

HEAVY METALS CONCENTRATIONS IN THE BIOPHYSICAL ENVIRONMENT AROUND THE Ni-Cu MINE AND THE SMELTER/CONCENTRATOR PLANT, SELEBI PHIKWE, BOTSWANA.

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ABSTRACT

The present work involves the study of heavy metals concentrations in the biophysical environment of a Ni-Cu mining and smelting area in Botswana, Africa. Samples of tailings dump, soils, particulate air matter (PAM), *Imbrasia belina*, and *Colophospermum mopane* were analysed for concentrations of heavy metals. Elements analysed were those associated with Ni-Cu mining and smelting included Cd, Cr, Co, Cu, Fe, Ni, Se and Zn, which were likely to be found in Ni-Cu orebodies and released into the biophysical environment through mining and smelting activities. Results depicted higher concentration levels of heavy metals in samples obtained close to the mine and the concentrator/smelter plant compared to samples obtained further away from where mining and smelting activities are being carried out. It is anticipated that these findings may be useful in interpreting biophysical environments where Ni-Cu mining and smelting activities are being conducted.

KEYWORDS: Selebi Phikwe; biophysical; heavy metals; environment

INTRODUCTION

The area of contaminated soils in the world is estimated to range from 50 000 to 200 000 hectares, and this may be over 100 000 sites consumption. Some of these soils which have been contaminated with heavy metals such as Cd, Co, Cr, Cu, Fe, Ni, Se and Zn produce apparently normal crops that are unsafe for both human and animal consumption (Benner *et al.*, 1999). Contamination of land due to industrial pollution, fall out from smelters and mine spoil are of increasing concern because the inorganic contaminants have the potential of entering food chains, and affecting human health among other environmental concerns.

Mining and smelting of Ni-Cu at Selebi Phikwe, Botswana is likely to affect the quality of the biophysical environment through the introduction of different types of contaminants. This study attempted to consolidate this hypothesis by investigating the heavy metals chemistry of the biophysical environment around the Selebi Phikwe Ni-Cu mine and smelter/concentrator plant. The study aimed at chemically characterising the heavy metals in the tailings dump, soil, particulate air matter (PAM), mopane and phane around the Selebi Phikwe area in order to understand how mining and extraction metallurgical activities affect the biophysical environmental quality of the surroundings.

DESCRIPTION OF THE STUDY AREA

The study area, Selebi Phikwe, is one of the main urbanised townships of Botswana (Figure 1), rated after Gaborone, Francistown, Maun, and Lobatse (Grant and Grant, 1995). It is located in the north-eastern part of Botswana between longitudes 27° 47'E and 27° 53'E, and latitudes 22° 55'S and 22° 00'S. The study area of about 250 km² has a population of about 50,000 with a 2.4% constant growth rate since 1991 (National Census, 1991).

In this study, the biophysical environment refers to the soils, particulate air matter (PAM), plants and animals. The soils at Selebi Phikwe are classified as Eutric Regosols and Haplic Luvisols as illustrated and described by the Soil Mapping and Advisory Service Project (1990). The Eutric Regosols are deep to very deep, very dark greyish brown to brown fine sandy loam soil. The Haplic Luvisols are shallow to moderate well-

drained, reddish brown to strong brown sandy clay to clay, undulating to rolling on basalt. Both soils are shallow with an average depth of 1 m. The primary minerals (quartz, mica and feldspars) and secondary minerals (kaolin, illite and smectites) are the main mineral components in the types of soils found at Selebi Phikwe (Tan, 1998).

The vegetation cover of the Selebi Phikwe area is the savanna type. The area is covered with mopane, *Colophospermum mopane* and a variety of acacia species namely the *Acacia Karoo*, *Acacia galpinti*, and *Acacia tortilis*. Other identified vegetation types are *Combretum sp.*, *Zizphus mucronata*, *Commiphora kirkia*, and *Burkea sp.*, which are commonly found on the rocky outcrops (Timberlake *et al.*, 1993). The mopane plant is a tree known as *Colophospermum mopane*. Its vegetation cover dominates the northern Botswana, Zimbabwe, and the Northern Province and lowveld of South Africa. Mopane vegetation grows on most soil types (Tietema *et al.*, 1991). Its glossy, rich-green leaves look like green butterflies. During the summer months, the leaves attract hundreds of brightly coloured caterpillars that feed on them. Browsers such as elephants, giraffes and kudus also eat the leaves. The wood of *Colophospermum mopane* is very hard and durable. In the past, it was used for props in mineshafts and for bridges in the Okavango Delta Area in Botswana. It is useful as wood fuel for cooking and heating of homes during winter months.

The phane caterpillar also known in Botswana as phane worm, mopane worm and phane, derives its common name from its host plant, the *Colophospermum mopane*. The caterpillar is the larva stage of *Imbrasia belina*, which is commonly known as the Emperor Moth (Ditlhogo, 1996; Oberpreiler, 1995). The moth flies in the mopane veld from late December to early February, and could extend to March. Individual female moths lay single layered clusters of eggs on branches and leaf stalks of *Colophospermum mopane*. Caterpillars usually grow for about forty days before pupating. During these days, the gregarious larvae feed on *Colophospermum mopane*, and sometimes defoliate entire trees. Their growth is strongly influenced by rainfall and leaf-water (Taylor and Moss, 1982; Scriber, 1977). Ecllosion is from underground pupae.

