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Studies on the Contribution of Fertilizers to Heavy Metal Levels in Soils and Cocoa from some Cocoa Farms in the Western Region of Ghana

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Abstract

Continuous applications of fertilizers to soils are known to increase heavy metal concentrations to levels that may eventually exceed natural levels in soils. In this study, the levels of heavy metals comprising, Cu, Pb, Mn, Zn, Ni, Cd, Cr, and Fe in five major fertilizers namely, Cocoa Asaasewura; Sidalco Balanced; Sidalco Potassium Rich; Cocofeed; and Nitrabor usually supplied by Ghana Cocoa Board (COCOBOD) to cocoa farmers, were determined. In order to assess the possible contributions of these fertilizers to the background levels in the soil and cocoa beans, the levels of the heavy metals were also determined in farm soils and cocoa bean samples from farms that have been fertilized for at least three years. Results from the analyses indicated that in general, Sidalco Balanced and Sidalco Potassium Rich had relatively very high levels of Mn, Cu and Zn but low levels of Pb, Ni and Cd. Cocofeed and Asaase-wura also had very high levels of Fe, Ni, Pb and Cd. Nitrabor generally had the least levels for almost all the metals. Fe occurred as the highest metal in all cases while Zn was the least recorded metal in the fertilizers. In general, contributions from the fertilizers to the metal levels in the soil and in the cocoa beans have been found to be minimal and fall within acceptable limits in the cocoa beans.
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Keywords: Fertilizers, Heavy metals, Soils, Cocoa

1. Introduction

Fertilizers are soil nutrient enhancements applied to the soil to promote plant growth. Some of the main chemical components of fertilizers are nitrogen, phosphorus and potassium. They are the most effective means of increasing crop production and of improving the quality of food and fodder (http://www.transpaktrading.com). These elements are essential in the growth of plants and hence the addition of fertilizers mostly results in increase yields of crops. However other elements mostly heavy metals which either have no known use or may be toxic to man and plants are often found in minutes quantities in these fertilizers, most of which are responsible for many adverse health effects (Alloway, 1995).

A wide variety of unsafe metals may exist in fertilizers which may include: arsenic, lead, cadmium and mercury (Foster, 1998). According to the Environmental Protection Agency, of the USA, these metals are known to be potentially toxic to humans contributing to cancer, developmental effects, birth defects, reproductive problems, and liver and kidney damage. Children are particularly susceptible to the toxic effects of fertilizers as they spend more time on the ground and tend to put their hands in their mouths without washing them (Goyer and Clarkson, 2001). Exposure to heavy metals in adults may also occur through inhalation and skin contact when the fertilizer is applied using the bare hand (Minnesota Dept. of Health Control, 1999).

Ghana is known to produce well fermented cocoa beans that attract a high quality premium and must maintain if not improve the level of confidence and trust of buyers. One big challenge is to ensure consistency in the quality of cocoa that is supplied.In an effort to boost the country's cocoa production whiles maintaining this high quality standard, the Ghana Cocoa Board has embarked on a project known as the "cocoa hi-tech" in which the use of fertilizers is being highly encouraged among cocoa farmers. Thus currently the government of Ghana is the largest supplier of fertilizers to cocoa farmers in Ghana at little or no cost to the farmer (Osei, 2007). However, continuous application of fertilizers to the soil may increase the heavy metal contents making it exceed the natural abundances in soils, and transfer of these metals into the human food chain despite the fact that these heavy metals may be present in minute quantities in fertilizers (Lidia et al, 1997). Hence, the need to assess the level of heavy metals in these fertilizers and their build up in farm soils and food substances cannot be over-emphasized. This will further ensure that the quality of the cocoa produced is not sacrificed for quantity. Hence this work is aimed at assessing the concentration of heavy metals in fertilizers used by cocoa farmers and subsequently determining the levels of these heavy metals in the soil, the cocoa nibs, and the shells.

2.0 Materials and Methods

2.1 Geographical description of the sampling area.

Ghana is positioned between latitude 4^{o} 44'N and 11^{o} 11'N and 3^{o} 11'W and 1^{o}11' E, about 750Km north of the equator at the western coast of Africa. Ghana shares borders with Burkina Faso to the North, Togo to the East, La Cote d'Ivoire to the West and the Gulf of Guinea at the South (Dickson and Benneh, 1998).
The country is divided into ten political regions; in six of these regions cultivation of cocoa occurs in commercial quantities. These regions include: Western region, Central region, Eastern region, Brong Ahafo region, Ashanti and Volta regions (Benneh et al, 1990).
The Western region of Ghana which is the study area contributes more than 50% of the total production of cocoa in the country. It shares boundaries with Brong Ahafo region to the north, Ashanti region to the north-east, and Central region to the east, La Cote d'Iviore to the west and the Atlantic Ocean to the south. Figure 1 represents the western region and indicates the various areas of sampling.

