surface water. MA12 and MA 13 have the lowest concentration in both media.

Nickel is higher in stream sediments with a minimum of 136.71 ppm and a maximum of 1177.79 (Table 9b & Figure 5.9f) while the surface water has a minimum of 21.72 ppm and a maximum of 93.08 ppm (Table 12b and Figure 5.9f). MA 1 has the lowest chromium concentration in the two media.
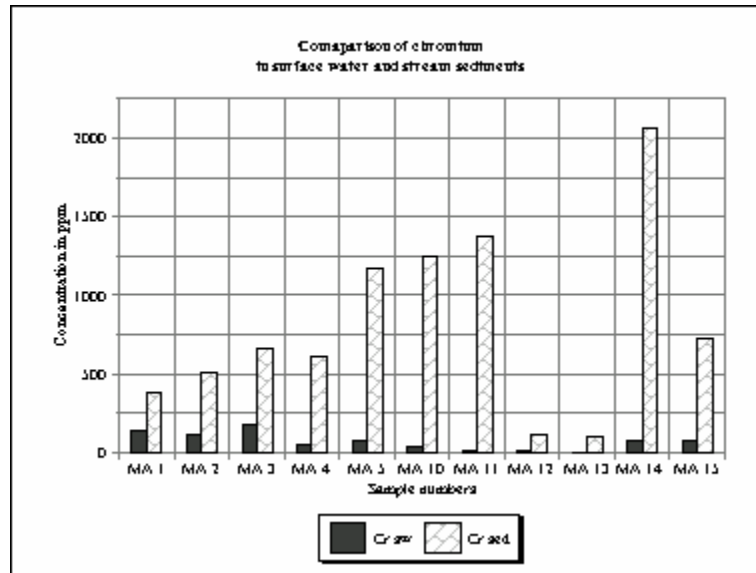

Figure 5.9g Comparison of cobalt concentration in the surface water and stream sediments during the wet season, at Athens mine.

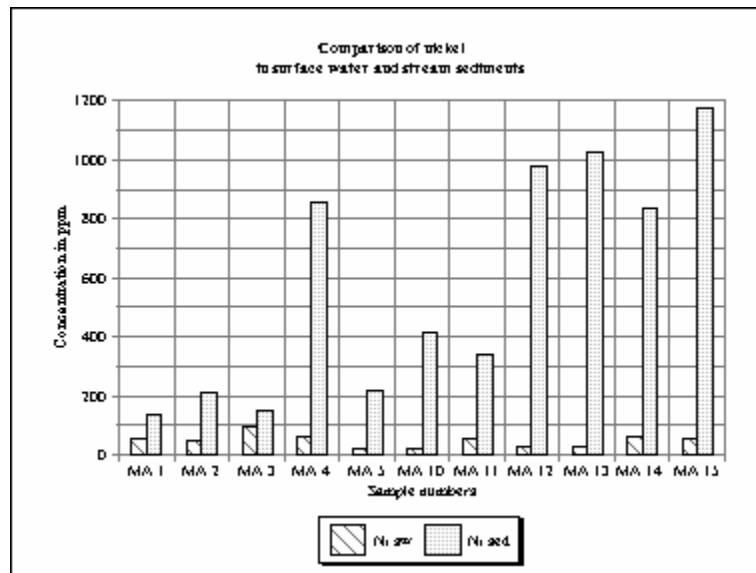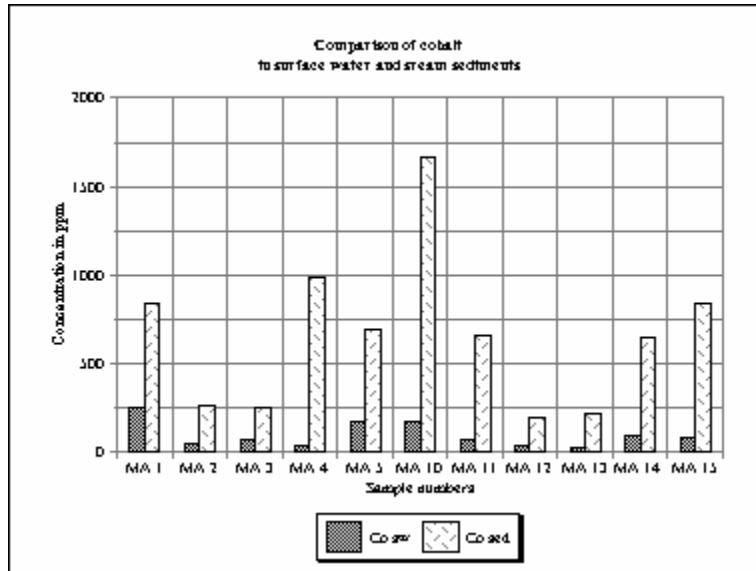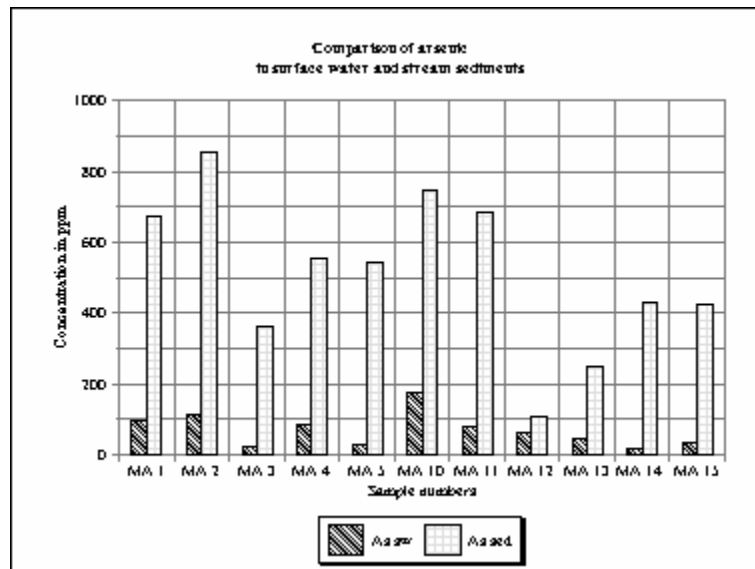**Figure 5.9h** Comparison of arsenic concentration in the surface water and stream sediments during the wet season, at Athens mine.