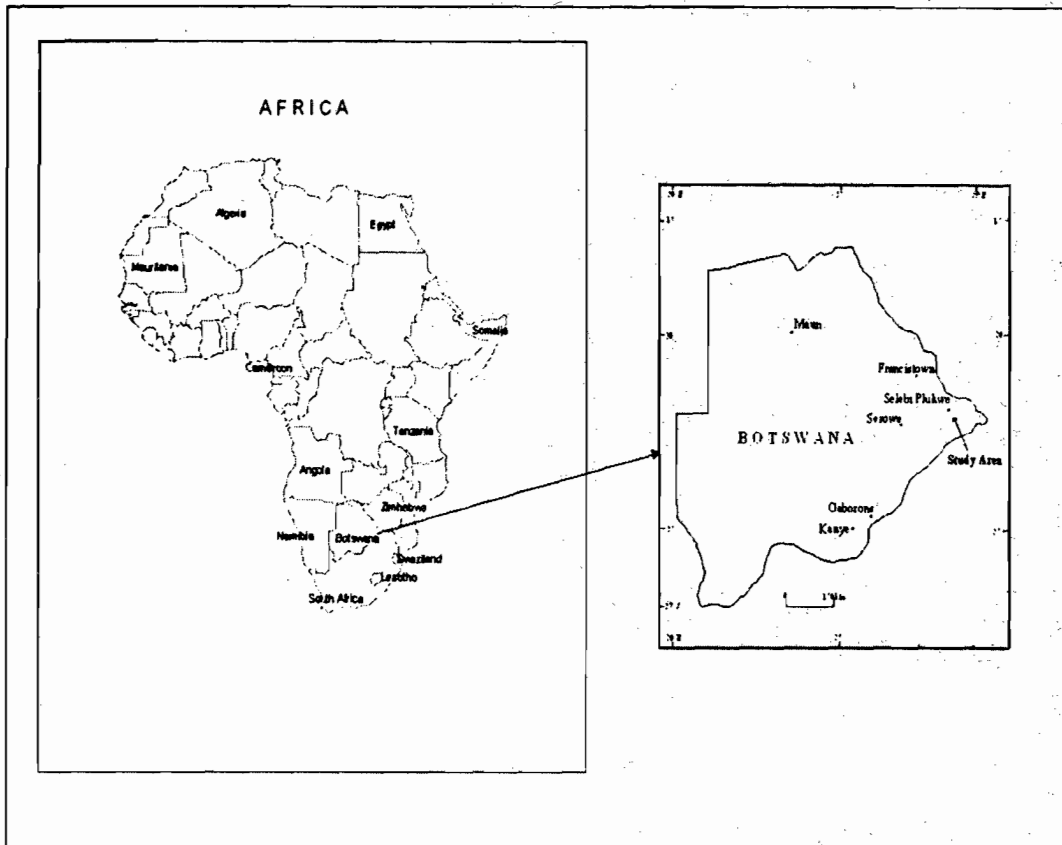


Figure 1: Map of Africa indicating Botswana, and of Botswana showing where Selebi Phikwe is located

Table 1: Location/characteristics of sampling sites at the Selebi Phikwe study site area.

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

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

SAMPLES AND SAMPLING

Sampling

There were 10 sampling areas, which included a chosen control site located close to the road juncture leading to Selebi Phikwe from the Gaborone-Francistown main road. This juncture is about 56 km from Selebi Phikwe. The soil lithology and vegetation cover of the control sampling site were very similar to those of Selebi Phikwe area. Nine sampling sites radiometrically distributed within the mine and smelter plant environments (Figure 2), and a control sampling site were identified (Table 1). Samples of soil, PAM, mopane leaves and phane caterpillar were obtained as close to one another as possible from the sampling sites during the sampling period. Tailings dump samples were obtained from the tailings dump mount close to the concentrator/smelter plant.

Sampling was done twice monthly from January 2000 to July 2000. Samples were collected from the tailings dump, soil, and mopane leaves on each of the fourteen field visits during

Table 2: Dates with corresponding types of study material sampled

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

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

sampling. The phane caterpillar was sampled only when available, namely on four visits because it is seasonal (Table 2). Samples of tailings dump, soils, mopane leaves and phane were obtained in the morning hours between 5.00 AM and 8.00 AM. Atmospheric conditions including temperature and wind direction at time of sampling were noted.

Tailings dump samples

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

Soil samples

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

Particulate air matter samples

Air samplers were placed at the same time in the early morning hours and removed in the evening, after twelve hours of PAM collection. Samples of PAM were obtained according to US NIOSH method 0500 for elemental analyses. Six Gilian Gilair - 3 personal air sampling system (South African version) for low flow and two Air con 2 constant medium flow samplers were used for sampling of PAM. It was not possible to collect samples on a monthly basis due to unusually heavy rains during the wet season of the year.

The medium flow samplers were used to obtain samples over a period of three days at each of the sampling points. The samplers for low flow were placed at the various sampling points and allowed to run for 12 hours at a flow rate of 1.9 l/min, as specified by the NIOSH manual of analytical methods of 1995. The cellulose acetate filters were acclimatised in an atmospheric stabilising cabinet for 24 hours in a clean laboratory environment where it was to be weighed. The balances were kept in a dust free room. Weighing of filters was done to an accuracy of 0.01 mg on the chemical balance. The weighed filters were kept in a filter container. The filters with the open ends pointing upwards were linked to calibrated pumps at the sampling sites at Selebi Phikwe. After 12 hours, the open end of the filter system was sealed with a clip for heavy metals analyses. After 35 samples (12 - hour sampling time) were obtained and weighed, the masses of sample concentrations obtained were very low. All the collected samples were put together to constitute a composite sample which was analysed.

Mopane samples

Between 10 and 12 mature dark green leaves with leaf diameter ranging from 4 cm to 8 cm of *Colophospermum mopane* depending on the leaf diameter, which constituted a sample set, were harvested at the sampling sites for laboratory analyses. A total of 140 sample sets were obtained during the sampling period. The samples were transported Gaborone where they were aerated for one week or more, until there was an escape of leaf moisture.

Phane samples

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

METHODS AND ANALYTICAL TECHNIQUES

Field observations

A hand lens was used in the field to have a closer look of hand

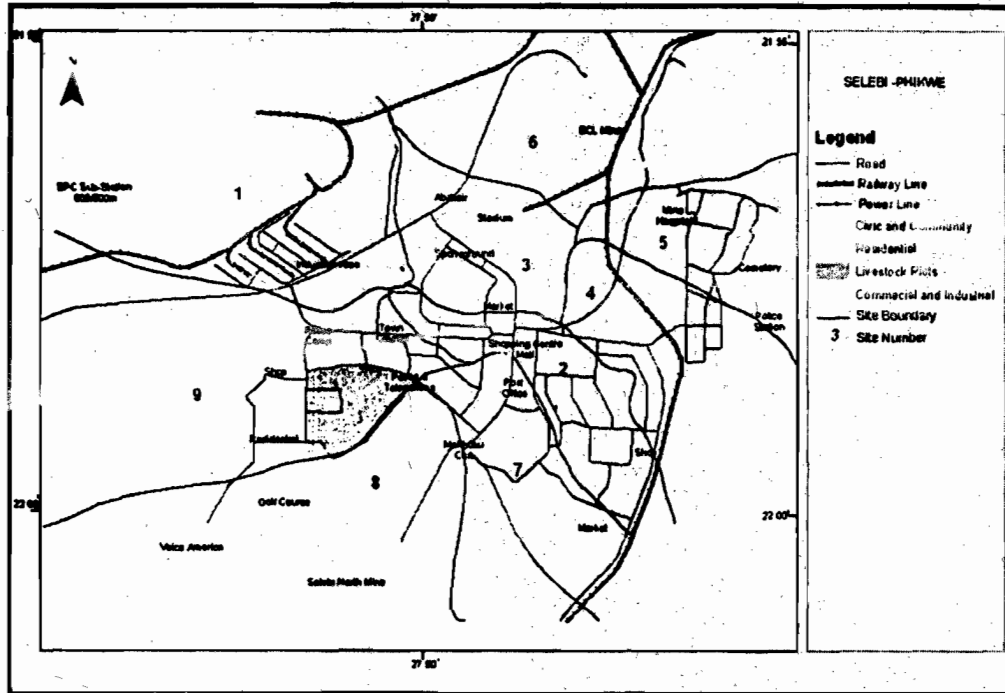


Figure 2: Map of Selebi Phikwe showing the different sampling sites

specimens of tailings dump and soils. The shape and size of the tailings dump mount were visually observed as well as the colour of the mineral crystals. Exposed soils at the study area were observed in terms of soil colour and texture. The atmosphere was visually inspected for PAM, in order to note any significant quantity, as well as attempts for possible detection of gas smell emanating from the smelter/concentrator plant. The shape and length of the leaves as well as colour were observed. Where possible, the worms were observed as they fed on mopane leaves. Other observations included leaves sites where leaves were eaten, and how was the eating of the leaves by the phane done. All the observations were carried out at the sampling sites on the same days and time that samples were obtained for laboratory analyses.

