

Impact of Cyanide Utilization in Mining on the Environment

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ABSTRACT: Cyanide (CN) is a toxic species that is found predominantly in industrial effluents generated by metallurgical operations. Cyanide's strong affinity for metals makes it favorable as an agent for metal finishing and treatment and also as a lixiviate for metal leaching, particularly gold. These technologies are environmentally sound but require safeguards to prevent accidental spills from contaminating soils as well as surface and ground waters. In this work, total cyanide, sodium, cadmium, iron, zinc and copper concentrations were determined in soil, cassava, hand dug wells and pipe-borne water from Bibiani, a gold mining town in the Western Region of Ghana. Total cyanide levels in soil ranged from 6.04 to 26.17 mg/kg and in water, from 2.17 to 7.83 mg/L. Total cyanide concentrations in raw cassava ranged from 82.45 to 142.91 mg/kg fresh weight. The cooked cassava had cyanide concentrations ranging from 6.79 to 24.91 mg/kg and the cassava peels, 360.05 to 509.51 mg/kg. Sodium concentrations ranged from 998.1 to 1794.7 mg/kg in the soil, 25.94 to 29.92 mg/L in the water and 114.7 to 159.6 mg/kg in cassava. The concentration of iron in the soil ranged from 77.88 to 302.08 mg/kg whilst in water and cassava, iron was below detection limit. Copper concentrations ranged from 12.4 mg/kg to 115.4 mg/kg in soil, 4.6 to 6.0 mg/kg in cassava and below detection in water. The zinc concentrations ranged from 24.1 to 170.3 and 7.6 to 11.6 mg/kg, in soil and cassava respectively. Zinc was below detection in most of the water samples and cadmium was generally low in all the samples. The pH of the soil, water and cassava ranged from 3.88 to 6.95, 3.14 to 7.44 and 5.42 to 5.60 respectively. The moisture content of the soil ranged between 2.47 and 35.40% and that of cassava, 56.08 to 56.87%. Electrical conductivity and total dissolved solids of water ranged from 34 to 155.5 $\mu\text{S}/\text{cm}$ and 31 to 89 mg/L respectively. The results showed a correlation between the metal and cyanide concentrations in all the samples.

Key words: Cyanide, Soil, Water, Cassava, Metals

INTRODUCTION

Cyanide is a fast acting poison because it binds to key iron-containing enzymes required for cells to use oxygen and as a result tissues are unable to take up oxygen from the blood (Ballantyne, 1975). In the absence of first aid, poisoning from gas inhalation, ingestion or absorption through the skin, can kill within minutes (Gosselin *et al.*, 1976). Some of the cyanide is changed to thiocyanate, which is less harmful, and leaves the body in the urine. Some can also combine with hydroxocobalamin to form vitamin B12. A small amount of cyanide is converted in the body to carbon dioxide, which leaves the body

in the breath. Most of the cyanide and its products leave the body within the first 24 hours after exposure (WHO, 1996).

The degree of dissociation of various metalocyanide complexes at equilibrium increases with decreased concentration and decreased pH, and is inversely related to their highly variable stability (APHA, 1998, Burdick *et al.*, 1948). The zinc- and cadmium- cyanide complexes dissociate almost completely in very dilute alkaline solutions; thus these complexes can result in acute toxicity to fish at pH 8 or below (APHA, 1998). In equally dilute solutions there is much less dissociation for the nickel-cyanide complex. The more stable

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cyanide complexes are formed with copper (I) and silver (I). The iron-cyanide complexes are very stable and therefore not toxic; in the dark, acute toxic levels of HCN are attained only in concentrated and aged solutions. However, dilute solutions of these complexes are subject to extensive and rapid photolysis on exposure to direct sunlight yielding toxic HCN (APHA, 1998, Smith, 1980 and Burdick *et al.*, 1948).

Between 1989 and 2003, Ghana recorded about eight accidental spills of cyanide in the mining industries (Amegbey and Adimado, 2003) and all these had adverse health effects on human beings and caused a lot of deaths to aquatic living organisms. A number of foodstuffs contain significant levels of cyanogenic compounds and can contribute to cyanide poisoning (Casadei *et al.*, 1984). They include lima beans, sorghum, sweet potatoes, maize, millet, bamboo shoots, and cassava, a staple foodstuff in many regions of Africa (Solomonson, 1982). These foodstuffs have the tendency to increase their cyanide content if the soils on which they are cultivated are

contaminated with cyanide. Gold mining has played a central role in the social, political and economic life of Ghana and its people for more than 500 years (Amegbey and Adimado, 2003). The favorable investment climate in Ghana has attracted a number of mining companies in the past 10-15 years. Currently, the majority of the mines in Ghana are surface mines, and the processing techniques adopted include carbon in column (CIC), carbon in leach (CIL) and biological oxidation (BIOX) (Flynn *et al.*, 1995). All these techniques employ cyanide and the method used to detoxify the cyanide is alkaline chlorination and occasionally, hydrogen peroxide (Ingles *et al.*, 1981; White, 1972; Dobson, 1947; Zaidi *et al.*, 1987; Staunton *et al.*, 1988).