2.2 Sample Collection

2.2.1 Soil sampling

Soils from cocoa farms were randomly sampled at a depth of 0 – 10 cm using plastic scrappers at the study sites into transparent clipper rubber bags in October 2010. At each site samples were collected at five different spots with each being about 50 meters apart.
Four different major cocoa growing towns in the region were considered for the work; two in the northern belt of the region (Sefwi Nkatieso and Sefwi Asawinso) and the other two being found in the southern belt of the region (Wassa Akropong and Bogoso). Sampling from these four cocoa growing towns was done with the aim of obtaining representative samples for the region.
Two main types of soil samples were taken; soil from farmlands which have seen at least 2 to 3 years of fertilizer amendment and farm lands with no fertilizer application. In this work, soil samples from farmlands with no fertilizer application are termed natural soil (NS) while soil samples obtained from farm lands with 2 to 3 years of fertilizer amendment are termed fertilizer amended soils (FS).
In each of these farms (where soil samples were taken), several cocoa fruits were plucked from the cocoa trees on the farms. Fertilizer samples namely, Cocoa Asaase-wura, Cocofeed and Sidalco Balanced were also obtained from the cocoa farmers. Nitrabor and Sidalco Potassium Rich were purchased from three different markets in Accra. The sampling locations, number of soils and cocoa fruits analyzed are summarized in Table 1.

2.3 Determination of Soil pH

Soil samples were weighed and mixed with distilled water in the water to soil ratio of 2.5: 1 (Lu, 1999) in the laboratory. Soil pH was then measured using pH meter DEMO 13702.93 manufactured by PHYWE of Germany. The mean values of pH obtained are as shown in Table 2.

2.4 Sample preparation for Atomic Absorption Spectrometer (AAS) analysis

Chemicals and Reagents

All reagents used for this work were of analytical grade. Digestion of samples was performed using concentrated nitric acid and 70% perchloric acid both obtained from Merk, Germany. Deionized water was used for all the analytical work.

2.4.1 Digestion of fertilizer samples

Nitric–perchloric acid digestion

Nitric – perchloric acid digestion was performed where 1.0 gm of the sample was placed in a 250 ml digestion tube

and 15.0 ml of concentrated nitric acid was added. The mixture was boiled gently for about 2 hours to oxidize all easily oxidizable matter. This was followed by 5.0 ml of 70% perchloric acid and the mixture boiled gently until dense white fumes appeared. After cooling, 20.0 ml of distilled water was added and the mixture boiled gently to release any fumes. The solution was cooled then filtered through whatman No. 42 filter paper and transferred quantitatively to a 100ml volumetric flask by adding distilled water (Zeng-Yei, 2004).
Atomic Absorption Spectrophotometer (Perkin Elmer A Analyst 400 AAS) was used to determine the following elements in each analyte; Copper, Manganese, Nickel, Cadmium, Chromium, Lead, Zinc and Iron.

2.4.2 Preparation of standards

Standard solutions of heavy metals were prepared for each element analysed from the stock solution obtained from BDH laboratory (supplies Poole BH15 LTD. England). The working standard solutions were all prepared by serial dilutions of the stock solution with de-ionized water in 100ml volumetric flasks.

2.5 Quality Assurance

NIVA SLP 1042 standard reference materials were subjected to the same treatment as the test materials and their heavy metal contents determined the same way as for the test materials. Table 3 contains the comparative levels of these elements obtained in this work.

2.6 Soil sample analysis using X-ray Fluorescence technique

Ten grams (10g) of each sample were made into thick sample pellets of diameter 2.5 cm using the hydraulic press (hydraulic Specac press) with an applied load of 10 metric tons. The elemental concentrations were determined using energy dispersive X-ray fluorescence (EDXRF) with a secondary target excitation arrangement and MCDWIN-(MC-A (1)) software for data collection.

EDXRF was preferred because it provides a rapid and non-destructive method for the analysis of trace and major elements in soil samples (Yeung et al, 2003). The compact 3K5 X-ray Generator EDXRF Spectrometer which was used for the elemental analysis has a molybdenum (Mo) secondary target arrangement coupled to pettier cooled silicon drift detector (SDD) with a 12µm beryllium window thickness. The SDD detector has a resolution of 136eV for 5.9KeV X-ray energy. IAEA Soil 7 Standard reference material was used for the validation of the analytical procedure and table 4 contains results obtained for this material.