Heavy metals analyses

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

were determined using a Varian Spectra AA 400 plus Atomic Absorption spectrometer with a Zeeman Graphite Tube Atomizer (GTA) 96 model whereas the ionic concentrations of Cu, Fe and Zn were measured with a Varian Spectra AA 10 Flame Atomic Absorption Spectrometer (FAAS).

The procedure for the determination of the concentrations of heavy metals used was adapted from both Beach (1989) for the Zeeman GFAAS and NIOSH (1995) manual of analytical methods for FAAS depending on the analyte being analysed. Analytical grade reagents were used in all the chemical analyses. Samples were homogenised and 0.5 g of sample was weighed into a 30 ml Teflon beaker. Samples were treated with HNO₃ digestion at a temperature not exceeding 500 °C. The derived solution was heated slowly at low temperature to dry. Then it was the ashing stage, which took place at a high temperature, and thirdly by atomisation. Zero point one gram of sample was weighed into a Pt crucible wetted with water. Each sample was digested with 0.5 ml of 72 % perchloric acid and 5 ml of 48 % hydrofluoric acid on a sand bath at 200 °C - 225 °C in a partially closed Pt crucible with lid. The residue was collected by boiling the sample with 5 ml of 60 % HCl and 10 to 15 ml of water. The contents of the crucible together with its lid were washed into a 100 ml volumetric flask filled to mark with ultra pure water, from which very small aliquots were aspirated into the spectrometer for atomisation and analysis of the heavy metal concentrations in the samples.

RESULTS AND INTERPRETATION

Field observations

Tailings dump

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

Table 3: Correlation coefficients between heavy metals in the tailings dump.

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

Soils

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

Particulate air matter

During the sampling period, the atmosphere was generally

very clear, to the extent that no PAM could be detected with the naked human eye. At sites one, two, three and eight the smell of sulphur rich gases (SO₂, H₂S) was very strong during most of the sampling periods. At the other sites (four, five, six, seven, nine and ten), sulphur smell could not easily be discerned.

Mopane leaves

It was observed that the plant leaves changed in colour probably due to deposition of sulphate particles on them. It was also noticed that leaves located at the periphery of the plant were more affected by the deposition of PAM than others. The peripheral leaves were the first to alter in colour.

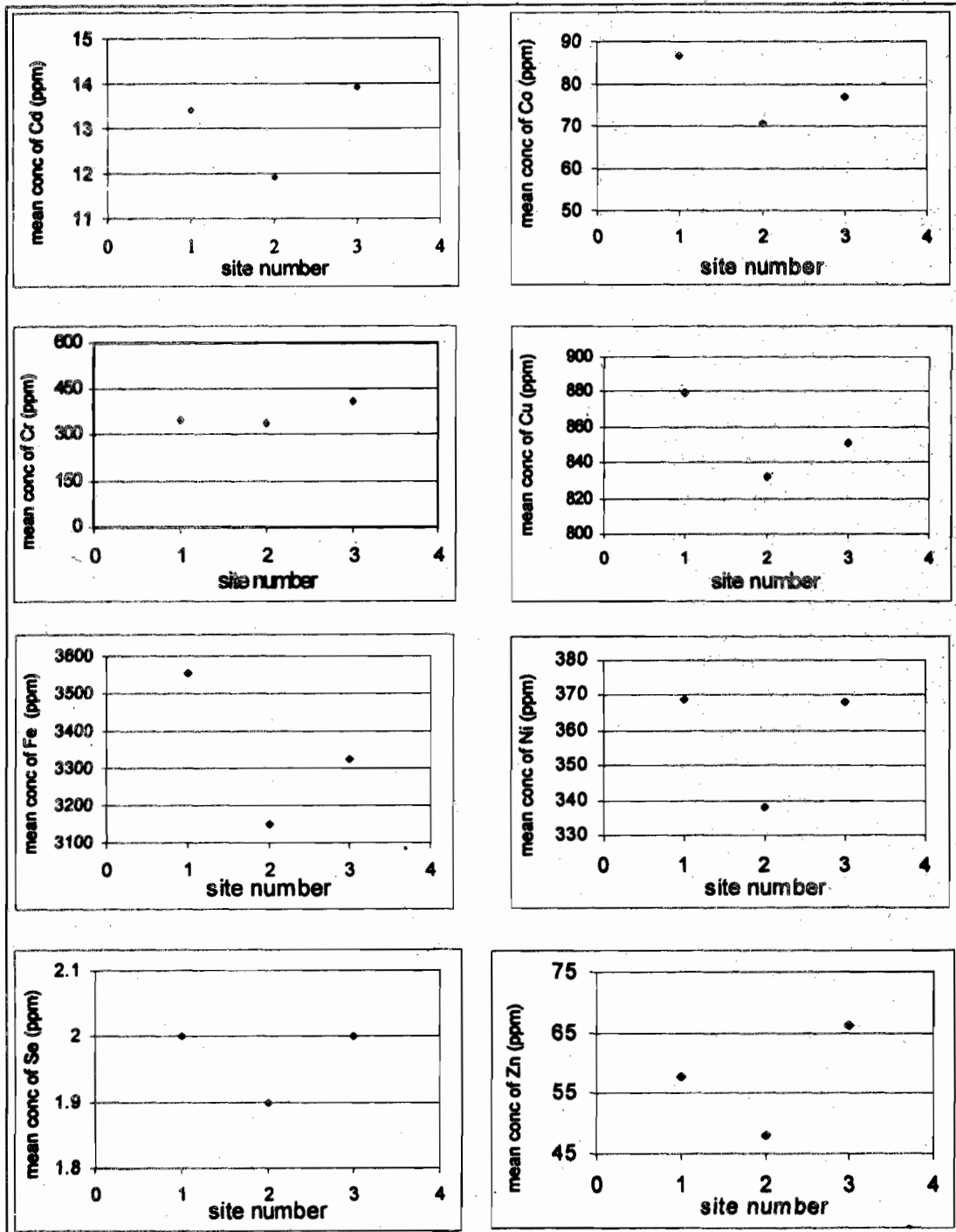


Figure 3: Mean concentrations of heavy metals in tailings dump around the Selebi Phikwe study area.