MATERIALS & METHODS

The soil, water and cassava samples were collected from Bibiani Old Town and Zongo which are between 100 and 1000 meters away from the mines. (Fig.1). below shows the map of Bibiani town, the mines and sampling sites.

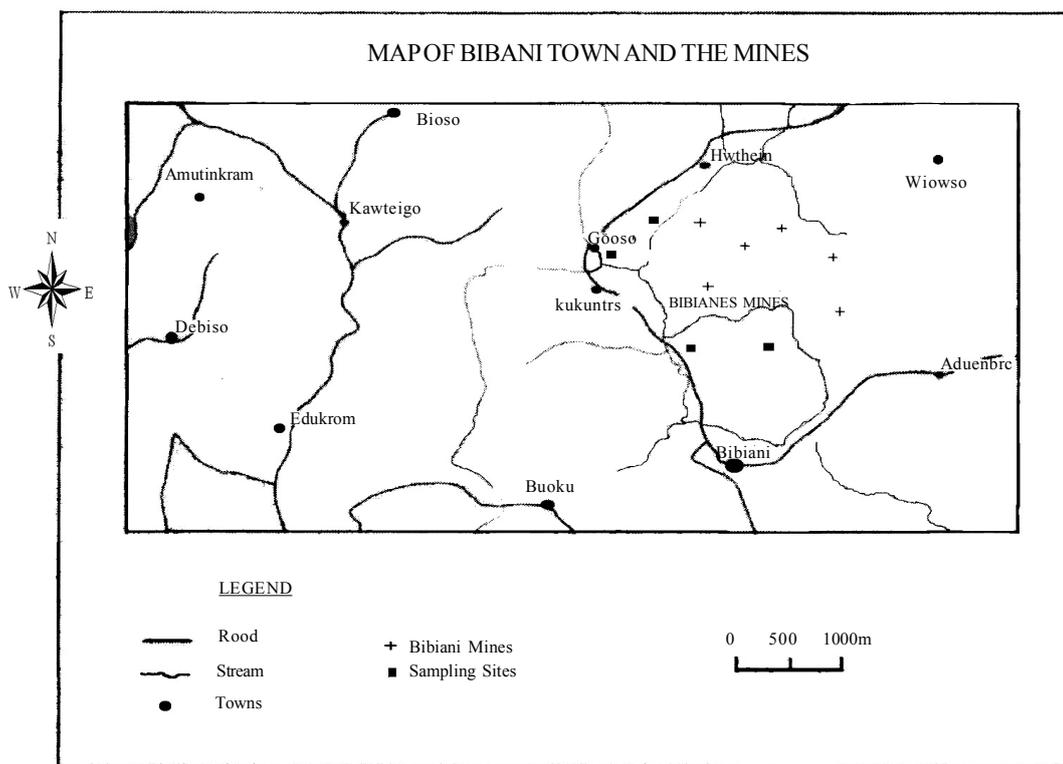


Fig. 1. Map of Bibiani town, the mines and sampling sites

About 500 to 1000g of soil samples were taken from four different farms located around the Bibiani mines. The soils were collected at depths corresponding to 0-15cm and 15-30cm on each farm with a sterilized soil auger which was rinsed with a lot of distilled water and dry cleaned after every sampling to avoid contamination. The samples were labeled F₁TS, F₁DS, F₂TS, F₂DS, F₃TS, F₃DS, F₄TS, and F₄DS. Control soil samples were taken from KNUST Agricultural Farm and labeled F₅TS and F₅DS. F₁, F₂, F₃, and F₄ represent the four farms from where the samples were taken at Bibiani, F₅, and the KNUST Agricultural Farm. TS and DS represent topsoil (0-15cm depth) and subsurface soil (15-30cm depth) respectively. All the soil samples were then put in a cool ice chest at 4°C and brought to the laboratory. The samples were then stored in a refrigerator at the same temperature.