3.0 Results and Discussions

3.1 Heavy metal levels in fertilizers

Results from the analysis show that generally Nitrabor had low concentrations of Mn, Cu, Cr and Zn with value, 1.90 µg/g for both Cu and Mn and 0.10 µg/g for Cr whiles Zn level was below the detectable limit of the instrument. Fe concentration was quite high in Nitrabor with a value of 54.90 µg/g, table 5.

As can be seen from table 5, Sidalco Balanced and Sidalco Potassium Rich had relatively the highest levels of Mn, Cu and Zn. Mn and Cu were slightly higher in Sidalco Balanced (301.00 mg/l and 153.00 mg/l respectively) than in Sidalco Potassium Rich. Zn level was also relatively higher in Sidalco Potassium Rich than in Sidalco Balanced. Generally the two liquid fertilizers (Sidalco Balanced and Sidalco Potassium Rich) had the least levels for Pb, Ni and Cd for all the samples. The levels of Fe, Ni, Pb and Cd were relatively higher in Cocofeed and Cocoa Asaase-wura compared with levels in Nitrabor and Sidalco Balanced and Sidalco Potassium Rich.

Levels of heavy metals were found to be well within the proposed limits by the Canadian Standards for fertilizers. Adopted levels for Pb, Cd, Ni, and Zn were 500 ppm, 20 ppm, 180 ppm, and 1850 ppm respectively (ATSDR, 1993; FAO/WHO, 2001).

3.2 Heavy metal levels in soils

Table 6, shows the heavy metal levels recorded in the soils. It can be found from this table that iron concentrations were relatively high in all the three sampling locations whiles Cd levels were the least since its concentrations were below detection limit of the instrument. Sefwi Asawinso/Nkatieso recorded the highest levels for Fe, Zn, Cu, Mn and Ni with values 8600.00 µg/g, 14.50 µg/g, 11.30 µg/g, 287.30 µg/g, and 29.70 µg/g respectively whiles the least levels of these metals were recorded in Wassa Akropong with values 1659.80 µg/g, 1.99 µg/g, 2.01 µg/g, 14.10 µg/g and 5.71 µg/g respectively. Cr levels range from 8.0 µg/g in Sefwi Asawinso/Nkatieso to a high of 13.60 µg/g in Bogoso. Lead (Pb), a very toxic metal ranges from 1.12 µg/g in Wassa Akropong to a high of 2.60 µg/g in Sefwi Asawinso/Nkatieso.

The relatively high levels of the heavy metals at Sefwi Asawinso/Nkatieso may be due to the elevated pH level of 6.45 as shown in Table 6. Metals remain adsorbed to soils at higher pH (i.e. > 7) as proposed by Chen et al, 1997. This prevents the metals from leaching into the soil but rather remain adsorbed to the soil surface.
The levels of heavy metals in the natural soil at Sefwi Asawinso/Nkatieso were found to follow the order: Fe>Mn>Ni>Zn>Cu>Cr>Pb>Cd. Similar order was observed for the metals in fertilizer amended soils (FS). The levels of heavy metals in the natural soil (NS) at Wassa Akropong were found to be in the order: Fe>Mn>Cr>Ni>Cu>Zn>Pb>Cd. The order of metal levels in the (FS) was also found to be Fe>Cr>Mn>Ni>Cu>Zn>Pb>Cd. Bogoso had Fe to have the highest occurrence of about 2410.00 µg/g; followed by Mn at 46.80 µg/g. Pb was the least of about 1.32 µg/g. The order for Bogoso soils was as follows: Fe>Mn>Cr>Ni>Cu>Zn>Pb>Cd. Fertilizer amended soils were also found to contain the same order of heavy metals.

Table 6 also shows that on the average, Wassa Akropong soils had the least heavy metal concentration. This could be attributed to the acidic nature of soils from this location. Soil pH of 4.21 is low enough to influence the ability of soils to retain the metals. Li and Wu, (1999) predicted that low soil pH may influence the ability of metals to be retained in soil but rather become more mobile and eventually increase their uptake by plants that grow on them. This may account for the low levels of the metals in top soils at Wassa Akropong as these heavy metals may be more easily taken up by plants or leached to lower depths rather than adhere to the surface soil.

