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Assessment of heavy metal pollution/contamination in soils east and west of the Bamangwato Concessions Ltd (BCL) Cu/Ni mine smelter in Selebi-Phikwe, Botswana

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Abstract

The current study evaluated the concentration and levels of pollution by heavy metals in soils around BCL Cu/Ni mine in Selebi-Phikwe, Botswana. Soil samples were collected from four different locations namely 2.5 km east, 2.5km west, 20km west and 55 km west of the mine smelter. Soils were analyzed for metals (Cu, Ni, Pb, Zn, Cr, Fe, Mn, As, Pt, Se, Li, Sn, Co, Cd and Mo) and soil pH was also determined. The results revealed that soil pH is very low (extremely acidic) closest to the mine on the western side and is related to distance from the mine smelter in the direction of prevailing winds which blow from the east towards the west. Heavy metal concentration of Cu, Ni and Fe were higher closer to the mine smelter (2.5 km west) and decreased exponentially with distance from the smelter towards the western side. These heavy metals were lower on the eastern side at 2.5km east compared to the west (2.5 km west). The concentration of heavy metals from the soil followed the order Fe>Cu>Ni>Mn>Cr>Pb>Zn>As>Pt>Se>Li>Sn>Co>Cd>Mo at 2.5 km west, Fe>Cu>Mn>Ni>Cr>As>Zn>Co>Li>Sn>Pb>Se>Cd>Pt>Mo at 20 km west, Fe>Mn>Cr>Co>Zn>Ni>Pb>As>Li>Cu>Sn>Cd>Se>Mo>Pt at 55 km west and Fe>Mn>Cu>Cr>Ni>Pb>Co>As>Zn>Li>Se>Pt>Sn>Cd>Mo at 2.5 km east. The concentrations of Mn, Cu, Ni and Fe were above permissible limits at all four sites for Mn, 2.5 km west for Cu and Ni and 2.5 km west, 20 km west and 2.5 km east for Fe. Mining and smelting in Selebi-Phikwe has resulted in accumulation of heavy metals and soil acidification.

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Introduction

Geographically, the BCL Cu-Ni mine is located in Selebi-Phikwe, Botswana between longitudes 27° 47' East and 27° 53' East, and latitude 22° 55' South 22° 00' South (Ekosse *et al.*, 2005). Mining of sulphidic nickel–copper–cobalt ore in the Selebi-Phikwe area started in 1973 and has been the main activity since. The mine excavates and smelts mixed copper-nickel ore from several shafts (Mc Cammon *et al.*, 2006). Mined ore is concentrated and smelted for its copper (Cu), nickel (Ni) and cobalt (Co) minerals (Nkoma and Ekosse, 1999).

The mine produces flue gases through smelting activities (fig 1) and this flue gas has been shown to be of acid nature. Particulate air matter (PAM) in the flue gas contains a variety of heavy metals: lead (Pb), arsenic (As), chromium (Cr), cadmium (Cd), nickel Ni, Cu, and zinc (Zn) and can travel greater distances (Ekosse *et al.*, 2004) The flue gas also contains H_2S and SO_2 which may combine with atmospheric moisture to release H_2SO_4, the primary chemical constituent of acid rain which can lower soil pH surrounding the mine.

The slopes of the tailings dumps around the mine serve as migratory pathways for anions of SO_4^{2-} (sulphate), CO_3^{2-} (carbonate), Cl^- (chloride), NO_3^- (nitrate), PO_4^2 (phosphate), Cd, Co, Cr, Cu, Fe (iron), Ni, Se, and Zn to the subsurface environments (Ekosse *et al.*, 2003) and fine metal-bearing dust particles from these tailings dumps could be blown and carried over long distances. Mining and smelting activities are therefore sources of environmental contamination as soils represent direct sinks for contaminants emitted to the atmosphere by smelters and this is of particular concern to the country (Ekosse *et al.*, 2004). Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem. This happens after direct ingestion or contact with contaminated soil; the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytotoxicity,

reduction in land usability for agricultural production causing food insecurity (Ling *et al.*, 2007).