Cobalt shows a similar trend as the other elements having higher concentrations in the sediments and lower concentration in the surface water (Figure 5.9g). MA 12 and MA 13

have the lowest concentrations in the stream sediments and surface water. MA 10 has the highest concentration and this is a contribution from stream 1 and stream 2 that is draining from the active slimes dump and the old slimes dump (Figure 4.1). MA 4 that is on stream 2 and MA 1 that is on stream 1, have the second and third highest respectively.

Arsenic concentration in the stream sediments is higher than in the surface water (Figure 5.9h) with a minimum of 108.77 ppm and a maximum of 852.79 ppm. The higher concentrations are from the slimes dumps as arsenic is associated with the copper and gold mineralisation at Athens. MA 10 shows a significant high arsenic concentration in surface water due to contribution from streams 1 and 2 (Figure 4.1).

Most of the analysed elements are found in the stream sediments as compared to the surface water. There is slight enrichment of copper and iron in the surface water and the sources are the dumps assisted by the acidic conditions in the stream and addition of $FeSO_4$ during gold processing.

5.10 Ground water

A total of twenty borehole water samples from ten boreholes were analysed and the results are shown in Tables 11a and 11b. Two of these samples were from the control borehole labelled CBH26 and the results were used as the natural background concentration for the area. All the boreholes were cased using iron casing.

The highest iron concentrations were recorded during the wet season with the highest concentration being at BH 4 and BH 3 as the second highest (Figure 5.10a). The water table in these two boreholes was six metres from the ground. The high concentrations were from the rusting iron casing and seepage from the old tailings into the ground water. BH 8 and BH 14 recorded the other high results and this was from the casing, mineralogy and the human activities (Figure 4.1) considering their locations. Their water tables were nine metres and eight and half metres respectively. All the other boreholes had concentrations lower than 10 ppm during the wet season.
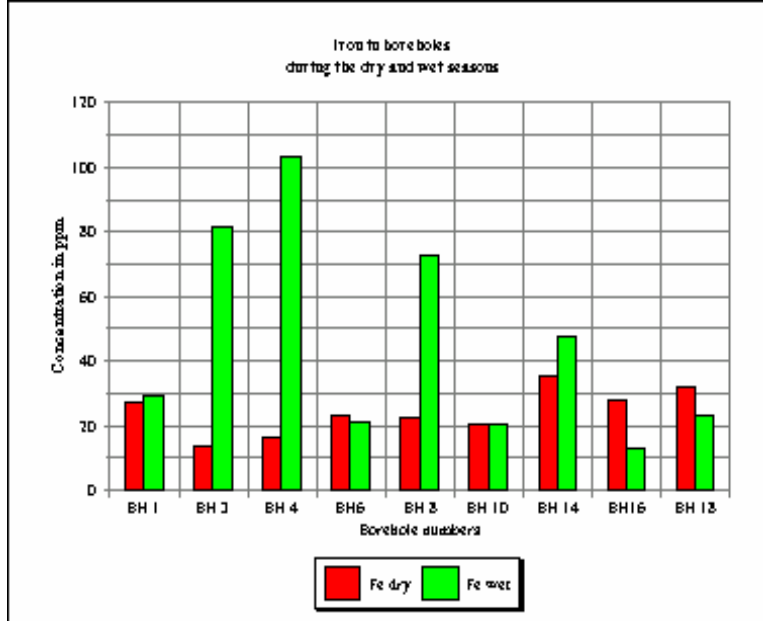
Figure 5.10a Iron concentration in boreholes

During the wet season, iron concentration in the boreholes is low with the highest lower than 30 ppm. This was because the groundwater is settled and the iron is in the sediments at the bottom of the boreholes.

Copper had a different trend with BH 3, BH 4, BH 6 and BH 18 having higher concentrations during the wet season and BH 1, BH 8, BH 10, BH 14 and BH 16 having higher concentrations during the dry season (Figure 5.10b). The higher concentrations were a result of seepage from the old slimes dumps (Figure 4.1).

Zinc concentrations in the boreholes are very low with the highest concentration as 1.3 ppm from BH1. All the other borehole concentrations are lower than 0.5 ppm during the wet season and 0.6 ppm during the dry season (Figure 5.10c). BH 3, BH 4 and BH 16 have higher concentrations during the wet season while BH 1, BH 6, BH 8, BH 10, BH 14 and BH 18 have higher concentration during the dry season. The Zinc concentrations in the boreholes are a result of leaching from rocks by the acidic ground water and possible seepage of leachate from the old slimes dumps within the mining area.
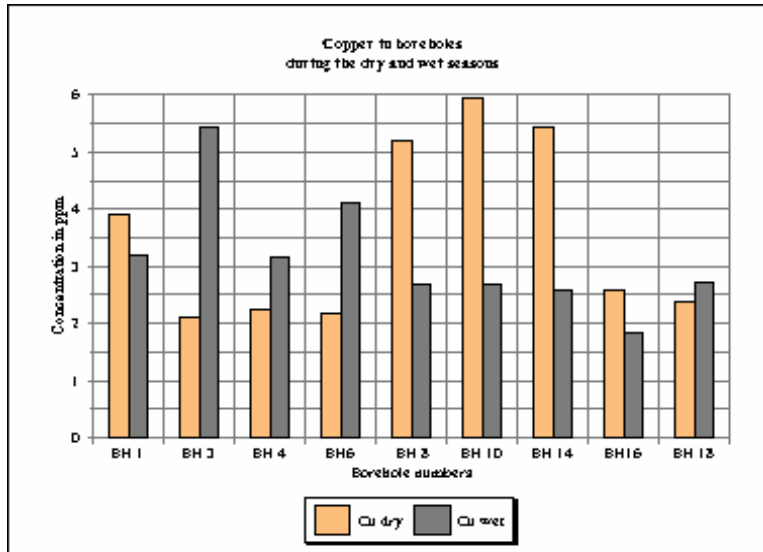
Figure 5.10b Copper concentration in boreholes
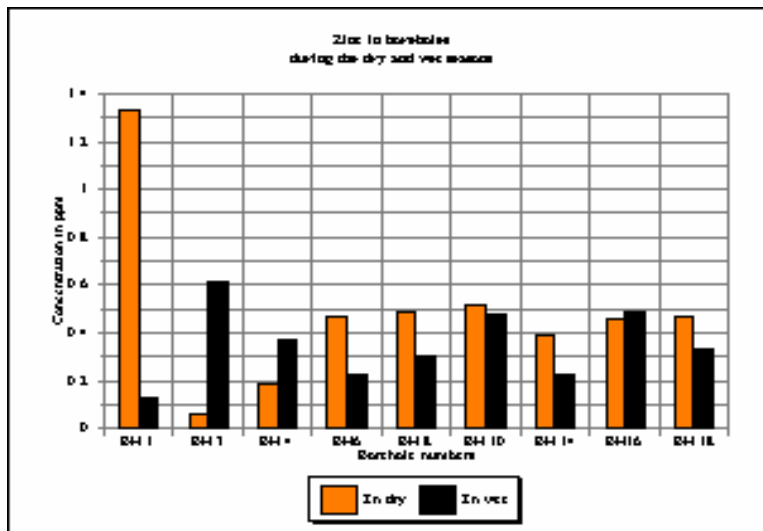
Figure 5.10c Zinc concentration in boreholes