It could also be seen from table 6 that, generally most of the heavy metals in fertilizer amended soils (FS) were higher when compared to those in natural soils (NS). This may be due to the fact that the soils could be retaining those heavy metals sourced from the applied fertilizers.

Table 2, shows that fertilizer amended soils (FS) have generally lower pH than natural soils (NS). This may be due to the fact that the fertilizer tends to lower soil pH due to the nitrates and phosphates content hence may influence heavy metal levels in fertilizer amended soils (FS). For this reason, metals such as Fe which are easily soluble in acids recorded lower levels in fertilizer amended soils at Sefwi Asawinso/Nkatieso than levels found in the natural soils (NS) of the same sampling area. The concentrations were 7890.00 µg/g and 8600.00 µg/g respectively. A similar trend was observed for Zn in the same sampling location. The fertilizer amended soil had Zn level of 14.40µg/g while the natural soil indicated 14.50 µg/g.

Manganese and Zn levels in soils at Wassa Akropong also followed a similar trend where the fertilizer amended soil levels were 14.10 µg/g for Mn and 1.99 µg/g for Zn and for the natural soils, 28.80 µg/g and 2.01 µg/g respectively. Just as observed for the case of Fe in soils from Sefwi Asawinso/Nkatieso, soils from Bogoso also showed a similar trend with Fe levels in the natural soils exceeding that in its fertilizer amended soils with, 2410.00 µg/g for natural soil and 2052.00 µg/g for fertilizer amended soil.

Generally, the mean values for the various elements analysed for the three sampling locations as can be seen in Table 6 shows that Fe levels were relatively high with values ranging between 8600.00 µg/g and 2410.00 µg/g for natural soils and 7890.00 µg/g and 2052.00 µg/g for fertilizer amended soils. Mn followed Fe with values 233.40 µg/g to 28.80 µg/g for natural soils and 287.00 µg/g to 57.40 µg/g for fertilizer amended soils. Copper levels were expected to be higher than observed due to the use of fungicides and pesticides on the farms. These agrochemicals are known to contain high levels of copper. The low levels of the metal recorded for samples within the 0 – 10 cm depth could be attributed to the leaching of the metal into soils at lower depths or it carried away through storm runoffs.

Again figure 2 shows that generally heavy metal levels in fertilizer amended soils were higher compared to those in the natural soils. Nevertheless these levels were far below the permissible limits for agricultural land use as stated by FAO/WHO, 2001; which gives the permissible limits as, Fe, 50,000 µg/g; Mn, 2000 µg/g; Zn, 300 µg/g; Pb, 50 µg/g and Cd, 3 µg/g. The permissible level for Cu was given as, 100 µg/g (FAO/WHO, 2001).

3.3 Heavy metal levels in cocoa nibs

There are no known permissible limits for these essential metals in cocoa nibs, but the levels obtained agree well with permissible levels in fruits and vegetables as in many literature.

Lead, one of the most toxic heavy metals recorded values ranging from 0.05 µg/g in sample from Sefwi Asawinso/Nkatieso to a level of 0.07 µg/g in samples from Wassa Akropong. The levels obtained were lower than what was proposed by CODEX which set the maximum allowable limit at 1.0 µg/g in cocoa. This level may also be comparable to those found in most fruits and vegetables. Generally soil water is known to contain about 0.05 to 0.13% of the total soil Pb concentrations. Pb^{2+} is known to be the dominant soluble form which also has the ability to form a number of highly insoluble precipitates including $Pb(OH)_2$, $Pb_3(PO_2)_2$, and $PbCO_3$. Hence Pb has very low water solubility in soil and low uptake by plants (Goyer and Clarkson, 2001).

Cadmium which is also rated a potentially toxic metal has 1.0 µg/g as allowable limit in cocoa by CODEX (FAO/WHO, 2001). The levels obtained in this work ranges from 0.13µg/g in samples from Sefwi Asawinso/Nkatieso to 0.58µg/g in samples from Bogoso for natural soils and 0.41 µg/g for samples from Sefwi Asawinso/Nkatieso to 0.71 µg/g in samples from Wassa Akropong for fertilizer amended soils, table 7.

The higher levels of Cd in the cocoa beans from fertilizer amended soils may be attributed to the decreased pH levels of the soils. Cd is known to have high mobility in soils at low pH (Alloway, 1995) thus its availability in soil solution for plant uptake may have been relatively higher than the other heavy metals. This may account for the low levels of the element in the soils for the various sampling locations but significant levels recorded in the cocoa nibs, tables 6 and 7.