It is therefore important to continuously monitor the status of soil around mining environments in order to prevent adverse effects on humans. The maximum permissible ranges/limits in soil in Botswana have not been set and therefore ranges/limits from various sources are tabulated in Table 1.Very high concentrations of heavy metals have been found in plants and soils adjacent to smelting works (Wuana and Okieimen, 2011) and heavy metal contamination is reported to diminish exponentially with distance from the smelter while soil pH is said to increase with distance from the mine smelter. Information about level of heavy metal contamination and soil pH around the mine smelter is therefore needed for an accurate assessment of site contamination and treatment (Jadia and Fulekar 2009). The analysis of heavy metal concentrations in soils is therefore critical for policy making orientated toward reducing heavy metal inputs to soil and guaranteeing the maintenance or even the improvement in soil quality

This study was therefore aimed to assess the level of contamination by heavy metals and soil acidity (estimated from pH level) from BCL Cu/Ni mine smelter on soils on the eastern and western side of the mine smelter. The study is also aimed to compare the metal contents of soils with the maximum permissible ranges/limits set by various standard regulatory bodies.

Materials and methods

Soil sample collection

Soil was sampled (Crépin and Johnson, 1993) from four different sites around the BCL Cu/Ni mine in Selebi-Phikwe, Botswana: 2.5 km east, 2.5 km west, 20 km west and 55 km west of the BCL Cu/Ni mine smelter. The exact locations for all sampled sites were determined using global positioning system as follows: 2.5 km east (21°56´32.88"S; 27°53´9.95"E), 2.5 km west (21°57´16.93"S; 27°50´20.71"E, 20 km west (21°58´6.25"S; 27°40´5.90"E) and 55 km west

(21°55´55.57"S; 27°20´12.07"E). At each of these sites, soil was sampled from within ten randomly selected quadrants (100 m²). Five samples were collected (15cm in depth) per quadrant and all twenty samples were pooled to make a single site composite sample. Sampling was done yearly for three years from 2012 to 2014 in the month of October. The soil samples were bulked and transported to the laboratory at University of Botswana, Department of Biological Sciences in well labeled polythene bags. Foreign bodies like twigs and stones were removed and samples were air dried to constant weight and sieved (through 2mm sieve) in preparation for heavy metal analysis.

Soil analyses
In the laboratory, soil pH was measured in five replicates according to Hendershot *et al* (1993). 10 g of air dried soil (<2mm) was added to a beaker and to it 20ml of distilled water was added. The suspension was starred intermittently for 30 minutes and left to stand for 1 hour. Soil pH was then measured afterwards by immersing the electrode into the clear supernatant. Calibration of the pH meter was done using two buffer solutions of pHs 3, 7 and 10.

For heavy metal analysis, 0.05g of sieved soil was weighed and 3 acids were added for digestion: 0.5ml nitric acid, 2.5 ml hydrofluoric acid and 0.5 ml perchloric acid. Digestion was carried out in an ultrasonic bath at 50°C for 2 hours. The samples were then dried on a hotplate at 150°C. Another set of the three acids were then added for another digestion at the same ratios as the first cycle and the same procedure for digestion was done as described in the first cycle. After drying, 2 g of nitric acid was added to each sample and left to dissolve in a water bath at 50°c for 2 hours. After dissolving, 8g of deionized water was added to 2 g of the sample to make 10 g. This was used for heavy metal measurements and 15 elements [Cu, Ni, Fe, Mn(manganese) , Zn, As, Cd, Co, Cr, Mo (molybedenum), Pb, Se, Sn (tin), Li (lithium) and Pt (platinum)] were measured. Heavy metal content was then measured using a Thermo

Scientific™ iCAP™ 7400 ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry). The whole process was carried out on 5 replicates of each of the samples.

Quality control
For quality control, standard reference material for soil samples NCSDC 73319 (China national analysis Center for Iron and Steel) and AVG-2 (United States Geological survey) were used. Heavy metal limits of detections (LOD) were calculated using the formulae by Shrivastava and Gupta (2011).

$$LOD = X_{b1} + 3\ S_{b1}$$
Where X_{b1} is the mean concentration of the blank and S_{b1} is the standard deviation of the blank.

Statistical analysis
All the above procedures were repeated on samples collected in three different sampling periods (2012, 2013 and 2014) and pooled data is presented. The data was analyzed statistically with IBM SPSS statistics 22. In order to detect differences in the determined parameters, analysis of variance (ANOVA) was performed. Significant differences between the mean values of variables of treatments were determined according to Least Significant Difference (LSD) test at P=0.05 level. All values are means ± standard error.