Two liters each of five water samples were taken from hand-dug well, borehole and pipe-borne water sources at five different sites in Bibiani for the determination of cyanide and physicochemical parameters. Of the five water samples collected in Bibiani, two were from hand-dug wells, one from pipe-borne water and two from boreholes. The two water samples from hand-dug wells were labeled HS₁ and HS₂, the pipe-borne water, HS₃ and the two water samples from boreholes as CM₁ and CM₂. The same volumes of water were collected from KNUST as control samples and labeled HS₄. The control water sample was pipe-borne water. Each water sample was collected into a white sterilized plastic gallon. The water samples from the hand-dug wells were fetched with a black plastic bag tied to a nylon rope measuring about 10 meters in length. Water from the bore-holes was fetched by means of a pump. The pipe-borne water samples were fetched directly from the tap. Water samples were tested qualitatively for sulfides on the field with lead acetate paper. pH of the water samples were done on site with a portable pH meter. The plastic containers were then covered with air-tight lids and put into an ice box and taken to the laboratory. The samples were then stored in a refrigerator at 8°C prior to chemical analyses.

On the average, three cassava root tubers weighing 600 to 800g were obtained from each plant. Cassava samples were taken from the same

farms as the soil samples and labeled F₁C, F₂C, F₃C and F₄C. A control cassava sample labeled F₅C was taken from KNUST Agricultural Farm. The root tubers were uprooted with a stainless steel machete. The cassava samples were put in black polyethylene bags and placed in an ice box at 4°C before conveying them to the laboratory. The pH and moisture content of the soil and cassava samples, total ash content of the cassava sample, pH, total dissolved solids and conductivity of water samples were determined. Soil, water and cassava samples were individually digested with concentrated sulphuric acid and Magnesium chloride and distilled. The distillate was collected in 1.25N sodium hydroxide. Colorimetric method using Pyridine-Barbituric acid reagent as coupling agent and UV-Visible spectrophotometer was used to measure the cyanide concentration. A recovery was done to check the reproducibility of the method.

All the water, soil, and cassava samples were acid digested with concentrated hydrochloric acid and were analyzed for sodium using JENWAY PFP7 flame photometer. Iron, zinc, copper and cadmium were determined after acid digestion of fresh water, soil and cassava samples with concentrated nitric acid and concentrated sulfuric acid at a ratio of 4:1 using Buck Scientific 210 VGP Flame Atomic Absorption Spectrophotometer.

RESULTS & DISCUSSION

The physicochemical properties, metals concentrations and levels of cyanide in soil, water and cassava samples are presented in (Tables 1, 2 & 3) respectively. Each value is the mean of three replicate samples. The interpretations of the findings are also discussed. The pH of soil samples ranged from 3.88 to 6.95 which fall within the acidic region. The soil samples from Bibiani had low pHs (below pH 6) with the exceptions of F₃TS which was 6.26 and F₄TS giving 6.05. The control samples from KNUST, F₅TS and F₅DS gave pH of 6.95 and 6.54 respectively, which were almost neutral. From the results obtained, it can be observed that the pH decreased with increasing depth (Table 1). The top soils had higher pH than their subsurface soils. Metal adsorption to soils increases with increase in pH, so desorption and solution concentration of metals are greatest in acid

soils (Alan, 1994). The mobility and solubility of metals increase with decreasing pH. At low pH, hydrogen ions compete with metals for exchange sites on soil particles. Cadmium and zinc are relatively mobile within a pH range of 4.2 to 6.6 while copper is only slightly mobile at this pH (McEldowney *et al.*, 1993). Lower pH also favors the dissociation of metalocyanides which frees cyanide initially bonded to metals (APHA, 1998). Free cyanide has a boiling point of 25.6°C and will volatilize at temperatures above the boiling point. Cyanide concentrations were high in soil samples that had pH close to neutral and low in soil samples that had low pH. At neutral pH, the rate of dissociation of metalocyanides is slow and very stable metalocyanides such as Ferro cyanide complexes will not dissociate. The volatilization of the cyanide in these soils will be low and hence these soils will have higher total cyanide concentrations.