As stated earlier, the average pH levels of fertilizer amended soils were lower than those of natural soils for the samples. Metals easily enter soil solution at low pH levels and become mobile; as such their intake by plant may increase (Kabata-Pendias and Pendias, 1992). This phenomenon may contribute to the elevated levels of heavy metals in cocoa nibs from fertilizer amended soils.

For instance Mn, Ni, Pb, Zn and Fe levels in soils of Sefwi Asawinso/Nkatieso were relatively higher than those in soils of Wassa Akropong and Bogoso; but the levels of these metals in the cocoa nibs from Wassa Akropong and Bogoso were relatively higher than their levels in cocoa nibs from Sefwi Asawinso/Nkatieso, tables 6 and 7.

3.4 Heavy metal levels in cocoa shells

Generally, levels of heavy metals in cocoa shells were found to be higher than those in the cocoa nibs and this is evident from tables 7 and 8. Figure 3 a graphical presentation of the comparision of the mean levels of the heavy metals for the cocoa nibs and cocoa shells of the fertilizer amended soils (FS). As can be seen, generally, levels in shells were higher than in nibs.

Figures 3 also shows that differences in recorded levels between the nibs and shells were not huge among the essential metals as compared to what happens for the potentially toxic metals (Cd and Pb).

For instance, Cd levels increased 12 fold and Pb also had 14 fold increase in the shells as compared to the cocoa nibs from the natural soils, however, 17 fold and 30 fold increases were observed for Cd and Pb respectively in cocoa shells from fertilizer amended soils, tables 7 and 8.

Cocoa shells probably may serve as a natural sink for these contaminants thereby protecting the nibs. The higher levels in shells may be due to atmospheric deposition during the drying periods. Cocoa shells also contain organic compounds such as alkaloids, furfural, theobromine and some natural pigments. These compounds are complexing ligands that have the ability to hold most heavy metals in their matrixes.

4.0 CONCLUSION AND RECOMMENDATION

4.1 CONCLUSION

The results show that fertilizers (Cocofeed, Asaase-wura, Nitrabor, Sidalco Balance and Sidalco Potassium Rich) employed by farmers on their cocoa farms contain some levels of heavy metals. The concentrations of these metals in the fertilizers analyzed in this work were well within the recommended maximum limits set by Canadian Standards for Fertilizers in Canada.

Cocoa nibs from Wassa Akropong were observed to contain relatively high levels of the metals and Sefwi Asawinso/Nkatieso recorded the least. Continuous application of fertilizer may influence soil pH, however this may not have direct impact on heavy metal build-up in cocoa nibs or shells but only metals that leach into the soil solution with their subsequent uptake by plants may influence metal build-up in cocoa nibs and shells.

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Table 1: Sampling locations, sets of soil and cocoa fruits used for analysis.

Sampling location	Soils	Cocoa fruits
Sefwi Asawinso	2	2
Sefwi Nkatieso	2	2
Wassa Akropong	4	7
Bogoso	4	6

Table 2: Mean values for Soil pH

Sampling location	**Soil type**	**pH values**
Sefwi Asawinso/Nkatieso	NS	6.45±1.86
	FS	5.90±0.95
Wassa Akropong	NS	4.21±0.65
	FS	3.87±0.12
Bogoso	NS	5.43±1.20
	FS	5.01±0.71

NS - Natural soil; FS – Fertilizer amended soil

Table 3: Comparative levels of heavy metals in NIVA SLP 1042 standard reference material.

Metal	**Cu**	**Mn**	**Ni**	**Cd**	**Pb**	**Zn**	**Fe**
This work (mg/l)	0.318	1.160	0.348	0.030	0.136	0.553	2.000
Expected values (mg/l)	0.320	1.090	0.492	0.032	0.128	0.520	1.970

Table 4: Levels of heavy metals in IAEA soil 7 standard reference materials.

Metal	Cu	Mn	Ni	Cd	Cr	Pb	Zn	Fe
Certified values (mg/g)	11.00±0.55	631.00±32.00	26.00±1.30	0.031±0.002	60.00±3.00	60.00±3.00	04.00±5.20	25700.00±1285.00
This work (mg/g)	11.30±0.70	651.00±33.00	26.70±1.30	0.030±0.002	61.70±3.10	61.80±3.10	07.00±5.30	26576.00±1329.00

Table 5: Mean values(µg/g) of heavy metal levels in fertilizers used by cocoa farmers