Results and discussion
The results obtained showed significant differences in soil pH between the soils around the mine (p<0.05) as shown in figure 3. Soil pH is lowest (3.86) in soil closest to the mine on the western side at 2.5 km and this is considered as extremely acidic. A similar finding was reported in a study by Chopin and Alloway (2007) in Spain. Soil pH significantly increases with distance from the mine smelter towards the west with pH values of 4.3 (also considered extremely acidic) and 6.28 (slightly acidic) from 20km and 55 km west of the mine smelter respectively. These findings are consistent with the findings of studies on other mines (Klumpp *et al.*,

2003) where soil pH increased with distance from the mine. However soil pH is significantly higher (5.36)(strongly acidic) ($p<0.05$) in soil collected from the eastern side at 2.5 km from the mine smelter compared to samples from 2.5 km West of the same smelter (3.36) (Figure 2). This is because in Selebi-Phikwe there are easterly prevailing winds which may be blowing smelter flumes from the east of the mine smelter towards the west. Gases from smelter flumes may react with water resulting in acid rain which falls on the western side thus reducing soil pH. Smelter flumes are seldom blown towards the east thus there are lower chances of the eastern side receiving acid rain and so the soil pH is higher than the western side. Very low soil pH on the western side (2.5km west and 20km west) as shown in figure 2 indicate that acidification took place.

Table 1. Heavy metals permissible range/limits in soils.

Metal	Permissible range/limit
Cu	13-24 mg/kg (Kabata-Pendias, 2001)
	100 mg/kg (Kabata-Pendias and Pendias, 2001)[a]
Zn	45-100 mg/kg (Kabata-Pendias, 2001)
	300 mg/kg (Kabata-Pendias and Pendias, 2001)[a]
Cr	12-83 mg/kg (Kabata-Pendias, 2001)
	100 mg/kg (Kabata-Pendias and Pendias, 2001)[a]
	0-100 mg/kg (Sattar,1996)[e]
Cd	0.37-0.78 mg/kg (Kabata-Pendias, 2001)
	5 mg/kg (Kabata-Pendias and Pendias, 2001)[a]
	0-1 mg/kg (Sattar, 1996)[e]
Ni	100 mg/kg (Kabata-Pendias and Pendias, 2001)[a]
	0-20 mg/kg (Sattar, 1996)[e]
Pb	22-44 mg/kg (Kabata-Pendias, 2001)(Essington ,2004)[b]
	100 mg/kg (Kabata-Pendias and Pendias, 2001)[a]
Co	50 mg/kg (Kabata-Pendias and Pendias, 2001)[a]
Fe	1000 mg/kg (Kabata-Pendias, 2010)[d]
Mn	0.27-0.53 mg/kg (Kabata-Pendias, 2001)(Essington ,2004)[b]
	0-500 mg/kg (Sattar, 1996)[e]
As	>10 mg/kg (Adriano,2001)[c]

[a]maximum permissible agricultural soil concentration in European countries

[b]mean values for worldwide normal surface soils

[c] maximum permissible soil concentration

[d]safe limits for heavy metals in soil

[e]typical values for uncontaminated soil.

Table 2 shows the results of heavy metal concentrations on two certified standard reference materials (NCSDC 73319 and AVG-2) for Cd, Pb, Li, Mo, Co, Ni, Cu Zn, Sn, Mn and As. There was concordance between the results and certified concentrations in Table 2 and the recoveries obtained ranged from 91 % (As) to 106 % (Pb) for NCSDC 73319 and 94 % (Cu) for AVG-2 to 109 % (N).

Table 3 shows limit of detection (LOD) of Ba, Cd, Pb, Li, Mo, Ni, Zn, Sn, Mn, As, Cu, Pt, Cr, Se and Co. LOD is expressed as the analyte concentration corresponding to the sample blank value plus three standard deviation.

Table 2. Heavy metal analysis of reference soil samples. Each value is the mean ± standard error.

	NCSDC 73319 (Soil reference)				AVG-2 (Soil reference)		
Metal	Certified value (mg/kg)	Measured (mg/kg)	Recovery (%)	Metal	Certified value (mg/kg)	Measured (mg/kg)	Recovery (%)
Cd	4.3 ±0.23	3.97 ±0.3	92	Cr	17 ±0.18	16.3 ±0.15	96
Pb	98 ±2.6	103.4 ±3.4	106	Pb	13 ±0.3	13.8 ± 0.3	106
Li	35 ±0.7	36.42 ± 0.66	104	Li	11 ±0.29	11.31 ±0.2	103
Mo	1.4±0.06	1.21±0.04	86	Co	16±0.18	17±0.17	106
Ni	20.4 ±0.2	20.82 ±0.19	102	Ni	19 ±0.21	20.7 ±0.18	109
Zn	680± 8.9	658 ±7.8	97	Zn	86 ±2.1	91.5 ±3.2	106
Sn	6.1 ±0.09	6.43 ±0.08	105	Cu	53 ±0.86	49.7 ±0.55	94
Mn	1760±43.4	1741 ±46.7	99				
As	34 ±0.65	30.8±0.71	91				
Cu	21 ±0.37	21.5 ±0.6	102				