Lead concentration in boreholes is less than 1.4 ppm during the wet and dry seasons (Figure 5.10d). Boreholes BH 1, BH 6, BH 8, BH 10, BH 14 and BH 18 have higher concentrations during the dry season with BH 1 having the highest concentration of 1.30 ppm. BH 3, BH 4 and BH 16 had higher concentration during the wet season with BH 3 having the highest concentration of 0.59 ppm (Table 11a & b and Figure 5.10d).
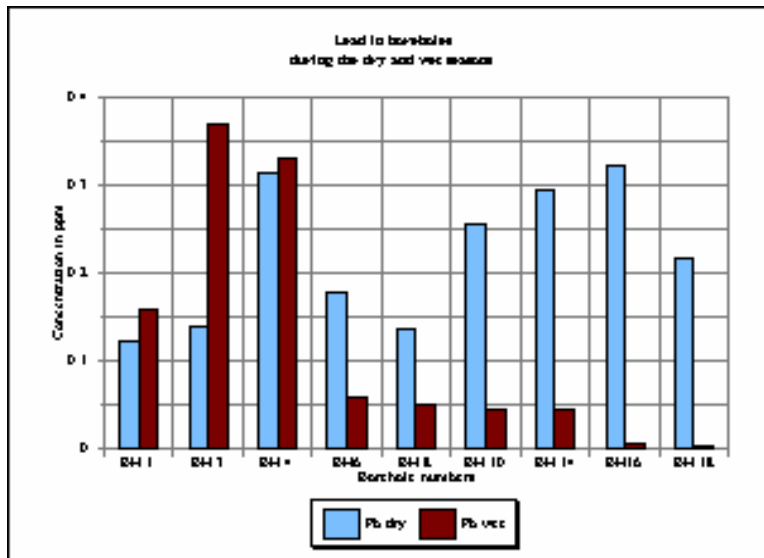
Figure 5.10d Lead concentration in boreholes.

Chromium concentrations in the boreholes are generally low with the highest concentration of 1.37 ppm during the two seasons (Tables 11a and 11b and Figure 5.10e). BH 4, BH 6, BH 14 and BH 18 have the higher concentration of lead during the dry season with BH 1, BH 3, BH 8, BH 10 and BH 16 having higher concentration in the wet seasons.
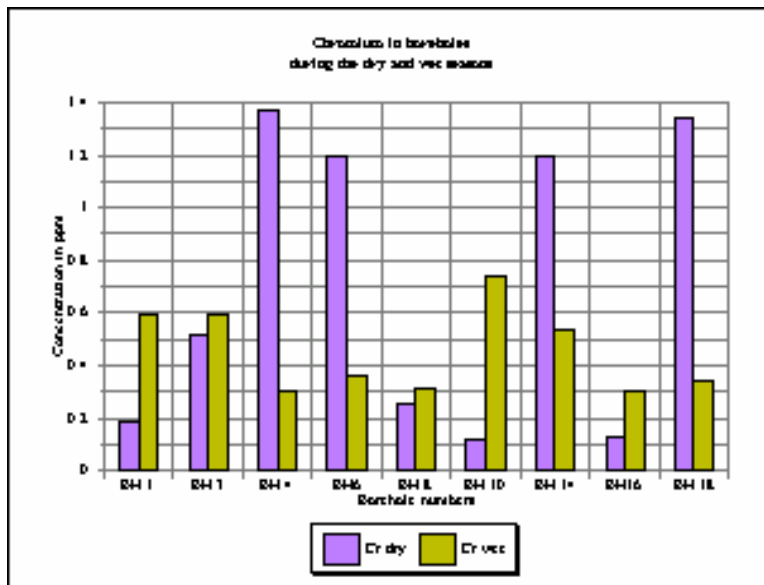
Figure 5.10e Chromium concentration in boreholes.