Fertilizer types	Cu	Mn	N i	Cd	Cr	Pb	Zn	Fe
Nitrabor (µg/g)	1.90±0.70	1.90±1.10	2.65±0.70	2.00±0.60	0.10±0.20	0.15±0.20	ND	54.90±0.10
Cocofeed (µg/g)	2.00±0.10	14.10±3.30	2.80±0.10	12.60±0.60	12.50±0.30	10.90±0.10	27.90±0.30	1192.00±4.00
Asaase-wura(µg/g)	8.90±1.50	7.60±1.40	4.30±0.50	6.20±0.10	10.30±0.10	22.60±3.40	23.90±3.40	1093.00±11.00
Sid. Balanced(µg/g)	153.00±9.50	301.00±33.00	2.05±0.30	0.02±0.30	0.15±0.02	ND	28.90±2.80	52.40±1.50
Sid. Pot. Rich(µg/g)	146.00±6.12	279.00±12.00	0.06±0.01	0.11±0.01	0.32±0.10	0.05±0.02	39.20±3.40	41.30±3.60
Mean	62.40±3.58	121.00±10.20	2.37±0.30	4.19±0.30	4.67±0.14	8.40±0.90	24.00±2.50	487±4.04

Table 6: Mean values for heavy metal levels(µg/g) in Natural soils (NS) and fertilizer amended soils (FS)

Sampling town	Cocoa type	Cu	Mn	Ni	Cd	Cr	Pb	Zn	Fe
Sefwi A/N	NS	8.14±0.01	233.40±9.20	20.60±1.30	ND	5.25±4.85	2.38±0.01	14.50±5.50	8600.00±1000
	FS	11.30±3.60	287.00±61.90	29.70±4.40	ND	8.00±7.00	2.60±0.30	14.40±0.60	7890.00±1880
Wassa Akr.	NS	2.01±0.47	28.80±2.03	5.71±0.06	ND	12.80±2.63	1.12±0.16	2.01±0.25	1659.80±440
	FS	2.82±0.22	14.10±2.90	7.03±1.62	ND	19.60±0.40	1.52±0.55	1.99±0.05	2500.00±230
Bogoso	NS	2.77±0.35	46.80±14.40	5.99±0.44	ND	13.60±0.57	1.32±0.41	2.43±0.83	2410.00±180
	FS	3.25±0.53	57.40±8.24	6.27±1.05	ND	13.00±1.20	1.76±0.36	2.76±0.17	2052.00±18

Asawinso/Nkatieso (A/N), Akropong (Akr).

Table 7: Mean values for heavy metal levels in cocoa nibs of cocoa from natural soil (NS) and fertilizer amended soil (FS) (µg/g)

Sampling locations	Cocoa type	Cu	Mn	Ni	Cd	Cr	Pb	Zn	Fe
Sefwi A/N	NS	19.15±5.59	25.30±9.76	0.25±0.13	0.13±0.01	ND	0.05±0.07	33.60±1.27	28.75±7.28
	FS	17.80±3.11	13.05±2.05	0.18±0.01	0.41±0.31	ND	0.07±0.04	38.96±7.14	36.75±2.76
Wassa Akropong	NS	11.70±2.59	26.33±3.71	0.38±0.05	0.43±0.26	ND	0.07±0.05	43.97±1.39	38.50±10.41
	FS	15.73±5.43	33.60±7.89	0.27±0.07	0.71±0.13	ND	0.16±0.02	47.17±9.67	38.73±10.8
Bogoso	NS	16.25±3.24	25.60±5.52	0.32±0.04	0.58±0.25	ND	0.07±0.14	44.35±1.06	29.33±5.67
	FS	16.95±2.05	24.75±6.57	0.32±0.12	0.54±0.23	ND	0.07±0.04	43.65±1.91	28.20±5.87

Table 8: Mean values for heavy metal levels in cocoa shells of cocoa from natural soil (NS) and fertilizer amended soil (FS) (μg/g).

Sampling locations	Cocoa type	Cu	Mn	Ni	Cd	Cr	Pb	Zn	Fe
Sefwi A/N	NS	22.75±4.17	17.65±10.8	1.85±0.34	6.20±2.40	0.01±0.01	0.56±0.14	37.85±3.75	105.80±22.40
	FS	24.00±6.51	18.45±13.2	2.35±0.21	5.65±0.35	0.015±0.01	1.02±0.03	36.45±0.21	101.60±1.69
Wassa Akr.	NS	21.80±4.22	37.27±6.76	1.50±0.65	7.30±1.37	0.04±0.01	3.51±0.46	35.60±0.61	141.90±29.20
	FS	22.03±5.56	34.17±4.27	1.18±0.79	6.83±1.51	0.57±0.09	2.04±1.57	38.25±4.70	188.07±32.90
Bogoso	NS	20.40±3.83	27.85±3.77	2.30±1.20	5.83±0.69	0.06±0.05	1.48±0.11	40.28±3.06	152.85±37.60
	FS	27.95±11.1	26.20±3.11	2.40±0.14	7.00±1.41	0.06±0.06	1.05±0.34	42.00±4.38	198.80±14.90