Heavy metals were found in soils from the four locations around Selelebi-Phikwe mine smelter. In figure 3, heavy metal concentration of Cu, Ni and Fe is higher at 2.5 km west of the mine smelter and it decreases exponentially with distance from the smelter towards the western side. They followed the order 2.5 km west> 20km west> 2.5 km east> 55 km west. Other elements however did not decrease exponentially with distance from the mine smelter as was the case with the ones mentioned above. This shows that the greatest pollution impact occurs towards the west in the direction of prevailing winds.

The windward sites (West) are assumed to be polluted whereas the leeward site (East) is assumed to be sheltered from pollution by smelter emissions. Several studies have shown that contaminant concentrations are greatest near the smelter, with the highest levels corresponding to the prevailing wind direction (Fernandez-Camacho *et al.*, 2010; Taylor *et al.*, 2010; Ojelede *et al.*, 2012. Most heavy metals did not follow the expected trend (Figure 3) and this shows that their presence is not due to mine smelter pollution but the geology of the area.

Table 3. Heavy metal limit of detection.

Metal	Limit of detection (mg/kg)
Cd	0.0113
Pb	0.0436
Li	0.1257
Mo	0
Ni	0.2537
Zn	0
Sn	0.0327
Mn	0.1157
As	0.1801
Cu	0
Pt	0
Cr	0.0331
Se	0
Co	0

The concentration of heavy metals from the soil at 2.5km West followed the order Fe>Cu>Ni>Mn>Cr>Pb>Zn>As>Pt>Se>Li>Sn>Co>C

d>Mo. 20km west followed the order Fe>Cu>Mn>Ni>Cr>As>Zn>Co>Li>Sn>Pb>Se>Cd>Pt>Mo. 55km west followed the order

Fe>Mn>Cr>Co>Zn>Ni>Pb>As>Li>Cu>Sn>Cd>Se> Mo>Pt and 2.5km east followed the order Fe>Mn>Cu>Cr>Ni>Pb>Co>As>Zn>Li>Se>Pt>Sn>Cd>Mo (figure 3).

Cu, Ni and Zn concentration closest to the mine on the western side were slightly lower than findings from studies by Ngole and Ekosse, (2012) where Cu was 252.4 mg/kg, Ni 153 mg/kg and Zn 30.4 whereas in our study Cu was 113 mg/kg, Ni 67mg/kg and Zn 3.23 mg/kg. Even though the sites where the soils

were sampled are all on western side of the mine smelter, difference in heavy metal concentration may be attributed to differences in geology of sampling sites. The other reason may be that Ngole and Ekosse (2012) sampled soil between January and July while in our study soil was sampled in October. These findings are however parallel to those by Likuku *et al* (2013) who got very low concentrations of Cu, Ni, Pb, Zn, Mn, Fe and Co at both the leeward and windward side as compared to our study. This difference may also be allotted differences in sampling sites.

Fig. 1. Smelter emissions at the BCL Cu-Ni mine in Selebi-Phikwe, Botswana (Picture taken by Raviro Vurayai, year 2014).

There was a negative correlation between levels of Cu, Ni and Fe found in the soil, and distance from the mine smelter towards the west. A positive correlation was also observed between pH of samples and distance from the mine smelter in the western direction. This implicates the smelter as the source of air pollutants; copious amounts heavy metals being deposited in heavier particulate matter closer to the site. Highly acidic soil closest to the smelter on the western side (figure 2) may be attributed to the undiluted fumes interacting with atmospheric moisture and falling rain to form acids. As the fumes are blown over long distances from the smelter, dilution effect on acid gases consequently results in

reduction on the amount of acid produced.