Nickel is higher in all the boreholes with the exception of BH 1 during the dry season with a highest concentration of 1.27 ppm (Table 11a & b and figure 5.10f). BH 1 is the only borehole with a higher concentration during the wet season (Figure 5.10f). Nickel is lower during the wet season due to dilution.
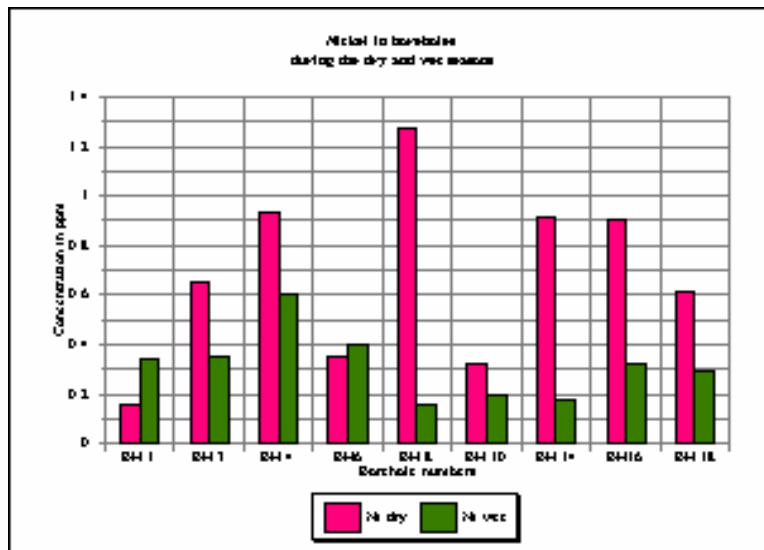
Figure 5.10f Nickel concentration in boreholes.
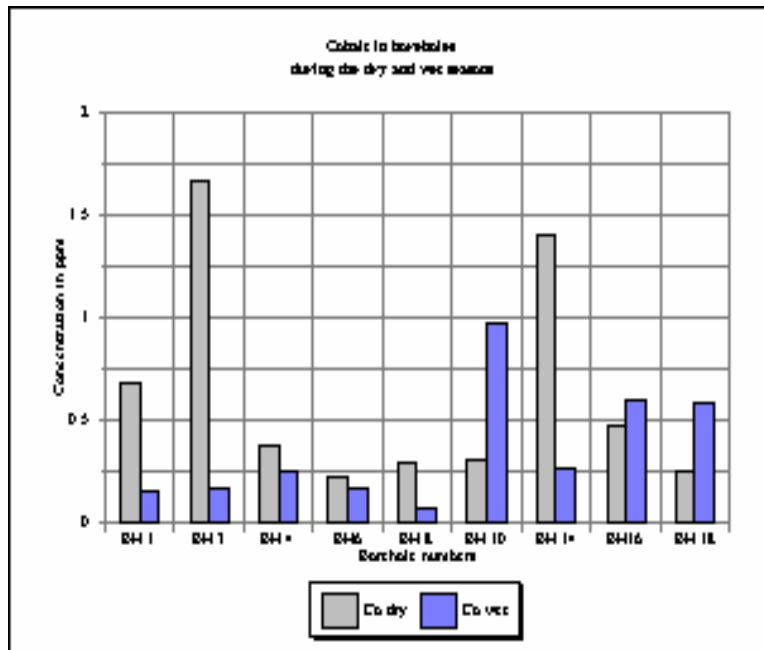
Figure 5.10g Cobalt concentration in boreholes

Cobalt show slightly higher concentrations during the dry season compared to the wet season, with the highest concentrations from borehole BH 3 and BH 14 with concentrations of 1.67 ppm and 1.40 ppm respectively (Figure 5.10g and Tables 11a and

11b). All the other concentrations during the dry season were lower than 1 ppm. During the wet season, BH 14 had the highest concentration of 0.98 ppm while BH 16 and BH 18 had a concentration of 0.59 ppm as the boreholes with concentrations higher than in the dry season.

BH 6, BH 10, BH 14, BH 16 and BH 18 had higher arsenic concentration during the dry with 1.88 ppm as the highest concentration (Figure 5.10h and Table 11a). During the wet season, BH 1, BH 3, BH 4 and BH 8 had higher concentrations with BH 8 with the highest concentration of 0.99 ppm (Figure 5.10h and Table 11b). All arsenic concentrations during the wet season were lower than 1 ppm due to dilution.
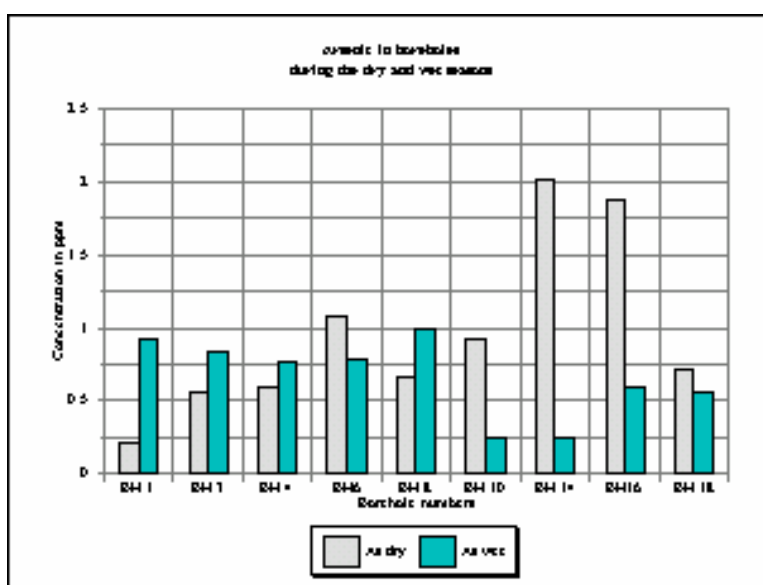
Figure 5.10h Arsenic concentration in boreholes

Table 11a. Element concentration in the ground water during the dry season.

Sample no.	Fe(mg/l)	Cu(mg/l)	Zn(mg/l)	Pb(mg/l)	Cr(mg/l)	Ni(mg/l)	Co(mg/l)	As(mg/l)	TDS(g/l)	pH
BH 1	27.05	3.91	1.33	0.12	0.19	0.16	0.68	0.21	117.23	4.96
BH 3	13.69	2.12	0.06	0.14	0.52	0.65	1.67	0.55	115.58	5.07
BH 4	16.07	2.24	0.18	0.31	1.37	0.93	0.38	0.59	175.45	5.01
BH6	22.97	2.17	0.47	0.18	1.20	0.35	0.23	1.08	112.55	4.75
BH 8	22.70	5.19	0.48	0.14	0.25	1.27	0.29	0.66	207.00	5.15
BH 10	20.26	5.95	0.52	0.26	0.12	0.32	0.31	0.92	97.67	5.11
BH 14	34.95	5.43	0.39	0.29	1.20	0.91	1.40	2.01	124.09	5.97
BH16	27.81	2.58	0.45	0.32	0.13	0.90	0.48	1.88	237.66	6.01
BH 18	31.71	2.36	0.47	0.22	1.34	0.61	0.25	0.72	239.81	6.03
CBH26	7.77	0.89	0.03	0.11	0.09	0.10	0.02	0.10	109.76	6.89

Table 11b. Element concentration in groundwater during the wet season.