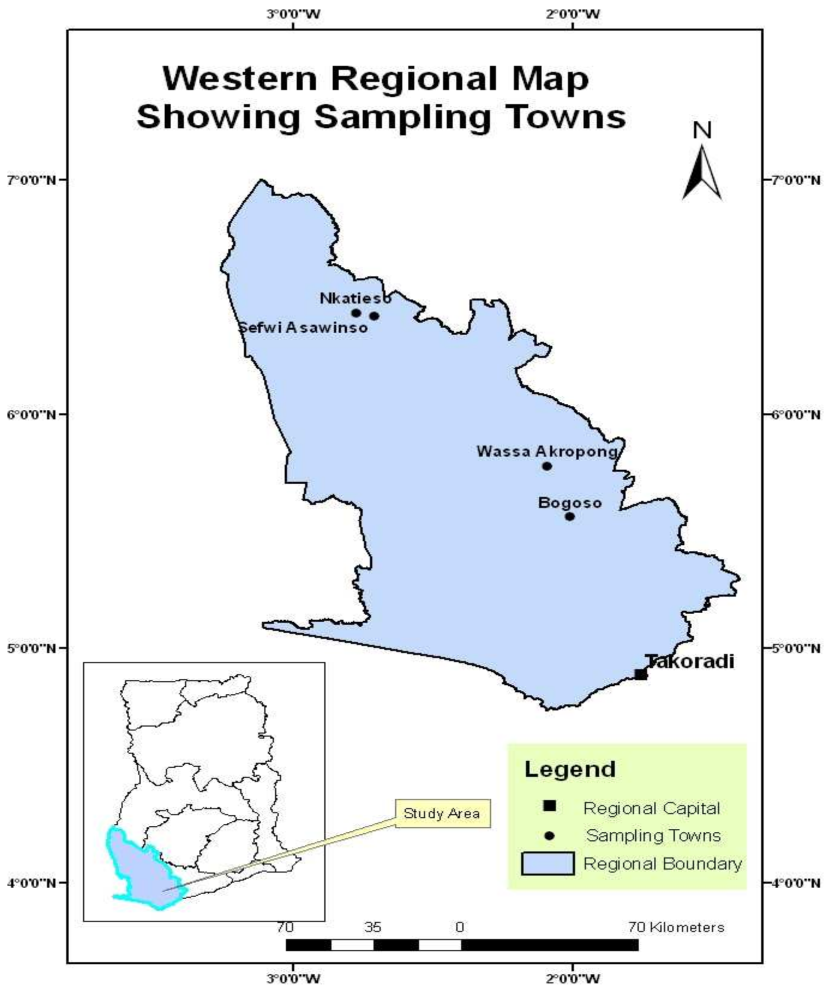

Figure 1: Map of Ghana and western region indicating the sampling locations.