The moisture content for the top soils (depth of 0-15cm) was higher than those of the subsurface soils (depth of 15-30cm). The trend was not different for the soil samples from KNUST (F₅). The soil samples from KNUST had the lowest soil moisture content for both the top soil and the subsurface soil. The top soil (F₅TS) recorded 3.84% and the subsurface soil (F₅DS), 2.47%. The highest moisture content for the top soils was 35.40% for the sample from farm 1 (F₁TS) at Bibiani while the highest for the subsurface soils was 21.36% for the sample from farm 2 (F₂DS) also at Bibiani. Cyanide concentrations in the soils were high in the top soils as compared to their subsurface soils with the exception of farm 4 (F₄) which was vice versa. The pH of the soils decreased as moisture content decreased and increased as moisture content increased. Soil moisture content is increased by rainfall and irrigation and the increase in soil water dilutes the acid in the soil and thereby increases the pH. As the pH increases, the total cyanide concentration of the soil also increases. The soil water may cause leaching of the water soluble metalocyanides such as zinc-cyanide and Ferro cyanide complexes from the topsoil into the subsurface soil and below.

The total cyanide concentration in the soils ranged from 6.04 mg/kg to 26.17 mg/kg. Cyanide concentrations were generally higher in the soil

samples with high pH and high moisture content than those with low pH and low moisture content with the exception of soil samples from farm 4 (F₄) which had a cyanide concentration of 22.14 mg/kg, pH of 6.05 and moisture content of 20.00% for the top soil (F₄TS) and a cyanide concentration of 26.17 mg/kg, pH of 5.79 and moisture content of 12.00% for the subsurface soil (F₄DS). This anomaly in the trend could be due to leaching and migration of sodium cyanide from the mines at Bibiani. This assertion can be supported with the concentrations of sodium in F₄TS and F₄DS which are 1097.7 mg/kg and 1346.6 mg/kg respectively.

With the exception of soil samples from farm 2 (F₂TS and F₂DS) and farm 3 (F₃TS and F₃DS) which had their subsurface soils (DS) having lower sodium concentrations than their topsoil (TS), the subsurface soils had higher sodium concentrations than their top soils. Though most soil nutrients are found in the top soil, leaching could take place and could cause the nutrients to get to the subsurface soil below. A high concentration of sodium in the soil can lead to the formation of sodium cyanide with cyanide in the soil at an alkaline pH. However, the pH of all the soil samples fell within the acid and neutral region which wouldn't favor the formation of sodium cyanide. Sodium in the Bibiani soils might come from the sodium cyanide used in the mines and application of sodium containing fertilizer. Since most of the soils had acidic pH, sodium cyanide would dissociate and hydrogen cyanide could be formed. This would volatilize because of its low boiling point leaving sodium ions in the soil.

The highest iron concentrations were obtained from soil samples collected from farm 4 (F₄). The top soil (F₄TS) recorded 302.1mg/kg and the subsurface soil (F₄DS) recorded 291.5 mg/kg. The abundance of iron in the soil will cause the formation of hexacyanoferrate complexes which are very stable. Cadmium concentrations were below detection limit of 0.25mg/kg in farm 4 top and subsurface soils (F₄TS and F₄DS). It could be inferred from the results that cadmium is not prevalent in soils in the areas where the soil samples were collected. Therefore, cadmium-cyanide complexes are rare in these areas. The highest concentrations of copper were recorded in the soil samples from farm 4 (F₄) with the top

soil (F₄TS) having 115.4mg/kg and subsurface soil (F₄DS) having 97.2 mg/kg. The other soil samples from Bibiani recorded copper concentrations below 53mg/kg in both their top soils and subsurface soils. High copper concentrations in the soil samples will favor copper-cyanide complex formation causing cyanide to stay in the soil without volatilizing.

Zinc concentrations were higher than copper and cadmium in the soil samples. With the exception of farm 3 where the topsoil (F₃TS) had a lower concentration of 24.1mg/kg than the subsurface soil (F₃DS) which had 28.8mg/kg, the top soils recorded higher zinc concentrations of

zinc than the subsurface soils. This observation may be due to excessive application of zinc containing fertilizers on the farms. Slow leaching process due to poor porosity of the soils could be a factor for lower concentrations of zinc in the subsurface soils. High concentration of zinc in the soils favors the formation of zinc-cyanide complexes which are stable and do not cause the release of cyanide in the soils. Results (table 1) generally indicate that the top soils had higher concentrations of the metals (Fe, Cu and Zn) than the subsurface soils. Similarly, the cyanide concentrations in the top soils were higher than those in the subsurface soils.