Sample no.	Fe(mg/l)	Cu(mg/l)	Zn(mg/l)	Pb(mg/l)	Cr(mg/l)	Ni(mg/l)	Co(mg/l)	As(mg/l)	TDS(g/l)	pH
BH 1	28.86	3.19	0.13	0.157	0.60	0.34	0.15	0.93	343.30	5.52
BH 3	81.37	5.43	0.61	0.371	0.59	0.35	0.17	0.83	280.02	3.93
BH 4	103.45	3.15	0.37	0.329	0.31	0.60	0.25	0.76	352.00	4.17
BH6	21.17	4.10	0.23	0.058	0.36	0.40	0.17	0.79	175.10	6.10
BH 8	72.61	2.69	0.30	0.051	0.31	0.16	0.07	0.99	118.22	5.88
BH 10	20.50	2.67	0.48	0.046	0.74	0.19	0.98	0.25	122.94	6.60
BH 14	47.30	2.57	0.23	0.045	0.53	0.17	0.27	0.25	122.60	6.58
BH16	12.78	1.82	0.48	0.006	0.30	0.32	0.59	0.59	120.98	6.19
BH 18	23.14	2.73	0.33	0.004	0.34	0.30	0.59	0.56	129.24	5.32
CBH26	22.40	0.73	0.02	0.002	0.30	0.05	0.02	0.05	101.30	6.97
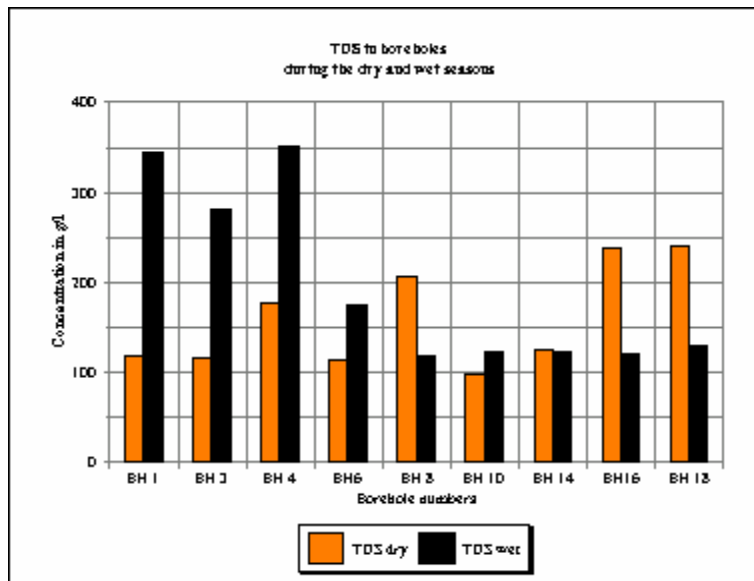
Figure 5.10i Total dissolved solids in borehole water samples from Athens mine.

BH 1, BH 3, BH 4, BH 6,and BH 10 had higher TDS content during the wet season while BH 8, BH 16 and BH 18 had higher TDS content during the wet season (Figure 5.10i and Tables 11a and 11b). There were very little variations during the two seasons. Higher TDS content during the wet season indicated more water flowing into the boreholes disturbing the sediments, which release the fine particles into the ground water. Reduced TDS indicate settling of the ground water resulting in most particles in the water settling at the bottom.

The general trend is that there is a slight increase in the elements analysed during the wet season as shown in Figure 5.10a to Figure 5.10h. Iron has the highest concentration and there is some significant contribution from the iron casing and pump components used in

the boreholes (Tables 11a and 11b, Appendix13 and Figure 5.10a). There are some seepages into borehole 3, 4 and 8 during the wet season otherwise there is very little variation in the other boreholes. Obtaining representative samples of the groundwater, for iron analysis presented problems due to oxidation or reduction of the water, which occurred when the water was brought from the boreholes to the surface.

All the other analysed elements are very low and show little variations with maximum values of less than 2mg/l (Figures 5.10b to 5.10h).

5.11 Quality control

Five types of controls were run with samples in order to guarantee quality of analysis and to maintain comparable accuracy with the results from other laboratories. These were The 5 ppm Cu standard solution, three in house standard (GEOKM1, GEOKM2 and GEOKM3, duplicate samples, laboratory duplicates and reagent blank.

5.11.1 5 ppm Cu standard solution

The 5 ppm standard was used to test the instrument performance before and during the analysis of the samples. The Chemistry and Geology UZ departments produced signal read out of 0.247 and 0.249 absorption units. This was within the acceptable range (0.235 to 0.250) if an instrument is working as required.

5.11.2 Reagent blanks

The blank was analysed to check the noise in reading measurements. The results from most of the solutions produced a reading of zero parts per million (0 ppm).

5.11.3: In house standards:

 The in house standards (GEOKM1, GEOKM2 and GEOKM3) were used to monitor systematic errors as a result of instrumental drift and contamination. The standards were for iron, copper, zinc, lead, nickel and antimony. No in house standards for arsenic, chromium and cobalt were available during the analysis.

 It can be seen that most of the results lie between the ranges of mean plus / minus one standard deviations, with the exception of antimony (Figure 5.11a to c). Percentage

deviation for copper, lead and zinc in the three standards is less than ten percent with iron slightly higher. Antimony has slightly higher percentage errors and this could be because some of the antimony values are below detection limit. The full results given in Appendix 12c and are summarised in Tables 12a to 12c. Results of the standards showed that the analyses are acceptable.

Table 12a: Showing a summary of the analytical results for **GEOKM1**. The average concentration of iron is in percentage while all the other elements are in ppm.

Element	Measurement	Average Concentration	Standard Deviation	Percentage Std. Deviation
Fe	27	3.28	0.54	10.54
Cu	29	20.55	1.20	5.79
Zn	28	333.45	15.38	4.61
Pb	28	229.35	15.78	6.88
Ni	5	53.00	5.76	10.87
Sb	24	98.59	18.48	18.75

Table 12b: Showing a summary of the analytical results for **GEOKM2**. The average concentration iron is in percentage while all the other elements are in ppm.