The coloration on leaves varied with location and with season. At the beginning of the field season, most of the leaves at the area were generally green. Where discoloration occurred, the leaves were initially green in the months of January, February and March, and they turned to pale yellow and later golden yellow in the subsequent months during the field season. Both the leaves and the stems of the mopane plants at site one were stunted. At site two, the leaves were initially green and changed to brownish green and eventually golden yellow. At site three the mature leaves were very short, between 2 cm and 2.5 cm in length. At site four, the leaves were constantly very broad and they exhibited full growths both in colour (rich green) and length (6 cm to 7 cm). At sites seven, nine and ten,

the leaves were constantly green and of full-length between 4 cm and 6 cm.

Phane caterpillar

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

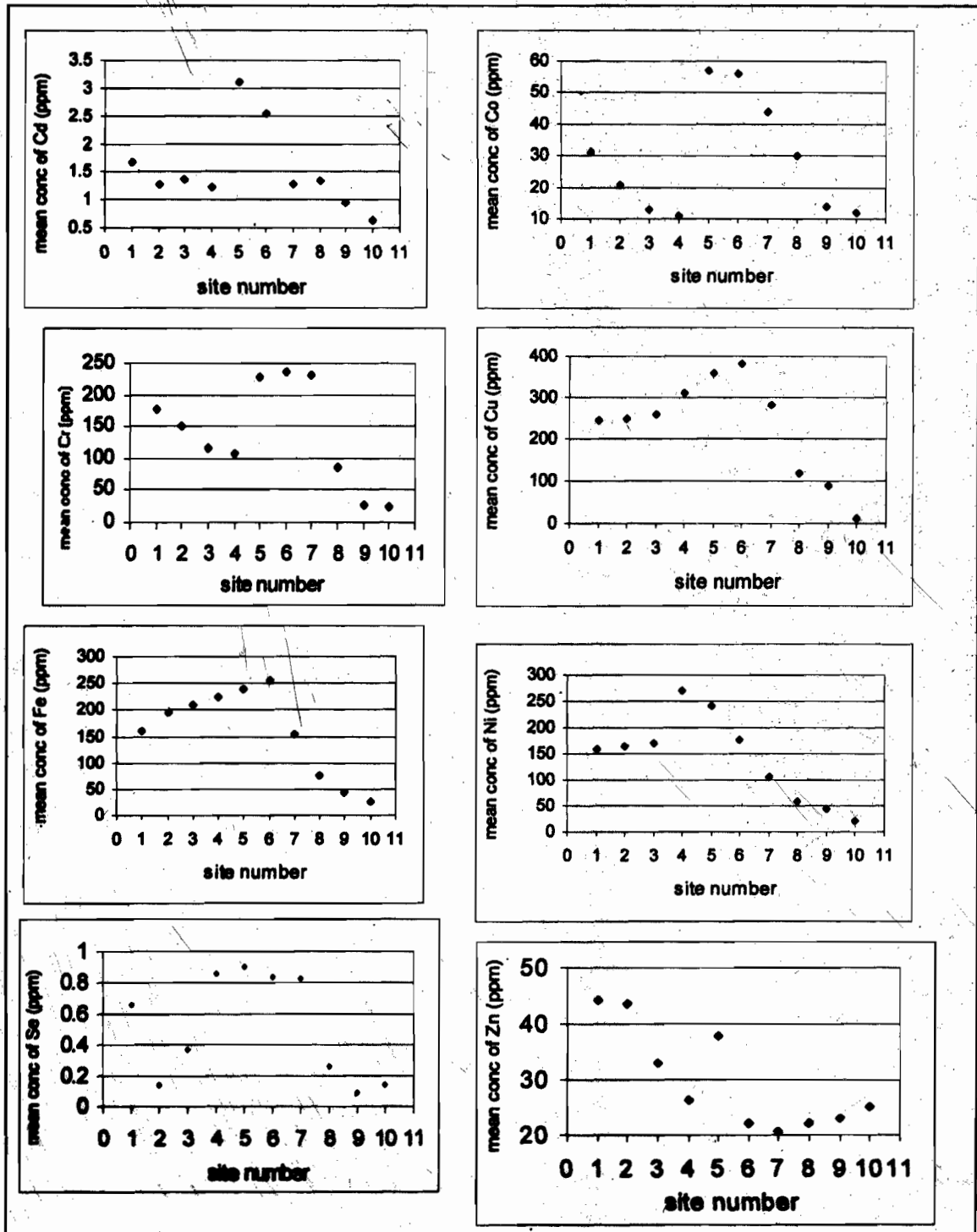


Figure 4: Mean concentrations of heavy metals in soil around the Selebi Phikwe study area.

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

Heavy metals concentrations

Tailings dump

Concentration values obtained for analysed heavy metals in samples of tailings dump were as follows: Cd was between 9 ppm and 16 ppm, Co was between 66 ppm and 89 ppm, Cr was between 312 ppm and 431 ppm, Cu was between 779 ppm and 896 ppm, Fe was between 3100 ppm and 3555 ppm,

Ni was between 328 ppm and 389 ppm, Se was between 1.7 ppm and 2.2 ppm, and Zn was between 46 ppm and 77 ppm. The correlation coefficients are depicted in Table 3.

The mean concentration values, as reflected in Figure 3 indicated lower concentration values at the centre of the tailings dump compared to higher concentration values at the sides of the waste mount. Most correlations between heavy metals in the tailings dump were very strong with a few exceptions. Very strong correlations included Cr/Cd, Fe/Cu, Ni/Cd, Ni/Co, Ni/Cu, Se/Cd, Se/Co, Se/Cr, Se/Fe, Zn/Cd, Zn/Cr, Zn/Ni and Zn/Se. Very insignificant associations occurred for Cr/Co and Cu/Cr with a correlation coefficient value of 0.06.