Table 1. Physiochemical properties, metals concentrations and levels of cyanide in soil

Sample	pH	Moisture %	Na (mg/kg)	Fe (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	CN (mg/kg)
F ₁ TS	4.56	35.40	1396.4	151.4	0.2	42.0	159.0	6.04
F ₁ DS	4.06	14.49	1695.1	155.6	0.2	31.1	142.8	6.04
F ₂ TS	4.71	25.98	1794.7	200.4	1.9	52.2	170.3	14.09
F ₂ DS	3.88	21.36	1745.0	159.6	0.4	42.2	159.1	10.06
F ₃ TS	6.26	10.00	1595.5	110.8	2.8	12.4	24.1	22.14
F ₃ DS	5.95	8.00	998.1	96.9	2.8	14.7	28.8	22.14
F ₄ TS	6.05	20.00	1097.7	302.1	bd	115.4	128.4	22.14
F ₄ DS	5.79	12.00	1346.6	291.5	bd	97.2	87.7	26.17
F ₅ TS	6.95	3.84	1446.2	115.4	0.5	30.3	49.7	10.06
F ₅ DS	6.54	2.47	1545.7	77.9.0	0.6	35.2	39.0	10.06

TS- Top soil, DS- Subsurface soil, bd-below detection limit

Table 2. Physiochemical properties, metals concentrations and levels of cyanide in water

Sample	pH	EC (µS _{cm} ⁻¹)	TDS (mg/L)	Na (mg/L)	Zn (mg/L)	Cd (mg/L)	CN (mg/L)
HS ₁	3.14	155.5	89	25.94	bd	bd	5.22
HS ₂	3.22	128.3	73	29.92	bd	bd	5.22
HS ₃	7.44	54.5	31	25.94	1.24	bd	3.47
CM ₁	3.43	106.4	61	28.92	bd	bd	7.83
CM ₂	3.27	109.3	62	29.92	bd	bd	7.83
HS ₄	7.41	34.5	24	25.94	0.8	bd	2.17

bd-below detection limit

Table 3. Physiochemical properties, metals concentrations and levels of cyanide in cassava

Sample	pH	Moisture (%)	Ash (%)	CN (flesh) (mg/kg)	CN(peels) (mg/kg)	Na (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)
F ₁ C	5.42	56.08	0.97	82.45	373.64	149.6	4.6	7.6	1.4
F ₂ C	5.50	56.82	1.12	158.54	400.82	159.6	6.0	9.4	1.2
F ₃ C	5.60	56.79	0.95	140.61	509.51	134.7	5.4	11.6	0.6
F ₄ C	5.45	56.87	1.24	138.97	464.22	114.7	5.9	10.8	0.4
F ₅ C	5.56	56.19	0.98	142.91	360.05	134.7	4.6	7.8	0.4

The pH of the borehole and hand-dug water samples show that they are highly acidic. The high acidity will lead to an increase in the dissociation of available cyanide complexes and hence to an increase in the release of free cyanide into the water. The effect will be an increase in the concentration of free cyanide in the water. The acidic nature of the ground water could be due to the type of bedrock since all the soil samples from Bibiani were found to be acidic. The high conductivity measurement of a cyanide containing solution with low pH shows that there could be a reduction of cyanide concentration in the solution through volatilization of free cyanide at temperatures above 25°C.

The ground water samples recorded TDS measurements ranging from 61 to 89mg/L. Pipe-borne water sample from Bibiani, HS₃ recorded a TDS measurement of 31mg/L. As the total dissolved solids increase, conductivity also increases. The total cyanide concentration was determined for all the water samples. The cyanide levels in the water samples ranged from 2.47 to 7.87mg/L. The data on tolerable total cyanide concentration level in drinking water is not available however the acceptable free cyanide level for drinking water is 0.2mg /L [USEPA, 1994]. The pipe-borne water samples, HS₃ and HS₄ had total cyanide concentrations of 3.47mg/L and 2.17mg/L respectively. These levels are lower than that of the borehole water. Cyanide in the soil may leach into the subsurface ground water and thereby causing an increase in the cyanide concentration. Sodium and other alkali metals in the water would also aid the formation of metalocyanides which would not volatilize at ambient temperature.