Element	Measurement	Average Concentration	Standard Deviation	Percentage Std. Deviation
Fe	29	2.09	0.19	9.09
Cu	30	18.73	1.59	8.50
Zn	30	122.03	8.99	7.37
Pb	30	85.70	5.88	6.86
Ni	6	26.83	2.34	8.72
Sb	25	134.08	19.88	14.83

Table 12c: Showing a summary of the analytical results for **GEOKM3**. The average concentration iron is in percentage while all the other elements are in ppm.

Element	Measurement	Average Concentration	Standard Deviation	Percentage Std. Deviation
Fe	28	1.30	0.16	12.31
Cu	29	10.07	0.87	8.64
Zn	27	780.52	21.76	2.79
Pb	24	483.42	36.74	7.60
Ni	6	17.50	1.26	7.20
Sb	24	19.79	7.07	35.73

5.11.4: Laboratory duplicates

The soil duplicates show a very good co-relationship between the analysed duplicates (Figures 5.8t and 5.8u). The analytical results of the duplicates are shown in Appendix 9a and 9b. The results as shown in figures 5.8t and 5.8u, reveal that all the elements with the exception of iron, the sampling precision is less than ten percent. It is concluded that in general the representativity of samples is satisfactory.

Soils Duplicates

$$y = 0.9571x - 0.0127$$
$$R^2 = 0.9999$$

MA 4SDup (y-axis)

MA 4S (x-axis)
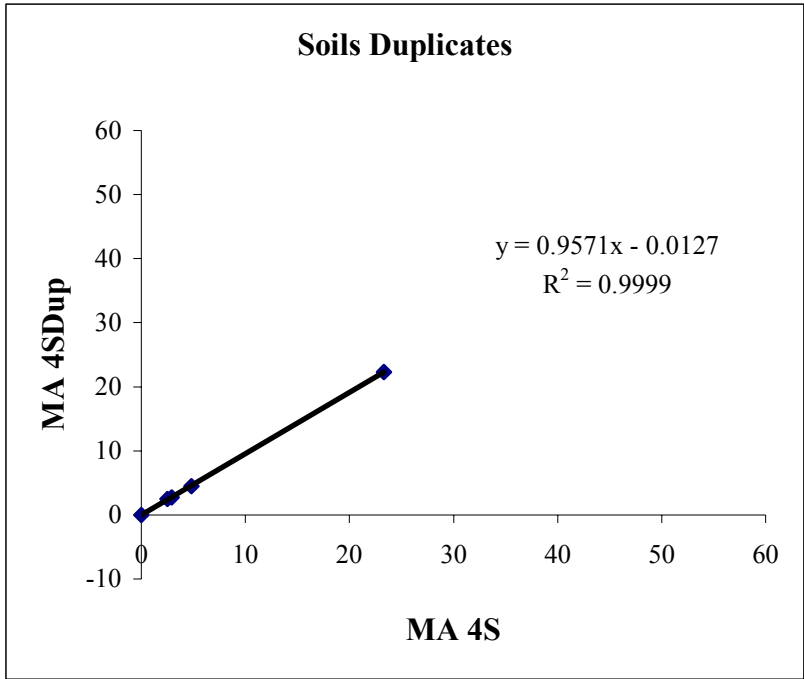
Figure 5.11T Relationship between soil duplicates MA 4S and MA 4Sdup excluding iron.

SOIL DUPLICATES

$$y = 0.9638x - 0.0406$$
$$R^2 = 0.9923$$

MA 9Dup (20m E) (y-axis)

MA 9 (20m E) (x-axis)
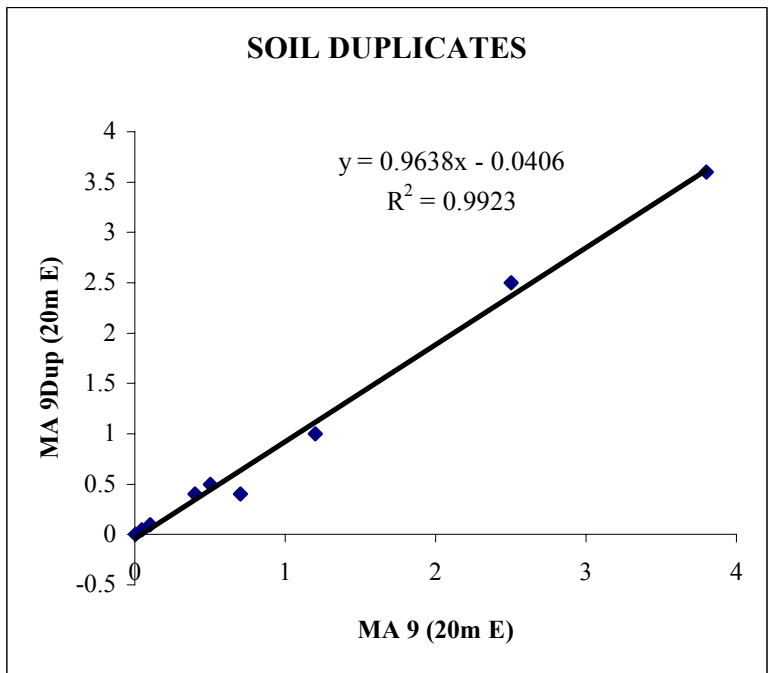
Figure 5.11u Relationship between soil duplicates MA 9 (20m W) and MA 9Dup (20m W) excluding iron.

116

The stream sediments duplicates (Figures 5.11v and 5.11w) show that the errors are less than ten percent as in the stream sediments. The two duplicates show a very good co-relationship and the precision is therefore generally satisfactory.