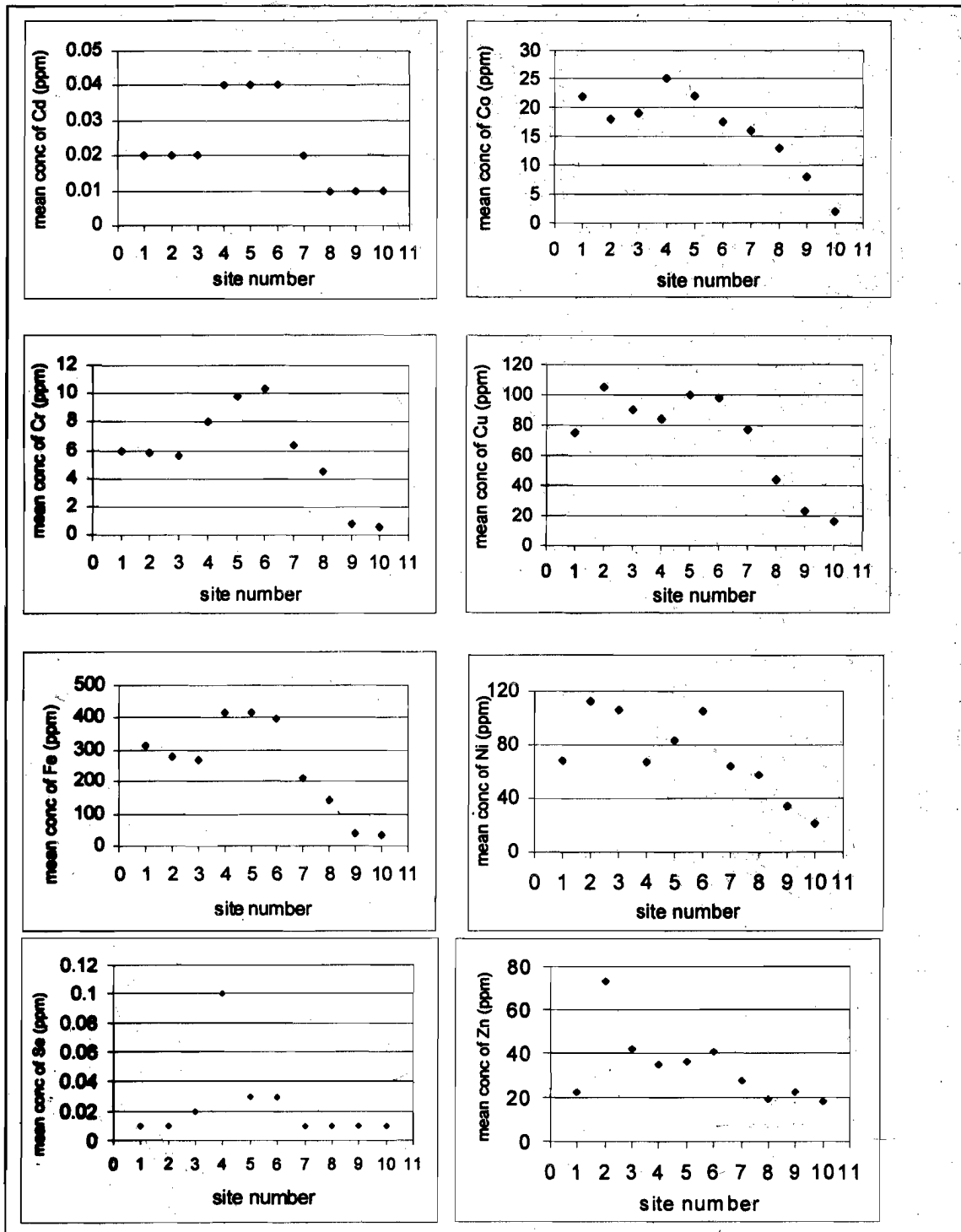
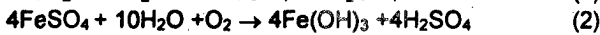
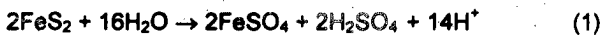


Figure 5: Mean concentrations of heavy metals in Mopane leaves around the Selebi Phikwe study area.

The lower values obtained for heavy metals at the centre of the dump compared to the sides suggested leaching of ions occurring more vigorously and high concentration values at the sides was as a result of enrichment of ions which were displaced from the top of the dump. The high concentration levels of heavy ions in the tailings dump were indicative of the mount being a major source for the introduction of contaminants into the physical environment. Bertsch and Seaman (1999), Bowles and Jambor (1990), Bowles *et al.* (1992; 1995) and De Vos *et al.* (1995) have demonstrated that the tailings dump of sulphide mines promote acid mine drainage (AMD) and introduce heavy metals into the environment (Bowles and Jambor, 1994). Groundwater, fauna and flora of the environment are affected Bowles *et al.* (1995). The rocks become acidic in a low pH environment, leading to precipitation of ions including those of heavy metals. Pyrrhotite ($\text{Fe}_7\text{S}_8\text{-FeS}$) and pyrite (FeS_2) in tailings dump are oxidised on exposure to water to form sulphate and sulphuric acid as indicated in equations 1 and 2 below (Bowles *et al.* 1995; Al *et al.*, 1994; 1994a; Benner *et al.*, 1997, 1999):



The acidification reactions could be accelerated by the bacterium *Thiobacillus ferrooxidans*, the absence of neutralising minerals such as calcite (CaCO_3), and the release of heavy metals into their ionic state (Bowles *et al.*, 1998). Piles of tailings dump from around the mines at Selebi Phikwe and the concentrator/smelter plant stay for years probably without proper disposal. During stockpiling, ions of heavy metals leached into the soils and water bodies, and could eventually be absorbed by plants. Finer particles from the tailings dump could be windblown to distant environments, and eventually affect the ecosystem. Tailings dump from Ni-Cu mines and smelter/concentrator plants leach out ions of heavy metals that could contaminate soils and cause the development of dead zones; depletion of vegetation growth where plants died due to heavy metal poisoning.

Soils

The concentration values obtained for analysed heavy metals in tailings dump samples were as follows: Cd was between 0.01 ppm and 0.05 ppm, Co was between 1 ppm and 28 ppm, Cr was between 0.03 ppm and 14 ppm, Cu was between 11 ppm and 116 ppm, Fe was between 31 ppm and 430 ppm, Ni

was between 19 ppm and 120 ppm, Se was between 0.01 ppm and 0.03 ppm, and Zn was between 17 ppm and 68 ppm. The correlation coefficients are shown in Table 4. The mean concentration values as reflected in Figure 4 indicated that the lowest concentrations occurred at the control site. Other low concentration values of the different heavy metals were further away from the smelter/concentrator plant (sites eight, nine and the control site, ten). The soils close to the plant, more specifically site four, five and six were the most contaminated.

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

Accumulation of heavy ions is more rapid in clear terrains than where vegetation cover is available (Berthelsen and Steiness, 1995). The precipitates accumulated from constant leaching of ions of heavy metals emanating from tailings dump caused the soils to be over saturated with heavy metals. In this regard, as vegetation was depleted due to the formation of dead zones, heavy metals concentrations in soils increased correspondingly.

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

Particulate air matter

Only one composite sample was chemically analysed. The concentration values were given in Table 5. The concentrations of the heavy metals in PAM were parallel to those in the soil samples and the tailings dump. Concentration

Table 4: Correlation coefficients between heavy metals in soil

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

Table 5: Concentrations of heavy metals contained in particulate air matter.