In comparison with heavy metals permissible ranges/limits in soils in Table 1, Zn, Cd, Cd, Pb, Co, and As concentrations in all the four sites were below the permissible limits. Mn was above the permissible limits at all four sites while Cu and Ni were above the permissible limits at 2.5km west only. Fe was above permissible limits at 2.5 km west (4.55x), 20 km west (1.81x) and 2.5 km east (1.01). Mn, Cu, Fe and Ni are toxic to plants at high concentrations. High concentrations of Mn may pose a serious health threat for communities around the mine. Previous researches have shown that Mn could be linked to the

initial symptoms of Parkinson's disease (Normandin and Hazell, 2002) while exposure to high levels of Cu can result in a number of adverse health effects. Cu has been associated indirectly with a number of neurological disorders, including Alzheimer's disease and prion diseases (Llanos & Mercer, 2002).
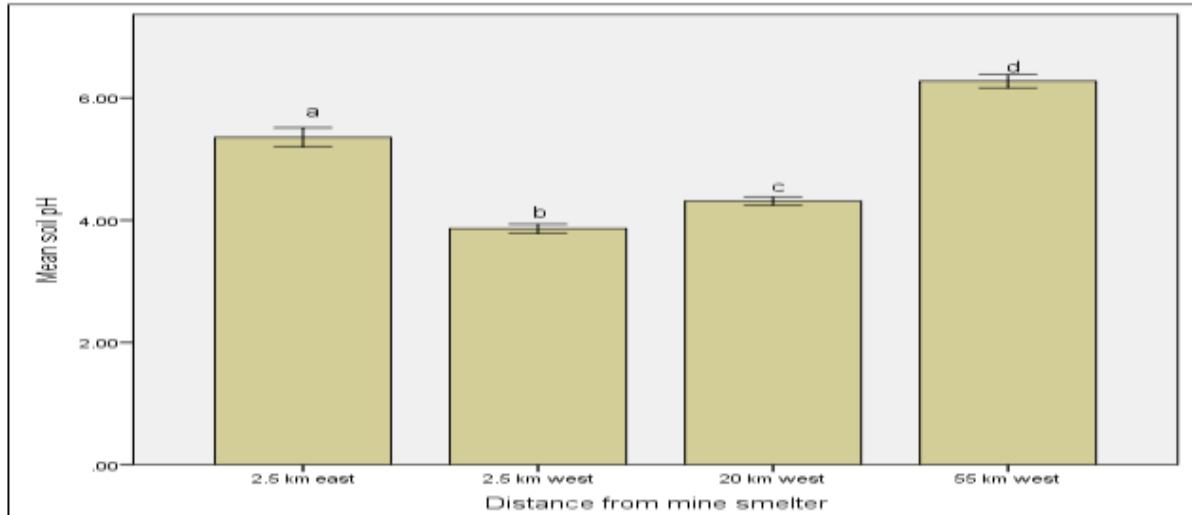

Fig. 2. Soil pH around Selebi-Phikwe Cu/Ni mine. Error bars indicate ± standard error and bars with different letters are significantly different at p ≤ 0.05 based on F test and LSD.
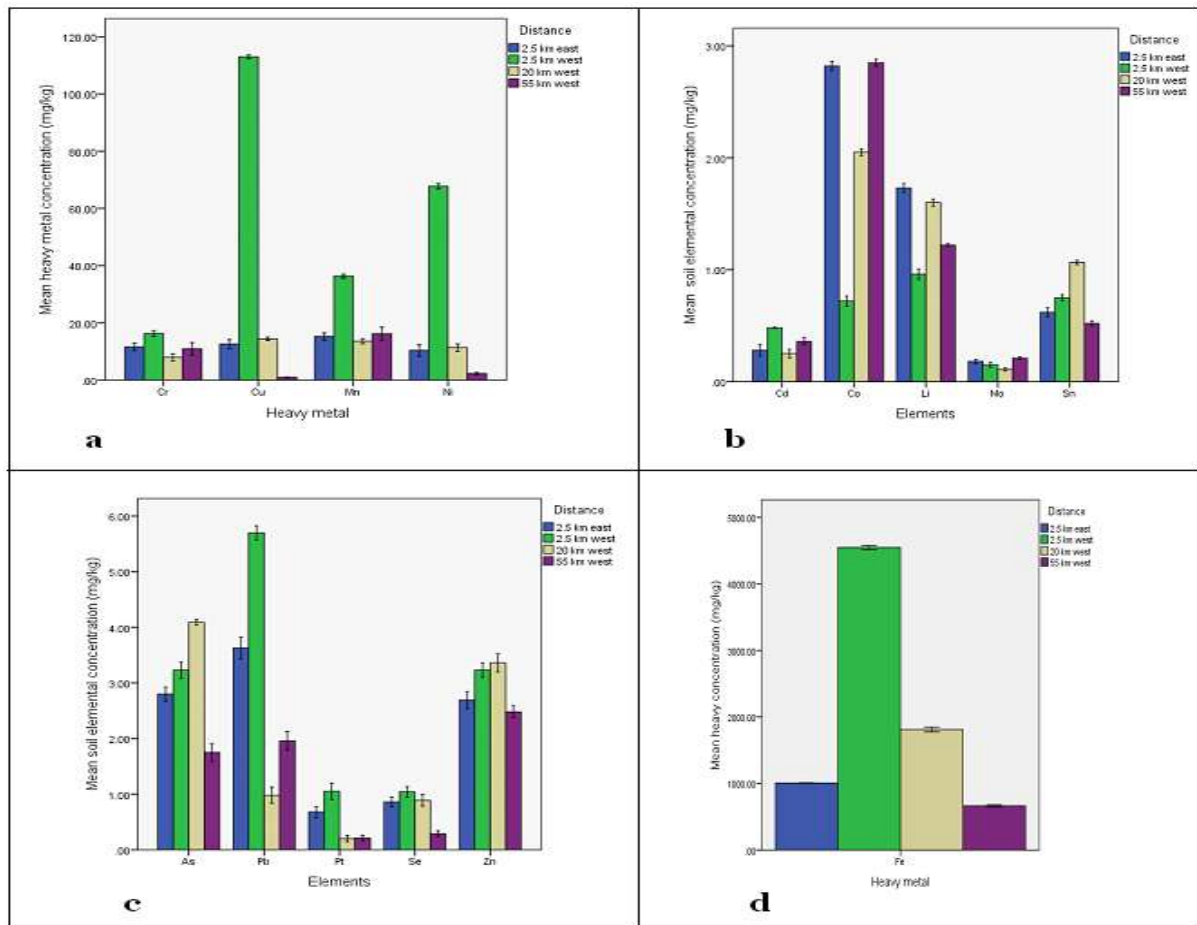