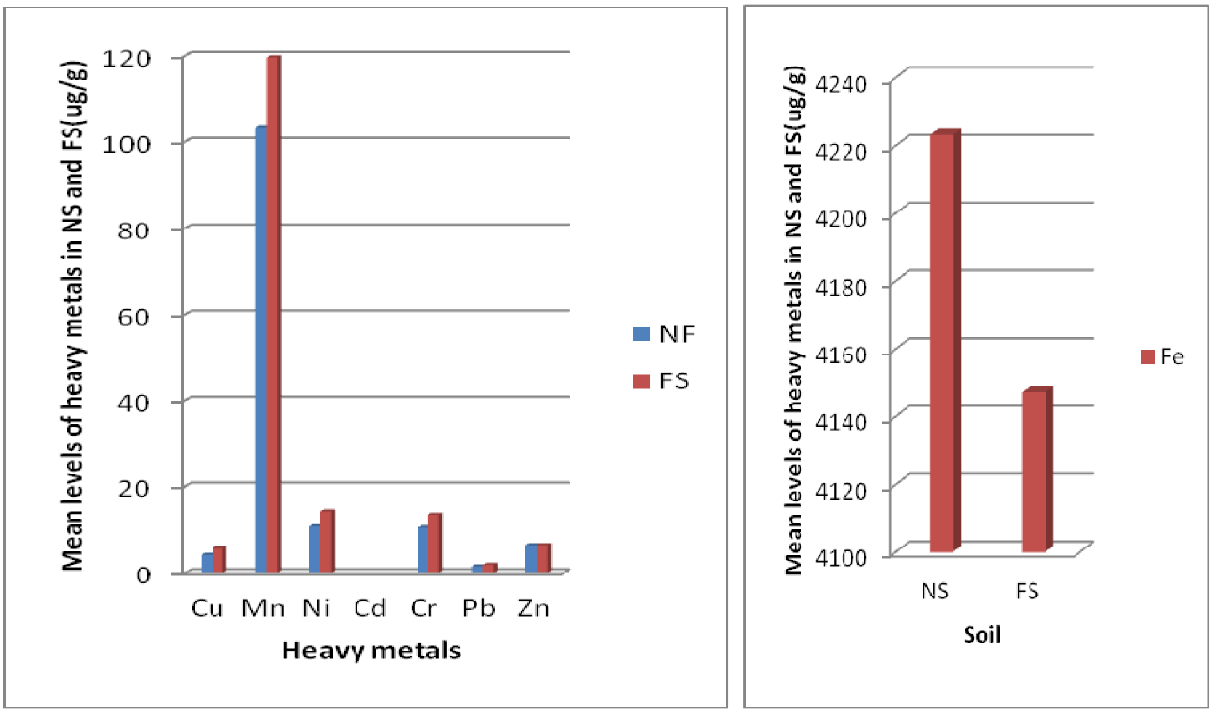

Figure 2: The mean levels of heavy metals in natural soils (NS) and fertilizer amended Soils (FS).

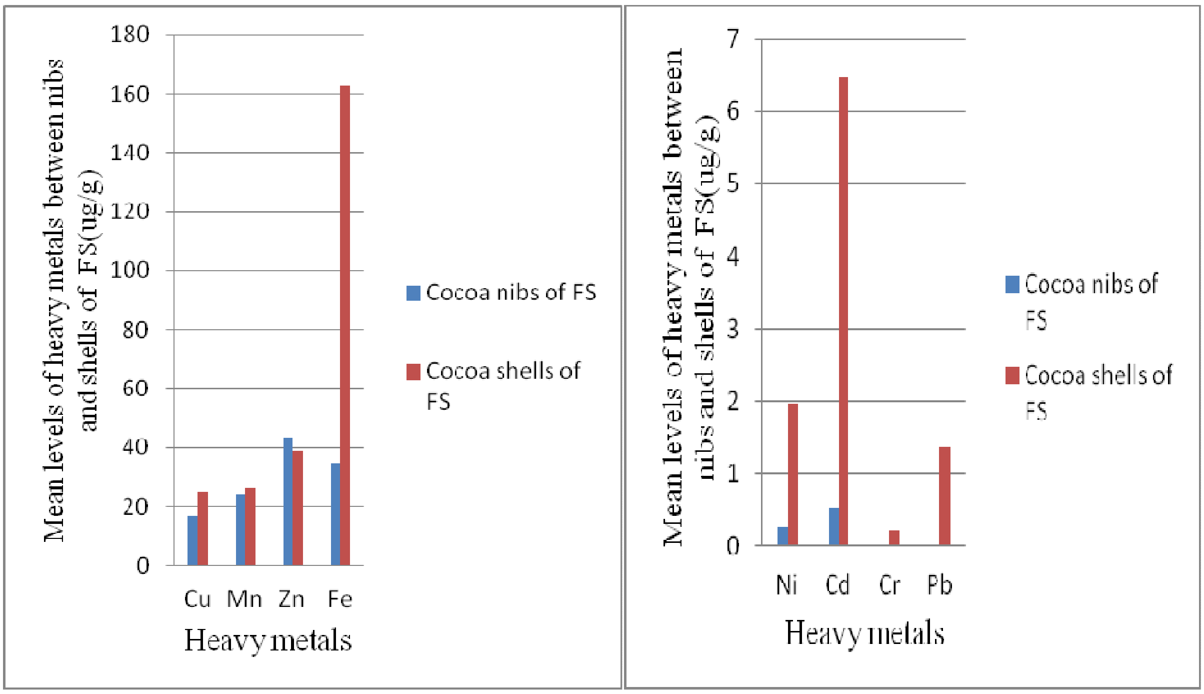

Figure 3: Chart showing the mean levels of heavy metals between nibs and shells of fertilizer amended soils (FS).