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

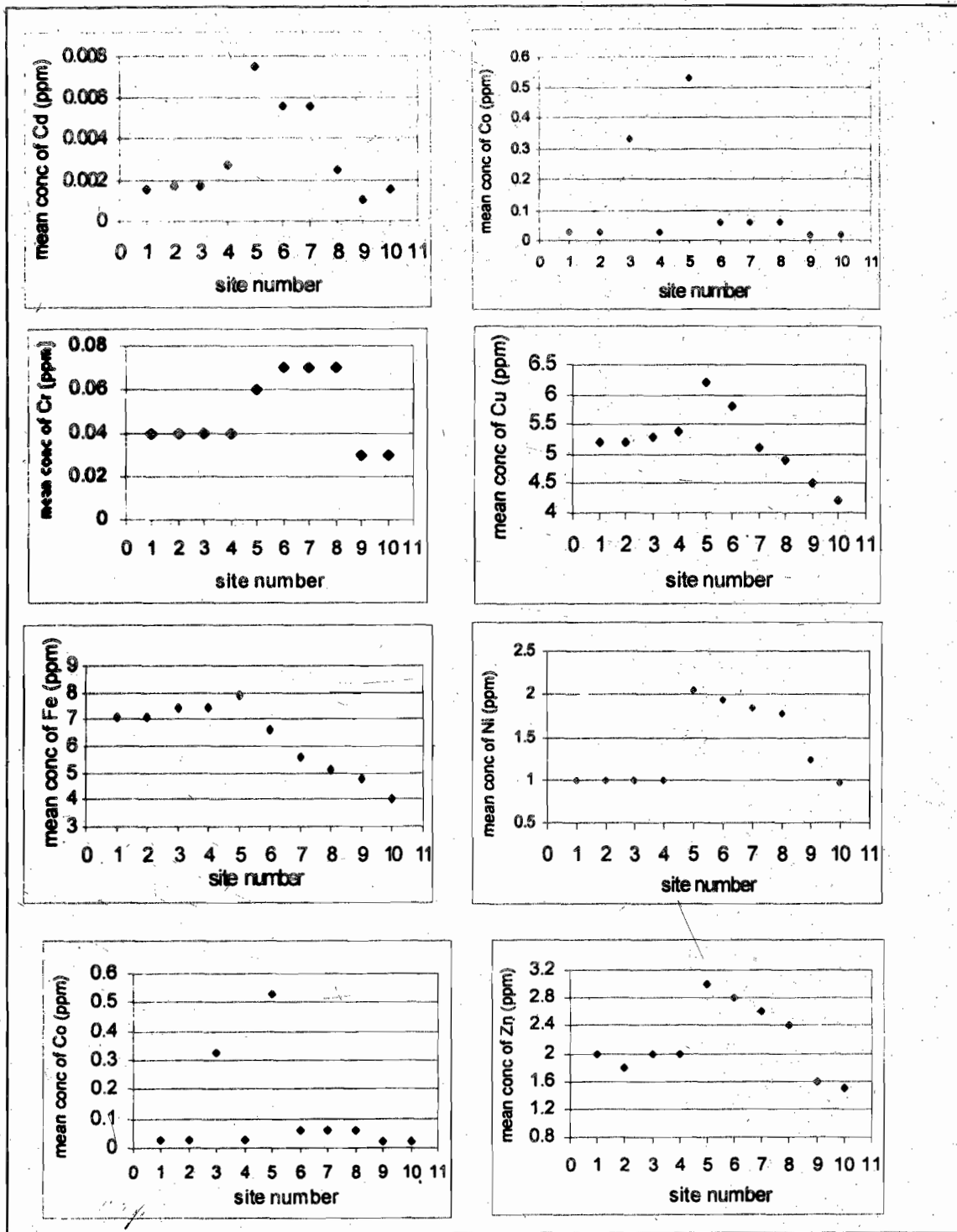


Figure 6: Mean concentrations of heavy metals in phane caterpillar around the Selebi Phikwe study area.

values for Co, Cr, Cu, Fe, Ni and Zn in PAM were higher than usual for residential areas.

Particulate air matter may consist of one or more of the following: dust, soot, smoke, and liquid droplets emitted directly into the atmosphere from sources such as factories, power plants, mines, transportation media, construction activity, fires, and windblown dust (USA – EPA, 1995). These particulate matter are known as primary PAM pollutants (PPAMP). Secondary PAM pollutants (SPAMP) result from the condensation or transformation of PPAMP into secondary gases and minerals. PAM refers to the solid or aerosol state at

ambient conditions and the particulate should have an euهدral spherical diameter (esd) of $\leq 100 \mu\text{m}$ (USA – EPA, 1995).

PAM may damage metal surfaces, fabrics, buildings, bridges and roads. PAM may damage crops, trees and shrubs. It may congest the leaves and make it difficult for photosynthesis to take place. The plants become distorted and eventually die through suffocation. Visual reduction is enhanced by finer particles causing haze, which may be dangerous to motorists, and diminish crop yield. Previous air pollution studies conducted (USA – EPA, 1995) show that PAM with an

Table 6: Correlation coefficients between heavy metals in the leaves of mopane plant

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

Table 7: Correlation coefficients between normalised heavy metals in the phane caterpillars

	Cd	Co	Cr	Cu	Fe	Ni	Se	Zn
Cd	1							
Co	0.54	1						
Cr	0.51	0.33	1					
Cu	0.66	0.63	0.54	1				
Fe	0.17	0.54	0.11	0.85	1			
Ni	0.65	0.38	0.89	0.53	0.03	1		
Se	0.67	0.84	0.68	0.61	0.60	0.51	1	
Zn	0.64	0.50	0.87	0.81	0.40	0.92	0.58	1

equivalent spherical diameter (esd) of $\leq 10 \mu\text{m}$ could be inhaled into the human respiratory system and could be deposited on the lungs. The Environment Protection Agency (US-EPA) has set a mean annual standard (MAS) of $50 \mu\text{g}/\text{m}^3$ of PAM provided sampling is calculated on 24 hrs/day and only one day value in the whole year exceeds $150 \mu\text{g}/\text{m}^3$. The PAM depicted levels of contamination as a result of mining and smelting activities.

Mopane leaves

The concentration values obtained for analysed mopane leaves were as follows: Cd was between 0.01 ppm and 0.05 ppm, Co was between 1 ppm and 28 ppm, Cr was between 0.03 ppm and 11 ppm, Cu was between 4 ppm and 116 ppm, Fe was between 31 ppm and 430 ppm, Ni was between 19 ppm and 120 ppm, Se was between 0.01 ppm and 0.03 ppm, and Zn was between 17 ppm and 79 ppm. The correlation coefficients are shown in Table 5. The mean concentration values of heavy metals in leaves as reflected in Figure 5 indicated that the lowest concentration values occurred at the control site. Other low concentration values of the different heavy metals were further away from the smelter/concentrator plant (sites seven, eight, nine and ten). The leaves close to the smelter/concentrator plant; more specifically sites four, five and six were the most contaminated.