Water samples were analyzed for sodium, iron, copper, zinc and cadmium. Iron and copper were below detection in all the water samples. The results of sodium, zinc, and cadmium analyses in the water samples are shown in the table below. HS₃ and HS₄ had 1.24mg Zn/L and 0.8mg Zn/L respectively and HS₃ had 0.08mg Cd/L. Both samples came from pipe-borne water sources. The effect of iron, copper, cadmium and zinc complexes on the total cyanide content of the water samples is negligible. Sodium levels in the water samples from Bibiani boreholes ranged from 25.94 to 29.92 mg/L. The control sample from KNUST had sodium concentration of 25.94mg/L. The amount

of sodium in the water is in excess of the amount of total cyanide obtained. This shows that not all the sodium in the water is in the form of sodium cyanide. Cyanide may also be lost through volatilization in the water because of the low pHs of the borehole water leaving sodium ions in the water. The sodium in the borehole water samples may come from the soil which may be contaminated with sodium cyanide from the mining activities.

The pH of the cassava samples ranged from 5.42 to 5.60 which make them slightly acidic. The final step in cyanide production which is the conversion of acetone cyanohydrins (the deglycosylation product of linamarin) to cyanide and acetone occurs at pH's greater than 5.0 (White *et al.*, 1998). This means that the cassava samples at the pH range quoted above will have all the acetone cyanohydrins present in them converted to free cyanide and acetone. The cyanide concentration will therefore be reduced since free cyanide will volatilize at temperatures above 25.6°C. The available cyanide in the cassava will be due to the linamarin present.

The moisture content of cassava from the four different farms at Bibiani and one farm from KNUST, Kumasi are shown in the table above. The moisture content of the cassava samples from Bibiani ranged from 56.08% to 56.87% and that from KNUST (F₅C) was 56.19%. The moisture content of the soils from which the cassava samples were taken shows that the moisture in cassava is not affected much by the soil moisture content, however, the moisture in cassava could cause the migration of free cyanide from the cassava tuber to the surrounding soil solution after the conversion of acetone cyanohydrin to acetone and cyanide. The ash content of the cassava from Bibiani ranged from 0.95 to 1.24% and that of F₅C was 0.98 which fell within the range of that from Bibiani. The ash content generally reflects the overall level of the mineral status (mineral salts, carbonates, phosphates, silicates, silica, etc) of the cassava. From the results obtained, it can be deduced that cassava contains mainly carbohydrates and other organic materials and minute amounts of minerals. The percentage ash content may be due to the presence of sodium and low concentrations of heavy metals in the cassava samples.

The cyanide concentration in cassava ranged from 82.45 to 158.54 mg/kg. The range falls within the WHO cyanide range of 40 to 400 mg/kg fresh weight (WHO, 1996). The cyanide concentration in cassava is caused mainly by the conversion of acetone cyanohydrins in cassava to acetone and cyanide and the presence of linamarin in the cassava. Cyanide in the soil may also increase the cyanide concentration in the root tuber through osmosis. Factors such as the nature of soil, climatic conditions and cyanide contamination of the soil can also affect the cyanide concentration. The peels had cyanide concentrations ranging from 360.05 to 509.51 mg/kg. The cyanogenic levels in the cassava peels could pose as health risks to livestock such as goats and sheep which feed on it. Iron in all the cassava samples was below a detection limit of 1.5 mg/kg. Sodium concentrations in the cassava samples from Bibiani ranged from 114.7 to 159.6 mg/kg and that of KNUST (F₅C) was 134.7 mg/kg. The zinc concentrations ranged from 7.6 to 11.6 mg/kg, copper concentrations, 4.6 to 6.0 mg/kg and cadmium, 0.4 to 1.4mg/kg. Generally, in comparison to soils, the levels of the heavy metals were low in the cassava samples. Iron even though had the highest concentration in the soils was below detection in the cassava. The possibility of the presence of some minerals and heavy metals in the cassava tuber is dependent on the solubility of the metals and their complexes in water. Cassava roots absorb water from the soil for photosynthesis and subsequently absorb water soluble minerals and heavy metals. The sodium concentration in the cassava is dependent on the concentration of sodium in the soil. The high concentration of sodium in the cassava could possibly come from contamination of the soil with sodium cyanide from the mining activities. This could contribute to the increase in the cyanide concentration in cassava from Bibiani. Cyanide in cassava is mainly from the presence of acetone cyanohydrins and linamarin in the cassava however, pollution of the soil with cyanide will increase its amount.

CONCLUSION

Free cyanide would volatilize at temperatures slightly above ambient temperatures because its boiling point is 25.6°C. However, the availability of metals would stabilize cyanide in the metallic

complex forms and thereby cause its retention in the environments at temperatures far above ambient temperature. Results obtained shows that as levels of metals increased, the cyanide levels also increased in most cases in all the samples analyzed. Even though most cyanide complexes are not poisonous, poisonous cyanide may be released if environmental conditions such as pH should change.

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