Fig. 3. Mean soil elemental concentration (mg/kg) in soil collected from different directions from the BCL-Cu/Ni mine smelter in Selebi-Phikwe, Botswana. Error bars indicate ±standard error.

Ni has been shown to be carcinogenic in high concentrations. Exposure to Ni compounds causes irreversible damage to the central nervous system, cardiovascular system, lungs and gastrointestinal tract (Axtell *et al.*, 2003). In plants Ni is responsible for chlorosis, yellowing and necrosis of leaves, deformation of plant parts, stunted growth and generation of free radicals (Halliwell and Gutteridge, 1999). Effect of Fe in plants at high concentrations results in dark green foliage, stunted top and root growth, thickening of roots, brown spots on leaves starting from tip of lower leaves, dark brown and purple leaves sometimes in the same plant (Prasad, 2013). In humans Fe toxicity causes pulmonary siderosis, a kind of pneumoconiosis caused by the long-term inhalation of iron dust (Banerjee *et al*, 2006).

Heavy metals introduced in soils remains even after their addition to soils have been stopped due to persistence and non-degradability (Gutiérrez-Ginés *et al.*, 2010, Ezeh and Chukwu, 2012). Elevated metal concentrations can cause negative effects on soil such as reduction of soil microbial biomass levels which are responsible for maintenance of soil fertility for optimum crop yield, affecting nitrogen-fixation and reduction in certain enzyme activities (Hesterberg, 1998 and Jung, 2008).

Conclusion

The results of this study indicates that Mn (at 2.5km east, 2.5 km west, 20km west and 55 km west), Cu and Ni (at 2.5km west) and Fe (at 2.5 km west, 20 km west and 2.5 km east) concentrations are above the critical values reported by various environmental protection agencies for these particular elements. Soil around Selebi-Phikwe mine is not polluted with Pb, Zn, Cr, As, Pt, Se, Li, Sn, Co, Cd and Mo but with gradual build up they could become polluted. There was a negative correlation between levels of Cu, Ni and Fe found in the soil, and distance from the mine smelter towards the west, implicating the smelter as the source of air pollutants. Mining and smelting in Selebi-Phikwe, Botswana resulted in soil acidification

around the mine smelter. Soil pH is lowest closest to the mine on the western side of the mine smelter where pH is extremely acidic. Soil pH is also related to distance from the source of metal particulates in line with direction of prevailing winds which blow from east towards the west.

There is also a positive correlation between soil pH and distance from the mine smelter towards the west, implicating the smelter as the source of acidic air pollutants more concentrated closer to the smelter.

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