The correlation coefficients between heavy metals in plants reflected very good associations for more than 75 % of the relationships. Very strong correlations included Cr/Cd, Cr/Co, Cu/Cd, Cu/Co, Cu/Cr, Fe/Cd, Fe/Co, Fe/Cr, Fe/Cu, Ni/Cu, Ni/Fe, Zn/Cu and Zn/Ni. The lowest correlation coefficient was at 0.1 with Zn/Se. The correlation coefficient values for Se/Co, Zn/Cd and Zn/Cr were the same. Mopane leaves were enriched from wash-offs, PAM, plant uptake from soils, and other wastes due to mining and smelting activities.

Phane caterpillars

The concentration values obtained for heavy metals in phane caterpillars were as follows: Cd was between 0.01 ppm and 0.05 ppm, Co was between 0.01 ppm and 0.6 ppm, Cr was between 0.03 ppm and 1.03 ppm, Cu was between 1.3 ppm and 9.79 ppm, Fe was between 1 ppm and 13.5 ppm, Ni was between 1.2 ppm and 4.20 ppm, Se was between 0.01 ppm and 0.03 ppm, and Zn was between 0.6 ppm and 5.79 ppm. The correlation coefficients are shown in Table 6.

The mean concentration values of heavy metals in phane, as reflected in Figure 6, indicated the lowest concentration values occurring at the control site. Other lower concentration values of the different heavy metals were further away from the smelter/concentrator plant (sites seven, eight, nine and ten).

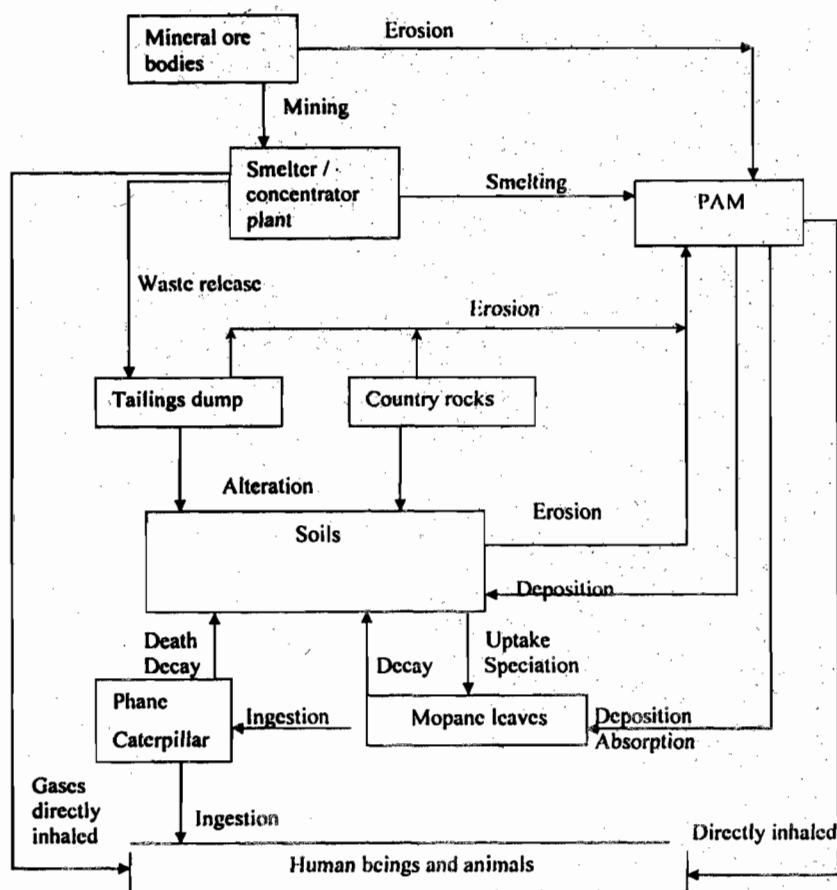


Figure 7: Schematic diagram showing physico-chemical processes and relationships of environmental constituents at the Selebi Phikwe study area

The worms close to the plant; more specifically sites four, five and six were the most contaminated. The correlation coefficients between heavy metals in phane caterpillar reflected very good associations. Strong correlations included Fe/Cu, Ni/Cr, Se/Co, Zn/Cu and Zn/Ni. The lowest correlation coefficient was at 0.03 with Ni/Fe. The concentrated heavy metal content in the phane caterpillars at these sites was attributed to the fact that the leaves they fed on were heavily contaminated.

DISCUSSIONS

Discussions in this section cover effects of heavy metals concentrations in soils, atmosphere and vegetation. Aspects of heavy metals concentrations on animals has not been addressed because they relate to animal health; which is beyond the scope of this present work.

Effects of heavy metals concentrations in soils

Cadmium is usually found in the soil as cadmium oxide, cadmium chloride and cadmium sulphide. At Selebi Phikwe the sulphide form is most likely to occur. Cadmium is quite soluble, and mobile. Cadmium in soils is readily bioavailable for plant uptake, and also exists in soluble forms in water. Research carried out indicated that Cd mobility is a greater threat to the human food chain than any of the other heavy metal (Alloway and Ayres, 1993).

Cobalt occurs in different ionic species in soils. The high levels of Co in Selebi Phikwe soils, provide contaminant trends for mineral uptake of plants. Cobalt migrates quite slowly, therefore it has the tendency to be retained in soils for longer periods compared to several other heavy metals.

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

Copper enrichment and retention in soils is dependent on soil pH, soil texture, and soil sorption properties. Copper is not easily adsorbed at low pH due to competition with Mg^{2+} , Fe^{3+} , H^+ and Al^{3+} for sorption sites, but its content in soils increase with increasing pH. Soil Cu content is between 2-100 ppm with an average of 30 ppm, and a recommended accumulation of 250 ppm in the upper 15 cm of soil (Alloway and Ayres, 1993). The levels obtained for Selebi Phikwe were higher.

Iron is commonly found in most soils as oxides. At Selebi Phikwe, it exists mainly in the form of sulphides. Iron content in soils affects plant growth, and promotes soil acidity (Nkoma and Ekosse, 1999). Unfortunately, Fe is a major accessory element present in the Ni-Cu ore, which is being mined at Selebi Phikwe. The Selebi Phikwe soils have high levels of Fe; as depicted in previous XRPD study which reflected pyrite and pyrrhotite acidity (Nkoma and Ekosse, 1999; Ekosse *et al*, 2003).