SEDIMENT DUPLICATES

$y = 1.0622x - 0.0651$

$R^2 = 0.9998$
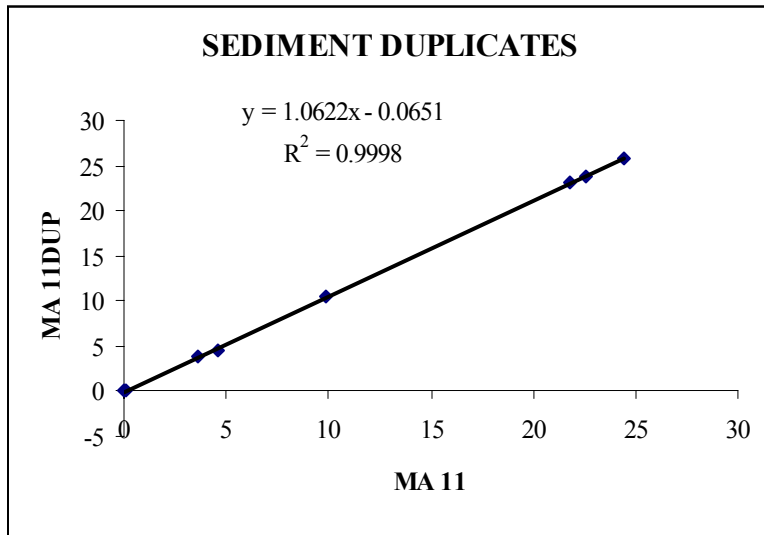
Figure 5.11v Relationship between sediment duplicates MA 11 and MA11 DUP excluding iron and copper.

SEDIMENT DUPLICATES

$y = 0.9241x - 0.225$

$R^2 = 0.9921$
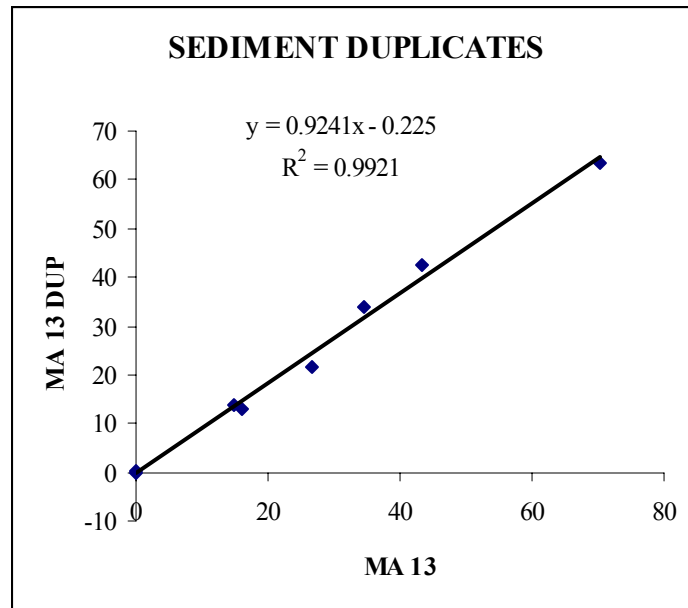
Figure 5.11w Relationship between sediment duplicates MA 13 and MA13 DUP excluding iron and copper.

The quality control program results show that the quality of most of the results is quite satisfactory. The laboratory environments of the two laboratories used were also good in the sense that there was no external contamination. The percentage errors are very low and within the permissible limits of less than ten percent error.

Chapter 6: Conclusions and Recommendations

6.1 Introduction

This chapter gives a summary of the findings of the project and suggests management options to contain the problem at Athens mine.

6.2 Conclusions

The chemical analysis of the slimes, leachate, sediments, soils, surface and groundwater, showed elevated concentrations of iron, copper, lead, arsenic chromium, nickel and cobalt. Mineralogically these elements are present in the mine ore body as element sulphides. The elements are present in easily extractable forms that are potentially mobile during both seasons.

Acid mine drainage is the main environmental problem at Athens which is mainly a result of the oxidation of the sulphide minerals. The oxidation process is aided by the presence of bacteria (Appendix 3) and continuous supply of oxygen during the two seasons. The acidic environment promotes the dissolution of the elements into the environment. Neutralisation of the produced sulphuric acid by addition of lime was only successful at the pump back point during the dry season only. During the wet season, there is an increase in the amount of acid generated and an increase in the volume of flow of water from the storage ponds. This results in the elements transported over a larger area mostly along streams. Most of the sulphides on the top part of the slimes have been oxidised and the acid generation is taking place at three metres from the top of the dump.

The chemicals used in processing, such as ferrous sulphate and lead nitrate are contributing significantly to the pollution of surface water, stream sediments, soils and ground water.

Iron, copper, nickel, zinc, lead, cobalt, chromium and arsenic are the main pollutants being released from the slimes dump. No alarming levels for antimony and cyanide were recorded from the all the samples.

The slimes are responsible for siltation of the streams and Mackenzie dam, most of the acid generation and releasing of elements into the environment. The siltation and

elemental pollution can be traced down in all the streams into Mackenzie dam during both the wet and dry seasons.

The secondary minerals are moderately to highly soluble and are responsible for the increased element concentration in receiving streams during the wet season. They are intermediates in the precipitation of more insoluble minerals with the potential for even greater long-term impact on the environment around Athens mining area. Finally, the secondary minerals serve as indicators of drainage geochemistry due to the incorporation of a variety of trace elements in their structures.

The sediments contain more elements than the water in the streams during the two seasons. In the wet season, the element plume extends to Mackenzie dam and all the streams within the mining area. Elements that reach the water are quickly diluted, either decompose into carbonates, sulphates and sulphides, or mineral and organic sediments adsorb them. This results in element content increase. The highly polluted stream sediments, through resuspension and mobilisation, will continue to pollute the localised environment at Athens mine even after the life of the mine and reworking of the old dumps.

Soil pollution is mostly restricted around the active dump where it has affected the vegetation and made revegetation difficult. The soils have been acidified by the acidic leachate seeping into them from the slimes. Acid from this source is hindering the buffering capacity of the soil. Low pH inhibits the development of microoganisms in the humus soil. The soil acidic environment has caused reduced plant growth in both the forest and cultivated crops.