Nickel occurs in soils as sulphides and oxides of which the sulphides were more prevalent in the Selebi Phikwe soils. The

Ni found in soils is usually embedded with minerals and is not readily bioavailable for plant uptake. Tolerant levels for Ni in soils are between 4 ppm and 80 ppm (Alloway and Ayres, 1993; Suechka and Zielonka, 1995), although values can reach 9000 ppm where Ni is extracted from ore. Concentration values obtained for the Selebi Phikwe soils implied that the soils were Ni-contaminated. Ni in soils is precipitated as Ni hydroxyoxides at alkaline pH. In lower oxidation states, Ni precipitates as Ni carbonate and Ni sulphide. The quantity and type of clay, and the soil CEC do not have any direct influence on Ni retention in soils. Fe and Mn oxides are positively correlated to Ni sorption. Organic matter can hold Ni at levels up to 2000 ppm. Soil accumulation of 100 ppm Ni appears to be acceptable based on phytotoxicity and microbial toxicity (Li *et al.*, 2000; Wang and Chen, 1998).

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

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

Effects of heavy metals concentrations in the atmosphere
Mineral dust at Selebi Phikwe consisted of particulate released into the atmosphere from mining and smelting activities, as well as spatially-transported aeolian particulate. Regional climatic and geomorphic factors such as draught and desertification encroachment tended to increase the quantity of mineral dust that enters into both the atmosphere and troposphere (Ringrose *et al.*, 1995). This phenomenon might dilute the proportions of heavy metals contained in mineral dust (PAM).

Secondary PAM is formed by atmospheric chemistry, by reactions of primary PAM with atmospheric gases and fluids. Mineral dust can force both cooling and warming effects on its environment locally, regionally and globally depending on the quantity contained in air as explained by Prospero (1999) and discussed by Buseck and Posfai (1999). Mineral particles absorb light creating a heating effect as explained by Buseck and Posfai (1999). The surfaces of mineral dust particles are used as reactive milieus for a wide variety of chemical reactions in the atmosphere, which significantly influence the cycles of N, S, and oxidants in the air. When mineral particles are associated with hygroscopic S compounds, they act as cloud condensation nuclei (CCN) and modify the cloud radiative properties of sunlight (1999). In this regard, they promote precipitation and concentration of ice. This phenomenon may explain why Selebi Phikwe has slightly more rain than its neighboring areas even though they are classified within the same climate type.

Effects of heavy metals concentrations on vegetation

Cadmium, Cr, Se and Zn in mopane leaves occurred in levels, which bear general trends, although concentration levels of Cr were higher. The Co, Cu, Fe and Ni in mopane leaves at Selebi Phikwe were quite high and levels are indicative of

phytotoxicity. The concentration levels for Ni were at an early stage of phytotoxicity. Plants are intermediate reservoirs for heavy metals, whereby they migrate from soils to animals and human beings. The availability of heavy metals to plants depends on the metal species, among several other plant and soil conditions. Only part of the total amount of heavy metals in soils is bioavailable for plant uptake. Certain plant species are hyperaccumulators of specific heavy metals, and serve as geobotanical-biochemical indicators (Chaney *et al.*, 1995). High concentrations of heavy metals with values exceeding plant tolerant levels are indicative channels of potential phytotoxicity.

Excessive concentrations of heavy metals affect biochemical processes in plants. Cadmium, Co and Se affect plant metabolism more than other heavy metals. From this study, it is shown that Co, Cr, Cu, Fe and Ni occurred at toxic concentration levels in the sampled mopane leaves. High Co causes plant chlorosis and together with Cr, Fe and Ni, they affect phosphate affinity. The presence of Cu and Fe result in dark green leaves in plants. Copper also affects permeability of cell membranes. The concentrated levels of Cu and Fe thus resulted in the mopane plants with dark green leaves and stunted growth. The copper concentrations in plants are 4 -15 ppm. Soil Cu content is the most important level in controlling the Cu content in plant leaves (Alloway and Ayres, 1993). Copper is toxic to plants and animals. At 20 ppm and above, Cu content in the leaves of plants is considered to be toxic. Other investigators suggest soil Cu concentration to be > 80 ppm for plant growth to be adversely affected (Rauta *et al.*, 1995). It has also been proved that large amounts of organic matter reduce soil Cu concentrations. Small quantities of Cu activate certain enzymes required for respiration, redox reactions and protein synthesis (Tan, 1998).

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

CONCLUSIONS

Strong correlation of heavy ions especially those of Fe, Ni, Cu and Co in tailings dump, soils, PAM, plants and caterpillar is indicative of interaction of contaminants from the mining and smelting activities to the physical environment. High acidity of soils is reflected by on-going AMD activity which is depicted by the formation of dead zones. In the tailings dump and soils the mobility of the ions depended on the pH, which in turn was controlled by precipitation, dissolution, solid-solution substitution, and adsorption/desorption reactions (Coggans *et al.*, 1999). The relative mobilities of the heavy metals were as follows: Fe = Ni = Co > Cu. Low soil pH promotes the leaching and precipitation of ions including those of heavy metals namely Cd, Co, Cr, Cu, Fe, Ni, Se and Zn. Pyrrhotite (Fe₇Se₈-FeS) and pyrite (FeS₂) in tailings dump are oxidized on exposure to water to form sulphate and sulphuric acid. Other observable phenomena in the study area were stunted growth of *Colophospermum mopane* (mopane tree) and *Imbrasia belina* (phane caterpillar) as a result of high concentrations of heavy metals in their organic systems.

Air pollution resulting from particulate matter of SO_x gases, metals and minerals has led to deposition and increasing acidity of soils. This might cause an increased bioavailability of

metal ions in soils and more uptake by plants (Tagami and Uchida, 1997). Concentration levels of plant nutrients in the surrounding mining environment increased due to the introduction of contaminants; a condition that might eventually lead to certain vegetation type becoming either endangered or locally extinct (Chaney *et. al.*, 1995).

The mining of and processing of sulphide minerals at Selebi Phikwe is accompanied by mine waste. These wastes led to the formation of different gas and PAM contents, deposition of tailings dump, and contamination of surrounding soils, vegetation and animals. A schematic presentation of the likely environmental implications at different stages is depicted in Figure 7. Fumes rich in sulphur, nitrous oxides (NO_x) and other associated gases were found to be deleterious to human life as well as cattle and game (Prospero, 1999). The emissions of SO₂, CO, CO₂, and other gases from concentrator and smelter plants affect people, plants, wildlife, rocks and soils, buildings and landscape topography Buseck and Posfai (1999).

Results obtained from chemical analyses of the tailings dump, soils, mopane leaves and phane worms were indicative of an increase in concentration of heavy metals at the study sites close to the smelter/concentrator plant compared to sites further away from the smelter plant. This work has investigated the heavy metals status of the biophysical environment due to mining and smelting activities. It is anticipated that the findings of this study may serve as useful guidelines in interpreting the biophysical environment of Selebi Phikwe and possibly similar settings around the world.

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