There is little contamination of groundwater by the slimes during the dry and very little seepages into groundwater takes place during the wet season. This is evident from the geophysics carried out around the active slimes dump and the chemistry of the samples from BH 4. The water is not suitable for human and animal consumption as all the analysed elements exceed the World Health Organisation (WHO) drinking water standards and Zimbabwe effluent of 2000 standards (see Appendix 13). The natural background levels are higher than the set levels for drinking water.

The pollution at Athens mine is localised to the areas around the mining, dumps, waste rock piles, slimes dumps and storage ponds but it is transported by streams during the wet season beyond the mining area. During the dry season the elemental pollution is restricted to the mining area. There is a significant contribution to the contamination of the Sanyati catchment from mining activities at Athens mine.

6.3 Recommendations

AMD has to be reduced in the active slimes dump and acidic water in the ponds should be treated. Oxygen penetration (by air or in water) can be minimised by using covers or sealant, restricting the water penetration into slimes and waste rock that are exposed to weathering, pH control by adding lime, limestone or phosphates to inhibit iron-oxidizing bacterial attack of sulphides (Ritcey, 1989). To achieve the desired properties of a cover, at least two layers (30-60cm thick) of fine-grained material such as bentonite (swelling clay) can be used because one material seldom has all the needed properties for a cover. A low-permeability sealing bottom layer is required for the purpose of decreasing the diffusion of oxygen and to hold large quantities of water, also under dry periods and in this way act as a barrier to oxygen. Clays are however prone to cracking during dry conditions which is a disadvantage because oxygen and water can pass into the slimes. Organic material could possibly be used instead provided the layer is thick enough. Some artificial materials, like plastic membranes have a higher impenetrability than natural materials and can be used (Palmer, 1991). A drain layer can be placed above the low permeability layer and its main purpose will be to protect the low permeability layer from destruction by erosion, drying, freezing, influence from man, animals and plants, microbiological destruction and can act as a capillary break to prevent upward migration of elements and salts (Swedish Environmental Protection Agency, 1993).

One other potential control technique is the addition of excess neutralizing material, particularly carbonate and hydroxide compounds, which produce a neutral to alkaline pH in the associated water, such as limestone ($CaCO_3$), lime (CaO or Ca $(OH)_2$) and sodium hydroxide (NaOH) (Sengupta, 1993). $CaCO_3$ consumes acid through the creation of HCO_3^- or $H_2CO_3^0$ (equations 6.1 and 6.2). The limestone to be used should contain less magnesium content because the higher the magnesium content the slower the rate of

neutralization. The additives should be in solid rather than dissolved form because the liquid represents a less concentrated source through solubility constraints. The fact that the slimes are no longer active at Athens mine, using limestone is an advantage because it will continue reacting with acidic water from the slimes and in the ponds. Calcium oxide must be applied also in the streams and receiving ponds. The success of the base additives to control acid drainage depends primarily on the movement of water through the system, nature of contact of acidic rock or water with neutralising additives or water, proportion of excess neutral material and type and purity of the neutralising additive (Sengupta, 1993).

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \qquad \text{(Sengupta, 1993)} \qquad (6.1)$$

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3^0 \qquad \text{(Sengupta, 1993)} \qquad (6.2)$$

The phosphate would inhibit the oxidation of pyrite by the conversion of iron sulphide to calcium sulphate and iron (II) phosphate $\{Fe_3(PO_4)_2\}$. The iron (II) phosphate precipitate provides a coating around the sulphide mineral grains (Watkin and Watkin, 1983). Fly ash, blast furnace slag, Portland cement and cement kiln dust are some of the inhibitors that could be used to reduce the acid drainage. The neutral or alkaline siliceous material renders iron (III) insoluble (Sengupta, 1993).

Phosphate chemicals (Renton et al., 1988) and phosphate clay (Chiado et al.,1988) restrict oxygen and reduce permeability within slimes. A slurry of clay and apatite can be used as a cover over the slimes to neutralise the acid. Such a cover also reduce the permeability of the surface, thereby reducing the amount of water entering into the slimes resulting in low effluent production. The clay also reduce permeability of iron, manganese, magnesium, aluminium, pH and sulphates in the effluent (Ritcey, 1989).

The slimes ponds after assessment and treatment can be converted to wetlands. Maintaining a high water Table and growing a wetland bog on the surface provides for reducing bacterial activity and oxidation is severely reduced (Sengupta, 1993).
A revegetation on and around all slimes dumps at Athens mine should be embarked on. Vegetation can decrease acid production (Sobek et al, 1990) by affecting several processes; (i) the roots system would compete for oxygen and moisture with acid producing bacteria; (ii) the populations of beneficial heterotrophic soil bacteria and fungi

are established, possibly resulting in additional oxygen consumption and formation of organic acids which may inhibit *T. ferrooxidans* and (iii) the carbon dioxide levels in the slimes is increased by plant root respiration and heterotrophic bacterial activity which would create an unfavourable micro-environment for *T. ferrooxidans*. The vegetation stabilizes the cover that is protecting it from wind, erosion and water infiltration. Gumtrees apart from being barriers to dust can also absorb water and deepen the groundwater level below the indicated zones (see figures 5.6a − k) (Sengupta, 1993). Efforts to revegetate the dumps must be continued using more or less metal tolerant genotypes on the waste or by adding sewage sludge, compost or similar wastes to the surface of the tailings to facilitate revegetation. Revegetation and planting of gumtrees has been successfully carried out at a few mines in Zimbabwe such as Shamva mine, Iron duke and Mazowe mine.

A dust monitoring system must be set-up around the mining area especially on the western side of the active dump, downwind of the prevailing wind direction from northeast to east. Dust fallout gauges can be can be used to collect the dust at designated monitoring location points. The quantity, composition, and the effects of the dust must be determined at the mine.

The streams passing through the mining area can be diverted so that they do not pass through the mining area or close to the slimes dumps and waste dumps. This will reduce the effects of mining activities in the streams.

A Best Practise Environmental Management (BPEM) (Ritcey, 1989 and Wills, 1997) system should be adopted at the mine so that many environmental problems can be detected and rectified early. The system must include biological monitoring in streams and dams. This will help in the development of the rehabilitation and closure plans.

Element speciation studies are required to determine the level of contamination and seriousness of the element levels. This would give the information on the toxicity of the elements and their bioavailability.

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